CHAPTER 14
CHEMICAL KINETICS

PRACTICE EXAMPLES

1A **(E)** The rate of consumption for a reactant is expressed as the negative of the change in molarity divided by the time interval. The rate of reaction is expressed as the rate of consumption of a reactant or production of a product divided by its stoichiometric coefficient.

$$\text{rate of consumption of A} = \frac{-\Delta[\text{A}]}{\Delta t} = \frac{-(0.3187\ \text{M} - 0.3629\ \text{M})}{8.25\ \text{min}} \times \frac{1\,\text{min}}{60\ \text{s}} = 8.93\times10^{-5}\ \text{M s}^{-1}$$

$$\text{rate of reaction} = \text{rate of consumption of A} \div 2 = \frac{8.93\times10^{-5}\ \text{M s}^{-1}}{2} = 4.46\times10^{-5}\ \text{M s}^{-1}$$

1B **(E)** We use the rate of reaction of A to determine the rate of formation of B, noting from the balanced equation that 3 moles of B form (+3 moles B) when 2 moles of A react (–2 moles A). (Recall that "M" means "moles per liter.")

$$\text{rate of B formation} = \frac{0.5522\,\text{M A} - 0.5684\,\text{M A}}{2.50\,\text{min} \times \frac{60\,\text{s}}{1\,\text{min}}} \times \frac{+3\,\text{moles B}}{-2\,\text{moles A}} = 1.62\times10^{-4}\ \text{M s}^{-1}$$

2A **(M)**

(a) The 2400-s tangent line intersects the 1200-s vertical line at 0.75 M and reaches 0 M at 3500 s. The slope of that tangent line is thus

$$\text{slope} = \frac{0\ \text{M} - 0.75\ \text{M}}{3500\ \text{s} - 1200\ \text{s}} = -3.3\times10^{-4}\ \text{M s}^{-1} = -\ \text{instantaneous rate of reaction}$$

The instantaneous rate of reaction = $3.3\times10^{-4}\ \text{M s}^{-1}$.

(b) At 2400 s, $[\text{H}_2\text{O}_2] = 0.39$ M. At 2450 s, $[\text{H}_2\text{O}_2] = 0.39\ \text{M} + \text{rate}\times\Delta t$

$$\text{At 2450 s,}\ [\text{H}_2\text{O}_2] = 0.39\ \text{M} + \left[-3.3\times10^{-4}\,\text{mol H}_2\text{O}_2\ \text{L}^{-1}\text{s}^{-1}\times 50\text{s}\right]$$
$$= 0.39\ \text{M} - 0.017\ \text{M} = 0.37\ \text{M}$$

2B **(M)** With only the data of Table 14.2 we can use only the reaction rate during the first 400 s, $-\Delta[\text{H}_2\text{O}_2]/\Delta t = 15.0\times10^{-4}\ \text{M s}^{-1}$, and the initial concentration, $[\text{H}_2\text{O}_2]_0 = 2.32$ M. We calculate the change in $[\text{H}_2\text{O}_2]$ and add it to $[\text{H}_2\text{O}_2]_0$ to determine $[\text{H}_2\text{O}_2]_{100}$.

$$\Delta[\text{H}_2\text{O}_2] = \text{rate of reaction of H}_2\text{O}_2 \times \Delta t = -15.0\times10^{-4}\ \text{M s}^{-1}\times 100\ \text{s} = -0.15\ \text{M}$$

$$[\text{H}_2\text{O}_2]_{100} = [\text{H}_2\text{O}_2]_0 + \Delta[\text{H}_2\text{O}_2] = 2.32\ \text{M} + (-0.15\ \text{M}) = 2.17\ \text{M}$$

This value differs from the value of 2.15 M determined in *text* Example 14-2b because the *text* used the initial rate of reaction $(17.1\times10^{-4}\ \text{M s}^{-1})$, which is a bit faster than the average rate over the first 400 seconds.

3A **(M)** We write the equation for each rate, divide them into each other, and solve for *n*.

$$R_1 = k\times[\mathrm{N_2O_5}]_1^n = 5.45\times10^{-5}\ \mathrm{M\ s^{-1}} = k(3.15\ \mathrm{M})^n$$

$$R_2 = k\times[\mathrm{N_2O_5}]_2^n = 1.35\times10^{-5}\ \mathrm{M\ s^{-1}} = k(0.78\ \mathrm{M})^n$$

$$\frac{R_1}{R_2} = \frac{5.45\times10^{-5}\ \mathrm{M\ s^{-1}}}{1.35\times10^{-5}\ \mathrm{M\ s^{-1}}} = 4.04 = \frac{k\times[\mathrm{N_2O_5}]_1^n}{k\times[\mathrm{N_2O_5}]_2^n} = \frac{k(3.15\ \mathrm{M})^n}{k(0.78\ \mathrm{M})^n} = \left(\frac{3.15}{0.78}\right)^n = (4.0\underline{4})^n$$

We kept an extra significant figure (4) to emphasize that the value of $n = 1$. Thus, the reaction is first-order in $\mathrm{N_2O_5}$.

3B **(E)** For the reaction, we know that $\text{rate} = k[\mathrm{HgCl_2}]^1[\mathrm{C_2O_4}^{2-}]^2$. Here we will compare Expt. 4 to Expt. 1 to find the rate.

$$\frac{\text{rate}_4}{\text{rate}_1} = \frac{k[\mathrm{HgCl_2}]^1[\mathrm{C_2O_4}^{2-}]^2}{k[\mathrm{HgCl_2}]^1[\mathrm{C_2O_4}^{2-}]^2} = \frac{0.025\ \mathrm{M}\times(0.045\ \mathrm{M})^2}{0.105\ \mathrm{M}\times(0.150\ \mathrm{M})^2} = 0.0214 = \frac{\text{rate}_4}{1.8\times10^{-5}\ \mathrm{M\,min^{-1}}}$$

The desired rate is $\text{rate}_4 = 0.0214\times1.8\times10^{-5}\ \mathrm{M\ min^{-1}} = 3.9\times10^{-7}\ \mathrm{M\,min^{-1}}$.

4A **(E)** We place the initial concentrations and the initial rates into the rate law and solve for k.

$$\text{rate} = k[\mathrm{A}]^2[\mathrm{B}] = 4.78\times10^{-2}\ \mathrm{M\ s^{-1}} = k(1.12\ \mathrm{M})^2(0.87\ \mathrm{M})$$

$$k = \frac{4.78\times10^{-2}\ \mathrm{M\ s^{-1}}}{(1.12\ \mathrm{M})^2\,0.87\ \mathrm{M}} = 4.4\times10^{-2}\ \mathrm{M^{-2}\ s^{-1}}$$

4B **(E)** We know that $\text{rate} = k[\mathrm{HgCl_2}]^1[\mathrm{C_2O_4}^{2-}]^2$ and $k = 7.6\times10^{-3}\ \mathrm{M^{-2}min^{-1}}$.

Thus, insertion of the starting concentrations and the *k* value into the rate law yields:

$$\text{Rate} = 7.6\times10^{-3}\ \mathrm{M^{-2}\ min^{-1}}(0.050\ \mathrm{M})^1(0.025\ \mathrm{M})^2 = 2.4\times10^{-7}\ \mathrm{M\ min^{-1}}$$

5A **(E)** Here we substitute directly into the integrated rate law equation.

$$\ln[\mathrm{A}]_t = -kt + \ln[\mathrm{A}]_0 = -3.02\times10^{-3}\ \mathrm{s^{-1}}\times325\ \mathrm{s} + \ln(2.80) = -0.982 + 1.030 = 0.048$$

$$[\mathrm{A}]_t = e^{0.048} = 1.0\ \mathrm{M}$$

5B **(M)** This time we substitute the provided values into text Equation 14.13.

$$\ln\frac{[\mathrm{H_2O_2}]_t}{[\mathrm{H_2O_2}]_0} = -kt = -k\times600\ \mathrm{s} = \ln\frac{1.49\ \mathrm{M}}{2.32\ \mathrm{M}} = -0.443 \qquad k = \frac{-0.443}{-600\ \mathrm{s}} = 7.38\times10^{-4}\ \mathrm{s^{-1}}$$

Now we choose $[\mathrm{H_2O_2}]_0 = 1.49$ M, $[\mathrm{H_2O_2}]_t = 0.62$, $\quad t = 1800\ \mathrm{s} - 600\ \mathrm{s} = 1200\ \mathrm{s}$

$$\ln\frac{[\mathrm{H_2O_2}]_t}{[\mathrm{H_2O_2}]_0} = -kt = -k\times1200\ \mathrm{s} = \ln\frac{0.62\ \mathrm{M}}{1.49\ \mathrm{M}} = -0.88 \qquad k = \frac{-0.88}{-1200\ \mathrm{s}} = 7.3\times10^{-4}\ \mathrm{s^{-1}}$$

These two values agree within the limits of the experimental error and thus, the reaction is first-order in $[\mathrm{H_2O_2}]$.

6A **(M)** We can use the integrated rate equation to find the ratio of the final and initial concentrations. This ratio equals the fraction of the initial concentration that remains at time *t*.

$$\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt = -2.95\times10^{-3}\ \mathrm{s}^{-1}\times150\ \mathrm{s} = -0.443$$

$$\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = e^{-0.443} = 0.642; \quad 64.2\%\ \text{of}\ [\mathrm{A}]_0\ \text{remains.}$$

6B **(M)** After two-thirds of the sample has decomposed, one-third of the sample remains. Thus $[\mathrm{H_2O_2}]_t = [\mathrm{H_2O_2}]_0 \div 3$, and we have

$$\ln\frac{[\mathrm{H_2O_2}]_t}{[\mathrm{H_2O_2}]_0} = -kt = \ln\frac{[\mathrm{H_2O_2}]_0 \div 3}{[\mathrm{H_2O_2}]_0} = \ln(1/3) = -1.099 = -7.30\times10^{-4}\ \mathrm{s}^{-1}t$$

$$t = \frac{-1.099}{-7.30\times10^{-4}\ \mathrm{s}^{-1}} = 1.51\times10^{3}\ \mathrm{s}\times\frac{1\ \mathrm{min}}{60\ \mathrm{s}} = 25.1\ \mathrm{min}$$

7A **(M)** At the end of one half-life the pressure of DTBP will have been halved, to 400 mmHg. At the end of another half-life, at 160 min, the pressure of DTBP will have halved again, to 200 mmHg. Thus, the pressure of DTBP at 125 min will be intermediate between the pressure at 80.0 min (400 mmHg) and that at 160 min (200 mmHg). To obtain an exact answer, first we determine the value of the rate constant from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{80.0\ \mathrm{min}} = 0.00866\ \mathrm{min}^{-1}$$

$$\ln\frac{(P_{\mathrm{DTBP}})_t}{(P_{\mathrm{DTBP}})_0} = -kt = -0.00866\ \mathrm{min}^{-1}\times125\ \mathrm{min} = -1.08$$

$$\frac{(P_{\mathrm{DTBP}})_t}{(P_{\mathrm{DTBP}})_0} = e^{-1.08} = 0.340$$

$$(P_{\mathrm{DTBP}})_t = 0.340\times(P_{\mathrm{DTBP}})_0 = 0.340\times800\ \mathrm{mmHg} = 272\ \mathrm{mmHg}$$

7B **(M)**

(a) We use partial pressures in place of concentrations in the integrated first-order rate equation. Notice first that more than 30 half-lives have elapsed, and thus the ethylene oxide pressure has declined to at most $(0.5)^{30} = 9\times10^{-10}$ of its initial value.

$$\ln\frac{P_{30}}{P_0} = -kt = -2.05\times10^{-4}\ \mathrm{s}^{-1}\times30.0\ \mathrm{h}\times\frac{3600\ \mathrm{s}}{1\ \mathrm{h}} = -22.1 \quad \frac{P_{30}}{P_0} = e^{-22.1} = 2.4\times10^{-10}$$

$$P_{30} = 2.4\times10^{-10}\times P_0 = 2.4\times10^{-10}\times782\ \mathrm{mmHg} = 1.9\times10^{-7}\ \mathrm{mmHg}$$

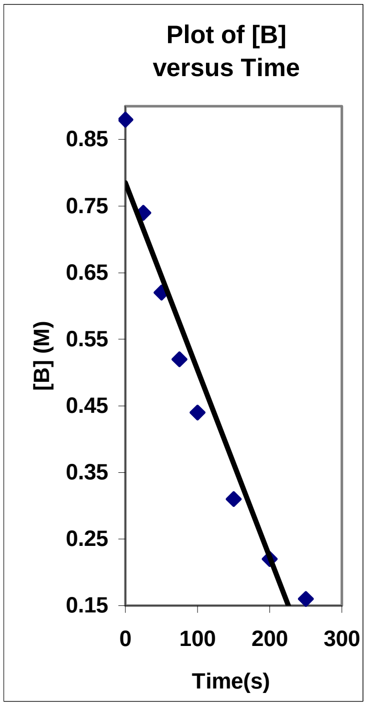
(b) $P_{\text{ethylene oxide}}$ initially 782 mmHg → 1.9×10^{-7} mmHg (~ 0). Essentially all of the ethylene oxide is converted to CH_4 and CO. Since pressure is proportional to moles, the final pressure will be twice the initial pressure (1 mole gas → 2 moles gas; 782 mmHg → 1564 mmHg). The final pressure will be 1.56×10^3 mmHg.

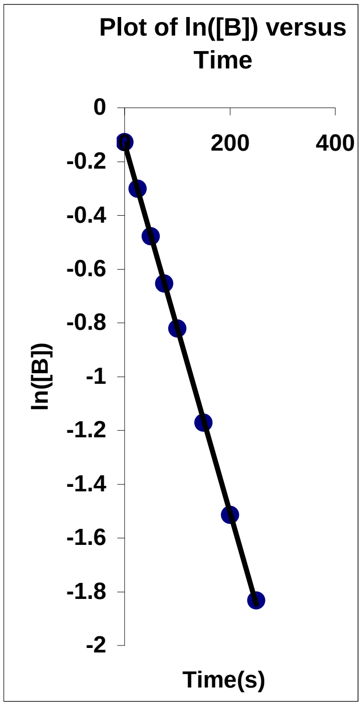
8A **(D)** We first begin by looking for a constant rate, indicative of a zero-order reaction. If the rate is constant, the concentration will decrease by the same quantity during the same time period. If we choose a 25-s time period, we note that the concentration decreases $(0.88\text{ M} - 0.74\text{ M} =)$ 0.14 M during the first 25 s, $(0.74\text{ M} - 0.62\text{ M} =)$ 0.12 M during the second 25 s, $(0.62\text{ M} - 0.52\text{ M} =)$ 0.10 M during the third 25 s, and $(0.52\text{ M} - 0.44\text{ M} =)$ 0.08 M during the fourth 25-s period. This is hardly a constant rate and we thus conclude that the reaction is not zero-order.

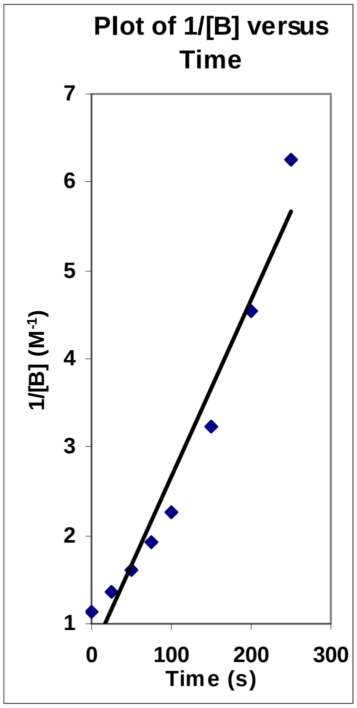
We next look for a constant half-life, indicative of a first-order reaction. The initial concentration of 0.88 M decreases to one half of that value, 0.44 M, during the first 100 s, indicating a 100-s half-life. The concentration halves again to 0.22 M in the second 100 s, another 100-s half-life. Finally, we note that the concentration halves also from 0.62 M at 50 s to 0.31 M at 150 s, yet another 100-s half-life. The rate is established as first-order. The rate constant is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100\text{ s}} = 6.93 \times 10^{-3}\text{ s}^{-1}.$$

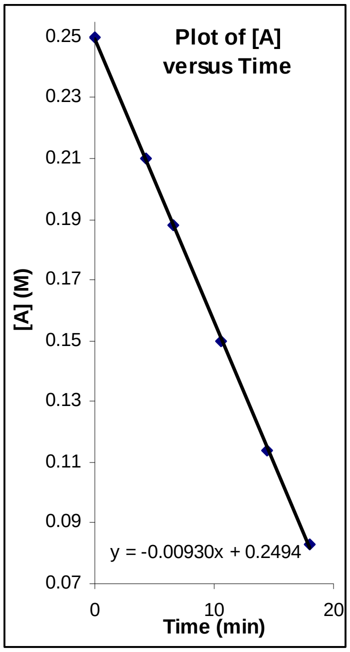
That the reaction is first-order is made apparent by the fact that the ln[B] vs time plot is a straight line with slope = $-k$ ($k = 6.85 \times 10^{-3}\text{ s}^{-1}$).

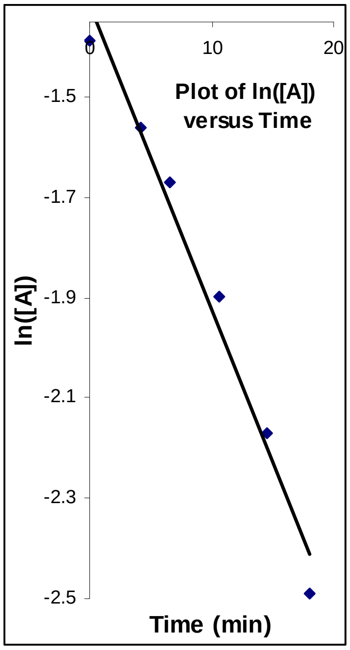

Plot of [B] versus Time

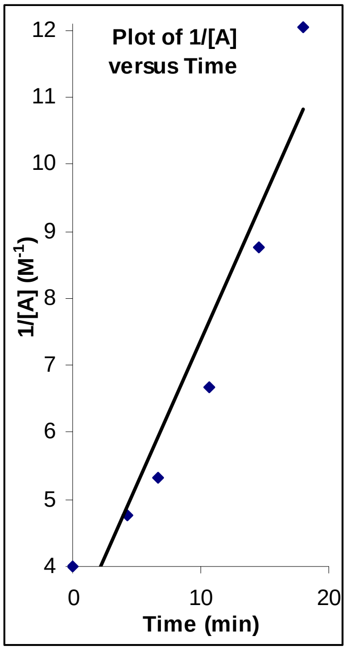

Plot of ln([B]) versus Time


Plot of 1/[B] versus Time

8B **(D)** We plot the data in three ways to determine the order. (1) A plot of [A] vs. time is linear if the reaction is zero-order. (2) A plot of ln [A] vs. time will be linear if the reaction is first-order. (3) A plot of 1/[A] vs. time will be linear if the reaction is second-order. It is obvious from the plots below that the reaction is zero-order. The negative of the slope of the line equals $k = -(0.083\ \text{M} - 0.250\ \text{M}) \div 18.00\ \text{min} = 9.28 \times 10^{-3}$ M/min ($k = 9.30 \times 10^{-3}$ M/min using a graphical approach).







9A **(M)** First we compute the value of the rate constant at 75.0 °C with the Arrhenius equation. We know that the activation energy is $E_a = 1.06 \times 10^5$ J/mol, and that $k = 3.46 \times 10^{-5}\ \text{s}^{-1}$ at 298 K. The temperature of $75.0\ ^\circ\text{C} = 348.2$ K.

$$\ln\frac{k_2}{k_1} = \ln\frac{k_2}{3.46 \times 10^{-5}\ \text{s}^{-1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{1.06 \times 10^5\ \text{J / mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{298.2\ \text{K}} - \frac{1}{348.2\ \text{K}}\right) = 6.14$$

$$k_2 = 3.46 \times 10^{-5}\ \text{s}^{-1} \times e^{+6.14} = 3.46 \times 10^{-5}\ \text{s}^{-1} \times 4.6 \times 10^2 = 0.016\ \text{s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.016\ \text{s}^{-1}} = 43\ \text{s at } 75\ ^\circ\text{C}$$

9B **(M)** We use the integrated rate equation to determine the rate constant, realizing that one-third remains when two-thirds have decomposed.

$$\ln\frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = \ln\frac{[\text{N}_2\text{O}_5]_0 \div 3}{[\text{N}_2\text{O}_5]_0} = \ln\frac{1}{3} = -kt = -k(1.50\ \text{h}) = -1.099$$

$$k = \frac{1.099}{1.50\ \text{h}} \times \frac{1\ \text{h}}{3600\ \text{s}} = 2.03 \times 10^{-4}\ \text{s}^{-1}$$

Now use the Arrhenius equation to determine the temperature at which the rate constant is 2.04 × $10^{-4}\ \text{s}^{-1}$.

$$\ln\frac{k_2}{k_1}=\ln\frac{2.04\times10^{-4}\ \text{s}^{-1}}{3.46\times10^{-5}\ \text{s}^{-1}}=1.77=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{1.06\times10^{5}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{298\ \text{K}}-\frac{1}{T_2}\right)$$

$$\frac{1}{T_2}=\frac{1}{298\ \text{K}}-\frac{1.77\times8.3145\ \text{K}^{-1}}{1.06\times10^{5}}=3.22\times10^{-3}\ \text{K}^{-1}\qquad T_2=311\ \text{K}$$

10A **(M)** The two steps of the mechanism must add, in a Hess's law fashion, to produce the overall reaction.

$$\begin{array}{lll}
\text{Overall reaction: } CO+NO_2\longrightarrow CO_2+NO & \text{or} & CO+NO_2\longrightarrow CO_2+NO\\
\text{Second step:} -\left(NO_3+CO\longrightarrow NO_2+CO_2\right) & \text{or} & +\left(NO_2+CO_2\longrightarrow NO_3+CO\right)\\
\text{First step:} & & \overline{2\ NO_2\longrightarrow NO+NO_3}
\end{array}$$

If the first step is the slow step, then it will be the rate-determining step, and the rate of that step will be the rate of the reaction, namely, rate of reaction = $k_1[NO_2]^2$.

10B **(M)**

(1) The steps of the mechanism must add, in a Hess's law fashion, to produce the overall reaction. This is done below. The two intermediates, $NO_2F_2(g)$ and F(g), are each produced in one step and consumed in the next one.

$$\begin{array}{ll}
\text{Fast:} & NO_2(g)+F_2(g)\rightleftharpoons NO_2F_2(g)\\
\text{Slow:} & NO_2F_2(g)\rightarrow NO_2F(g)+F(g)\\
\text{Fast:} & F(g)+NO_2(g)\rightarrow NO_2F(g)\\
\text{Net:} & 2\ NO_2(g)+F_2(g)\rightarrow 2\ NO_2F(g)
\end{array}$$

(2) The proposed mechanism must agree with the rate law. We expect the rate-determining step to determine the reaction rate: Rate = $k_3[NO_2F_2]$. To eliminate $[NO_2F_2]$, we recognize that the first elementary reaction is very fast and will have the same rate forward as reverse: $R_f=k_1[NO_2][F_2]=k_2[NO_2F_2]=R_r$. We solve for the concentration of intermediate: $[NO_2F_2]=k_1[NO_2][F_2]/k_2$. We now substitute this expression for $[NO_2F_2]$ into the rate equation: Rate = $(k_1k_3/k_2)[NO_2][F_2]$. Thus the predicted rate law agrees with the experimental rate law.

INTEGRATIVE EXAMPLE

A. **(M)**

(a) The time required for the fixed (*c*) process of souring is three times as long at 3 °C refrigerator temperature (276 K) as at 20 °C room temperature (293 K).

$$\ln\frac{c/t_2}{c/t_1}=\ln\frac{t_1}{t_2}=\ln\frac{64\text{ h}}{3\times 64\text{ h}}=-1.10=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{E_a}{R}\left(\frac{1}{293\text{ K}}-\frac{1}{276\text{ K}}\right)=\frac{E_a}{R}(-2.10\times 10^{-4})$$

$$E_a=\frac{1.10\,R}{2.10\times 10^{-4}\text{ K}^{-1}}=\frac{1.10\times 8.3145\text{ J mol}^{-1}\text{ K}^{-1}}{2.10\times 10^{-4}\text{ K}^{-1}}=4.4\times 10^{4}\text{ J/mol}=44\text{ kJ/mol}$$

(b) Use the E_a determined in part **(a)** to calculate the souring time at 40 °C = 313 K.

$$\ln\frac{t_1}{t_2}=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{4.4\times 10^{4}\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{313\text{ K}}-\frac{1}{293\text{ K}}\right)=-1.15=\ln\frac{t_1}{64\text{ h}}$$

$$\frac{t_1}{64\text{ h}}=e^{-1.15}=0.317\qquad t_1=0.317\times 64\text{ h}=20.\text{ h}$$

B. **(M)** The species A^* is a reactive intermediate. Let's deal with this species by using a steady state approximation.

$d[A^*]/dt = 0 = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$. Solve for $[A^*]$. $k_{-1}[A^*][A] + k_2[A^*] = k_1[A]^2$

$$[A^*]=\frac{k_1[A]^2}{k_{-1}[A]+k_2}\qquad\text{The rate of reaction is: Rate}=k_2[A^*]=\frac{k_2k_1[A]^2}{k_{-1}[A]+k_2}$$

At low pressures ($[A] \sim 0$ and hence $k_2 \gg k_{-1}[A]$), the denominator becomes $\sim k_2$ and the rate law is

$$\text{Rate}=\frac{k_2k_1[A]^2}{k_2}=k_1[A]^2\quad\text{Second-order with respect to [A]}$$

At high pressures ([A] is large and $k_{-1}[A] \gg K_2$), the denominator becomes $\sim k_{-1}[A]$ and the rate law is

$$\text{Rate}=\frac{k_2k_1[A]^2}{k_{-1}[A]}=\frac{k_2k_1[A]}{k_{-1}}\quad\text{First-order with respect to [A]}$$

EXERCISES

Rates of Reactions

1. **(M)** $2A + B \rightarrow C + 3D$ $\qquad -\frac{\Delta[A]}{\Delta t} = 6.2\times 10^{-4}\text{ M s}^{-1}$

(a) $\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = 1/2(6.2\times 10^{-4}\text{ M s}^{-1}) = 3.1\times 10^{-4}\text{ M s}^{-1}$

(b) Rate of disappearance of B $= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = 1/2(6.2\times 10^{-4}\text{ M s}^{-1}) = 3.1\times 10^{-4}\text{ M s}^{-1}$

(c) Rate of appearance of D $= -\frac{3}{2}\frac{\Delta[A]}{\Delta t} = 3(6.2\times 10^{-4}\text{ M s}^{-1}) = 9.3\times 10^{-4}\text{ M s}^{-1}$

2. **(M)** In each case, we draw the tangent line to the plotted curve.

(a) The slope of the line is $\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1.7\text{ M} - 0.6\text{ M}}{400\text{ s} - 1600\text{ s}} = -9.2\times10^{-4}\text{ M s}^{-1}$

reaction rate = $-\frac{\Delta[H_2O_2]}{\Delta t} = 9.2\times10^{-4}\text{ M s}^{-1}$

(b) Read the value where the horizontal line $[H_2O_2]$ = 0.50 M intersects the curve, $\approx 21\underline{5}0$ s or ≈ 36 minutes

<u>3</u>. **(E)** Rate $= -\frac{\Delta[A]}{\Delta t} = -\frac{(0.474\text{ M} - 0.485\text{ M})}{82.4\text{ s} - 71.5\text{ s}} = 1.0\times10^{-3}\text{ M s}^{-1}$

4. **(M)**

(a) Rate $= -\frac{\Delta[A]}{\Delta t} = -\frac{0.1498\text{ M} - 0.1565\text{ M}}{1.00\text{ min} - 0.00\text{ min}} = 0.0067\text{ M min}^{-1}$

Rate $= -\frac{\Delta[A]}{\Delta t} = -\frac{0.1433\text{ M} - 0.1498\text{ M}}{2.00\text{ min} - 1.00\text{ min}} = 0.0065\text{ M min}^{-1}$

(b) The rates are not equal because, in all except zero-order reactions, the rate depends on the concentration of reactant. And, of course, as the reaction proceeds, reactant is consumed and its concentration decreases, so the rate of the reaction decreases.

<u>5.</u> **(M)**

(a) $[A] = [A]_i + \Delta[A] = 0.588\text{ M} - 0.013\text{ M} = 0.575\text{ M}$

(b) $\Delta[A] = 0.565\text{ M} - 0.588\text{ M} = -0.023\text{ M}$

$\Delta t = \Delta[A]\frac{\Delta t}{\Delta[A]} = \frac{-0.023\text{ M}}{-2.2\times10^{-2}\text{ M/min}} = 1.0\text{ min}$

time $= t + \Delta t = (4.40 + 1.0)\text{min} = 5.4\text{ min}$

6. **(M)** Initial concentrations are $[HgCl_2] = 0.105\text{ M}$ and $[C_2O_4{}^{2-}] = 0.300\text{ M}$.

The initial rate of the reaction is $7.1\times10^{-5}\text{ M min}^{-1}$. Recall that the reaction is:

$2\text{ HgCl}_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2\text{ Cl}^-(aq) + 2\text{ CO}_2(g) + Hg_2Cl_2(aq)$.

The rate of reaction equals the rate of disappearance of $C_2O_4^{2-}$. Then, after 1 hour, assuming that the rate is the same as the initial rate,

(a) $$[HgCl_2] = 0.105\text{ M} - \left(7.1\times10^{-5}\frac{\text{mol } C_2O_4{}^{2-}}{\text{L}\cdot\text{ s}}\times\frac{2\text{ mol HgCl}_2}{1\text{ mol } C_2O_4{}^{2-}}\times1\text{ h}\times\frac{60\text{ min}}{1\text{ h}}\right) = 0.096\text{ M}$$

(b) $$[C_2O_4^{2-}] = 0.300\text{ M} - \left(7.1\times10^{-5}\frac{\text{mol}}{\text{L}\cdot\text{min}}\times1\text{ h}\times\frac{60\text{ min}}{1\text{ h}}\right) = 0.296\text{ M}$$

7. (M)

(a) Rate $= \dfrac{-\Delta[\mathrm{A}]}{\Delta t} = \dfrac{\Delta[\mathrm{C}]}{2\Delta t} = 1.76\times10^{-5}\ \mathrm{M\ s^{-1}}$

$$\frac{\Delta[\mathrm{C}]}{\Delta t} = 2\times1.76\times10^{-5}\ \mathrm{M\ s^{-1}} = 3.52\times10^{-5}\ \mathrm{M/s}$$

(b) $\dfrac{\Delta[\mathrm{A}]}{\Delta t} = -\dfrac{\Delta[\mathrm{C}]}{2\Delta t} = -1.76\times10^{-5}\ \mathrm{M\ s^{-1}}$ Assume this rate is constant.

$$[\mathrm{A}] = 0.3580\ \mathrm{M} + \left(-1.76\times10^{-5}\ \mathrm{M\ s^{-1}}\times1.00\,\mathrm{min}\times\frac{60\ \mathrm{s}}{1\,\mathrm{min}}\right) = 0.357\ \mathrm{M}$$

(c) $\dfrac{\Delta[\mathrm{A}]}{\Delta t} = -1.76\times10^{-5}\ \mathrm{M\ s^{-1}}$

$$\Delta t = \frac{\Delta[\mathrm{A}]}{-1.76\times10^{-5}\ \mathrm{M/s}} = \frac{0.3500\ \mathrm{M} - 0.3580\ \mathrm{M}}{-1.76\times10^{-5}\ \mathrm{M/s}} = 4.5\times10^{2}\ \mathrm{s}$$

8. **(M)**

(a) $\dfrac{\Delta n[\mathrm{O_2}]}{\Delta t} = 1.00\ \mathrm{L\ soln}\times\dfrac{5.7\times10^{-4}\ \mathrm{mol\ H_2O_2}}{1\ \mathrm{L\ soln}\cdot\ \mathrm{s}}\times\dfrac{1\ \mathrm{mol\ O_2}}{2\ \mathrm{mol\ H_2O_2}} = 2.9\times10^{-4}\ \mathrm{mol\ O_2/s}$

(b) $\dfrac{\Delta n[\mathrm{O_2}]}{\Delta t} = 2.9\times10^{-4}\ \dfrac{\mathrm{mol\ O_2}}{\mathrm{s}}\times\dfrac{60\ \mathrm{s}}{1\,\mathrm{min}} = 1.7\times10^{-2}\ \mathrm{mol\ O_2\ /\ min}$

(c) $\dfrac{\Delta V[\mathrm{O_2}]}{\Delta t} = 1.7\times10^{-2}\ \dfrac{\mathrm{mol\ O_2}}{\mathrm{min}}\times\dfrac{22{,}414\ \mathrm{mL\ O_2\ at\ STP}}{1\ \mathrm{mol\ O_2}} = \dfrac{3.8\times10^{2}\ \mathrm{mL\ O_2\ at\ STP}}{\mathrm{min}}$

9. **(M)** Notice that, for every 1000 mmHg drop in the pressure of A(g), there will be a corresponding 2000 mmHg rise in the pressure of B(g) plus a 1000 mmHg rise in the pressure of C(g).

(a) We set up the calculation with three lines of information below the balanced equation: (1) the initial conditions, (2) the changes that occur, which are related to each other by reaction stoichiometry, and (3) the final conditions, which simply are initial conditions + changes.

	A(g)	→	2B(g)	+	C(g)
Initial	1000. mmHg		0. mmHg		0. mmHg
Changes	–1000. mmHg		+2000. mmHg		+1000. mmHg
Final	0. mmHg		2000. MmHg		1000. mmHg

Total final pressure = 0. mmHg + 2000. mmHg + 1000. mmHg = 3000. mmHg

(b)

	A(g)	→	2B(g)	+	C(g)
Initial	1000. mmHg		0. mmHg		0. mmHg
Changes	–200. mmHg		+400. mmHg		+200. mmHg
Final	800 mmHg		400. mmHg		200. mmHg

Total pressure = 800. mmHg + 400. mmHg + 200. mmHg = 1400. mmHg

10. **(M)**

(a) We will use the ideal gas law to determine N_2O_5 pressure

$$P\{N_2O_5\} = \frac{nRT}{V} = \frac{\left(1.00\ g \times \frac{1\ mol\, N_2O_5}{108.0\, g}\right) \times 0.08206 \frac{L\ atm}{mol\ K} \times (273 + 65)\ K}{15\ L} \times \frac{760\ mmHg}{1\ atm} = 13\ mmHg$$

(b) After 2.38 min, one half-life passes. The initial pressure of N_2O_5 decreases by half to 6.5 mmHg.

(c) From the balanced chemical equation, the reaction of 2 mol $N_2O_5(g)$ produces 4 mol $NO_2(g)$ and 1 mol $O_2(g)$. That is, the consumption of 2 mol of reactant gas produces 5 mol of product gas. When measured at the same temperature and confined to the same volume, pressures will behave as amounts: the reaction of 2 mmHg of reactant produces 5 mmHg of product.

$$P_{total} = 13\ mmHg\ N_2O_5\ _{(initially)} - 6.5\ mmHg\ N_2O_5\ _{(reactant)} + \left(6.5\ mmHg_{(reactant)} \times \frac{5\ mmHg_{(product)}}{2\ mmHg_{(reactant)}}\right)$$

$$= (13 - 6.5 + 16)\ mmHg = 23\ mmHg$$

Method of Initial Rates

11. **(M)**

(a) From Expt. 1 to Expt. 3, [A] is doubled, while [B] remains fixed. This causes the rate to increases by a factor of $\frac{6.75 \times 10^{-4}\ M\ s^{-1}}{3.35 \times 10^{-4}\ M\ s^{-1}} = 2.01 \approx 2$.

Thus, the reaction is first-order with respect to A.

From Expt. 1 to Expt. 2, [B] doubles, while [A] remains fixed. This causes the rate to increases by a factor of $\frac{1.35 \times 10^{-3}\ M\ s^{-1}}{3.35 \times 10^{-4}\ M\ s^{-1}} = 4.03 \approx 4$.

Thus, the reaction is second-order with respect to B.

(b) Overall reaction order = order with respect to A + order with respect to B = 1 + 2 = 3. The reaction is third-order overall.

(c) $\text{Rate} = 3.35 \times 10^{-4}\ M\ s^{-1} = k(0.185\ M)(0.133\ M)^2$

$$k = \frac{3.35 \times 10^{-4}\ M\ s^{-1}}{(0.185\ M)(0.133\ M)^2} = 0.102\ M^{-2}\ s^{-1}$$

12. **(M)** From Expt. 1 and Expt. 2 we see that [B] remains fixed while [A] triples. As a result, the initial rate increases from 4.2×10^{-3} M/min to 1.3×10^{-2} M/min, that is, the initial reaction rate triples. Therefore, the reaction is first-order in [A]. Between Expt. 2 and Expt. 3, we see that [A] doubles, which would double the rate, and [B] doubles. As a consequence, the initial rate goes from 1.3×10^{-2} M/min to 5.2×10^{-2} M/min, that is, the rate quadruples. Since an additional doubling of the rate is due to the change in [B], the reaction is first-order in [B]. Now we determine the value of the rate constant.

$$\text{Rate} = k[\text{A}]^1[\text{B}]^1 \qquad k = \frac{\text{Rate}}{[\text{A}][\text{B}]} = \frac{5.2\times10^{-2}\ \text{M/min}}{3.00\ \text{M}\times 3.00\ \text{M}} = 5.8\times10^{-3}\ \text{L mol}^{-1}\text{min}^{-1}$$

The rate law is $\text{Rate} = (5.8\times10^{-3}\ \text{L mol}^{-1}\text{min}^{-1})[\text{A}]^1[\text{B}]^1$.

13. **(M)** From Experiment 1 to 2, [NO] remains constant while [Cl_2] is doubled. At the same time the initial rate of reaction is found to double. Thus, the reaction is first-order with respect to [Cl_2], since dividing reaction 2 by reaction 1 gives $2 = 2^x$ when $x = 1$. From Experiment 1 to 3, [Cl_2] remains constant, while [NO] is doubled, resulting in a quadrupling of the initial rate of reaction. Thus, the reaction must be second-order in [NO], since dividing reaction 3 by reaction 1 gives $4 = 2^x$ when $x = 2$. Overall the reaction is third-order: Rate = $k\,[\text{NO}]^2[\text{Cl}_2]$. The rate constant may be calculated from any one of the experiments. Using data from Exp. 1,

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{Cl}_2]} = \frac{2.27\times10^{-5}\ \text{M s}^{-1}}{(0.0125\ \text{M})^2(0.0255\,\text{M})} = 5.70\ \text{M}^{-2}\,\text{s}^{-1}$$

14. **(M)**

(a) From Expt. 1 to Expt. 2, [B] remains constant at 1.40 M and [C] remains constant at 1.00 M, but [A] is halved $(\times 0.50)$. At the same time the rate is halved $(\times 0.50)$. Thus, the reaction is first-order with respect to A, since $0.50^x = 0.50$ when $x = 1$.
From Expt. 2 to Expt. 3, [A] remains constant at 0.70 M and [C] remains constant at 1.00 M, but [B] is halved $(\times 0.50)$, from 1.40 M to 0.70 M. At the same time, the rate is quartered $(\times 0.25)$. Thus, the reaction is second-order with respect to B, since $0.50^y = 0.25$ when $y = 2$.

From Expt. 1 to Expt. 4, [A] remains constant at 1.40 M and [B] remains constant at 1.40 M, but [C] is halved $(\times 0.50)$, from 1.00 M to 0.50 M. At the same time, the rate is increased by a factor of 2.0.

$$\left[\text{Rate}_4 = 16\ \text{Rate}_3 = 16\times\frac{1}{4}\text{Rate}_2 = 4\ \text{Rate}_2 = 4\times\frac{1}{2}\text{Rate}_1 = 2\times\text{Rate}_1.\right]$$

Thus, the order of the reaction with respect to C is -1, since $0.5^z = 2.0$ when $z = -1$.

(b) $$\text{rate}_5 = k(0.70\ \text{M})^1(0.70\ \text{M})^2(0.50\ \text{M})^{-1} = k\left(\frac{1.40\ \text{M}}{2}\right)^1\left(\frac{1.40\ \text{M}}{2}\right)^2\left(\frac{1.00\ \text{M}}{2}\right)^{-1}$$

$$= k\,\tfrac{1}{2}^1(1.40\ \text{M})^1\,\tfrac{1}{2}^2(1.40\ \text{M})^2\,\tfrac{1}{2}^{-1}(1.00\ \text{M})^{-1} = \text{rate}_1\left(\frac{1}{2}\right)^{1+2-1} = \text{rate}_1\left(\frac{1}{2}\right)^2 = \tfrac{1}{4}\text{rate}_1$$

This is based on $\text{rate}_1 = k(1.40\ \text{M})^1(1.40\ \text{M})^2(1.00\ \text{M})^{-1}$

First-Order Reactions

15. **(E)**

(a) TRUE The rate of the reaction does decrease as more and more of B and C are formed, but not because more and more of B and C are formed. Rather, the rate decreases because the concentration of A must decrease to form more and more of B and C.

(b) FALSE The time required for one half of substance A to react—the half-life—is independent of the quantity of A present.

16. **(E)**

(a) FALSE For first-order reactions, a plot of ln [A] or log [A] vs. time yields a straight line. A graph of [A] vs. time yields a curved line.

(b) TRUE The rate of formation of C is related to the rate of disappearance of A by the stoichiometry of the reaction.

17. **(M)**

(a) Since the half-life is 180 s, after 900 s five half-lives have elapsed, and the original quantity of A has been cut in half five times.

$$\text{final quantity of A} = (0.5)^5 \times \text{ initial quantity of A} = 0.03125 \times \text{ initial quantity of A}$$

About 3.13% of the original quantity of A remains unreacted after 900 s.

or

More generally, we would calculate the value of the rate constant, k, using

$k = \dfrac{\ln 2}{t_{1/2}} = \dfrac{0.693}{180\text{ s}} = 0.00385\text{ s}^{-1}$ Now ln(% unreacted) = $-kt = -0.00385\text{ s}^{-1} \times (900\text{s}) = -3.46\underline{5}$

(% unreacted) = 0.0313 × 100% = 3.13% of the original quantity.

(b) $\text{Rate} = k[\text{A}] = 0.00385\text{ s}^{-1} \times 0.50\text{ M} = 0.00193\text{ M/s}$

18. **(M)**

(a) The reaction is first-order, thus

$$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln\frac{0.100\text{ M}}{0.800\text{ M}} = -54\,\text{min}(k) \qquad k = -\frac{-2.08}{54\text{ min}} = 0.038\underline{5}\text{ min}^{-1}$$

We may now determine the time required to achieve a concentration of 0.025 M

$$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln\frac{0.025\text{ M}}{0.800\text{ M}} = -0.038\underline{5}\text{ min}^{-1}(t) \qquad t = \frac{-3.4\underline{7}}{-0.038\underline{5}\text{ min}^{-1}} = 90.\text{ min}$$

(b) Since we know the rate constant for this reaction (see above),

$$\text{Rate} = k[\text{A}]^1 = 0.038\underline{5}\text{ min}^{-1} \times 0.025\text{ M} = 9.6 \times 10^{-4}\text{ M/min}$$

19. **(M)**

(a) The mass of A has decreased to one fourth of its original value, from 1.60 g to 0.40 g. Since $\frac{1}{4}=\frac{1}{2}\times\frac{1}{2}$, we see that two half-lives have elapsed.

Thus, $2\times t_{1/2}=38\text{ min}$, or $t_{1/2}=19\text{ min}$.

(b) $k = 0.693/t_{1/2} = \dfrac{0.693}{19\,\text{min}} = 0.036\,\text{min}^{-1}$ $\quad \ln\dfrac{[\text{A}]_t}{[\text{A}]_0} = -kt = -0.036\text{ min}^{-1}\times 60\,\text{min} = -2.2$

$$\frac{[\text{A}]_t}{[\text{A}]_0} = \text{e}^{-2.2} = 0.1\underline{1} \quad \text{or} \quad [\text{A}]_t = [\text{A}]_0\; e^{-kt} = 1.60\text{ g A}\times 0.1\underline{1} = 0.1\underline{8}\text{ g A}$$

20. **(M)**

(a) $\ln\dfrac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln\dfrac{0.632\text{ M}}{0.816\text{ M}} = -0.256 \qquad k = -\dfrac{-0.256}{16.0\text{ min}} = 0.0160\text{ min}^{-1}$

(b) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.0160\text{ min}^{-1}} = 43.3\text{ min}$

(c) We need to solve the integrated rate equation to find the elapsed time.

$$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln\frac{0.235\text{ M}}{0.816\text{ M}} = -1.245 = -0.0160\,\text{min}^{-1}\times t \qquad t = \frac{-1.245}{-0.0160\,\text{min}^{-1}} = 77.8\,\text{min}$$

(d) $\ln\dfrac{[\text{A}]}{[\text{A}]_0} = -kt$ becomes $\dfrac{[\text{A}]}{[\text{A}]_0} = e^{-kt}$ which in turn becomes

$$[\text{A}] = [\text{A}]_0\; e^{-kt} = 0.816\text{ M}\ \exp\left(-0.0160\,\text{min}^{-1}\times 2.5\text{ h}\times\frac{60\,\text{min}}{1\text{ h}}\right) = 0.816\times 0.0907 = 0.074\text{ M}$$

21. **(M)** We determine the value of the first-order rate constant and from that we can calculate the half-life. If the reactant is 99% decomposed in 137 min, then only 1% (0.010) of the initial concentration remains.

$$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln\frac{0.010}{1.000} = -4.61 = -k\times 137\text{min} \qquad k = \frac{-4.61}{-137\text{ min}} = 0.0336\text{ min}^{-1}$$

$$t_{1/2} = \frac{0.0693}{k} = \frac{0.693}{0.0336\text{ min}^{-1}} = 20.6\text{ min}$$

22. **(E)** If 99% of the radioactivity of ${}^{32}\text{P}$ is lost, 1% (0.010) of that radioactivity remains. First we compute the value of the rate constant from the half-life. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{14.3\text{ d}} = 0.0485\text{ d}^{-1}$

Then we use the integrated rate equation to determine the elapsed time.

$$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt \quad t = -\frac{1}{k}\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -\frac{1}{0.0485\text{ d}^{-1}}\ln\frac{0.010}{1.000} = 95\text{ days}$$

23. **(D)**

(a) $$\ln\left(\frac{\frac{35}{100}[\text{A}]_0}{[\text{A}]_0}\right) = \ln(0.35) = -kt = (-4.81\times10^{-3}\text{ min}^{-1})t \qquad t = 218\text{ min.}$$

Note: We did not need to know the initial concentration of acetoacetic acid to answer the question.

(b) Let's assume that the reaction takes place in a 1.00L container.

$$10.0\text{ g acetoacetic acid}\times\frac{1\text{ mol acetoacetic acid}}{102.090\text{ g acetoacetic acid}} = 0.0979\underline{5}\text{ mol acetoacetic acid.}$$

After 575 min. (~ 4 half lives, hence, we expect ~ 6.25% remains as a rough approximation), use integrated form of the rate law to find $[\text{A}]_t$ = 575 min.

$$\ln\left(\frac{[\text{A}]_t}{[\text{A}]_0}\right) = -kt = (-4.81\times10^{-3}\text{ min}^{-1})(575\text{ min}) = -2.76\underline{6}$$

$$\frac{[\text{A}]_t}{[\text{A}]_0} = e^{-2.76\underline{6}} = 0.0629\underline{3}\ (\sim 6.3\%\text{ remains}) \qquad \frac{[\text{A}]_t}{0.09795\,\text{moles}} = 0.063 \quad [\text{A}]_t = 6.2\times10^{-3}$$

moles.

$[\text{A}]_{\text{reacted}} = [\text{A}]_\text{o} - [\text{A}]_\text{t} = (0.098 - 6.2\times10^{-3})$ moles = 0.092 moles acetoacetic acid. The stoichiometry is such that for every mole of acetoacetic acid consumed, one mole of CO_2 forms. Hence, we need to determine the volume of 0.0918 moles CO_2 at 24.5 °C (297.6$\underline{5}$ K) and 748 torr (0.984 atm) by using the Ideal Gas law.

$$V = \frac{nRT}{P} = \frac{0.0918\,\text{mol}\left(0.08206\,\frac{\text{L atm}}{\text{K mol}}\right)297.65\,\text{K}}{0.984\,\text{atm}} = 2.3\text{ L CO}_2$$

24. **(M)**

(a) $$\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt = \ln\frac{2.5\text{ g}}{80.0\text{ g}} = -3.47 = -6.2\times10^{-4}\text{ s}^{-1}t$$

$$t = \frac{3.47}{6.2\times10^{-4}\text{ s}^{-1}} = 5.6\times10^{3}\text{ s} \approx 93\text{ min}$$

We substituted masses for concentrations, because the same substance (with the same molar mass) is present initially at time t, and because it is a closed system.

(b) $$\text{amount } O_2 = 77.5 \text{ g } N_2O_5 \times \frac{1 \text{ mol } N_2O_5}{108.0 \text{ g } N_2O_5} \times \frac{1 \text{ mol } O_2}{2 \text{ mol } N_2O_5} = 0.359 \text{ mol } O_2$$

$$V = \frac{nRT}{P} = \frac{0.359 \text{ mol } O_2 \times 0.08206 \ \frac{\text{L atm}}{\text{mol K}} \times (45+273) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 9.56 \text{ L } O_2$$

<u>25.</u> **(D)**

(a) If the reaction is first-order, we will obtain the same value of the rate constant from several sets of data.

$$\ln\frac{[A]_t}{[A]_0} = -kt = \ln\frac{0.497 \text{ M}}{0.600 \text{ M}} = -k \times 100 \text{ s} = -0.188, \quad k = \frac{0.188}{100 \text{ s}} = 1.88 \times 10^{-3} \text{ s}^{-1}$$

$$\ln\frac{[A]_t}{[A]_0} = -kt = \ln\frac{0.344 \text{ M}}{0.600 \text{ M}} = -k \times 300 \text{ s} = -0.556, \quad k = \frac{0.556}{300 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

$$\ln\frac{[A]_t}{[A]_0} = -kt = \ln\frac{0.285 \text{ M}}{0.600 \text{ M}} = -k \times 400 \text{ s} = -0.744, \quad k = \frac{0.744}{400 \text{ s}} = 1.86 \times 10^{-3} \text{ s}^{-1}$$

$$\ln\frac{[A]_t}{[A]_0} = -kt = \ln\frac{0.198 \text{ M}}{0.600 \text{ M}} = -k \times 600 \text{ s} = -1.109, \quad k = \frac{1.109}{600 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

$$\ln\frac{[A]_t}{[A]_0} = -kt = \ln\frac{0.094 \text{ M}}{0.600 \text{ M}} = -k \times 1000 \text{ s} = -1.854, \quad k = \frac{1.854}{1000 \text{ s}} = 1.85 \times 10^{-3} \text{ s}^{-1}$$

The virtual constancy of the rate constant throughout the time of the reaction confirms that the reaction is first-order.

(b) For this part, we assume that the rate constant equals the average of the values obtained in part (a).

$$k = \frac{1.88 + 1.85 + 1.86 + 1.85}{4} \times 10^{-3} \text{ s}^{-1} = 1.86 \times 10^{-3} \text{ s}^{-1}$$

(c) We use the integrated first-order rate equation:

$$[\text{ A}]_{750} = [\text{ A}]_0 \exp(-kt) = 0.600 \text{ M} \exp\left(-1.86 \times 10^{-3} \text{ s}^{-1} \times 750 \text{ s}\right)$$

$$[\text{ A}]_{750} = 0.600 \text{ M } e^{-1.40} = 0.148 \text{ M}$$

26. **(D)**

(a) If the reaction is first-order, we will obtain the same value of the rate constant from several sets of data.

$$\ln\frac{P_t}{P_0} = -kt = \ln\frac{264 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 390 \text{ s} = -0.167, \quad k = \frac{0.167}{390 \text{ s}} = 4.28 \times 10^{-4} \text{ s}^{-1}$$

$$\ln\frac{P_t}{P_0} = -kt = \ln\frac{224 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 777 \text{ s} = -0.331, \quad k = \frac{0.331}{777 \text{ s}} = 4.26 \times 10^{-4} \text{ s}^{-1}$$

$$\ln\frac{P_t}{P_0} = -kt = \ln\frac{187 \text{ mmHg}}{312 \text{ mmHg}} = -k \times 1195 \text{ s} = -0.512, \quad k = \frac{0.512}{1195 \text{ s}} = 4.28 \times 10^{-4} \text{ s}^{-1}$$

$$\ln\frac{P_t}{P_0} = -kt = \ln\frac{78.5\text{ mmHg}}{312\text{ mmHg}} = -k \times 3155\text{ s} = -1.38, \qquad k = \frac{1.38}{3155\text{ s}} = 4.37\times10^{-4}\ \text{s}^{-1}$$

The virtual constancy of the rate constant confirms that the reaction is first-order.

(b) For this part we assume the rate constant is the average of the values in part (a): $4.3\times10^{-4}\ \text{s}^{-1}$.

(c) At 390 s, the pressure of dimethyl ether has dropped to 264 mmHg. Thus, an amount of dimethyl ether equivalent to a pressure of $(312\text{ mmHg} - 264\text{ mmHg} =)$ 48 mmHg has decomposed. For each 1 mmHg pressure of dimethyl ether that decomposes, 3 mmHg of pressure from the products is produced. Thus, the increase in the pressure of the products is $3\times48 = 144$ mmHg. The total pressure at this point is $264\text{ mmHg} + 144\text{ mmHg} = 408$ mmHg. Below, this calculation is done in a more systematic fashion:

	$(CH_3)_2O(g)$ $\rightarrow$	$CH_4(g)$ +	$H_2(g)$ +	$CO(g)$
Initial	312 mmHg	0 mmHg	0 mmHg	0 mmHg
Changes	– 48 mmHg	+ 48 mmHg	+ 48 mmHg	+ 48 mmHg
Final	264 mmHg	48 mmHg	48 mmHg	48 mmHg

$$P_{\text{total}} = P_{\text{DME}} + P_{\text{methane}} + P_{\text{hydrogen}} + P_{\text{CO}}$$
$$= 264\text{ mmHg} + 48\text{ mmHg} + 48\text{ mmHg} + 48\text{ mmHg} = 408\text{ mmHg}$$

(d) This question is solved in the same manner as part (c). The results are summarized below.

	$(CH_3)_2O(g)$ $\rightarrow$	$CH_4(g)$ +	$H_2(g)$ +	$CO(g)$
Initial	312 mmHg	0 mmHg	0 mmHg	0 mmHg
Changes	-312 mmHg	$+312$ mmHg	$+312$ mmHg	$+312$ mmHg
Final	0 mmHg	312 mmHg	312 mmHg	312 mmHg

$$P_{\text{total}} = P_{\text{DME}} + P_{\text{methane}} + P_{\text{hydrogen}} + P_{\text{CO}}$$
$$= 0\text{ mmHg} + 312\text{ mmHg} + 312\text{ mmHg} + 312\text{ mmHg} = 936\text{ mmHg}$$

(e) We first determine P_{DME} at 1000 s. $\ln\dfrac{P_{1000}}{P_0} = -kt = -4.3\times10^{-4}\ \text{s}^{-1}\times1000\text{ s} = -0.43$

$$\frac{P_{1000}}{P_0} = e^{-0.43} = 0.65 \qquad P_{1000} = 312\text{ mmHg}\times0.65 = 203\text{ mmHg}$$

Then we use the same approach as was used for parts (c) and (d)

	$(CH_3)_2O(g)$ $\rightarrow$	$CH_4(g)$ +	$H_2(g)$ +	$CO(g)$
Initial	312 mmHg	0 mmHg	0 mmHg	0 mmHg
Changes	-109 mmHg	$+109$ mmHg	$+109$ mmHg	$+109$ mmHg
Final	203 mmHg	109 mmHg	109 mmHg	109 mmHg

$$P_{\text{total}} = P_{\text{DME}} + P_{\text{methane}} + P_{\text{hydrogen}} + P_{\text{CO}}$$
$$= 203\text{ mmHg} + 109\text{ mmHg} + 109\text{ mmHg} + 109\text{ mmHg} = 530.\text{ mmHg}$$

Reactions of Various Orders

27. **(M)**

(a) Set II is data from a zero-order reaction. We know this because the rate of set II is constant. $0.25\ \text{M}/25\ \text{s} = 0.010\ \text{M s}^{-1}$. Zero-order reactions have constant rates of reaction.

(b) A first-order reaction has a constant half-life. In set I, the first half-life is slightly less than 75 sec, since the concentration decreases by slightly more than half (from 1.00 M to 0.47 M) in 75 s. Again, from 75 s to 150 s the concentration decreases from 0.47 M to 0.22 M, again by slightly more than half, in a time of 75 s. Finally, two half-lives should see the concentration decrease to one-fourth of its initial value. This, in fact, is what we see. From 100 s to 250 s, 150 s of elapsed time, the concentration decreases from 0.37 M to 0.08 M, i.e., to slightly less than one-fourth of its initial value. Notice that we cannot make the same statement of constancy of half-life for set III. The first half-life is 100 s, but it takes more than 150 s (from 100 s to 250 s) for [A] to again decrease by half.

(c) For a second-order reaction, $1/[\text{A}]_t - 1/[\text{A}]_0 = kt$. For the initial 100 s in set III, we have

$$\frac{1}{0.50\ \text{M}} - \frac{1}{1.00\ \text{M}} = 1.0\ \text{L mol}^{-1} = k\,100\ \text{s}, \qquad k = 0.010\ \text{L mol}^{-1}\ \text{s}^{-1}$$

For the initial 200 s, we have

$$\frac{1}{0.33\ \text{M}} - \frac{1}{1.00\ \text{M}} = 2.0\ \text{L mol}^{-1} = k\ 200\ \text{s}, \qquad k = 0.010\ \text{L mol}^{-1}\ \text{s}^{-1}$$

Since we obtain the same value of the rate constant using the equation for second-order kinetics, set III must be second-order.

28. **(E)** For a zero-order reaction (set II), the slope equals the rate constant:
$k = -\Delta[\text{A}]/\Delta t = 1.00\ \text{M}/100\ \text{s} = 0.0100\ \text{M/s}$

29. **(M)** Set I is the data for a first-order reaction; we can analyze those items of data to determine the half-life. In the first 75 s, the concentration decreases by a bit more than half. This implies a half-life slightly less than 75 s, perhaps 70 s. This is consistent with the other time periods noted in the answer to Review Question 18 (b) and also to the fact that in the 150-s interval from 50 s to 200 s, the concentration decreases from 0.61 M to 0.14 M, which is a bit more than a factor-of-four decrease. The factor-of-four decrease, to one-fourth of the initial value, is what we would expect for two successive half-lives. We can determine the half-life more accurately, by obtaining a value of k from the relation $\ln\left([\text{A}]_t/[\text{A}]_0\right) = -kt$ followed by $t_{1/2} = 0.693/k$ For instance, $\ln(0.78/1.00) = -k\,(25\ \text{s})$;
$k = 9.9\underline{4} \times 10^{-3}\ \text{s}^{-1}$. Thus, $t_{1/2} = 0.693/9.9\underline{4} \times 10^{-3}\ \text{s}^{-1} = 70\ \text{s}$.

30. **(E)** We can determine an approximate initial rate by using data from the first 25 s.

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.80\ \text{M} - 1.00\ \text{M}}{25\ \text{s} - 0\ \text{s}} = 0.0080\ \text{M s}^{-1}$$

31. **(M)** The approximate rate at 75 s can be taken as the rate over the time period from 50 s to 100 s.

(a) $\text{Rate}_{\text{II}} = -\dfrac{\Delta[\text{A}]}{\Delta t} = -\dfrac{0.00\ \text{M} - 0.50\ \text{M}}{100\ \text{s} - 50\ \text{s}} = 0.010\ \text{M s}^{-1}$

(b) $\text{Rate}_{\text{I}} = -\dfrac{\Delta[\text{A}]}{\Delta t} = -\dfrac{0.37\ \text{M} - 0.61\ \text{M}}{100\ \text{s} - 50\ \text{s}} = 0.0048\ \text{M s}^{-1}$

(c) $\text{Rate}_{\text{III}} = -\dfrac{\Delta[\text{A}]}{\Delta t} = -\dfrac{0.50\ \text{M} - 0.67\ \text{M}}{100\ \text{s} - 50\ \text{s}} = 0.0034\ \text{M s}^{-1}$

Alternatively we can use [A] at 75 s (the values given in the table) in the relationship $\text{Rate} = k[\text{A}]^m$, where $m = 0$, 1, or 2.

(a) $\text{Rate}_{\text{II}} = 0.010\ \text{M s}^{-1} \times (0.25\ \text{mol/L})^0 = 0.010\ \text{M s}^{-1}$

(b) Since $t_{1/2} = 70\,\text{s}$, $k = 0.693/70\,\text{s} = 0.0099\,\text{s}^{-1}$

$\text{Rate}_{\text{I}} = 0.0099\,s^{-1} \times (0.47\,\text{mol/L})^1 = 0.0047\,\text{M}\,\text{s}^{-1}$

(c) $\text{Rate}_{\text{III}} = 0.010\ \text{L mol}^{-1}\ \text{s}^{-1} \times (0.57\ \text{mol/L})^2 = 0.0032\ \text{M s}^{-1}$

32. **(M)** We can combine the approximate rates from Exercise 31, with the fact that 10 s have elapsed, and the concentration at 100 s.

(a) $[\text{A}]_{\text{II}} = 0.00\ \text{M}$ There is no reactant left after 100 s.

(b) $[\text{A}]_{\text{I}} = [\text{A}]_{100} - (10\ \text{s} \times\ \text{rate}) = 0.37\ \text{M} - (10\ \text{s} \times 0.0047\ \text{M s}^{-1}) = 0.32\ \text{M}$

(c) $[\text{A}]_{\text{III}} = [\text{A}]_{100} - (10\ \text{s} \times\ \text{rate}) = 0.50\ \text{M} - (10\ \text{s} \times 0.0032\ \text{M s}^{-1}) = 0.47\ \text{M}$

33. **(E)** Substitute the given values into the rate equation to obtain the rate of reaction.

$\text{Rate} = k[\text{A}]^2[\text{B}]^0 = (0.0103\ \text{M}^{-1}\text{min}^{-1})(0.116\ \text{M})^2\,(3.83\ \text{M})^0 = 1.39 \times 10^{-4}\ \text{M}/\text{min}$

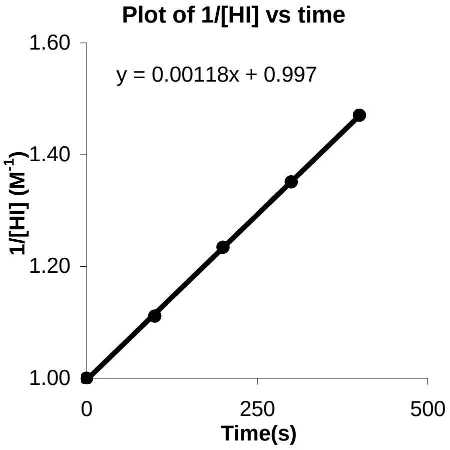
34. **(M)**

(a) A first-order reaction has a constant half-life. Thus, half of the initial concentration remains after 30.0 minutes, and at the end of another half-life—60.0 minutes total—half of the concentration present at 30.0 minutes will have reacted: the concentration has decreased to one-quarter of its initial value. Or, we could say that the reaction is 75% complete after two half-lives—60.0 minutes.

(b) A zero-order reaction proceeds at a constant rate. Thus, if the reaction is 50% complete in 30.0 minutes, in twice the time—60.0 minutes—the reaction will be 100% complete. (And in one-fifth the time—6.0 minutes—the reaction will be 10% complete. Alternatively, we can say that the rate of reaction is 10%/6.0 min.) Therefore, the time required for the reaction to be 75% complete $= 75\% \times \dfrac{60.0\ \text{min}}{100\%} = 45\ \text{min}.$

35. **(M)** For reaction: $HI(g) \rightarrow 1/2\ H_2(g) + 1/2\ I_2(g)$ (700 K)

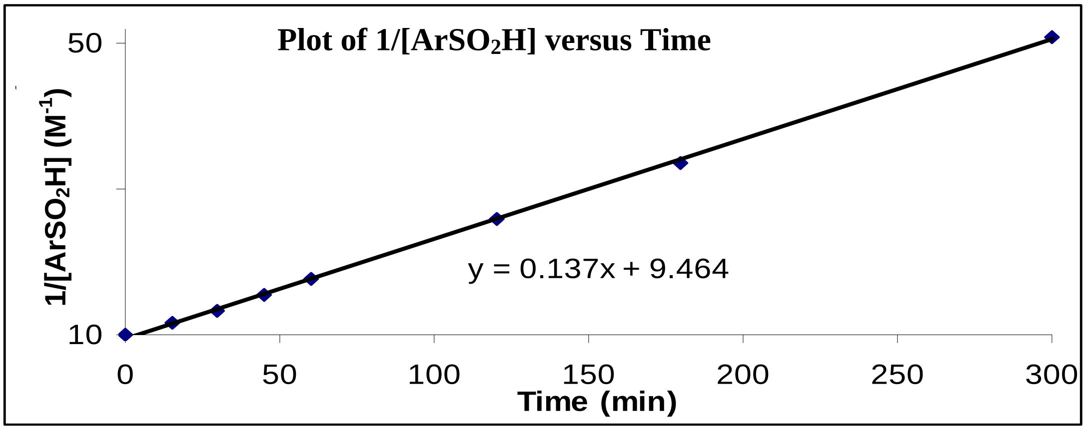
Time (s)	[HI] (M)	ln[HI]	1/[HI](M^{-1})
0	1.00	0	1.00
100	0.90	–0.105	1.11
200	0.81	–0.211	$1.23\underline{5}$
300	0.74	–0.301	1.35
400	0.68	–0.386	1.47



From data above, a plot of 1/[HI] vs. *t* yields a straight line. The reaction is second-order in HI at 700 K. Rate = $k[HI]^2$. The slope of the line = $k = 0.00118\ M^{-1}s^{-1}$

36. **(D)**

(a) We can graph $1/[ArSO_2H]$ vs. time and obtain a straight line. We can also graph $[ArSO_2H]$ vs. time and $\ln([ArSO_2H])$ vs. time to demonstrate that they do not yield a straight line. Only the plot of $1/[ArSO_2H]$ versus time is shown.



The linearity of the line indicates that the reaction is second-order.

(b) We solve the rearranged integrated second-order rate law for the rate constant, using the longest time interval. $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$ $\qquad \frac{1}{t}\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = k$

$$k = \frac{1}{300\text{ min}}\left(\frac{1}{0.0196\text{ M}} - \frac{1}{0.100\text{ M}}\right) = 0.137\text{ L mol}^{-1}\text{min}^{-1}$$

(c) We use the same equation as in part (b), but solved for t, rather than k.

$$t = \frac{1}{k}\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = \frac{1}{0.137\text{ L mol}^{-1}\text{min}^{-1}}\left(\frac{1}{0.0500\text{ M}} - \frac{1}{0.100\text{ M}}\right) = 73.0\text{ min}$$

(d) We use the same equation as in part (b), but solve for t , rather than k .

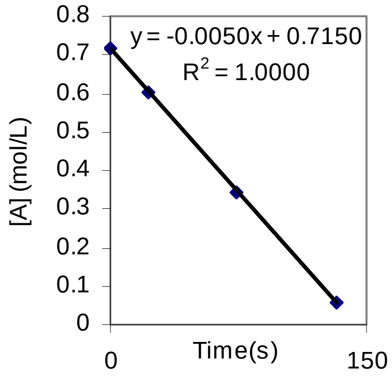
$$t=\frac{1}{k}\left(\frac{1}{[\mathrm{A}]_t}-\frac{1}{[\mathrm{A}]_0}\right)=\frac{1}{0.137\ \mathrm{L\ mol^{-1}min^{-1}}}\left(\frac{1}{0.0250\ \mathrm{M}}-\frac{1}{0.100\ \mathrm{M}}\right)=219\ \mathrm{min}$$

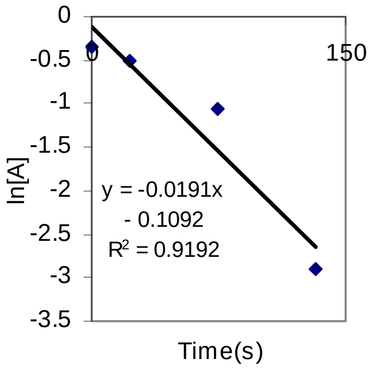
(e) We use the same equation as in part (b), but solve for t , rather than k .

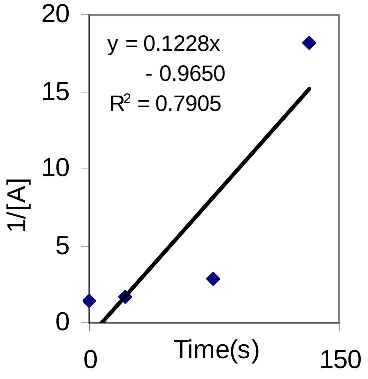
$$t=\frac{1}{k}\left(\frac{1}{[\mathrm{A}]_t}-\frac{1}{[\mathrm{A}]_0}\right)=\frac{1}{0.137\ \mathrm{L\ mol^{-1}min^{-1}}}\left(\frac{1}{0.0350\ \mathrm{M}}-\frac{1}{0.100\ \mathrm{M}}\right)=136\ \mathrm{min}$$

37. **(M)**

(a) Plot [A] vs *t*, ln[A] vs *t*, and 1/[A] vs *t* and see which yields a straight line.







Clearly we can see that the reaction is zero-order in reactant A with a rate constant of 5.0×10^{-3}.

(b) The half-life of this reaction is the time needed for one half of the initial [A] to react.

Thus, $\Delta[\mathrm{A}]=0.715\ \mathrm{M}\div 2=0.358\,\mathrm{M}$ and $t_{1/2}=\dfrac{0.358\ \mathrm{M}}{5.0\times10^{-3}\ \mathrm{M/s}}=72\ \mathrm{s}$.

38. **(D)**

(a) We can either graph $1/[C_4H_6]$ vs. time and obtain a straight line, or we can determine the second-order rate constant from several data points. Then, if k indeed is a constant, the reaction is demonstrated to be second-order. We shall use the second technique in this case. First we do a bit of algebra.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \qquad \frac{1}{t}\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = k$$

$$k = \frac{1}{12.18 \text{ min}}\left(\frac{1}{0.0144 \text{ M}} - \frac{1}{0.0169 \text{ M}}\right) = 0.843 \text{ L mol}^{-1}\text{min}^{-1}$$

$$k = \frac{1}{24.55 \text{ min}}\left(\frac{1}{0.0124 \text{ M}} - \frac{1}{0.0169 \text{ M}}\right) = 0.875 \text{ L mol}^{-1}\text{min}^{-1}$$

$$k = \frac{1}{42.50 \text{ min}}\left(\frac{1}{0.0103 \text{ M}} - \frac{1}{0.0169 \text{ M}}\right) = 0.892 \text{ L mol}^{-1}\text{min}^{-1}$$

$$k = \frac{1}{68.05 \text{ min}}\left(\frac{1}{0.00845 \text{ M}} - \frac{1}{0.0169 \text{ M}}\right) = 0.870 \text{ L mol}^{-1}\text{min}^{-1}$$

The fact that each calculation generates similar values for the rate constant indicates that the reaction is second-order.

(b) The rate constant is the average of the values obtained in part (a).

$$k = \frac{0.843 + 0.875 + 0.892 + 0.870}{4} \text{ L mol}^{-1}\text{min}^{-1} = 0.87 \text{ L mol}^{-1}\text{min}^{-1}$$

(c) We use the same equation as in part (a), but solve for t, rather than k.

$$t = \frac{1}{k}\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = \frac{1}{0.870 \text{ L mol}^{-1}\text{min}^{-1}}\left(\frac{1}{0.00423 \text{ M}} - \frac{1}{0.0169 \text{ M}}\right) = 2.0\times10^2 \text{ min}$$

(d) We use the same equation as in part (a), but solve for t, rather than k.

$$t = \frac{1}{k}\left(\frac{1}{[A]_t} - \frac{1}{[A]_0}\right) = \frac{1}{0.870 \text{ L mol}^{-1}\text{min}^{-1}}\left(\frac{1}{0.0050 \text{ M}} - \frac{1}{0.0169 \text{ M}}\right) = 1.6\times10^2 \text{ min}$$

39. **(E)**

(a) $$\text{initial rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1.490 \text{ M} - 1.512 \text{ M}}{1.0 \text{ min} - 0.0 \text{ min}} = +0.022 \text{ M/min}$$

$$\text{initial rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{2.935 \text{ M} - 3.024 \text{ M}}{1.0 \text{ min} - 0.0 \text{ min}} = +0.089 \text{ M/min}$$

(b) When the initial concentration is doubled $(\times 2.0)$, from 1.512 M to 3.024 M, the initial rate quadruples $(\times 4.0)$. Thus, the reaction is second-order in A (since $2.0^x = 4.0$ when $x = 2$).

40. **(M)**

(a) Let us assess the possibilities. If the reaction is zero-order, its rate will be constant. During the first 8 min, the rate is $-(0.60\text{ M}-0.80\text{ M})/8\text{ min}=0.03\text{ M/min}$. Then, during the first 24 min, the rate is $-(0.35\text{ M}-0.80\text{ M})/24\text{ min}=0.019\text{ M/min}$. Thus, the reaction is not zero-order. If the reaction is first-order, it will have a constant half-life that is consistent with its rate constant. The half-life can be assessed from the fact that 40 min elapse while the concentration drops from 0.80 M to 0.20 M, that is, to one-fourth of its initial value. Thus, 40 min equals two half-lives and $t_{1/2}=20\text{ min}$.

This gives $k=0.693/t_{1/2}=0.693/20\text{ min}=0.035\text{ min}^{-1}$. Also

$$kt=-\ln\frac{[\text{A}]_t}{[\text{A}]_0}=-\ln\frac{0.35\text{ M}}{0.80\text{ M}}=0.827=k\times 24\text{ min}\qquad k=\frac{0.827}{24\text{ min}}=0.034\text{ min}^{-1}$$

The constancy of the value of k indicates that the reaction is first-order.

(b) The value of the rate constant is $k=0.034\text{ min}^{-1}$.

(c) Reaction $\text{rate}=\frac{1}{2}\text{ (rate of formation of B) }=k[\text{A}]^1$ First we need [A] at $t=30.$ min

$$\ln\frac{[\text{A}]}{[\text{A}]_0}=-kt=-0.034\text{ min}^{-1}\times 30.\text{ min}=-1.0_2\qquad \frac{[\text{A}]}{[\text{A}]_0}=e^{-1.02}=0.36$$

$$[\text{A}]=0.36\times 0.80\text{ M}=0.29\text{ M}$$

$$\text{rate of formation of B}=2\times 0.034\text{ min}^{-1}\times 0.29\text{ M}=2.0\times 10^{-2}\text{ M min}^{-1}$$

<u>41.</u> **(M)** The half-life of the reaction depends on the concentration of A and, thus, this reaction cannot be first-order. For a second-order reaction, the half-life varies inversely with the reaction rate: $t_{1/2}=1/(k[\text{ A}]_0)$ or $k=1/(t_{1/2}[\text{ A}]_0)$. Let us attempt to verify the second-order nature of this reaction by seeing if the rate constant is fixed.

$$k=\frac{1}{1.00\text{ M}\times 50\text{ min}}=0.020\text{ L mol}^{-1}\text{min}^{-1}$$

$$k=\frac{1}{2.00\text{ M}\times 25\text{ min}}=0.020\text{ L mol}^{-1}\text{min}^{-1}$$

$$k=\frac{1}{0.50\text{ M}\times 100\text{ min}}=0.020\text{ L mol}^{-1}\text{ min}^{-1}$$

The constancy of the rate constant demonstrates that this reaction indeed is second-order. The rate equation is $\text{Rate}=k[\text{A}]^2$ and $k=0.020\text{ L mol}^{-1}\text{min}^{-1}$.

42. **(M)**

(a) The half-life depends on the initial $\left[\mathrm{NH_3}\right]$ and, thus, the reaction cannot be first-order. Let us attempt to verify second-order kinetics.

$k = \dfrac{1}{\left[\mathrm{NH_3}\right]_0 t_{1/2}}$ for a second-order reaction $\quad k = \dfrac{1}{0.0031\ \mathrm{M} \times 7.6\ \mathrm{min}} = 42\ \mathrm{M^{-1}min^{-1}}$

$k = \dfrac{1}{0.0015\ \mathrm{M} \times 3.7\ \mathrm{min}} = 180\ \mathrm{M^{-1}min^{-1}} \quad k = \dfrac{1}{0.00068\ \mathrm{M} \times 1.7\mathrm{min}} = 865\ \mathrm{M^{-1}min^{-1}}$

The reaction is not second-order. But, if the reaction is zero-order, its rate will be constant.

$$\text{Rate} = \frac{[\mathrm{A}]_0/2}{t_{1/2}} = \frac{0.0031\ \mathrm{M} \div 2}{7.6\ \mathrm{min}} = 2.0 \times 10^{-4}\ \mathrm{M/min}$$

$$\text{Rate} = \frac{0.0015\ \mathrm{M} \div 2}{3.7\ \mathrm{min}} = 2.0 \times 10^{-4}\ \mathrm{M/min}$$

$$\text{Rate} = \frac{0.00068\ \mathrm{M} \div 2}{1.7\ \mathrm{min}} = 2.0 \times 10^{-4}\ \mathrm{M/min} \qquad \text{Zero-order reaction}$$

(b) The constancy of the rate indicates that the decomposition of ammonia under these conditions is zero-order, and the rate constant is $k = 2.0 \times 10^{-4}\ \mathrm{M/min}$.

<u>43.</u> **(M)** Zero-order: $t_{1/2} = \dfrac{[\mathrm{A}]_0}{2k}$ Second-order: $t_{1/2} = \dfrac{1}{k[\mathrm{A}]_0}$

A zero-order reaction has a half life that varies proportionally to $[\mathrm{A}]_0$, therefore, increasing $[\mathrm{A}]_0$ increases the half-life for the reaction. A second-order reaction's half-life varies inversely proportional to $[\mathrm{A}]_0$, that is, as $[\mathrm{A}]_0$ increases, the half-life decreases. The reason for the difference is that a zero-order reaction has a constant rate of reaction (independent of $[\mathrm{A}]_0$). The larger the value of $[\mathrm{A}]_0$, the longer it will take to react. In a second-order reaction, the rate of reaction increases as the square of the $[\mathrm{A}]_0$, hence, for high $[\mathrm{A}]_0$, the rate of reaction is large and for very low $[\mathrm{A}]_0$, the rate of reaction is very slow. If we consider a bimolecular elementary reaction, we can easily see that a reaction will not take place unless two molecules of reactants collide. This is more likely when the $[\mathrm{A}]_0$ is large than when it is small.

44. **(M)**

(a) $\dfrac{[\mathrm{A}]_0}{2k} = \dfrac{0.693}{k}$ Hence, $\dfrac{[\mathrm{A}]_0}{2} = 0.693$ or $[\mathrm{A}]_0 = 1.39\ \mathrm{M}$

(b) $\dfrac{[\mathrm{A}]_0}{2k} = \dfrac{1}{k[\mathrm{A}]_0}$, Hence, $\dfrac{[\mathrm{A}]_0^{\,2}}{2} = 1$ or $[\mathrm{A}]_0^{2} = 2.00\ \mathrm{M}$ $\quad [\mathrm{A}]_0 = 1.41\underline{4}\ \mathrm{M}$

(c) $\dfrac{0.693}{k} = \dfrac{1}{k[\mathrm{A}]_o}$, Hence, $0.693 = \dfrac{1}{[\mathrm{A}]_0}$ or $[\mathrm{A}]_0 = 1.44\ \mathrm{M}$

Collision Theory; Activation Energy

45. **(M)**

(a) The rate of a reaction depends on at least two factors other than the frequency of collisions. The first of these is whether each collision possesses sufficient energy to get over the energy barrier to products. This depends on the activation energy of the reaction; the higher it is, the smaller will be the fraction of successful collisions. The second factor is whether the molecules in a given collision are properly oriented for a successful reaction. The more complex the molecules are, or the more freedom of motion the molecules have, the smaller will be the fraction of collisions that are correctly oriented.

(b) Although the collision frequency increases relatively slowly with temperature, the fraction of those collisions that have sufficient energy to overcome the activation energy increases much more rapidly. Therefore, the rate of reaction will increase dramatically with temperature.

(c) The addition of a catalyst has the net effect of decreasing the activation energy of the overall reaction, by enabling an alternative mechanism. The lower activation energy of the alternative mechanism, (compared to the uncatalyzed mechanism), means that a larger fraction of molecules have sufficient energy to react. Thus the rate increases, even though the temperature does not.

46. **(M)**

(a) The activation energy for the reaction of hydrogen with oxygen is quite high, too high, in fact, to be supplied by the energy ordinarily available in a mixture of the two gases at ambient temperatures. However, the spark supplies a suitably concentrated form of energy to initiate the reaction of at least a few molecules. Since the reaction is highly exothermic, the reaction of these first few molecules supplies sufficient energy for yet other molecules to react and the reaction proceeds to completion or to the elimination of the limiting reactant.

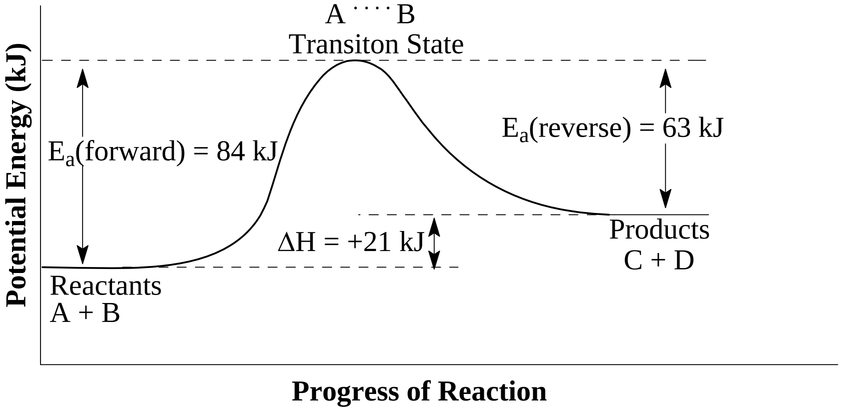
(b) A larger spark simply means that a larger number of molecules react initially. But the eventual course of the reaction remains the same, with the initial reaction producing enough energy to initiate still more molecules, and so on.

47. **(M)**

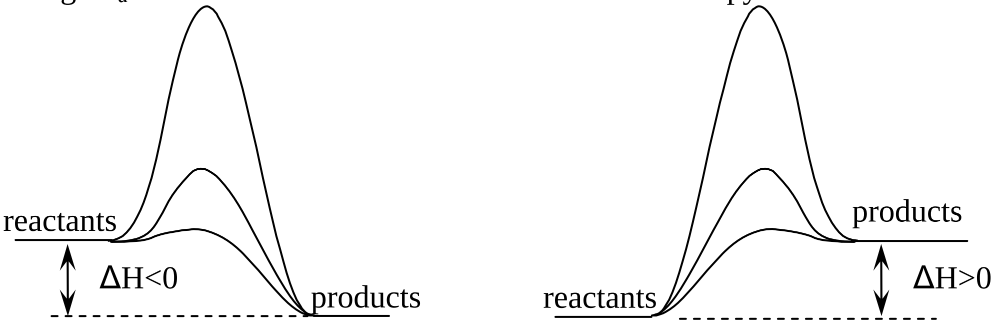
(a) The products are 21 kJ/mol closer in energy to the energy activated complex than are the reactants. Thus, the activation energy for the reverse reaction is

$$84 \text{ kJ/mol} - 21 \text{ kJ/mol} = 63 \text{ kJ/mol}.$$

(b) The reaction profile for the reaction in Figure 14-10 is sketched below.



48. **(M)** In an endothermic reaction (right), E_a must be larger than the ΔH for the reaction. For an exothermic reaction (left), the magnitude of E_a may be either larger or smaller than that of ΔH. In other words, a small activation energy can be associated with a large decrease in the enthalpy, or a large E_a can be connected to a small decrease in enthalpy.



49. **(E)**

(a) There are two intermediates (B and C).

(b) There are three transition states (peaks/maxima) in the energy diagram.

(c) The fastest step has the smallest E_a, hence, step 3 is the fastest step in the reaction with step 2 a close second.

(d) Reactant A (step 1) has the highest E_a, and therefore the slowest smallest constant

(e) Endothermic; energy is needed to go from A to B.

(f) Exothermic; energy is released moving from A to D.

50. **(E)**

(a) There are two intermediates (B and C).

(b) There are three transition states (peaks/maxima) in the energy diagram.

(c) The fastest step has the smallest E_a, hence, step 2 is the fastest step in the reaction.

(d) Reactant A (step 1) has the highest E_a, and therefore the slowest smallest constant

(e) Endothermic; energy is needed to go from A to B.

(f) Endothermic, energy is needed to go from A to D.

Effect of Temperature on Rates of Reaction

51. **(M)**

$$\ln\frac{k_1}{k_2}=\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=\ln\frac{5.4\times10^{-4}\text{ L mol}^{-1}\text{ s}^{-1}}{2.8\times10^{-2}\text{ L mol}^{-1}\text{ s}^{-1}}=\frac{E_a}{R}\left(\frac{1}{683\text{ K}}-\frac{1}{599\text{ K}}\right)$$

$$-3.95R=-E_a\times2.05\times10^{-4}$$

$$E_a=\frac{3.95\ R}{2.05\times10^{-4}}=1.93\times10^{4}\text{ K}^{-1}\times8.3145\text{ J mol}^{-1}\text{ K}^{-1}=1.60\times10^{5}\text{ J / mol}=160\text{ kJ / mol}$$

52. **(M)**

$$\ln\frac{k_1}{k_2}=\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=\ln\frac{5.0\times10^{-3}\text{ L mol}^{-1}\text{ s}^{-1}}{2.8\times10^{-2}\text{ L mol}^{-1}\text{ s}^{-1}}=\frac{1.60\times10^{5}\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{683\text{ K}}-\frac{1}{T}\right)$$

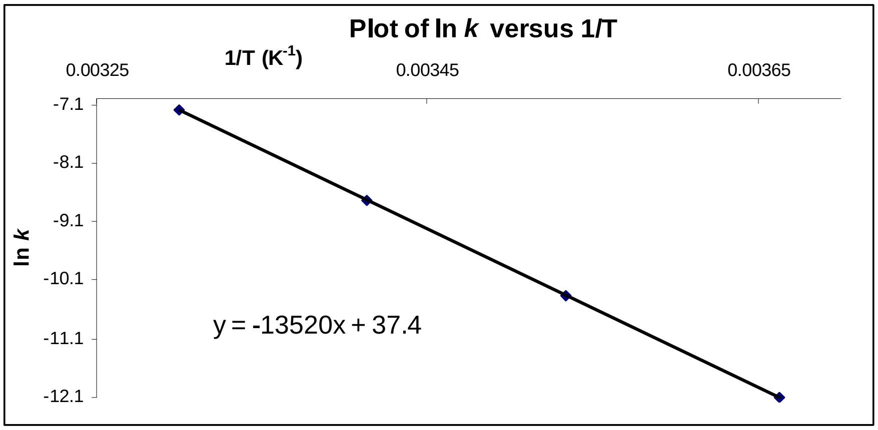
$$-1.72=1.92\times10^{4}\left(\frac{1}{683\text{ K}}-\frac{1}{T}\right)\qquad\left(\frac{1}{683\text{ K}}-\frac{1}{T}\right)=\frac{-1.72}{1.92\times10^{4}}=-8.96\times10^{-5}$$

$$\frac{1}{T}=8.96\times10^{-5}+1.46\times10^{-3}=1.55\times10^{-3}\qquad T=645\text{ K}$$

53. **(D)**

(a) First we need to compute values of ln k and $1/T$. Then we plot the graph of ln k versus 1/T.

T, °C	0 °C	10 °C	20 °C	30 °C
T, K	273 K	283 K	293 K	303 K
$1/T$, K^{-1}	0.00366	0.00353	0.00341	0.00330
k, s^{-1}	5.6×10^{-6}	3.2×10^{-5}	1.6×10^{-4}	7.6×10^{-4}
ln k	−12.09	−10.35	−8.74	−7.18



(b) The slope $= -E_a / R$.

$$E_a = -R \times \text{ slope} = -8.3145 \frac{\text{J}}{\text{mol K}} \times -1.35_2 \times 10^4 \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 112 \frac{\text{kJ}}{\text{mol}}$$

(c) We apply the Arrhenius equation, with $k = 5.6 \times 10^{-6} \text{ s}^{-1}$ at $0\,^\circ\text{C}$ (273 K), $k = ?$ at $40\,^\circ\text{C}$ (313 K), and $E_a = 113 \times 10^3$ J/mol.

$$\ln \frac{k}{5.6 \times 10^{-6} \text{ s}^{-1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{112 \times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}}\left(\frac{1}{273 \text{ K}} - \frac{1}{313 \text{ K}}\right) = 6.30\underline{6}$$

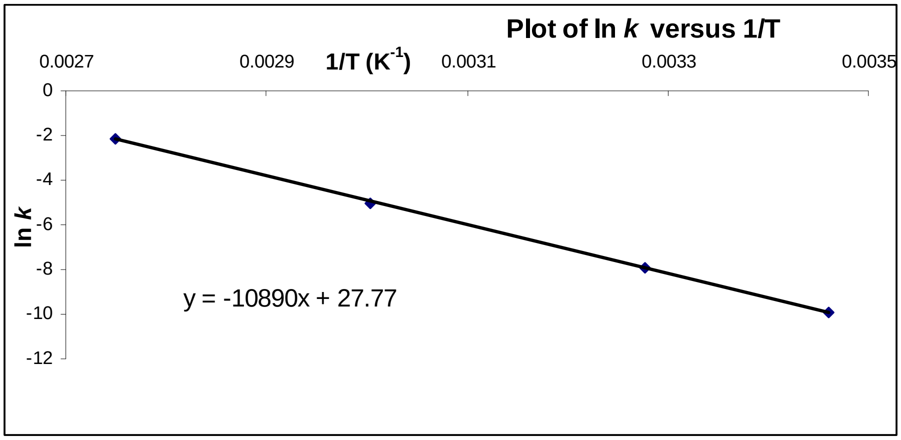
$$e^{6.30\underline{6}} = 548 = \frac{k}{5.6 \times 10^{-6} \text{ s}^{-1}} \qquad k = 548 \times 5.6 \times 10^{-6} \text{ s}^{-1} = 3.0\underline{7} \times 10^{-3} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.0\underline{7} \times 10^{-3} \text{ s}^{-1}} = 2.3 \times 10^2 \text{ s}$$

54. (D)

(a) Here we plot $\ln k$ vs. $1/T$. The slope of the straight line equals $-E_a / R$. First we tabulate the data to plot. (the plot is shown below).

T, °C	15.83	32.02	59.75	90.61
T, K	288.98	305.17	332.90	363.76
$1/T$, K^{-1}	0.0034604	0.0032769	0.0030039	0.0027491
k, $\text{M}^{-1}\text{s}^{-1}$	5.03×10^{-5}	3.68×10^{-4}	6.71×10^{-3}	0.119
$\ln k$	-9.898	-7.907	-5.004	-2.129



The slope of this graph $= -1.09 \times 10^4\ \text{K} = E_a / R$

$$E_a = -\left(-1.089 \times 10^4\ \text{K}\right) \times 8.3145\ \frac{\text{J}}{\text{mol K}} = 9.054 \times 10^4\ \frac{\text{J}}{\text{mol}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 90.5\ \frac{\text{kJ}}{\text{mol}}$$

(b) We calculate the activation energy with the Arrhenius equation using the two extreme data points.

$$\ln\frac{k_2}{k_1} = \ln\frac{0.119}{5.03\times10^{-5}} = +7.77 = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{E_a}{R}\left(\frac{1}{288.98\ \text{K}}-\frac{1}{363.76\ \text{K}}\right)$$

$$= 7.1138\times10^{-4}\ \text{K}^{-1}\frac{E_a}{R} \qquad E_a = \frac{7.769\times8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}{7.1138\times10^{-4}\ \text{K}^{-1}} = 9.0\underline{8}\times10^4\ \text{J/mol}$$

$E_a = 91\,\text{kJ/mol}$. The two E_a values are in quite good agreement, within experimental limits.

(c) We apply the Arrhenius equation, with $E_a = 9.080 \times 10^4\ \text{J/mol}$,

$k = 5.03\times10^{-5}\ \text{M}^{-1}\ \text{s}^{-1}$ at $15.83\ °\text{C}$ (288.98 K), and $k = ?$ at $100.0\ °\text{C}$ (373.2 K).

$$\ln\frac{k}{5.03\times10^{-5}\ \text{M}^{-1}\ \text{s}^{-1}} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{90.80\times10^3\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{288.98\ \text{K}}-\frac{1}{373.2\ \text{K}}\right)$$

$$\ln\frac{k}{5.03\times10^{-5}\ \text{M}^{-1}\ \text{s}^{-1}} = 8.528 \qquad e^{8.528} = 5.05\times10^3 = \frac{k}{5.03\times10^{-5}\ \text{M}^{-1}\ \text{s}^{-1}}$$

$$k = 5.05\times10^3\times5.03\times10^{-5}\ \text{M}^{-1}\ \text{s}^{-1} = 0.254\ \text{M}^{-1}\ \text{s}^{-1}$$

55. **(M)** The half-life of a first-order reaction is inversely proportional to its rate constant: $k = 0.693/t_{1/2}$. Thus we can apply a modified version of the Arrhenius equation to find E_a.

(a)
$$\ln\frac{k_2}{k_1} = \ln\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \ln\frac{46.2\ \text{min}}{2.6\ \text{min}} = \frac{E_a}{R}\left(\frac{1}{298\ \text{K}}-\frac{1}{(102+273)\ \text{K}}\right)$$

$$2.88 = \frac{E_a}{R}6.89\times10^{-4} \quad E_a = \frac{2.88\times8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}{6.89\times10^{-4}\ \text{K}^{-1}}\times\frac{1\ \text{kJ}}{1000\ \text{J}} = 34.8\ \text{kJ/mol}$$

(b)
$$\ln\frac{10.0\ \text{min}}{46.2\ \text{min}} = \frac{34.8\times10^3\ \text{J / mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{T}-\frac{1}{298}\right) = -1.53 = 4.19\times10^3\left(\frac{1}{T}-\frac{1}{298}\right)$$

$$\left(\frac{1}{T}-\frac{1}{298}\right) = \frac{-1.53}{4.19\times10^3} = -3.65\times10^{-4} \qquad \frac{1}{T} = 2.99\times10^{-3} \qquad T = 334\ \text{K} = 61\ ^\circ\text{C}$$

56. **(M)** The half-life of a first-order reaction is inversely proportional to its rate constant: $k = 0.693/t_{1/2}$. Thus, we can apply a modified version of the Arrhenius equation.

(a)
$$\ln\frac{k_2}{k_1} = \ln\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \ln\frac{22.5\ \text{h}}{1.5\ \text{h}} = \frac{E_a}{R}\left(\frac{1}{293\ \text{K}}-\frac{1}{(40+273)\ \text{K}}\right)$$

$$2.71 = \frac{E_a}{R}2.18\times10^{-4}, \qquad E_a = \frac{2.71\times8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}{2.18\times10^{-4}\ \text{K}^{-1}}\times\frac{1\ \text{kJ}}{1000\ \text{J}} = 103\ \text{kJ/mol}$$

(b) The relationship is $k = A\ \exp\left(-E_a / RT\right)$

$$k = 2.05\times10^{13}\ \text{s}^{-1}\exp\left(\frac{-103\times10^{3}\ \text{J mol}^{-1}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\times\left(273+30\right)\ \text{K}}\right) = 2.05\times10^{13}\ \text{s}^{-1}\times\ e^{-40.9} = 3.5\times10^{-5}\ \text{s}^{-1}$$

57. **(M)**

(a) It is the change in the value of the rate constant that causes the reaction to go faster. Let k_1 be the rate constant at room temperature, $20\ ^\circ\text{C}$ (293 K). Then, ten degrees higher (30° C or 303 K), the rate constant $k_2 = 2\times k_1$.

$$\ln\frac{k_2}{k_1} = \ln\frac{2\times k_1}{k_1} = 0.693 = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{E_a}{R}\left(\frac{1}{293}-\frac{1}{303\ \text{K}}\right) = 1.13\times10^{-4}\ \text{K}^{-1}\frac{E_a}{R}$$

$$E_a = \frac{0.693\times8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}{1.13\times10^{-4}\ \text{K}^{-1}} = 5.1\times10^{4}\ \text{J / mol} = 51\ \text{kJ / mol}$$

(b) Since the activation energy for the depicted reaction (i.e., $N_2O + NO \rightarrow N_2 + NO_2$) is 209 kJ/mol, we would not expect this reaction to follow the rule of thumb.

58. **(M)** Under a pressure of 2.00 atm, the boiling point of water is approximately $121\ ^\circ\text{C}$ or 394 K. Under a pressure of 1 atm, the boiling point of water is $100^\circ\ \text{C}$ or 373 K. We assume an activation energy of $5.1\times10^{4}\ \text{J / mol}$ and compute the ratio of the two rates.

$$\ln\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{5.1\times10^{4}\ \text{J / mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{373}-\frac{1}{394\ \text{K}}\right) = 0.88$$

$\text{Rate}_2 = e^{0.88}\ \text{Rate}_1 = 2.4\ \text{Rate}_1$. Cooking will occur 2.4 times faster in the pressure cooker.

Catalysis

59. **(E)**

(a) Although a catalyst is *recovered unchanged from the reaction mixture*, it does "take part in the reaction." Some catalysts actually slow down the rate of a reaction. Usually, however, these negative catalysts are called inhibitors.

(b) The function of a catalyst is to *change the mechanism of a reaction*. The new mechanism is one that has a different (lower) activation energy (and frequently a different A value), than the original reaction.

60. **(M)** If the reaction is first-order, its half-life is 100 min, for in this time period [S] decreases from 1.00 M to 0.50 M, that is, by one half. This gives a rate constant of

$k = 0.693 / t_{1/2} = 0.693 / 100\ \text{min} = 0.00693\ \text{min}^{-1}$.

The rate constant also can be determined from any two of the other sets of data.

$$kt = \ln\frac{[\text{A}]_0}{[\text{A}]_t} = \ln\frac{1.00\ \text{M}}{0.70\ \text{M}} = 0.357 = k\times60\ \text{min} \qquad k = \frac{0.357}{60\ \text{min}} = 0.00595\ \text{min}^{-1}$$

This is not a very good agreement between the two *k* values, so the reaction is probably not first-order in [A]. Let's try zero-order, where the rate should be constant.

$$\text{Rate} = -\frac{0.90\ \text{M} - 1.00\ \text{M}}{20\ \text{min}} = 0.0050\ \text{M/min} \qquad \text{Rate} = -\frac{0.50\ \text{M} - 1.00\ \text{M}}{100\ \text{min}} = 0.0050\ \text{M/min}$$

$$\text{Rate} = -\frac{0.20\ \text{M} - 0.90\ \text{M}}{160\ \text{min} - 20\ \text{min}} = 0.0050\ \text{M/min} \qquad \text{Rate} = -\frac{0.50\ \text{M} - 0.90\ \text{M}}{100\ \text{min} - 20\ \text{min}} = 0.0050\ \text{M/min}$$

Thus, this reaction is zero-order with respect to [S].

61. **(E)** Both platinum and an enzyme have a metal center that acts as the active site. Generally speaking, platinum is not dissolved in the reaction solution (heterogeneous), whereas enzymes are generally soluble in the reaction media (homogeneous). The most important difference, however, is one of specificity. Platinum is rather nonspecific, catalyzing many different reactions. An enzyme, however, is quite specific, usually catalyzing only one reaction rather than all reactions of a given class.

62. **(E)** In both the enzyme and the metal surface cases, the reaction occurs in a specialized location: either within the enzyme pocket or on the surface of the catalyst. At high concentrations of reactant, the limiting factor in determining the rate is not the concentration of reactant present but how rapidly active sites become available for reaction to occur. Thus, the rate of the reaction depends on either the quantity of enzyme present or the surface area of the catalyst, rather than on how much reactant is present (i.e., the reaction is zero-order). At low concentrations or gas pressures the reaction rate depends on how rapidly molecules can reach the available active sites. Thus, the rate depends on concentration or pressure of reactant and is first-order.

63. **(E)** For the straight-line graph of Rate versus [Enzyme], an excess of substrate must be present.

64. **(E)** For human enzymes, we would expect the maximum in the curve to appear around 37°C, i.e., normal body temperature (or possibly at slightly elevated temperatures to aid in the control of diseases (37 - 41 °C). At lower temperatures, the reaction rate of enzyme-activated reactions decreases with decreasing temperature, following the Arrhenius equation. However, at higher temperatures, these temperature sensitive biochemical processes become inhibited, probably by temperature-induced structural modifications to the enzyme or the substrate, which prevent formation of the enzyme-substrate complex.

Reaction Mechanisms

65. **(E)** The molecularity of an elementary process is the number of reactant molecules in the process. This molecularity is equal to the order of the overall reaction only if the elementary process in question is the slowest and, thus, the rate-determining step of the overall reaction. In addition, the elementary process in question should be the only elementary step that influences the rate of the reaction.

66. **(E)** If the type of molecule that is expressed in the rate law as being first-order collides with other molecules that are present in much larger concentrations, the reaction will seem to depend only on the amount of those types of molecules present in smaller concentration, since the larger concentration will be essentially unchanged during the course of the reaction. Such a situation is quite common, and has been given the name pseudo first-order. It is also possible to have molecules which, do not participate directly in the reaction— including product molecules—

strike the reactant molecules and impart to them sufficient energy to react. Finally, collisions of the reactant molecules with the container walls may also impart adequate energy for reaction to occur.

67. **(M)** The three elementary steps must sum to give the overall reaction. That is, the overall reaction is the sum of step 1 + step 2 + step 3. Hence, step 2 = overall reaction −step 1 −step 3. Note that all species in the equations below are gases.

Overall: $2\ NO + 2H_2 \rightarrow N_2 + 2\ H_2O$ $\qquad 2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$

−First: $-\left(2\ NO \rightleftharpoons N_2O_2\right)$ $\qquad N_2O_2 \rightleftharpoons 2NO$

−Third $-\left(N_2O + H_2 \rightarrow N_2 + H_2O\right)$ or $N_2 + H_2O \rightarrow N_2O + H_2$

The result is the second step, which is slow: $\qquad H_2 + N_2O_2 \rightarrow H_2O + N_2O$

The rate of this rate-determining step is: Rate = $k_2\left[H_2\right]\left[N_2O_2\right]$

Since N_2O_2 does not appear in the overall reaction, we need to replace its concentration with the concentrations of species that do appear in the overall reaction. To do this, recall that the first step is rapid, with the forward reaction occurring at the same rate as the reverse reaction. $k_1[NO]^2 =$ forward rate = reverse rate = $k_{-1}[N_2O_2]$. This expression is solved for $\left[N_2O_2\right]$, which then is substituted into the rate equation for the overall reaction.

$$\left[N_2O_2\right] = \frac{k_1[NO]^2}{k_{-1}} \qquad \text{Rate} = \frac{k_2 k_1}{k_{-1}}\left[H_2\right]\ [NO]^2$$

The reaction is first-order in $\left[H_2\right]$ and second-order in [NO]. This result conforms to the experimentally determined reaction order.

68. **(M)** Proposed mechanism: $I_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,I(g)$ Observed rate law:

$$\begin{array}{c} 2\ I(g) + H_2(g) \xrightarrow{k_2} 2\ HI(g) \\ \hline I_2(g) + H_2(g) \rightarrow 2\ HI(g) \end{array} \qquad \text{Rate} = k[I_2][H_2]$$

The first step is a fast equilibrium reaction and step 2 is slow. Thus, the predicted rate law is Rate = $k_2[I]^2[H_2]$. In the first step, set the rate in the forward direction for the equilibrium equal to the rate in the reverse direction. Then solve for $[I]^2$.

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$ Use: $\text{Rate}_{\text{forward}} = k_1[I_2]$ and $\text{Rate}_{\text{reverse}} = k_{-1}[I]^2$

From this we see: $k_1[I_2] = k_{-1}[I]^2$. Rearranging (solving for $[I]^2$)

$[I]^2 = \dfrac{k_1[I_2]}{k_{-1}}$ Substitute into Rate = $k_2[I]^2[H_2] = k_2\dfrac{k_1[I_2]}{k_{-1}}[H_2] = k_{obs}[I_2][H_2]$

Since the predicted rate law is the same as the experimental rate law, this mechanism is plausible.

69. **(M)** Proposed mechanism: $Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl(g)$ Observed rate law:

$$\begin{array}{c} 2\,Cl(g) + 2\,NO(g) \xrightarrow{k_2} 2\,NOCl(g) \\ \hline Cl_2(g) + 2NO(g) \rightarrow 2\,NOCl(g) \end{array} \qquad \text{Rate} = k[Cl_2][NO]^2$$

The first step is a fast equilibrium reaction and step 2 is slow. Thus, the predicted rate law is Rate = $k_2[Cl]^2[NO]^2$ In the first step, set the rate in the forward direction for the equilibrium equal to the rate in the reverse direction. Then express $[Cl]^2$ in terms of $k_{1,}\, k_{-1}$ and $[Cl_2]$. This mechanism is almost certainly not correct because it involves a tetra molecular second step.

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$ Use: $\text{Rate}_{\text{forward}} = k_1[Cl_2]$ and $\text{Rate}_{\text{reverse}} = k_{-1}[Cl]^2$
From this we see: $k_1[Cl_2] = k_{-1}[Cl]^2$. Rearranging (solving for $[Cl]^2$)

$$[Cl]^2 = \frac{k_1[Cl_2]}{k_{-1}} \quad \text{Substitute into Rate} = k_2[Cl]^2[NO]^2 = k_2\frac{k_1[Cl_2]}{k_{-1}}[NO]^2 = k_{obs}[Cl_2][NO_2]^2$$

There is another plausible mechanism. $Cl_2(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl(g) + Cl(g)$

$$\begin{array}{c} Cl(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl(g) \\ \hline Cl_2(g) + 2NO(g) \rightarrow 2\,NOCl(g) \end{array}$$

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$ Use: $\text{Rate}_{\text{forward}} = k_1[Cl_2][NO]$ and $\text{Rate}_{\text{reverse}} = k_{-1}[Cl][NOCl]$

From this we see: $k_1[Cl_2][NO] = k_{-1}[Cl][NOCl]$. Rearranging (solving for [Cl])

$$[Cl] = \frac{k_1[Cl_2][NO]}{k_{-1}[NOCl]} \quad \text{Substitute into Rate} = k_2[Cl][NO] = \frac{k_2k_1[Cl_2][NO]^2}{k_{-1}[NOCl]}$$

If [NOCl], the product is assumed to be constant (~ 0 M using method of initial rates), then $\frac{k_2k_1}{k_{-1}[NOCl]}$ = constant = k_{obs} Hence, the predicted rate law is $k_{obs}[Cl_2][NO]^2$ which agrees with the experimental rate law. Since the predicted rate law agrees with the experimental rate law, both this and the previous mechanism are plausible, however, the first is dismissed as it has a tetramolecular elementary reaction (extremely unlikely to have four molecules simultaneously collide).

70. **(M)** A possible mechanism is: Step 1: $O_3 \rightleftharpoons O_2 + O(\text{fast})$

Step 2: $O + O_3 \xrightarrow{k_3} 2\,O_2(\text{slow})$

The overall rate is that of the slow step: Rate = $k_3[O][O_3]$. But O is a reaction intermediate, whose concentration is difficult to determine. An expression for [O] can be found by assuming that the forward and reverse “fast” steps proceed with equal speed.

$$\text{Rate}_1 = \text{Rate}_2 \quad k_1[O_3] = k_2[O_2][O] \quad [O] = \frac{k_1[O_3]}{k_2[O_2]} \qquad \text{Rate} = k_3\frac{k_1[O_3]}{k_2[O_2]}[O_3] = \frac{k_3k_1}{k_2}\frac{[O_3]^2}{[O_2]}$$

Then substitute this expression into the rate law for the reaction. This rate equation has the same form as the experimentally determined rate law and thus the proposed mechanism is plausible.

71. (M)

$$S_1 + S_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (S_1 : S_2)^*$$

$$(S_1 : S_2)^* \xrightarrow{k_2} (S_1 : S_2)$$

$$\frac{d(S_1 : S_2)^*}{dt} = k_1[S_1][S_2] - k_{-1}(S_1 : S_2)^* - k_2(S_1 : S_2)^*$$

$$k_1[S_1][S_2] = (k_{-1} + k_2)(S_1 : S_2)^*$$

$$(S_1 : S_2)^* = \frac{k_1}{k_{-1} + k_2}[S_1][S_2]$$

$$\frac{d(S_1 : S_2)}{dt} = k_2(S_1 : S_2)^* = \frac{k_2 \cdot k_1[S_1][S_2]}{k_{-1} + k_2}$$

72. (M)

$$(CH_3)_2\,CO\text{ (aq)} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3C(O)CH_2^-\text{(aq)} + H_2O\text{ (l)}$$

$$CH_3C(O)CH_2^-\text{(aq)} + (CH_3)_2\,CO\text{ (aq)} \xrightarrow{k_2} \text{Prod}$$

We note that $CH_3C(O)CH_2^-$ is an intermediate species. Using the steady state approximation, while its concentration is not known during the reaction, the rate of change of its concentration is zero, except for the very beginning and towards the end of the reaction. Therefore,

$$\frac{d\left[CH_3C(O)CH_2^-\right]}{dt} = k_1\left[(CH_3)_2\,CO\right]\left[OH^-\right] - k_{-1}\left[CH_3C(O)CH_2^-\right][H_2O]$$
$$-k_2\left[CH_3C(O)CH_2^-\right]\left[(CH_3)_2\,CO\right] = 0$$

Rearranging the above expression to solve for $CH_3C(O)CH_2^-$ gives the following expression

$$\left[CH_3C(O)CH_2^-\right] = \frac{k_1\left[(CH_3)_2\,CO\right]\left[OH^-\right]}{k_{-1}[H_2O] + k_2\left[(CH_3)_2\,CO\right]}$$

The rate of formation of product, therefore, is:

$$\frac{d[\text{Prod}]}{dt} = k_2\left[CH_3C(O)CH_2^-\right]\left[(CH_3)_2\,CO\right]$$

$$= k_2\left[(CH_3)_2\,CO\right] \cdot \frac{k_1\left[(CH_3)_2\,CO\right]\left[OH^-\right]}{k_{-1}[H_2O] + k_2\left[(CH_3)_2\,CO\right]}$$

$$= \frac{k_2 k_1\left[(CH_3)_2\,CO\right]^2\left[OH^-\right]}{k_{-1}[H_2O] + k_2\left[(CH_3)_2\,CO\right]}$$

INTEGRATIVE AND ADVANCED EXERCISES

73. **(M)** The data for the reaction starting with 1.00 M being first-order or second-order as well as that for the first-order reaction using 2.00 M is shown below

Time (min)	$[A]_o$ = 1.00 M (second order)	$[A]_o$ = 1.00 M (first order)	$[A]_o$ = 2.00 M (second order)	$[A]_o$ = 2.00 M (first order)
0	1.00	1.00	2.00	2.00
5	0.63	0.55	0.91	1.10
10	0.46	0.30	0.59	0.60
15	0.36	$0.16\underline{5}$	$0.43\underline{5}$	0.33
25	0.25	0.05	$0.28\underline{6}$	0.10

Clearly we can see that when $[A]_o$ = 1.00 M, the first-order reaction concentrations will always be lower than that for the second-order case (assumes magnitude of the rate constant is the same). If, on the other hand, the concentration is above 1.00 M, the second-order reaction decreases faster than the first-order reaction (remember that the half-life shortens for a second-order reaction as the concentration increases, whereas for a first-order reaction, the half-life is constant).

From the data, it appears that the crossover occurs in the case where $[A]_0$ = 2.00 M at just over 10 minutes.

Second-order at 11 minutes: $\frac{1}{[A]} = \frac{1}{2} + \left(\frac{0.12}{\text{M min}}\right) \times (11\text{ min})$ [A] = 0.549 M

First-order at 11 minutes: $\ln[A] = \ln(2) - \left(\frac{0.12}{\text{min}}\right) \times (11\text{ min})$ [A] = 0.534 M

A quick check at 10.5 minutes reveals,

Second-order at 10.5 minutes: $\frac{1}{[A]} = \frac{1}{2} + \frac{0.12(10.5\text{ min})}{\text{M min}}$ [A] = 0.568 M

First-order at 10.5 minutes: $\ln[A] = \ln(2) - \frac{0.12(10.5\text{ min})}{\text{M min}}$ [A] = 0.567 M

Hence, at approximately 10.5 minutes, these two plots will share a common point (point at which the concentration versus time curves overlap).

74. **(M)**

(a) The concentration vs. time graph is not linear. Thus, the reaction is obviously not zero-order (the rate is not constant with time). A quick look at various half lives for this reaction shows the ~2.37 min (1.000 M to 0.5 M), ~2.32 min (0.800 M to 0.400 M), and ~2.38 min(0.400 M to 0.200 M). Since the half-life is constant, the reaction is probably first-order.

(b) average $t_{1/2} = \frac{(2.37 + 2.32 + 2.38)}{3} = 2.36\text{ min}$ $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.36\text{ min}} = 0.294\,\text{min}^{-1}$

or perhaps better expressed as $k = 0.29\text{ min}^{-1}$ due to imprecision.

(c) When $t = 3.5\,\text{min}, [\text{A}] = 0.352\ \text{M}$. Then, rate = $k[\text{A}] = 0.294\ \text{min}^{-1} \times 0.352\ \text{M} = 0.103\ \text{M/min}$.

(d) $\text{Slope} = \dfrac{\Delta[\text{A}]}{\Delta t} = -\text{Rate} = \dfrac{0.1480\ \text{M} - 0.339\ \text{M}}{6.00\ \ \text{min} - 3.00\ \ \text{min}} = -0.0637\ \text{M / min}$ Rate = 0.064 M/min.

(e) Rate = k[A] = $0.294\ \text{min}^{-1} \times 1.000\ \text{M} = 0.29_4$ M/min.

75. **(M)** The reaction being investigated is:

$$2\,\text{MnO}_4^-(\text{aq}) + 5\,\text{H}_2\text{O}_2(\text{aq}) + 6\,\text{H}^+(\text{aq}) \longrightarrow 2\,\text{Mn}^{2+}(\text{aq}) + 8\,\text{H}_2\text{O(l)} + 5\,\text{O}_2(\text{g})$$

We use the stoichiometric coefficients in this balanced reaction to determine [H_2O_2].

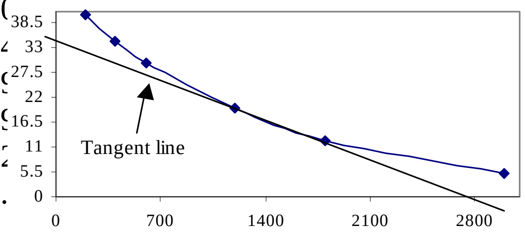
$$[\text{H}_2\text{O}_2] = \frac{37.1\ \text{mL titrant} \times \dfrac{0.1000\ \text{mmol MnO}_4^-}{1\ \text{mL titrant}} \times \dfrac{5\ \text{mmol H}_2\text{O}_2}{2\ \text{mmol MnO}_4^-}}{5.00\ \text{mL}} = 1.86\ \text{M}$$

76. **(D)** We assume in each case that 5.00 mL of reacting solution is titrated.

$$\text{volume MnO}_4^- = 5.00\ \text{mL} \times \frac{2.32\ \text{mmol H}_2\text{O}_2}{1\ \text{mL}} \times \frac{2\ \text{mmol MnO}_4^-}{5\ \text{mmol H}_2\text{O}_2} \times \frac{1\ \text{mL titrant}}{0.1000\ \text{mmol MnO}_4^-}$$

$$= 20.0 \times 2.32\ \text{M H}_2\text{O}_2 = 46.4\ \text{mL } 0.1000\ \text{M MnO}_4^-\ \text{titrant at 0 s}$$

At 200 s $V_{\text{titrant}} = 20.0 \times 2.01\ \text{M H}_2\text{O}_2 = 4$
At 400 s $V_{\text{titrant}} = 20.0 \times 1.72\ \text{M H}_2\text{O}_2 = 3$
At 600 s $V_{\text{titrant}} = 20.0 \times 1.49\ \text{M H}_2\text{O}_2 = 2$
At 1200 s $V_{\text{titrant}} = 20.0 \times 0.98\ \text{M H}_2\text{O}_2 = 1$
At 1800 s $V_{\text{titrant}} = 20.0 \times 0.62\ \text{M H}_2\text{O}_2 = 1$
At 3000 s $V_{\text{titrant}} = 20.0 \times 0.25\ \text{M H}_2\text{O}_2 = 5.$



The graph of volume of titrant vs. elapsed time is given above. This graph is of approximately the same shape as Figure 14-2, in which [H_2O_2] is plotted against time. In order to determine the rate, the tangent line at 1400 s has been drawn on the graph. The intercepts of the tangent line are at 34 mL of titrant and 2800 s. From this information we determine the rate of the reaction.

$$\text{Rate} = \frac{\dfrac{34\ \text{mL}}{2800\ \text{s}} \times \dfrac{1\ \text{L}}{1000\ \text{mL}} \times \dfrac{0.1000\ \text{mol MnO}_4^-}{1\ \text{L titrant}} \times \dfrac{5\ \text{mol H}_2\text{O}_2}{2\ \text{mol MnO}_4^-}}{0.00500\ \text{L sample}} = 6.1 \times 10^{-4}\ \ \text{M/s}$$

This is the same as the value of 6.1×10^{-4} obtained in Figure 14-2 for 1400 s. The discrepancy is due, no doubt, to the coarse nature of our plot.

77. **(M)** First we compute the change in [H_2O_2]. This is then used to determine the amount, and ultimately the volume, of oxygen evolved from the given quantity of solution. Assume the O_2(g) is dry.

$$\Delta[\mathrm{H_2O_2}] = -\frac{\Delta[\mathrm{H_2O_2}]}{\Delta t}\Delta t = -\left(-1.7\times10^{-3}\ \mathrm{M/s}\times1.00\ \mathrm{min}\times\frac{60\ \mathrm{s}}{1\ \mathrm{min}}\right) = 0.102\ \mathrm{M}$$

$$\text{amount } \mathrm{O_2} = 0.175\ \mathrm{L\ soln}\times\frac{0.102\ \mathrm{mol\ H_2O_2}}{1\ \mathrm{L}}\times\frac{1\ \mathrm{mol\ O_2}}{2\ \mathrm{mol\ H_2O_2}} = 0.00892\ \mathrm{mol\ O_2}$$

$$\text{Volume } \mathrm{O_2} = \frac{nRT}{P} = \frac{0.00892\ \mathrm{mol\ O_2}\times0.08206\,\frac{\mathrm{L\cdot atm}}{\mathrm{mol\cdot K}}\times(273+24)\ \mathrm{K}}{757\ \mathrm{mmHg}\times\frac{1\ \mathrm{atm}}{760\ \mathrm{mmHg}}} = 0.22\ \mathrm{L\ O_2}$$

<u>78</u>. **(M)** We know that rate has the units of M/s, and also that concentration has the units of M. The generalized rate equation is $\mathrm{Rate} = k\left[\mathrm{A}\right]_0$. In terms of units, this becomes M/s = {units of *k*} M_0. Therefore $\{\text{Units of } k\} = \frac{\mathrm{M/s}}{\mathrm{M_0}} = \mathrm{M_{1-0}}\ \mathrm{s^{-1}}$

79. **(M)**

(a) Comparing the third and the first lines of data, [I^-] and [OH^-]stay fixed, while [OCl^-] doubles. Also the rate for the third kinetics run is one half of the rate found for the first run. Thus, the reaction is <u>first-order</u> in [OCl^-]. Comparing the fourth and fifth lines, [OCl^-] and [I^-] stay fixed, while [OH^-] is halved. Also, the fifth run has a reaction rate that is twice that of the fourth run. Thus, the reaction is <u>*minus* first-order</u> in [OH^-]. Comparing the third and second lines of data, [OCl^-] and [OH^-] stay fixed, while the [I^-] doubles. Also, the second run has a reaction rate that is double that found for the third run. Thus, the reaction is <u>first-order</u> in [I^-].

(b) The reaction is first-order in [OCl^-] and [I^-] and minus first-order in [OH^-]. Thus, the overall order = 1 + 1 – 1 = 1. The reaction is first-order overall.

(c)

$$\mathrm{Rate} = k\frac{[\mathrm{OCl^-}][\mathrm{I^-}]}{[\mathrm{OH^-}]}$$

$$\text{using data from first run:}\frac{\mathrm{Rate}\ [\mathrm{OH^-}]}{[\mathrm{OCl^-}][\mathrm{I^-}]} = \frac{4.8\times10^{-4}\ \mathrm{M/s}\times1.00\ \mathrm{M}}{0.0040\ \mathrm{M}\times0.0020\ \mathrm{M}} = 60.\ \mathrm{s^{-1}}$$

80. **(M)** We first determine the number of moles of N_2O produced. The partial pressure of N_2O(g) in the "wet" N_2O is 756 mmHg – 12.8 mmHg = 743 mmHg.

$$\text{amount } \mathrm{N_2O} = \frac{PV}{RT} = \frac{743\,\mathrm{mmHg}\times\frac{1\,\mathrm{atm}}{760\,\mathrm{mmHg}}\times0.0500\,\mathrm{L}}{0.08206\,\mathrm{L\ atm\ mol^{-1}\ K^{-1}}\times(273+15)\,\mathrm{K}} = 0.00207\,\mathrm{mol\ N_2O}$$

Now we determine the change in [NH_2NO_2].

$$\Delta[NH_2NO_2] = \frac{0.00207 \text{ mol } N_2O \times \dfrac{1 \text{ mol } NH_2NO_2}{1 \text{ mol } N_2O}}{0.165 \text{ L soln}} = 0.0125 \text{ M}$$

$$[NH_2NO_2]_{\text{final}} = 0.105 \text{ M} – 0.0125 \text{ M} = 0.093 \text{ M} \qquad k = \frac{0.693}{123 \text{ min}} = 0.00563 \text{ min}^{-1}$$

$$t = -\frac{1}{k}\ \ln\frac{[A]_t}{[A]_0} = -\frac{1}{0.00563 \text{ min}^{-1}}\ln\frac{0.093 \text{ M}}{0.105 \text{ M}} = 22 \text{ min} = \text{elapsed time}$$

81. **(D)** We need to determine the partial pressure of ethylene oxide at each time in order to determine the order of the reaction. First, we need the initial pressure of ethylene oxide. The pressure at infinite time is the pressure that results when all of the ethylene oxide has decomposed. Because two moles of product gas are produced for every mole of reactant gas, this infinite pressure is twice the initial pressure of ethylene oxide. P_{initial} = 249.88 mmHg ÷ 2 = 124.94 mmHg. Now, at each time we have the following. $(CH_2)_2O(g) \longrightarrow CH_4(g) + CO(g)$

Initial: 124.94 mmHg Changes: $-x$ mmHg $+x$ mmHg $+x$ mmHg Final: 124.94 + x mmHg

Thus, $x = P_{\text{tot}} - 124.94$ and $P_{\text{EtO}} = 124.94 - x = 124.94 - (P_{\text{tot}} - 124.94) = 249.88 - P_{\text{tot}}$

Hence, we have, the following values for the partial pressure of ethylene oxide.

t, min	0	10	20	40	60	100	200
P_{EtO}, mmHg	124.94	110.74	98.21	77.23	60.73	37.54	11.22

For the reaction to be zero-order, its rate will be constant.

The rate in the first 10 min is: $\text{Rate} = \dfrac{-(110.74 - 124.94) \text{ mmHg}}{10 \text{ min}} = 1.42 \text{ mmHg/min}$

The rate in the first 40 min is: $\text{Rate} = \dfrac{-(77.23 - 124.94) \text{ mmHg}}{40 \text{ min}} = 1.19 \text{ mmHg/min}$

We conclude from the non-constant rate that the reaction is not zero-order. For the reaction to be first-order, its half-life must be constant. From 40 min to 100 min—a period of 60 min—the partial pressure of ethylene oxide is approximately halved, giving an approximate half-life of 60 min. And, in the first 60 min, the partial pressure of ethylene oxide is approximately halved. Thus, the reaction appears to be first-order. To verify this tentative conclusion, we use the integrated first-order rate equation to calculate some values of the rate constant.

$$k = -\frac{1}{t}\ln\frac{P}{P_0} = -\frac{1}{10 \text{ min}}\ln\frac{110.74 \text{ mmHg}}{124.94 \text{ mmHg}} = 0.0121 \text{ min}^{-1}$$

$$k = -\frac{1}{100 \text{ min}}\ln\frac{37.54 \text{ mmHg}}{124.94 \text{ mmHg}} = 0.0120 \text{ min}^{-1} \qquad k = -\frac{1}{60 \text{ min}}\ln\frac{60.73 \text{ mmHg}}{124.94 \text{ mmHg}} = 0.0120 \text{ min}^{-1}$$

The constancy of the first-order rate constant suggests that the reaction is first-order.

<u>82</u>. **(M)** For this first-order reaction $\ln\dfrac{P_t}{P_0} = -kt$ Elapsed time is computed as: $t = -\dfrac{1}{k}\ln\dfrac{P_t}{P_0}$

We first determine the pressure of DTBP when the total pressure equals 2100 mmHg.

Reaction: $C_8H_{18}O_2(g) \longrightarrow 2C_3H_6O(g) + C_2H_6(g)$ [Equation 15.16]

Initial: 800.0 mmHg

Changes: $-x$ mmHg $+2x$ mmHg $+x$ mmHg

Final: $(800.0-x)$ mmHg $2x$ mmHg x mmHg

Total pressure $= (800.0-x)+2x+x = 800.0+2x = 2100.$

$x = 650.$ mmHg $P\{C_8H_{18}O_2(g)\} = 800.\text{ mmHg} - 650.\text{ mmHg} = 150.\text{ mmHg}$

$$t = -\frac{1}{k}\ln\frac{P_t}{P_0} = -\frac{1}{8.7\times10^{-3}\ \text{min}^{-1}}\ \ln\frac{150.\text{ mmHg}}{800.\text{ mmHg}} = 19_2\ \text{min} = 1.9\times10^{2}\ \text{min}$$

83. **(D)** If we compare Experiment 1 with Experiment 2, we notice that [B] has been halved, and also that the rate, expressed as $\Delta[A]/\Delta t$, has been halved. This is most evident for the times 5 min, 10 min, and 20 min. In Experiment 1, [A] decreases from 1.000 × 10^{-3} M to 0.779 × 10^{-3} M in 5 min, while in Experiment 2 this same decrease in [A] requires 10 min. Likewise in Experiment 1, [A] decreases from 1.000 × 10^{-3} M to 0.607 M× 10^{-3} in 10 min, while in Experiment 2 the same decrease in [A] requires 20 min. This dependence of rate on the first power of concentration is characteristic of a first-order reaction. This reaction is first-order in [B]. We now turn to the order of the reaction with respect to [A]. A zero-order reaction will have a constant rate. Determine the rate

After over the first minute: $\text{Rate} = \dfrac{-(0.951-1.000)\times10^{-3}\ \text{M}}{1\,\text{min}} = 4.9\times10^{-5}\ \text{M/min}$

After over the first five minutes: $\text{Rate} = \dfrac{-(0.779-1.000)\times10^{-3}\ \text{M}}{5\,\text{min}} = 4.4\times10^{-5}\ \text{M/min}$

After over the first twenty minutes: $\text{Rate} = \dfrac{-(0.368-1.000)\times10^{-3}\ \text{M}}{20\,\text{min}} = 3.2\times10^{-5}\ \text{M/min}$

This is not a very constant rate; we conclude that the reaction is not zero-order. There are no clear half-lives in the data with which we could judge the reaction to be first-order. But we can determine the value of the first-order rate constant for a few data.

$$k = -\frac{1}{t}\ \ln\frac{[A]}{[A]_0} = -\frac{1}{1\text{ min}}\ln\frac{0.951\,\text{mM}}{1.000\text{ mM}} = 0.0502\ \text{min}^{-1}$$

$$k = -\frac{1}{10\text{ min}}\ln\frac{0.607\text{ mM}}{1.000\text{ mM}} = 0.0499\ \text{min}^{-1} \qquad k = -\frac{1}{20\text{ min}}\ln\frac{0.368\text{ mM}}{1.000\text{ mM}} = 0.0500\ \text{min}^{-1}$$

The constancy of the first-order rate constant indicates that the reaction indeed is first-order in [A]. (As a point of interest, notice that the concentrations chosen in this experiment are such that the reaction is pseudo-zero-order in [B]. Here, then it is not necessary to consider the variation of [B] with time as the reaction proceeds when determining the kinetic dependence on [A].)

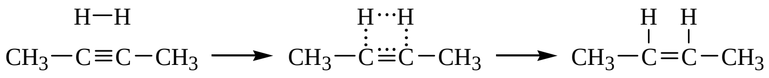
84. **(M)** In Exercise 79 we established the rate law for the iodine-hypochlorite ion reaction: $\text{Rate} = k[\text{OCl}^-][\text{I}^-][\text{OH}^-]^{-1}$. In the mechanism, the slow step gives the rate law; $\text{Rate} = k_3\,[\text{I}^-][\text{HOCl}]$. We use the initial fast equilibrium step to substitute for [HOCl] in this rate equation. We assume in this fast step that the forward rate equals the reverse rate.

$$k_1[\text{OCl}^-][\text{H}_2\text{O}] = k_{-1}[\text{HOCl}][\text{OH}^-] \qquad [\text{HOCl}] = \frac{k_1[\text{OCl}^-][\text{H}_2\text{O}]}{k_{-1}[\text{OH}^-]}$$

$$\text{Rate} = k_2\,[\text{I}^-]\frac{k_1[\text{OCl}^-][\text{H}_2\text{O}]}{k_{-1}[\text{OH}^-]} = \frac{k_2k_1[\text{H}_2\text{O}]}{k_{-1}}\frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]} = k\frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

This is the same rate law that we established in Exercise 79. We have incorporated $[\text{H}_2\text{O}]$ in the rate constant for the reaction because, in an aqueous solution, $[\text{H}_2\text{O}]$ remains effectively constant during the course of the reaction. (The final fast step simply involves the neutralization of the acid HOI by the base hydroxide ion, OH^-.)

85. **(M)** It is more likely that the *cis*-isomer, compound (I), would be formed than the *trans*-isomer, compound (II). The reason for this is that the reaction will involve the adsorption of both $\text{CH}_3\text{—C}\equiv\text{C—CH}_3$ and H_2 onto the surface of the catalyst. These two molecules will eventually be adjacent to each other. At some point, one of the π bonds in the C≡C bond will break, the H–H bond will break, and two C–H bonds will form. Since these two C–H bonds form on the same side of the carbon chain, compound (I) will be produced. In the sketches below, dotted lines (…) indicate bonds forming or breaking.



86. **(D)** $\text{Hg}_2^{2+} + \text{Tl}^{3+} \rightarrow 2\ \text{Hg}^{2+} + \text{Tl}^{+}$ Experimental rate law = $k\dfrac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$

Possible mechanism:

$$\text{Hg}_2^{2+} + \text{Tl}^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Hg}^{2+} + \text{HgTl}^{3+} \quad \text{(fast)}$$

$$\text{HgTl}^{3+} \xrightarrow{k_2} \text{Hg}^{2+} + \text{Tl}^{3+} \quad \text{(slow)}$$

$$\text{Hg}_2^{2+} + \text{Tl}^{3+} \rightarrow 2\ \text{Hg}^{2+} + \text{Tl}^{+} \qquad \text{Rate} = k_2[\text{HgTl}^{3+}]$$

$$k_1[\text{Hg}_2^{2+}][\text{Tl}^{3+}] = k_{-1}\,[\text{Hg}^{2+}][\text{HgTl}^{3+}] \quad \xrightarrow{\text{rearrange}} [\text{HgTl}^{3+}] = \frac{k_1}{k_{-1}}\frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$$

$$\text{Rate} = \text{k}_2[\text{HgTl}^{3+}] = \frac{k_2k_1}{k_{-1}}\frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]} = k_{\text{obs}}\frac{[\text{Hg}_2^{2+}][\text{Tl}^{3+}]}{[\text{Hg}^{2+}]}$$

87. (M)

$$\frac{\Delta \mathrm{CCl_3}}{\Delta \mathrm{t}} = \mathrm{rate_{formation}} + \mathrm{rate_{disappearance}} = 0 \qquad \text{so } \mathrm{rate_{formation}} = \mathrm{rate_{decomposition}}$$

$$k_2[\mathrm{Cl(g)}][\mathrm{CHCl_3}] = k_3[\mathrm{CCl_3}][[\mathrm{Cl(g)}] \text{ and, simplifying, } [\mathrm{CCl_3}] = \frac{k_2}{k_3}[\mathrm{CHCl_3}]$$

$$\text{since rate} = k_3[\mathrm{CCl_3}][\mathrm{Cl(g)}] = k_3\left(\frac{k_2}{k_3}[\mathrm{CHCl_3}]\right)[\mathrm{Cl(g)}] = k_2[\mathrm{CHCl_3}][\mathrm{Cl(g)}]$$

$$\text{We know: } [\mathrm{Cl(g)}] = \left(\frac{k_1}{k_{-1}}[\mathrm{Cl_2(g)}]\right)^{1/2} \text{ then } \mathrm{rate_{overall}} = k_2[\mathrm{CHCl_3}]\left(\frac{k_1}{k_{-1}}[\mathrm{Cl_2(g)}]\right)^{1/2}$$

$$\text{and the rate constant } k \text{ will be: } k = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2} = (1.3\times10^{-2})\left(\frac{4.8\times10^3}{3.6\times10^3}\right)^{1/2} = 0.015$$

88. (D)

$$\mathrm{Rate} = k[\mathrm{A}]^3 - \frac{\mathrm{d[A]}}{\mathrm{dt}} \qquad \text{Rearrange:} \qquad -k\mathrm{t} = \frac{\mathrm{d[A]}}{[\mathrm{A}]^3}$$

Integrate using the limits → time (0 to t) and concentration ($[\mathrm{A}]_0$ to $[\mathrm{A}]_t$)

$$-k\int_0^{t} \mathrm{t} = \int_{[\mathrm{A}]_o}^{[\mathrm{A}]_t} \frac{\mathrm{d[A]}}{[\mathrm{A}]^3} \quad \Rightarrow \quad -k\mathrm{t} - (-k(0)) = -\frac{1}{2}\frac{1}{[\mathrm{A}]_t^{\,2}} - \left(-\frac{1}{2}\frac{1}{[\mathrm{A}]_o^{\,2}}\right)$$

$$\text{Simplify: } -k\mathrm{t} = -\frac{1}{2[\mathrm{A}]_t^{\,2}} + \frac{1}{2[\mathrm{A}]_o^{\,2}} \qquad \text{Rearrange: } \frac{1}{2[\mathrm{A}]_t^{\,2}} = k\mathrm{t} + \frac{1}{2[\mathrm{A}]_0^{\,2}}$$

$$\text{Multiply through by 2 to give the integrated rate law: } \quad \frac{1}{[\mathrm{A}]_t^{\,2}} = 2k\mathrm{t} + \frac{1}{[\mathrm{A}]_o^{\,2}}$$

$$\text{To derive the half life}(\mathrm{t_{1/2}}) \text{ substitute } \mathrm{t} = \mathrm{t_{1/2}} \text{ and } [\mathrm{A}]_t = \frac{[\mathrm{A}]_o}{2}$$

$$\frac{1}{\left(\frac{[\mathrm{A}]_0}{2}\right)^2} = 2k\mathrm{t_{1/2}} + \frac{1}{[\mathrm{A}]_o^{\,2}} = \frac{1}{\frac{[\mathrm{A}]_o^{\,2}}{4}} = \frac{4}{[\mathrm{A}]_o^{\,2}} \qquad \text{Collect terms}$$

$$2k\mathrm{t_{1/2}} = \frac{4}{[\mathrm{A}]_o^{\,2}} - \frac{1}{[\mathrm{A}]_o^{\,2}} = \frac{3}{[\mathrm{A}]_o^{\,2}} \qquad \text{Solve for } \mathrm{t_{1/2}} \qquad \mathrm{t_{1/2}} = \frac{3}{2k[\mathrm{A}]_o^{\,2}}$$

89. (D) Consider the reaction: A + B → products (first-order in A, first-order in B). The initial concentration of each reactant can be defined as $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ Since the stoichiometry is 1:1, we can define *x* as the concentration of reactant A and reactant B that is removed (a variable that changes with time).

The $[\mathrm{A}]_t = ([\mathrm{A}]_o - x)$ and $[\mathrm{B}]_t = ([\mathrm{B}]_o - x)$.

Algebra note: $[\mathrm{A}]_o - x = -(x - [\mathrm{A}]_o)$ and $[\mathrm{B}]_o - x = -(x - [\mathrm{B}]_o)$.

As well, the calculus requires that we use the absolute value of $|x - [A]_o|$ and $|x - [B]_o|$ when taking the integral of the reciprocal of $|x - [A]_o|$ and $|x - [B]_o|$

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{dx}{dt} = k[A]_t[B]_t = k([A]_o\text{-x})([B]_o\text{-x}) \quad \text{or} \quad \frac{dx}{([A]_o\text{-x})([B]_o\text{-x})} = kdt$$

In order to solve this, partial fraction decomposition is required to further ease integration:

$$dx\underset{\text{Note: this is a constant}}{\left(\frac{1}{([B]_o\text{-}[A]_o)}\right)}\left(\frac{1}{([A]_o\text{-x})} - \frac{1}{([B]_o\text{-x})}\right) = kdt$$

From the point of view of integration, a further rearrangement is desirable (See algebra note above).

$$dx\underset{t}{\left(\frac{1}{([B]_o\text{-}[A]_o)}\right)}\left(\frac{-1}{|x\text{-}[A]_o|} - \frac{-1}{|x\text{-}[B]_o|}\right) = kdt$$

$$\text{Integrate both sides} \quad \left(\frac{1}{([B]_o\text{-}[A]_o)}\right)\left[-\ln|x\text{-}[A]_o| - (-\ln|x\text{-}[B]_o|)\right] = kt + C$$

$$|x\text{-}[A]_o| = [A]_o\text{-x} \ \text{ and } \ |x\text{-}[B]_o| = [B]_o\text{-x} \qquad \text{Substitute and simplify}$$

$$\left(\frac{1}{([B]_o\text{-}[A]_o)}\right)\ln\left(\frac{([B]_o\text{-x})}{[A]_o\text{-x}}\right) = kt + C \quad \text{Determine C by setting } x = 0 \text{ at t} = 0$$

$$C = \left(\frac{1}{([B]_o\text{-}[A]_o)}\right)\ln\frac{[B]_o}{[A]_o} \quad \text{Hence:} \left(\frac{1}{([B]_o\text{-}[A]_o)}\right)\ln\left(\frac{([B]_o\text{-x})}{([A]_o\text{-x})}\right) = kt + \left(\frac{1}{([B]_o\text{-}[A]_o)}\right)\ln\frac{[B]_o}{[A]_o}$$

$$\text{Multiply both sides by} ([B]_o\text{-}[A]_o)\text{, hence,} \quad \ln\left(\frac{([B]_o\text{-x})}{([A]_o\text{-x})}\right) = ([B]_o\text{-}[A]_o)\times kt + \ln\frac{[B]_o}{[A]_o}$$

$$\ln\left(\frac{([B]_o\text{-x})}{([A]_o\text{-x})}\right) - \ln\frac{[B]_o}{[A]_o} = ([B]_o\text{-}[A]_o)\times kt = \ln\frac{\left(\frac{([B]_o\text{-x})}{([A]_o\text{-x})}\right)}{\frac{[B]_o}{[A]_o}} = \ln\left(\frac{[A]_o([B]_o\text{-x})}{[B]_o([A]_o\text{-x})}\right)$$

$$\text{Set} ([A]_o\text{-x}) = [A]_t \ \text{ and } \ ([B]_o\text{-x}) = [B]_t \ \text{ to give } \ \ln\left(\frac{[A]_o\times[B]_t}{[B]_o\times[A]_t}\right) = ([B]_o\text{-}[A]_o)\times kt$$

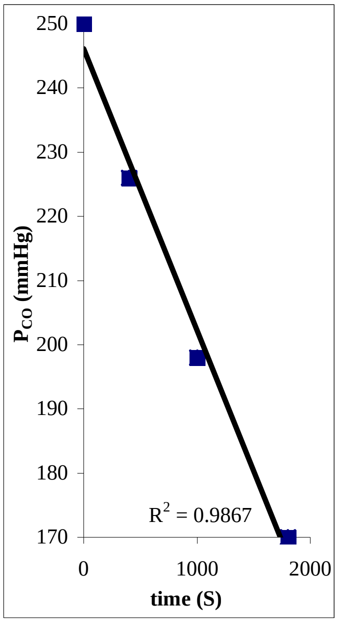
90. **(D)** Let 250-2x equal the partial pressure of CO(g) and x be the partial pressure of CO_2(g).

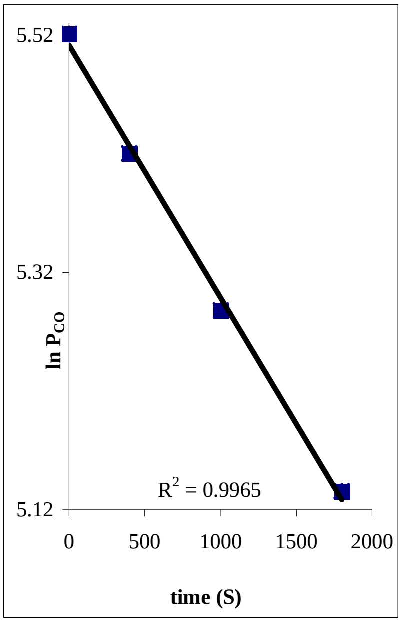
$$\begin{array}{cccc} 2CO & \rightarrow & CO_2 + & C(s) \\ 250-2x & & x & - \end{array}$$

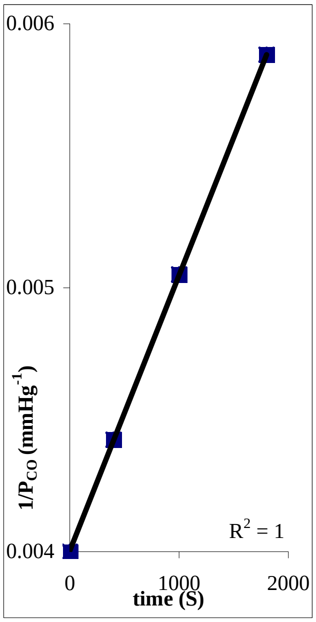
$$P_{tot} = P_{CO} + P_{CO2} = 250 - 2x + x = 250 - x$$

P_{tot} [torr]	Time [sec]	P_{CO2}	P_{CO} [torr]
250	0	0	250
238	398	12	226
224	1002	26	198
210	1801	40	170

The plots that follow show that the reaction appears to obey a second-order rate law.
Rate = $k[CO]^2$







ZERO ORDER PLOT

T	P_{CO}
0	250
398	226
1002	198
1801	170

1^{st} ORDER PLOT

T	$\ln P_{CO}$
0	5.521461
398	5.420535
1002	5.288267
1801	5.135798

2^{nd} ORDER PLOT

T	1/CO
0	0.004
398	0.004425
1002	0.005051
1801	0.005882

(Best correlation coefficient)

91. **(D)** Let 100-4x equal the partial pressure of $PH_3(g)$, x be the partial pressure of $P_4(g)$and 6x be the partial pressure of H_2 (g)

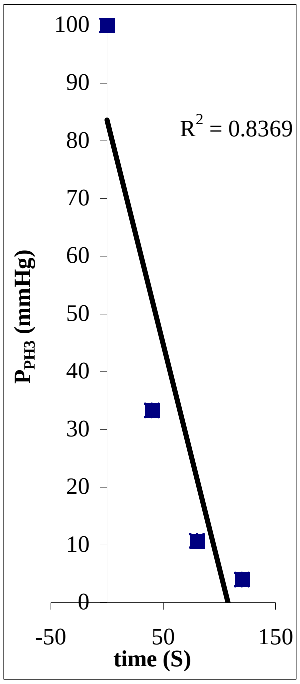
$$4\,PH_3(g) \rightarrow P_4(g) \quad + \quad 6\,H_2(g)$$

$$100 - 4x \qquad x \qquad\qquad 6x$$

$$P_{tot} = P_{PH_3} + P_{P_4} + P_{H_2} = 100 - 4x + x + 6x = 100 + 3x$$

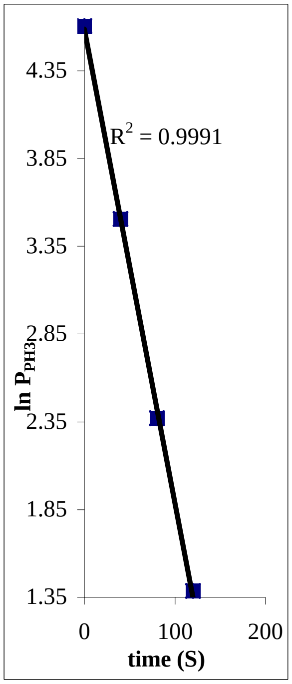
P_{tot} [torr]	Time [sec]	P_{P_4} [torr]	P_{PH_3} [torr]
100	0	0	100
150	40	50/3	100-(4)(50/3)
167	80	67/3	100-(4)(67/3)
172	120	72/3	100-(4)(72/3)

The plots to follow show that the reaction appears to obey a first-order rate law.
Rate = k[PH_3]



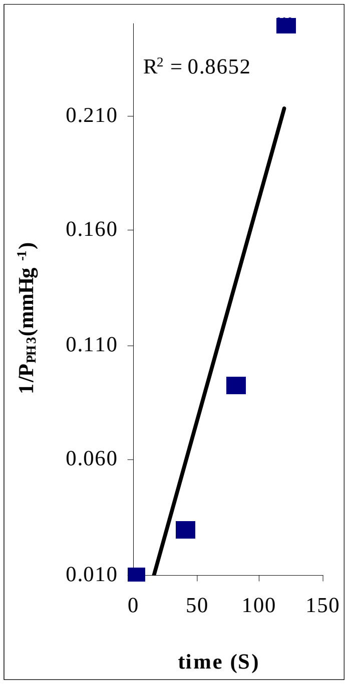
ZERO ORDER PLOT

T	P_{PH3}
0	100
40	33.3
80	10.7
120	4



1st ORDER PLOT

T	$\ln P_{PH3}$
0	4.61
40	3.51
80	2.37
120	1.39



2nd ORDER PLOT

T	$1/P_{PH3}$
0	0.010
40	0.030
80	0.093
120	0.250

92. **(D)** Consider the following equilibria.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P \qquad E + I \overset{K_I}{\rightleftharpoons} EI$$

Product production $\frac{d[P]}{dt} = k_2[ES]$ Use the steady state approximation for [ES]

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = k_1[E][S] - [ES](k_{-1} + k_2) = 0$$

solve for [ES] $\left(\text{Keep in mind } K_M = \frac{k_{-1} + k_2}{k_1}\right)$ $[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} = \frac{[E][S]}{K_M}$

Formation of EI: $K_I = \frac{[E][I]}{[EI]}$ $[EI] = \frac{[E][I]}{K_I}$

$$[E_o] = [E] + [ES] + [EI] = [E] + \frac{[E][S]}{K_M} + \frac{[E][I]}{K_I}$$

$[E_o] = [E]\left(1 + \frac{[S]}{K_M} + \frac{[I]}{K_I}\right)$ Solve for [E] $[E] = \frac{[E_o]}{\left(1 + \frac{[S]}{K_M} + \frac{[I]}{K_I}\right)}$

From above: $[ES] = \frac{[E][S]}{K_M}$ $[ES] = \frac{[E_o]\left(\frac{[S]}{K_M}\right)}{\left(1 + \frac{[S]}{K_M} + \frac{[I]}{K_I}\right)}$ multiplication by $\frac{K_M}{K_M}$ affords

$$[ES] = \frac{[E_o][S]}{\left(K_M + [S] + \frac{[I]K_M}{K_I}\right)} = \frac{[E_o][S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}$$

Remember $\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E_o][S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}$

If we substitute $k_2[E_o] = V_{max}$ then $\frac{d[P]}{dt} = \frac{V_{max}[S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}$

Thus, as [I] increases, the ratio $\frac{V_{max}[S]}{K_M\left(1 + \frac{[I]}{K_I}\right) + [S]}$ decreases;

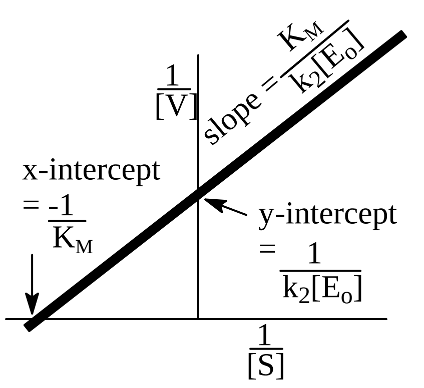
i.e., the rate of product formation decreases as [I] increases.

93. **(D)** In order to determine a value for K_M, we need to rearrange the equation so that we may obtain a linear plot and extract parameters from the slope and intercepts.

$$V = \frac{k_2[E_o][S]}{K_M+[S]} \qquad \frac{1}{V} = \frac{K_M+[S]}{k_2[E_o][S]} = \frac{K_M}{k_2[E_o][S]} + \frac{[S]}{k_2[E_o][S]}$$

$$\frac{1}{V} = \frac{K_M}{k_2[E_o][S]} + \frac{1}{k_2[E_o]}$$ We need to have this in the form of y = mx+b

Plot $\frac{1}{V}$ on the y-axis and $\frac{1}{[S]}$ on the x-axis. See result below:



The plot of 1/V vs 1/[S] should yield a slope of $\frac{K_M}{k_2[E_o]}$ and a y-intercept of $\frac{1}{k_2[E_o]}$. The x-intercept = $-1/K_M$

$$0 = \frac{K_M}{k_2[E_o]}\left(\frac{1}{[S]}\right) - \frac{1}{k_2[E_o]} \qquad \frac{1}{[S]} = \frac{-k_2[E_o]}{k_2[E_o]\times K_M} = \frac{-1}{K_M}$$

To find the value of K_M take the negative inverse of x-intercept. To find k_2, invert the y-intercept and divide by the $[E_o]$.

94. **(M)**

a) The first elementary step $HBr + O_2 \xrightarrow{k1} HOOBr$ is rate-determining if the reaction obeys reaction rate = k $[HBr][O_2]$ since the rate of this step is identical to that of the experimental rate law.

b) No, mechanisms cannot be shown to be absolutely correct, only consistent with experimental observations.

c) Yes; the sum of the elementary steps ($3\ HBr + O_2 \rightarrow HOBr + Br_2 + H_2O$) is not consistent with the overall stoichiometry (since HOBr is not detected as a product) of the reaction and therefore cannot be considered a valid mechanism.

95. **(M)**

(a) Both reactions are first-order, because they involve the decomposition of one molecule.

(b) k_2 is the slow reaction.

(c) To determine the concentration of the product, N_2, we must first determine how much reactant remains at the end of the given time period, from which we can calculate the amount of reactant consumed and therefore the amount of product produced. Since this is a first-order reaction, the concentration of the reactant, N_2O after time *t* is determined as follows:

$$[A]_t = [A]_0\, e^{-kt}$$

$$[N_2O]_{0.1} = (2.0\text{ M})\cdot \exp\left(-\left(25.7\text{ s}^{-1}\right)(0.1\text{ s})\right) = 0.153\text{ M } N_2O \text{ remaining}$$

The amount of N_2O consumed = 2.0 M – 0.153 M =1.847 M

$$[N_2] = 1.847\text{ M NO} \times \frac{1\text{ M }N_2}{2\text{ M NO}} = 0.9235\text{ M }N_2$$

(d) The process is identical to step (c).

$$\left[N_2O\right]_{0.1} = (4.0\text{ M}) \cdot \exp\left(-\left(18.2\text{ s}^{-1}\right)(0.025\text{ s})\right) = 2.538\text{ M }N_2O\text{ remaining}$$

The amount of N_2O consumed = 4.0 M – 2.538 M =1.462 M

$$[N_2O] = 1.462\text{ M NO} \times \frac{1\text{ M }N_2O}{2\text{ M NO}} = 0.731\text{ M }N_2O$$

FEATURE PROBLEMS

96. **(D)**

(a) To determine the order of the reaction, we need $\left[C_6H_5N_2Cl\right]$ at each time. To determine this value, note that 58.3 mL $N_2(g)$ evolved corresponds to total depletion of $C_6H_5N_2Cl$, to $\left[C_6H_5N_2Cl\right] = 0.000$ M .

Thus, at any point in time, $\left[C_6H_5N_2Cl\right] = 0.071\text{ M} - \left(\text{volume }N_2(g) \times \dfrac{0.071\text{ M }C_6H_5N_2Cl}{58.3\text{ mL }N_2(g)}\right)$

Consider 21 min: $\left[C_6H_5N_2Cl\right] = 0.071\text{ M} - \left(44.3\text{ mL }N_2 \times \dfrac{0.071\text{ M }C_6H_5N_2Cl}{58.3\text{ mL }N_2(g)}\right) = 0.017\text{ M}$

The numbers in the following table are determined with this method.

Time, min	0	3	6	9	12	15	18	21	24	27	30	∞
V_{N_2}, mL	0	10.8	19.3	26.3	32.4	37.3	41.3	44.3	46.5	48.4	50.4	58.3
$\left[C_6H_5N_2Cl\right]$, mM	71	58	47	39	32	26	21	17	14	12	10	0

[The concentration is given in thousandths of a mole per liter (mM).]

(b)

time(min) 0 3 6 9 12 15 18 21 24 27 30 ∞

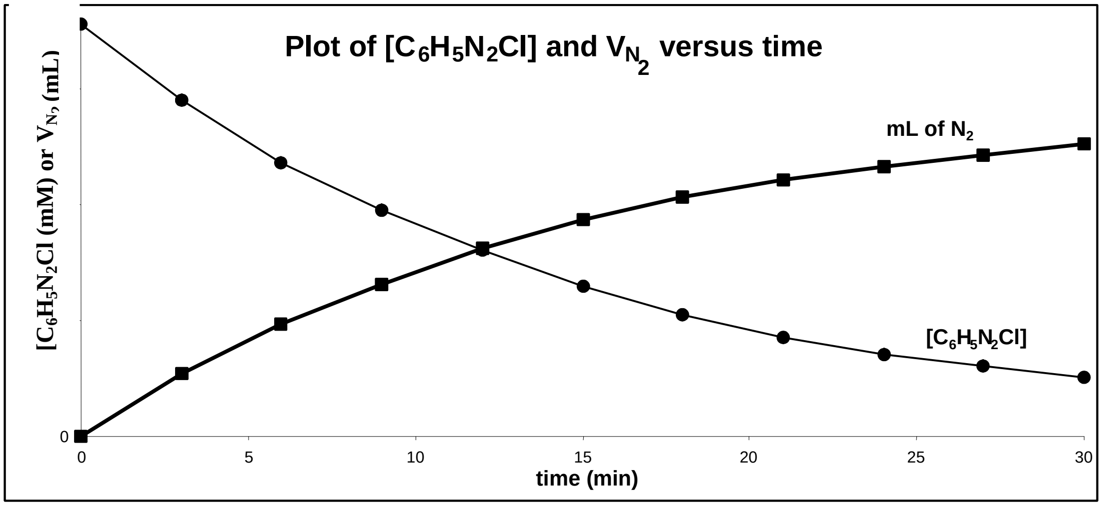
ΔT(min) 3 3 3 3 3 3 3 3 3 3

$[C_6H_5N_2Cl]$(mM) 71 58 47 39 32 26 21 17 14 12 10 ∞

$\Delta[C_6H_5N_2Cl]$(mM) -13 -11 -8 -7 -6 -5 -4 -3 -2 -2

Reaction Rate (mM min^{-1}) 4.3 3.7 2.7 2.3 2.0 1.7 1.3 1.0 0.7 0.7

(c) The two graphs are drawn on the same axes.



(d) The rate of the reaction at $t = 21$ min is the slope of the tangent line to the $[C_6H_5N_2Cl]$ curve. The tangent line intercepts the vertical axis at about $[C_6H_5N_2Cl] = 39$ mM and the horizontal axis at about 37 min

$$\text{Reaction rate} = \frac{39\times10^{-3}\text{ M}}{37\text{ min}} = 1.0_5\times10^{-3}\text{ M min}^{-1} = 1.1\times10^{-3}\text{ M min}^{-1}$$

The agreement with the reported value is very good.

(e) The initial rate is the slope of the tangent line to the $[C_6H_5N_2Cl]$ curve at $t = 0$. The intercept with the vertical axis is 71 mM, of course. That with the horizontal axis is about 13 min.

$$\text{Rate} = \frac{71\times10^{-3}\text{ M}}{13\text{ min}} = 5.5\times10^{-3}\text{ M min}^{-1}$$

(f) The first-order rate law is $\text{Rate} = k[C_6H_5N_2Cl]$, which we solve for *k:*

$$k = \frac{\text{Rate}}{[C_6H_5N_2Cl]} \qquad k_0 = \frac{5.5\times10^{-3}\text{ M min}^{-1}}{71\times10^{-3}\text{ M}} = 0.077\text{ min}^{-1}$$

$$k_{21} = \frac{1.1\times10^{-3}\text{ M min}^{-1}}{17\times10^{-3}\text{ M}} = 0.065\text{ min}^{-1}$$

An average value would be a reasonable estimate: $k_{\text{avg}} = 0.071\text{ min}^{-1}$

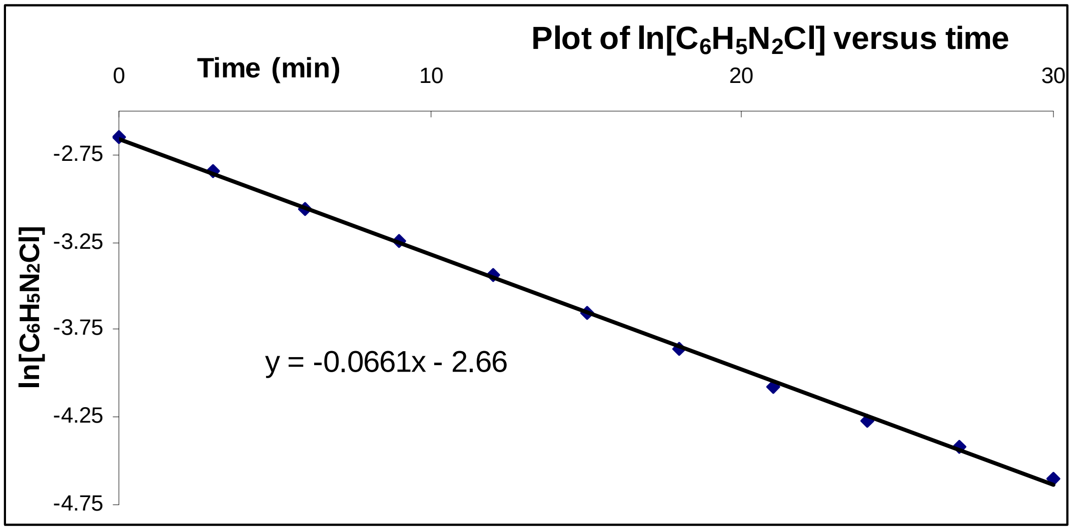
(g) The estimated rate constant gives one value of the half-life:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.071\text{ min}^{-1}} = 9.8\text{ min}$$

The first half-life occurs when $[C_6H_5N_2Cl]$ drops from 0.071 M to 0.0355 M. This occurs at about 10.5 min.

(h) The reaction should be three-fourths complete in two half-lives, or about 20 minutes.

(i) The graph plots $\ln[C_6H_5N_2Cl]$ (in millimoles/L) vs. time in minutes.



The linearity of the graph demonstrates that the reaction is first-order.

(j) $k = -\text{ slope} = -\left(-6.61\times10^{-2}\right)\text{ min}^{-1} = 0.0661\text{ min}^{-1}$

$t_{1/2} = \dfrac{0.693}{0.0661\text{ min}^{-1}} = 10.5\text{ min}$, in good agreement with our previously determined values.

97. **(D)**

(a) In Experiments 1 & 2, [KI] is the same (0.20 M), while $\left[(NH_4)_2S_2O_8\right]$ is halved, from 0.20 M to 0.10 M. As a consequence, the time to produce a color change doubles (i.e., the rate is halved). This indicates that reaction (a) is first-order in $S_2O_8{}^{2-}$. Experiments 2 and 3 produce a similar conclusion. In Experiments 4 and 5, $\left[(NH_4)_2S_2O_8\right]$is the same (0.20 M) while [KI] is halved, from 0.10 to 0.050 M. As a consequence, the time to produce a color change nearly doubles, that is, the rate is halved. This indicates that reaction (a) is also first-order in I^-. Reaction (a) is (1 + 1) second-order overall.

(b) The blue color appears when all the $S_2O_3^{2-}$ has been consumed, for only then does reaction (b) cease. The same amount of $S_2O_3^{2-}$ is placed in each reaction mixture.

$$\text{amount } S_2O_3{}^{2-} = 10.0\text{ mL}\times\frac{1\text{ L}}{1000\text{ mL}}\times\frac{0.010\text{ mol }Na_2S_2O_3}{1\text{ L}}\times\frac{1\text{ mol }S_2O_3{}^{2-}}{1\text{ mol }Na_2S_2O_3} = 1.0\times10^{-4}\text{ mol}$$

Through stoichiometry, we determine the amount of each reactant that reacts before this amount of $S_2O_3{}^{2-}$ will be consumed.

$$\text{amount } S_2O_8^{2-} = 1.0\times10^{-4}\text{ mol } S_2O_3^{2-}\times\frac{1\text{ mol } I_3^-}{2\text{ mol } S_2O_3^{2-}}\times\frac{1\text{ mol } S_2O_8^{2-}}{1\text{ mol } I_3^-}$$

$$= 5.0\times10^{-5}\text{ mol } S_2O_8^{2-}$$

$$\text{amount } I^- = 5.0\times10^{-5}\text{ mol } S_2O_8^{2-}\times\frac{2\text{ mol } I^-}{1\text{ mol } S_2O_8^{2-}} = 1.0\times10^{-4}\text{ mol } I^-$$

Note that we do not use “3 mol I^-” from equation (a) since one mole has not been oxidized; it simply complexes with the product I_2. The total volume of each solution is $(25.0\text{ mL} + 25.0\text{ mL} + 10.0\text{ mL} + 5.0\text{ mL} =)\ 65.0\text{ mL}$, or 0.0650 L.

The amount of $S_2O_8^{2-}$ that reacts in each case is 5.0×10^{-5} mol and thus

$$\Delta\left[S_2O_8^{2-}\right] = \frac{-5.0\times10^{-5}\text{ mol}}{0.0650\text{ L}} = -7.7\times10^{-4}\text{ M}$$

$$\text{Thus, Rate}_1 = \frac{-\Delta\left[S_2O_8^{2-}\right]}{\Delta t} = \frac{+7.7\times10^{-4}\text{ M}}{21\text{ s}} = 3.7\times10^{-5}\text{ M s}^{-1}$$

(c) For Experiment 2, $\text{Rate}_2 = \dfrac{-\Delta\left[S_2O_8^{2-}\right]}{\Delta t} = \dfrac{+7.7\times10^{-4}\text{ M}}{42\text{ s}} = 1.8\times10^{-5}\text{ M s}^{-1}$

To determine the value of k, we need initial concentrations, as altered by dilution.

$$\left[S_2O_8^{2-}\right]_1 = 0.20\text{ M}\times\frac{25.0\text{ mL}}{65.0\text{ mL total}} = 0.077\text{ M} \qquad \left[I^-\right]_1 = 0.20\text{ M}\times\frac{25.0\text{ mL}}{65.0\text{ mL}} = 0.077\text{ M}$$

$$\text{Rate}_1 = 3.7\times10^{-5}\text{ M s}^{-1} = k\left[S_2O_8^{2-}\right]^1\left[I^-\right]^1 = k(0.077\text{ M})^1(0.077\text{ M})^1$$

$$k = \frac{3.7\times10^{-5}\text{ M s}^{-1}}{0.077\text{ M}\times0.077\text{ M}} = 6.2\times10^{-3}\text{ M}^{-1}\text{ s}^{-1}$$

$$\left[S_2O_8^{2-}\right]_2 = 0.10\text{ M}\times\frac{25.0\text{ mL}}{65.0\text{ mL total}} = 0.038\text{ M} \qquad \left[I^-\right]_2 = 0.20\text{ M}\times\frac{25.0\text{ mL}}{65.0\text{ mL}} = 0.077\text{ M}$$

$$\text{Rate}_2 = 1.8\times10^{-5}\text{ M s}^{-1} = k\left[S_2O_8^{2-}\right]^1\left[I^-\right]^1 = k(0.038\text{ M})^1(0.077\text{ M})^1$$

$$k = \frac{1.8\times10^{-5}\text{ M s}^{-1}}{0.038\text{ M}\times0.077\text{ M}} = 6.2\times10^{-3}\text{ M}^{-1}\text{ s}^{-1}$$

(d) First we determine concentrations for Experiment 4.

$$\left[S_2O_8^{2-}\right]_4 = 0.20\text{ M}\times\frac{25.0\text{ mL}}{65.0\text{ mL total}} = 0.077\text{ M} \qquad \left[I^-\right]_4 = 0.10\times\frac{25.0\text{ mL}}{65.0\text{ mL}} = 0.038\text{ M}$$

We have two expressions for Rate; let us equate them and solve for the rate constant.

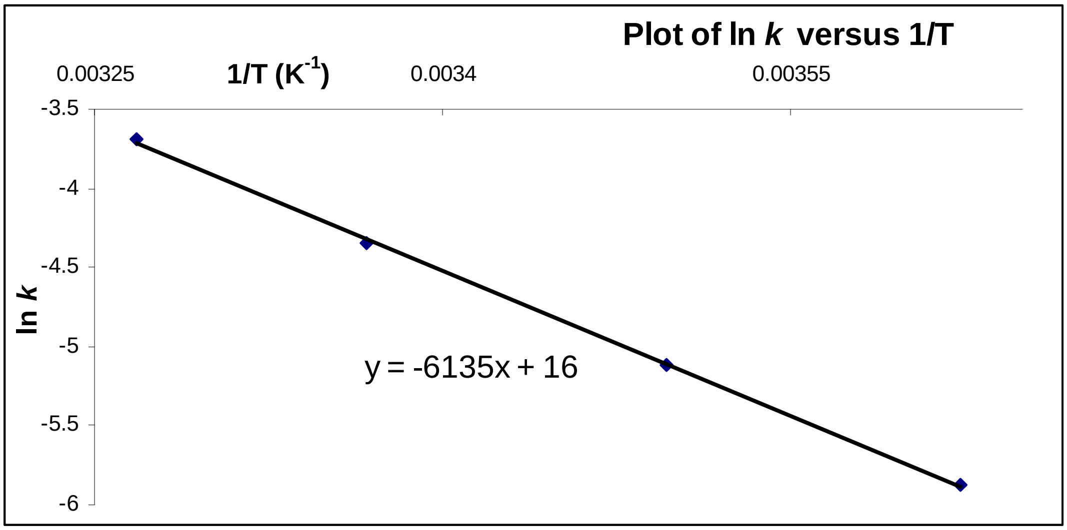
$$\text{Rate}_4 = \frac{-\Delta\left[S_2O_8^{2-}\right]}{\Delta t} = \frac{+7.7\times10^{-4}\text{ M}}{\Delta t} = k\left[S_2O_8^{2-}\right]_4^1\left[I^-\right]_4^1 = k(0.077\text{ M})(0.038\text{ M})$$

$$k = \frac{7.7\times10^{-4}\text{ M}}{\Delta t\times0.077\text{ M}\times0.038\text{ M}} = \frac{0.26\text{ M}^{-1}}{\Delta t} \qquad k_3 = \frac{0.26\text{ M}^{-1}}{189\text{ s}} = 0.0014\text{ M}^{-1}\text{ s}^{-1}$$

$$k_{13} = \frac{0.26\ \mathrm{M}^{-1}}{88\ \mathrm{s}} = 0.0030\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} \qquad k_{24} = \frac{0.26\ \mathrm{M}^{-1}}{42\ \mathrm{s}} = 0.0062\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

$$k_{33} = \frac{0.26\ \mathrm{M}^{-1}}{21\ \mathrm{s}} = 0.012\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

(e) We plot $\ln k$ vs. $1/T$ The slope of the $\text{line} = -E_a / R$.



$E_\mathrm{a} = +6135\ \mathrm{K} \times 8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}} = 51.0 \times 10^3\ \mathrm{J/mol} = 51.0\ \mathrm{kJ/mol}$

The scatter of the data permits only a two significant figure result: 51 kJ/mol

(f) For the mechanism to agree with the reaction stoichiometry, the steps of the mechanism must sum to the overall reaction, in the manner of Hess's law.

(slow) $\mathrm{I^- + S_2O_8^{2-} \rightarrow IS_2O_8^{3-}}$

(fast) $\mathrm{IS_2O_8^{3-} \rightarrow 2\ SO_4^{2-} + I^+}$

(fast) $\mathrm{I^+ + I^- \rightarrow I_2}$

(fast) $\mathrm{I_2 + I^- \rightarrow I_3^-}$

(net) $\mathrm{3\ I^- + S_2O_8^{2-} \rightarrow 2\ SO_4^{2-} + I_3^-}$

Each of the intermediates cancels: $\mathrm{IS_2O_8^{3-}}$ is produced in the first step and consumed in the second, $\mathrm{I^+}$ is produced in the second step and consumed in the third, $\mathrm{I_2}$ is produced in the third step and consumed in the fourth. The mechanism is consistent with the stoichiometry. The rate of the slow step of the mechanism is

$\mathrm{Rate}_1 = k_1\left[\mathrm{S_2O_8^{2-}}\right]^1\left[\mathrm{I^-}\right]^1$

This is exactly the same as the experimental rate law. It is reasonable that the first step be slow since it involves two negatively charged species coming together. We know that like charges repel, and thus this should not be an easy or rapid process.

SELF-ASSESSMENT EXERCISES

98. **(E)**

(a) $[A]_0$: Initial concentration of reactant A

(b) k: Reaction rate constant, which is the proportionality constant between reaction rate and reactant concentration

(c) $t_{1/2}$: Half-life of the reaction, the amount of time that the concentration of a certain reactant is reduced by half

(d) Zero-order reaction: A reaction in which the rate is not dependent on the concentration of the reactant

(e) Catalyst: A substance which speeds up the reaction by lowering the activation energy, but it does not itself get consumed

99. **(E)**

(a) Method of initial rates: A study of the kinetics of the reaction by measuring the initial reaction rates, used to determine the reaction order

(b) Activated complex: Species that exist in a transitory state between the reactants and the products

(c) Reaction mechanism: Sequential elementary steps that show the conversion of reactant(s) to final product(s)

(d) Heterogeneous Catalyst: A catalyst which is in a different physical phase than the reaction medium

(e) Rate-determining step: A reaction which occurs more slowly than other reactions in a mechanism and therefore usually controls the overall rate of the reaction

100. **(E)**

(a) First-order and second-order reactions: In a first-order reaction, the rate of the reaction depends on the concentration of only one substrate and in a 1-to-1 manner (doubling the concentration of the reactant doubles the rate of the reaction). In a second-order reaction, the rate depends on two molecules reacting with each other at the elementary level.

(b) Rate law and integrated rate law: Rate law describes how the rate relates to the concentration of the reactants and the overall rate of a reaction, whereas the integrated rate law expresses the concentration of a reactant as a function of time

(c) Activation energy and enthalpy of reaction: Activation energy is the minimum energy required for a particular reaction to take place, whereas enthalpy of reaction is the amount of heat generated (or consumed) by a reaction when it happens

(d) Elementary process and overall reaction: Individual steps of a reaction mechanism, which describes any molecular event that significantly alters a molecule’s energy or geometry or produces a new molecule

(e) Enzyme and substrate: An enzyme is a protein that acts as a catalyst for a biological reaction. A substrate is the reactant that is transformed in the reaction (in this context, by the enzyme).

101. **(E)** The answer is (c). The rate constant k is only dependent on temperature, not on the concentration of the reactants

102. **(E)** The answers are (b) and (e). Because half-life is 75 seconds, the quantity of reactant left at two half-lives (75 + 75 = 150) equals one-half of the level at 75 seconds. Also, if the initial concentration is doubled, after one half-life the remaining concentration would have to be twice as much as the original concentration.

103. **(E)** The answer is (a). Half-life $t_{½}$ = 13.9 min, k = ln 2/$t_{½}$ = 0.050 min^{-1}. Rate of a first-order reaction is as follows:

$$\frac{d[A]}{dt} = k[A] = (0.050\ \text{min}^{-1})(0.40\ \text{M}) = 0.020\ \text{M min}^{-1}$$

104. **(E)** The answer is (d). A second-order reaction is expressed as follows:

$$\frac{d[A]}{dt} = k[A]^2$$

If the rate of the reaction when [A] =0.50 is $k(0.50)^2 = k(0.25)$. If [A] = 0.25 M, then the rate is $k(0.0625)$, which is ¼ of the rate at [A] =0.50.

105. **(M)** The answer is (b). Going to slightly higher temperatures broadens the molecular speed distribution, which in turn increases the fraction of molecules at the high kinetic energy range (which are those sufficiently energetic to make a reaction happen).

106. **(E)** The answer is (c). Since the reaction at hand is described as an elementary one, the rate of the reaction is $k[A][B]$.

107. **(E)** We note that from the given data, the half-life of the reaction is 100 seconds (at t = 0, [A] = 0.88 M/s, whereas at t = 100, [A] = 0.44 M/s). Therefore, the rate constant k is:
k = ln 2/100 s = 0.00693 s^{-1}. We can now calculate instantaneous rate of the reaction:
d[A]/dt = (0.00693 s^{-1})(0.44 M) = 3.0×10^{-3} $\text{M}\cdot\text{s}^{-1}$

108. **(M)**

(a) For a first-order reaction,

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{30} = 0.0231\,\text{min}^{-1}$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$t = \frac{\ln[A]_t - \ln[A]_0}{-k} = \frac{\ln(0.25) - 0}{-0.0231\,\text{min}^{-1}} = 60.0\ \text{min}$$

(b) For a zero-order reaction,

$$k = \frac{0.5}{t_{1/2}} = \frac{0.5}{30} = 0.0167\ \text{min}^{-1}$$

$$[A]_t - [A]_0 = -kt$$

$$t = \frac{[A]_t - [A]_0}{-k} = \frac{0.25 - 1.00}{-0.0167\ \text{min}^{-1}} = 45.0\ \text{min}$$

109. **(M)** The reaction is second-order, because the half-life doubles with each successive half-life period.

110. **(M)**

(a) The initial rate = $\Delta M/\Delta t$ = (1.204 M – 1.180 M)/(1.0 min) = 0.024 M/min

(b) In experiment 2, the initial concentration is twice that of experiment A. For a second-order reaction:

$$\text{Rate} = k\,[A_{\text{exp }2}]^2 = k\,[2\times A_{\text{exp }1}]^2 = 4\,k\,[A_{\text{exp }1}]^2$$

This means that if the reaction is second order, its initial rate of experiment 2 will be 4 times that of experiment 1 (that is, 4 times as many moles of A will be consumed in a given amount of time). The initial rate is 4×0.024 M/min = 0.096 M/s. Therefore, at 1 minute, [A] = 2.408 – 0.0960 = 2.312 M.

(c) The half-life of the reaction, obtained from experiment 1, is 35 minutes. If the reaction is first-order, then k = ln 2/35 min = 0.0198 min^{-1}.

For a first-order reaction,

$$[A]_t = [A]_0\,e^{-kt}$$

$$[A]_{35\,\text{min}} = (2.408)\exp\left(-0.0198\ \text{min}^{-1}\cdot 30\ \text{min}\right) = 1.33\ \text{M}$$

111. **(D)** The overall stoichiometry of the reaction is determined by adding the two reactions with each other: $A + 2B \rightleftharpoons C + D$

(a) Since I is made slowly but is used very quickly, its rate of formation is essentially zero. The amount of I at any given time during the reaction can be expressed as follows:

$$\frac{d[I]}{dt} = 0 = k_1[A][B] - k_2[B][I]$$

$$[I] = \frac{k_1}{k_2}[A]$$

Using the above expression for [I], we can now determine the overall reaction rate law:

$$\frac{d[C]}{dt} = k_2[I][B] = k_2\cdot\frac{k_1}{k_2}[A]\cdot[B] = k_1[A][B]$$

(b) Adding the two reactions given, we still get the same overall stoichiometry as part (a). However, with the given proposed reaction mechanisms, the rate law for the product(s) is given as follows:

$$\frac{d[B_2]}{dt}=k_1[B]^2-k_{-1}[B_2]-k_2[A][B]=0$$

$$[B_2]=\frac{k_1[B]^2}{k_{-1}+k_2[A]}$$

Therefore,

$$\frac{d[C]}{dt}=k_2[A][B_2]=\frac{k_2k_1[A][B]^2}{k_{-1}+k_2[A]}$$

which does not agree with the observed reaction rate law.

112. **(M)** The answer is (b), first-order, because only in a first-order reaction is the half-life independent of the concentration of the reacting species.

113. **(E)** The answer is (a), zero-order, because in a zero-order reaction the relationship between concentration and time is: $[A]_t = kt + [A]_0$

114. **(M)** The answer is (d). The relationship between rate constant (and thus rate) between two reactions can be expressed as follows:

$$\frac{k_2}{k_1}=\exp\left(\frac{-Ea}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$$

If T_2 is twice T_1, the above expression gets modified as follows:

$$\ln\left(\frac{k_2}{k_1}\right)=\frac{-Ea}{R}\left(\frac{1}{T_1}-\frac{1}{2T_1}\right)$$

$$\left(\frac{R}{E_a}\right)\ln\left(\frac{k_2}{k_1}\right)=\frac{T_1-1}{2T_1},$$

$$\ln\left(\frac{k_2}{k_1}\right)^{\frac{R}{E_a}}=\frac{T_1-1}{2T_1}$$

For reasonably high temperatures,

$$\ln\left(\frac{k_2}{k_1}\right)^{\frac{R}{E_a}}=\frac{T_1}{2T_1}=\frac{1}{2}$$

Therefore,

$$\left(\frac{k_2}{k_1}\right)^{\frac{R}{E_a}}=e^{1/2}=1.64$$

115. **(E)** The answer is (c), remain the same. This is because for a zero-order reaction, $d[A]/dt = k[A]^0 = k$. Therefore, the reaction rate is independent of the concentration of the reactant.

116. **(M)** The overarching concept for this concept map is kinetics as a result of successful collision. The subtopics are collision theory, molecular transition theory. Molecular speed and orientation derive from collision theory. Transition complexes and partial bonds fall under the molecular transition theory heading. Deriving from the collision theory is another major topic, the Arrhenius relationship. The Arrhenius relationship encompasses the ideas of activation energy, Arrhenius collision factor, and exponential relationship between temperature and rate constant.

CHAPTER 15
PRINCIPLES OF CHEMICAL EQUILIBRIUM

PRACTICE EXAMPLES

1A **(E)** The reaction is as follows:

$$2Cu^{2+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Cu^{+}(aq) + Sn^{4+}(aq)$$

Therefore, the equilibrium expression is as follows:

$$K = \frac{\left[Cu^{+}\right]^2\left[Sn^{4+}\right]}{\left[Cu^{2+}\right]^2\left[Sn^{2+}\right]}$$

Rearranging and solving for Cu^{2+}, the following expression is obtained:

$$\left[Cu^{2+}\right] = \left(\frac{\left[Cu^{+}\right]^2\left[Sn^{4+}\right]}{K\left[Sn^{2+}\right]}\right)^{1/2} = \left(\frac{x^2 \cdot x}{(1.48)x}\right)^{1/2} = \frac{x}{1.22}$$

1B **(E)** The reaction is as follows:

$$2Fe^{3+}(aq) + Hg_2^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + 2Hg^{2+}(aq)$$

Therefore, the equilibrium expression is as follows:

$$K = \frac{\left[Fe^{2+}\right]^2\left[Hg^{2+}\right]^2}{\left[Fe^{3+}\right]^2\left[Hg_2^{2+}\right]} = \frac{(0.0025)^2(0.0018)^2}{(0.015)^2(x)} = 9.14\times10^{-6}$$

Rearranging and solving for Hg_2^{2+}, the following expression is obtained:

$$\left[Hg_2^{2+}\right] = \frac{\left[Fe^{2+}\right]^2\left[Hg^{2+}\right]^2}{\left[Fe^{3+}\right]^2 \cdot K} = \frac{(0.0025)^2(0.0018)^2}{(0.015)^2(9.14\times10^{-6})} = 0.009847 \approx 0.0098\text{ M}$$

2A **(E)** The example gives $\underline{K_c}$ = 5.8×10^5 for the reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$. The reaction we are considering is one-third of this reaction. If we divide the reaction by 3, we should take the cube root of the equilibrium constant to obtain the value of the equilibrium constant for the "divided" reaction: $K_{c3} = \sqrt[3]{K_c} = \sqrt[3]{5.8\times10^5} = 8.3\times10^2$

2B **(E)** First we reverse the given reaction to put $NO_2(g)$ on the reactant side. The new equilibrium constant is the inverse of the given one.

$$NO_2(g) \rightleftharpoons NO(g) + \tfrac{1}{2}O_2(g) \qquad K_c' = 1/(1.2\times10^2) = 0.0083$$

Then we double the reaction to obtain 2 moles of $NO_2(g)$ as reactant. The equilibrium constant is then raised to the second power.

$$2\ NO_2(g) \rightleftharpoons 2\ NO(g) + O_2(g) \qquad K_c = (0.00833)^2 = 6.9\times10^{-5}$$

3A **(E)** We use the expression $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$. In this case, $\Delta n_{gas} = 3+1-2 = 2$ and thus we have

$$K_p = K_c\left(RT\right)^2 = 2.8\times10^{-9}\times\left(0.08314\times298\right)^2 = 1.7\times10^{-6}$$

3B **(M)** We begin by writing the K_p expression. We then substitute $P = \left(n/V\right)RT = [concentration]RT$ for each pressure. We collect terms to obtain an expression relating K_c and K_p, into which we substitute to find the value of K_c.

$$K_p = \frac{\{P(H_2)\}^2\{P(S_2)\}}{\{P(H_2S)\}^2} = \frac{([H_2]RT)^2([S_2]RT)}{([H_2S]RT)^2} = \frac{[H_2]^2[S_2]}{[H_2S]^2}RT = K_cRT$$

The same result can be obtained by using $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$, since $\Delta n_{gas} = 2+1-2 = +1$.

$$K_c = \frac{K_p}{RT} = \frac{1.2\times10^{-2}}{0.08314\ \times\left(1065+273\right)} = 1.1\times10^{-4}$$

But the reaction has been reversed and halved. Thus $K_{final} = \sqrt{\frac{1}{K_c}} = \sqrt{\frac{1}{1.1\times10^{-4}}} = \sqrt{9091} = 95$

4A **(E)** We remember that neither solids, such as $Ca_5(PO_4)_3OH(s)$, nor liquids, such as $H_2O(l)$, appear in the equilibrium constant expression. Concentrations of products appear in the numerator, those of reactants in the denominator. $K_c = \frac{\left[Ca^{2+}\right]^5\left[HPO_4^{\ 2-}\right]^3}{\left[H^+\right]^4}$

4B **(E)** First we write the balanced chemical equation for the reaction. Then we write the equilibrium constant expressions, remembering that gases and solutes in aqueous solution appear in the K_c expression, but pure liquids and pure solids do not.

$$3\ Fe(s) + 4\ H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\ H_2(g)$$

$$K_p = \frac{\{P(H_2)\}^4}{\{P(H_2O)\}^4} \qquad K_c = \frac{[H_2]^4}{[H_2O]^4}$$

Because $\Delta n_{gas} = 4-4 = 0$, $K_p = K_c$

5A **(M)** We compute the value of Q_c. Each concentration equals the mass (m) of the substance divided by its molar mass (this quotient is the amount of the substance in moles) and further divided by the volume of the container.

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\dfrac{m \times \dfrac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2}}{V} \times \dfrac{m \times \dfrac{1 \text{ mol } H_2}{2.0 \text{ g } H_2}}{V}}{\dfrac{m \times \dfrac{1 \text{ mol CO}}{28.0 \text{ g CO}}}{V} \times \dfrac{m \times \dfrac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}}{V}} = \frac{\dfrac{1}{44.0 \times 2.0}}{\dfrac{1}{28.0 \times 18.0}} = \frac{28.0 \times 18.0}{44.0 \times 2.0} = 5.7 > 1.00 = K_c$$

(In evaluating the expression above, we cancelled the equal values of V , and we also cancelled the equal values of m.) Because the value of Q_c is larger than the value of K_c, the reaction will proceed to the left to reach a state of equilibrium. Thus, at equilibrium there will be greater quantities of reactants, and smaller quantities of products than there were initially.

5B **(M)** We compare the value of the reaction quotient, Q_p, to that of K_p.

$$Q_p = \frac{\{P(PCl_3)\}\{P(Cl_2)\}}{\{P(PCl_5\}} = \frac{2.19 \times 0.88}{19.7} = 0.098$$

$$K_p = K_c \left(RT\right)^{2-1} = K_c \left(RT\right)^1 = 0.0454 \times \left(0.08206 \times (261 + 273)\right)^1 = 1.99$$

Because $Q_c < K_c$, the net reaction will proceed to the right, forming products and consuming reactants.

6A **(E)** $O_2(g)$ is a reactant. The equilibrium system will shift right, forming product in an attempt to consume some of the added O_2(g) reactant. Looked at in another way, $[O_2]$ is increased above its equilibrium value by the addition of oxygen. This makes Q_c smaller than K_c. (The $[O_2]$ is in the denominator of the expression.) And the system shifts right to drive Q_c back up to K_c, at which point equilibrium will have been achieved.

6B **(M)**

(a) The position of an equilibrium mixture is affected only by changing the concentration of substances that appear in the equilibrium constant expression, $K_c = [CO_2]$. Since CaO(s) is a pure solid, its concentration does not appear in the equilibrium constant expression and thus adding extra CaO(s) will have no direct effect on the position of equilibrium.

(b) The addition of $CO_2(g)$ will increase $[CO_2]$ above its equilibrium value. The reaction will shift left to alleviate this increase, causing some $CaCO_3(s)$ to form.

(c) Since $CaCO_3$(s) is a pure solid like CaO(s), its concentration does not appear in the equilibrium constant expression and thus the addition of any solid $CaCO_3$ to an equilibrium mixture will not have an effect upon the position of equilibrium.

7A **(E)** We know that a decrease in volume or an increase in pressure of an equilibrium mixture of gases causes a net reaction in the direction producing the smaller number of moles of gas. In the reaction in question, that direction is to the left: one mole of $N_2O_4(g)$ is formed when two moles of $NO_2(g)$ combine. Thus, decreasing the cylinder volume would have the initial effect of doubling both $[N_2O_4]$ and $[NO_2]$. In order to reestablish equilibrium, some NO_2 will then be converted into N_2O_4. Note, however, that the NO_2 concentration will still ultimately end up being higher than it was prior to pressurization.

7B **(E)** In the balanced chemical equation for the chemical reaction, $\Delta n_{\text{gas}} = (1+1)-(1+1) = 0$. As a consequence, a change in overall volume or total gas pressure will have no effect on the position of equilibrium. In the equilibrium constant expression, the two partial pressures in the numerator will be affected to exactly the same degree, as will the two partial pressures in the denominator, and, as a result, Q_p will continue to equal K_p.

8A **(E)** The cited reaction is endothermic. Raising the temperature on an equilibrium mixture favors the endothermic reaction. Thus, $N_2O_4(g)$ should decompose more completely at higher temperatures and the amount of $NO_2(g)$ formed from a given amount of $N_2O_4(g)$ will be greater at high temperatures than at low ones.

8B **(E)** The NH_3(g) formation reaction is $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightarrow NH_3(g)$, $\Delta H^\circ = -46.11$ kJ/mol. This reaction is an exothermic reaction. Lowering temperature causes a shift in the direction of this exothermic reaction to the right toward products. Thus, the equilibrium $[NH_3(g)]$ will be greater at $100^\circ C$.

9A **(E)** We write the expression for K_c and then substitute expressions for molar concentrations.

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{0.22}{3.00}\right)^2 \frac{0.11}{3.00}}{\left(\frac{2.78}{3.00}\right)^2} = 2.3\times10^{-4}$$

9B **(M)** We write the equilibrium constant expression and solve for $[N_2O_4]$.

$$K_c = 4.61\times10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} \qquad [N_2O_4] = \frac{[NO_2]^2}{4.61\times10^{-3}} = \frac{(0.0236)^2}{4.61\times10^{-3}} = 0.121\text{ M}$$

Then we determine the mass of N_2O_4 present in 2.26 L.

$$N_2O_4 \text{ mass} = 2.26\text{ L} \times \frac{0.121\text{ mol } N_2O_4}{1\text{ L}} \times \frac{92.01\text{ g } N_2O_4}{1\text{ mol } N_2O_4} = 25.2\text{ g } N_2O_4$$

10A **(M)** We use the initial-change-equilibrium setup to establish the amount of each substance at equilibrium. We then label each entry in the table in the order of its determination (1st, 2nd, 3rd, 4th, 5th), to better illustrate the technique. We know the initial amounts of all substances (1st). There are no products at the start.
Because ‘‘initial’’+ ‘‘change’’= ‘‘equilibrium’’, the equilibrium amount (2nd) of $Br_2(g)$ enables us to determine “change” (3rd) for $Br_2(g)$. We then use stoichiometry to write other entries (4th) on the “change” line. And finally, we determine the remaining equilibrium amounts (5th).

Reaction:	$2\ NOBr(g)$ $\rightleftharpoons$	$2\ NO(g)$ +	$Br_2(g)$
Initial:	1.86 mol (1st)	0.00 mol (1st)	0.00 mol (1st)
Change:	−0.164 mol (4th)	+0.164 mol (4th)	+0.082 mol (3rd)
Equil.:	1.70 mol (5th)	0.164 mol (5th)	0.082 mol (2nd)

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{\left(\frac{0.164}{5.00}\right)^2\left(\frac{0.082\text{ mol}}{5.00}\right)}{\left(\frac{1.70}{5.00}\right)^2} = 1.5\times10^{-4}$$

Here, $\Delta n_{gas} = 2+1-2 = +1.$ $K_p = K_c\left(RT\right)^{+1} = 1.5\times10^{-4}\times\left(0.08314\times298\right) = 3.7\times10^{-3}$

10B **(M)** Use the amounts stated in the problem to determine the equilibrium concentration for each substance.

Reaction:	$2\ SO_3(g)$ $\rightleftharpoons$	$2\ SO_2(g)$ +	$O_2(g)$
Initial:	0 mol	0.100 mol	0.100 mol
Changes:	+0.0916 mol	−0.0916 mol	−0.0916/2 mol
Equil.:	0.0916 mol	0.0084 mol	0.0542 mol
Concentrations:	$\frac{0.0916\text{ mol}}{1.52\text{ L}}$	$\frac{0.0084\text{ mol}}{1.52\text{ L}}$	$\frac{0.0542\text{ mol}}{1.52\text{ L}}$
Concentrations:	0.0603 M	0.0055 M	0.0357 M

We use these values to compute K_c for the reaction and then the relationship $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$ (with $\Delta n_{gas} = 2+1-2 = +1$) to determine the value of K_p.

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(0.0055)^2(0.0357)}{(0.0603)^2} = 3.0\times10^{-4}$$

$$K_p = 3.0\times10^{-4}\times(0.08314\times900) \simeq 0.022$$

11A **(M)** The equilibrium constant expression is $K_p = P\{H_2O\}P\{CO_2\} = 0.231$ at $100\,^\circ C$. From the balanced chemical equation, we see that one mole of $H_2O(g)$ is formed for each mole of $CO_2(g)$ produced. Consequently, $P\{H_2O\} = P\{CO_2\}$ and $K_p = (P\{CO_2\})^2$. We solve this expression for $P\{CO_2\}$: $P\{CO_2\} = \sqrt{(P\{CO_2\})^2} = \sqrt{K_p} = \sqrt{0.231} = 0.481$ atm.

11B **(M)** The equation for the reaction is $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, $K_p = 0.108$ at $25\,^\circ C$. The two partial pressures do not have to be equal at equilibrium. The only instance in which they must be equal is when the two gases come solely from the decomposition of $NH_4HS(s)$. In this case, some of the $NH_3(g)$ has come from another source. We can obtain the pressure of $H_2S(g)$ by substitution into the equilibrium constant expression, since we are given the equilibrium pressure of $NH_3(g)$.

$$K_p = P\{H_2S\}P\{NH_3\} = 0.108 = P\{H_2S\} \times 0.500 \text{ atm } NH_3 \qquad P\{H_2S\} = \frac{0.108}{0.500} = 0.216 \text{ atm}$$

So, $P_{total} = P_{H_2S} + P_{NH_3} = 0.216$ atm + 0.500 atm = 0.716 atm

12A **(M)** We set up this problem in the same manner that we have previously employed, namely designating the equilibrium amount of HI as $2x$. (Note that we have used the same multipliers for x as the stoichiometric coefficients.)

Equation:	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial:	0.150 mol		0.200 mol		0 mol
Changes:	$-x$ mol		$-x$ mol		$+2x$ mol
Equil:	$(0.150-x)$ mol		$(0.200-x)$ mol		$2x$ mol

$$K_c = \frac{\left(\frac{2x}{15.0}\right)^2}{\frac{0.150-x}{15.0} \times \frac{0.200-x}{15.0}} = \frac{(2x)^2}{(0.150-x)(0.200-x)} = 50.2$$

We substitute these terms into the equilibrium constant expression and solve for *x*.

$$4x^2 = (0.150-x)(0.200-x)50.2 = 50.2(0.0300 - 0.350x + x^2) = 1.51 - 17.6x + 50.2x^2$$

$0 = 46.2x^2 - 17.6x + 1.51$ Now we use the quadratic equation to determine the value of *x*.

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{17.6 \pm \sqrt{(17.6)^2 - 4 \times 46.2 \times 1.51}}{2 \times 46.2} = \frac{17.6 \pm 5.54}{92.4} = 0.250 \text{ or } 0.131$$

The first root cannot be used because it would afford a negative amount of H_2 (namely, 0.150-0.250 = -0.100). Thus, we have $2 \times 0.131 = 0.262$ mol HI at equilibrium. We check by substituting the amounts into the K_c expression. (Notice that the volumes cancel.) The slight disagreement in the two values (52 compared to 50.2) is the result of rounding error.

$$K_c = \frac{(0.262)^2}{(0.150-0.131)(0.200-0.131)} = \frac{0.0686}{0.019 \times 0.069} = 52$$

12B **(D)**

(a) The equation for the reaction is $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ and $K_c = 4.61\times10^{-3}$ at $25^\circ C$. In the example, this reaction is conducted in a 0.372 L flask. The effect of moving the mixture to the larger, 10.0 L container is that the reaction will be shifted to produce a greater number of moles of gas. Thus, $NO_2(g)$ will be produced and $N_2O_4(g)$ will dissociate. Consequently, the amount of N_2O_4 will decrease.

(b) The equilibrium constant expression, substituting 10.0 L for 0.372 L, follows.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{10.0}\right)^2}{\frac{0.0240-x}{10.0}} = \frac{4x^2}{10.0(0.0240-x)} = 4.61\times10^{-3}$$

This can be solved with the quadratic equation, and the sensible result is $x = 0.0118$ moles. We can attempt the method of successive approximations. *First*, assume that $x << 0.0240$. We obtain:

$$x = \frac{\sqrt{4.61\times10^{-3}\times10.0\ (0.0240-0)}}{4} = \sqrt{4.61\times10^{-3}\times 2.50\ (0.0240-0)} = 0.0166$$

Clearly x is not much smaller than 0.0240. So, *second*, assume $x \approx 0.0166$. We obtain:

$$x = \sqrt{4.61\times10^{-3}\times2.50(0.0240-0.0166)} = 0.00925$$

This assumption is not valid either. So, *third*, assume $x \approx 0.00925$. We obtain:

$$x = \sqrt{4.61\times10^{-3}\times2.50(0.0240-0.00925)} = 0.0130$$

Notice that after each cycle the value we obtain for x gets closer to the value obtained from the roots of the equation. The values from the next several cycles follow.

Cycle	4th	5th	6th	7th	8th	9th	10th	11th
x value	0.0112	0.0121	0.0117	0.0119	0.01181	0.01186	0.01183	0.01184

The amount of N_2O_4 at equilibrium is 0.0118 mol, less than the 0.0210 mol N_2O_4 at equilibrium in the 0.372 L flask, as predicted.

13A **(M)** Again we base our solution on the balanced chemical equation.

Equation:	$Ag^{+}(aq)+$	$Fe^{2+}(aq) \rightleftharpoons$	$Fe^{3+}(aq)+ Ag(s)$	$K_c = 2.98$
Initial:	0 M	0 M	1.20 M	
Changes:	$+x$ M	$+x$ M	$-x$ M	
Equil:	x M	x M	$(1.20-x)$ M	

$$K_c = \frac{[Fe^{3+}]}{[Ag^{+}][Fe^{2+}]} = 2.98 = \frac{1.20-x}{x^2} \quad 2.98\ x^2 = 1.20-x \quad 0 = 2.98x^2 + x - 1.20$$

We use the quadratic formula to obtain a solution.

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-1.00 \pm \sqrt{(1.00)^2 + 4\times 2.98\times 1.20}}{2\times 2.98} = \frac{-1.00 \pm 3.91}{5.96} = 0.488 \text{ M or} -0.824 \text{ M}$$

A negative root makes no physical sense. We obtain the equilibrium concentrations from *x*.

$$[Ag^{+}] = [Fe^{2+}] = 0.488 \text{ M} \qquad [Fe^{3+}] = 1.20 - 0.488 = 0.71 \text{ M}$$

13B **(M)** We first calculate the value of Q_c to determine the direction of the reaction.

$$Q_c = \frac{[V^{2+}][Cr^{3+}]}{[V^{3+}][Cr^{2+}]} = \frac{0.150\times 0.150}{0.0100\times 0.0100} = 225 < 7.2\times 10^2 = K_c$$

Because the reaction quotient has a smaller value than the equilibrium constant, a net reaction to the right will occur. We now set up this solution as we have others, heretofore, based on the balanced chemical equation.

	$V^{3+}(aq)$	$+\ Cr^{2+}(aq)$	$\rightleftharpoons\ V^{2+}(aq)$	$+\ Cr^{3+}(aq)$
initial	0.0100 M	0.0100 M	0.150 M	0.150 M
changes	–*x* M	–*x* M	+*x* M	+*x* M
equil	(0.0100 – *x*)M	(0.0100 – *x*)M	(0.150 + *x*)M	(0.150 + *x*)M

$$K_c = \frac{[V^{2+}][Cr^{3+}]}{[V^{3+}][Cr^{2+}]} = \frac{(0.150+x)\times(0.150+x)}{(0.0100-x)\times(0.0100-x)} = 7.2\times 10^2 = \left(\frac{0.150+x}{0.0100-x}\right)^2$$

If we take the square root of both sides of this expression, we obtain

$$\sqrt{7.2\times 10^2} = \frac{0.150+x}{0.0100-x} = 27$$

0.150 + *x* = 0.27 – 27*x* which becomes $28x = 0.12$ and yields 0.0043 M. Then the equilibrium concentrations are: $[V^{3+}] = [Cr^{2+}] = 0.0100\text{ M} - 0.0043\text{ M} = 0.0057\text{ M}$

$$[V^{2+}] = [Cr^{3+}] = 0.150\text{ M} + 0.0043\text{ M} = 0.154\text{ M}$$

INTEGRATIVE EXAMPLE

A. **(E)** We will determine the concentration of F6P and the final enthalpy by adding the two reactions:

$$\begin{array}{c} C_6H_{12}O_6 + ATP \rightleftharpoons G6P + ADP \\ G6P \rightleftharpoons F6P \\ \hline C_6H_{12}O_6 + ATP \rightleftharpoons ADP + F6P \end{array}$$

$\Delta H_{TOT} = -19.74\ kJ \cdot mol^{-1} + 2.84\ kJ \cdot mol^{-1} = -16.9\ kJ \cdot mol^{-1}$

Since the overall reaction is obtained by adding the two individual reactions, then the overall reaction equilibrium constant is the product of the two individual K values. That is,
$K = K_1 \cdot K_2 = 1278$

The equilibrium concentrations of the reactants and products is determined as follows:

	$C_6H_{12}O_6$	+	ATP	$\rightleftharpoons$	ADP	+	F6P
Initial	1.20×10^{-6}		1×10^{-4}		1×10^{-2}		0
Change	$-x$		$-x$		$+x$		$+x$
Equil	$1.20\times10^{-6}-x$		$1\times10^{-4}-x$		$1\times10^{-2}+x$		x

$$K = \frac{[ADP][F6P]}{[C_6H_{12}O_6][ATP]}$$

$$1278 = \frac{(1\times10^{-2}+x)(x)}{(1.20\times10^{-6}-x)(1\times10^{-4}-x)} = \frac{1.0\times10^{-2}x + x^2}{1.2\times10^{-10} - 1.012\times10^{-4}x + x^2}$$

Expanding and rearranging the above equation yields the following second-order polynomial:
$1277x^2 - 0.1393x + 1.534\times10^{-7} = 0$
Using the quadratic equation to solve for x, we obtain two roots: $x = 1.113\times10^{-6}$ and 1.080×10^{-4}. Only the first one makes physical sense, because it is less than the initial value of $C_6H_{12}O_6$. Therefore, $[F6P]_{eq} = 1.113\times10^{-6}$.

During a fever, the body generates heat. Since the net reaction above is exothermic,
Le Châtelier's principle would force the equilibrium to the left, reducing the amount of F6P generated.

B. **(E)**

(a) The ideal gas law can be used for this reaction, since we are relating vapor pressure and concentration. Since K = 3.3×10^{-29} for decomposition of Br_2 to Br (very small), then it can be ignored.

$$V=\frac{nRT}{P}=\frac{(0.100\text{ mol})(0.08206\text{ L}\cdot\text{atm}\cdot\text{K}^{-1})(298.15\text{ K})}{0.289\text{ atm}}=8.47\text{ L}$$

(b) At 1000 K, there is much more Br being generated from the decomposition of Br_2. However, K is still rather small, and this decomposition does not notably affect the volume needed.

EXERCISES

Writing Equilibrium Constants Expressions

1. **(E)**

(a) $2\text{ COF}_2(g) \rightleftharpoons \text{CO}_2(g)+\text{CF}_4(g)$ $\qquad K_c=\dfrac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$

(b) $\text{Cu}(s)+2\text{ Ag}^+(aq) \rightleftharpoons \text{Cu}^{2+}(aq)+2\text{ Ag}(s)$ $\qquad K_c=\dfrac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$

(c) $\text{S}_2\text{O}_8{}^{2-}(aq)+2\text{ Fe}^{2+}(aq) \rightleftharpoons 2\text{ SO}_4{}^{2-}(aq)+2\text{ Fe}^{3+}(aq)$ $\qquad K_c=\dfrac{[\text{SO}_4{}^{2-}]^2[\text{Fe}^{3+}]^2}{[\text{S}_2\text{O}_8{}^{2-}][\text{Fe}^{2+}]^2}$

2. **(E)**

(a) $4\text{ NH}_3(g)+3\text{ O}_2(g) \rightleftharpoons 2\text{ N}_2(g)+6\text{ H}_2\text{O}(g)$ $\qquad K_P=\dfrac{P\{\text{N}_2\}^2\cdot P\{\text{H}_2\text{O}\}^6}{P\{\text{NH}_3\}^4\cdot P\{\text{O}_2\}^3}$

(b) $7\text{ H}_2(g)+2\text{ NO}_2(g) \rightleftharpoons 2\text{ NH}_3(g)+4\text{ H}_2\text{O}(g)$ $\qquad K_P=\dfrac{P\{\text{NH}_3\}^2\cdot P\{\text{H}_2\text{O}\}^4}{P\{\text{H}_2\}^7\cdot P\{\text{NO}_2\}^2}$

(c) $\text{N}_2(g)+\text{Na}_2\text{CO}_3(s)+4\text{ C}(s) \rightleftharpoons 2\text{ NaCN}(s)+3\text{ CO}(g)$ $\qquad K_c=\dfrac{[\text{CO}]^3}{[\text{N}_2]}$

3. **(E)**

(a) $K_c=\dfrac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$ $\qquad$ **(b)** $K_c=\dfrac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$ $\qquad$ **(c)** $K_c=\dfrac{[\text{OH}^-]^2}{[\text{CO}_3{}^{2-}]}$

4. **(E)**

(a) $K_p = \dfrac{P\{CH_4\}P\{H_2S\}^2}{P\{CS_2\}P\{H_2\}^4}$ **(b)** $K_p = P\{\ O_2\ \}^{1/2}$ **(c)** $K_p = P\{CO_2\}P\{H_2O\}$

5. **(E)** In each case we write the equation for the formation reaction and then the equilibrium constant expression, K_c, for that reaction.

(a) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightleftharpoons HF(g)$ $K_c = \dfrac{[HF]}{[H_2]^{1/2}[F_2]^{1/2}}$

(b) $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ $K_c = \dfrac{[\ NH_3]^2}{[N_2][H_2]^3}$

(c) $2\ N_2(g) + O_2(g) \rightleftharpoons 2\ N_2O(g)$ $K_c = \dfrac{[N_2O]^2}{[N_2]^2[O_2]}$

(d) $\frac{1}{2}Cl_2(g) + \frac{3}{2}F_2(g) \rightleftharpoons ClF_3(l)$ $K_c = \dfrac{1}{[Cl_2]^{1/2}[F_2]^{3/2}}$

6. **(E)** In each case we write the equation for the formation reaction and then the equilibrium constant expression, K_p, for that reaction.

(a) $\frac{1}{2}\ N_2(g) + \frac{1}{2}\ O_2(g) + \frac{1}{2}\ Cl_2(g) \rightleftharpoons NOCl(g)$ $K_p = \dfrac{[P_{NOCl}]}{[P_{N_2}]^{1/2}[P_{O_2}]^{1/2}[P_{Cl_2}]^{1/2}}$

(b) $N_2(g) + 2\ O_2(g) + Cl_2(g) \rightleftharpoons 2\ ClNO_2(g)$ $K_p = \dfrac{[P_{ClNO_2}]^2}{[P_{N_2}][P_{O_2}]^2[P_{Cl_2}]}$

(c) $N_2(g) + 2\ H_2(g) \rightleftharpoons N_2H_4(g)$ $K_p = \dfrac{P_{N_2H_4}}{[P_{N_2}][P_{H_2}]^2}$

(d) $\frac{1}{2}\ N_2(g) + 2\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightleftharpoons NH_4Cl(s)$ $K_p = \dfrac{1}{[P_{N_2}]^{1/2}[P_{H_2}]^2[P_{Cl_2}]^{1/2}}$

7. **(E)** Since $K_p = K_c(RT)^{\Delta n_g}$, it is also true that $K_c = K_p(RT)^{-\Delta n_g}$.

(a) $K_c = \dfrac{[SO_2][Cl_2]}{[SO_2Cl_2]} = K_p(RT)^{-(+1)} = 2.9 \times 10^{-2}(0.08206 \times 303)^{-1} = 0.0012$

(b) $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]} = K_p(RT)^{-(-1)} = 1.48 \times 10^4 \times (0.08206 \times 303) = 5.55 \times 10^5$

(c) $K_c = \dfrac{[H_2S]^3}{[H_2]^3} = K_p(RT)^0 = K_p = 0.429$

8. **(E)** $K_p = K_c\left(RT\right)^{\Delta n_g}$, with $R = 0.08206$ L · atm mol^{-1} K^{-1}

(a) $$K_p = \frac{P\{NO_2\}^2}{P\{N_2O_4\}} = K_c(RT)^{+1} = 4.61\times10^{-3}(0.08206\times298)^1 = 0.113$$

(b) $$K_p = \frac{P\{C_2H_2\}P\{H_2\}^3}{P\{CH_4\}^2} = K_c(RT)^{(+2)} = (0.154)(0.08206\times2000)^2 = 4.15\times10^3$$

(c) $$K_p = \frac{P\{H_2\}^4P\{CS_2\}}{P\{H_2S\}^2P\{CH_4\}} = K_c(RT)^{(+2)} = (5.27\times10^{-8})(0.08206\times973)^2 = 3.36\times10^{-4}$$

<u>9.</u> **(E)** The equilibrium reaction is $H_2O(l) \rightleftharpoons H_2O(g)$ with $\Delta n_{gas} = +1$. $K_p = K_c\left(RT\right)^{\Delta n_g}$ gives $K_c = K_p\left(RT\right)^{-\Delta n_g}$. $\quad K_p = P\{H_2O\} = 23.8 \text{ mmHg}\times\frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.0313$

$$K_c = K_p\left(RT\right)^{-1} = \frac{K_p}{RT} = \frac{0.0313}{0.08206\times298} = 1.28\times10^{-3}$$

10. **(E)** The equilibrium rxn is $C_6H_6(l) \rightleftharpoons C_6H_6(g)$ with $\Delta n_{gas} = +1$. Using $K_p = K_c\left(RT\right)^{\Delta n_g}$,

$$K_p = K_c\left(RT\right) = 5.12\times10^{-3}\left(0.08206\times298\right) = 0.125 = P\{C_6H_6\}$$

$$P\{C_6H_6\} = 0.125 \text{ atm}\times\frac{760 \text{ mmHg}}{1 \text{ atm}} = 95.0 \text{ mmHg}$$

<u>11</u>. **(E)** Add one-half of the reversed 1st reaction with the 2nd reaction to obtain the desired reaction.

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \qquad K_c = \frac{1}{\sqrt{2.1\times10^{30}}}$

$NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g) \qquad K_c = 1.4$

net: $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g) \qquad K_c = \frac{1.4}{\sqrt{2.1\times10^{30}}} = 9.7\times10^{-16}$

12. **(M)** We combine the several given reactions to obtain the net reaction.

$2\,N_2O(g) \rightleftharpoons 2\,N_2(g) + O_2(g) \qquad K_c = \frac{1}{\left(2.7\times10^{-18}\right)^2}$

$4\,NO_2(g) \rightleftharpoons 2\,N_2O_4(g) \qquad K_c = \frac{1}{\left(4.6\times10^{-3}\right)^2}$

$2N_2(g) + 4O_2(g) \rightleftharpoons 4NO_2(g) \qquad K_c = (4.1\times10^{-9})^4$

net: $2\,N_2O(g) + 3\,O_2(g) \rightleftharpoons 2\,N_2O_4(g) \quad K_{c(Net)} = \frac{\left(4.1\times10^{-9}\right)^4}{\left(2.7\times10^{-18}\right)^2\left(4.6\times10^{-3}\right)^2} = 1.8\times10^6$

13. **(M)** We combine the K_c values to obtain the value of K_c for the overall reaction, and then convert this to a value for K_p.

$$2\ CO_2(g) + 2H_2(g) \rightleftharpoons 2\ CO(g) + 2\ H_2O(g) \qquad K_c = (1.4)^2$$

$$2\ C(graphite) + O_2(g) \rightleftharpoons 2\ CO(g) \qquad K_c = (1\times10^8)^2$$

$$4\ CO(g) \rightleftharpoons 2\ C(graphite) + 2\ CO_2(g) \qquad K_c = \frac{1}{(0.64)^2}$$

$$\text{net:} \quad 2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K_{c(Net)} = \frac{(1.4)^2(1\times10^8)^2}{(0.64)^2} = 5\times10^6$$

$$K_p = K_c(RT)^{\Delta n} = \frac{K_c}{RT} = \frac{5\times10^{16}}{0.08206\times1200} = 5\times10^{14}$$

14. **(M)** We combine the K_p values to obtain the value of K_p for the overall reaction, and then convert this to a value for K_c.

$$2\ NO_2Cl(g) \rightleftharpoons 2\ NOCl(g) + O_2(g) \qquad K_p = \left(\frac{1}{1.1\times10^2}\right)^2$$

$$2\ NO_2(g) + Cl_2(g) \rightleftharpoons 2\ NO_2Cl(g) \qquad K_p = (0.3)^2$$

$$N_2(g) + 2\ O_2(g) \rightleftharpoons 2\ NO_2(g) \qquad K_p = (1.0\times10^{-9})^2$$

$$\text{net:}\ N_2(g) + O_2(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g) \qquad K_{p(Net)} = \frac{(0.3)^2(1.0\times10^{-9})^2}{(1.1\times10^2)^2} = 7.\underline{4}\times10^{-24}$$

$$K_p = K_c(RT)^{\Delta n} \qquad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{7.\underline{4}\times10^{-24}}{(0.08206\times298)^{2-3}} = 2\times10^{-22}$$

15. **(E)** $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

In terms of concentration, K = a(H_2CO_3)/a(CO_2)

In terms of concentration and partial pressure, $K = \dfrac{[H_2CO_3]/c^\circ}{P_{CO_2}/P^\circ}$

16. **(E)** $2\ Fe(s) + 3\ O_2(g) \rightleftharpoons Fe_2O_3(s)$

$K = \dfrac{a_{Fe_2O_3}}{a_{Fe}\cdot a_{O_2}}$. Since activity of solids and liquids is defined as 1, then the expression simplifies to $K = \dfrac{1}{a_{O_2}}$

Similarly, in terms of pressure and concentration, $K = 1/(P_{O_2}/P^\circ)$

Experimental Determination of Equilibrium Constants

<u>17.</u> **(M)** First, we determine the concentration of PCl_5 and of Cl_2 present initially and at equilibrium, respectively. Then we use the balanced equation to help us determine the concentration of each species present at equilibrium.

$$[PCl_5]_{initial} = \frac{1.00\times10^{-3}\text{ mol }PCl_5}{0.250\text{ L}} = 0.00400\text{ M} \qquad [Cl_2]_{equil} = \frac{9.65\times10^{-4}\text{ mol }Cl_2}{0.250\text{ L}} = 0.00386\text{ M}$$

Equation:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial:	0.00400M		0 M		0 M
Changes:	–xM		+xM		+xM
Equil:	0.00400M-xM		xM		xM ← 0.00386 M (from above)

At equilibrium, $[Cl_2] = [PCl_3] = 0.00386$ M and $[PCl_5] = 0.00400\text{M} - x\text{M} = 0.00014$ M

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.00386\,\text{M})(0.00386\,\text{M})}{0.00014\,\text{M}} = 0.10\underline{6}$$

18. **(M)** First we determine the partial pressure of each gas.

$$P_{\text{initial}}\{H_2(g)\} = \frac{nRT}{V} = \frac{1.00\,\text{g }H_2 \times \frac{1\,\text{mol }H_2}{2.016\,\text{g }H_2} \times \frac{0.08206\,\text{L atm}}{\text{mol K}} \times 1670\,\text{K}}{0.500\,\text{L}} = 136\,\text{atm}$$

$$P_{\text{initial}}\{H_2S(g)\} = \frac{nRT}{V} = \frac{1.06\,\text{g }H_2S \times \frac{1\,\text{mol }H_2S}{34.08\,\text{g }H_2S} \times \frac{0.08206\,\text{L atm}}{\text{mol K}} \times 1670\,\text{K}}{0.500\,\text{L}} = 8.52\,\text{atm}$$

$$P_{\text{equil}}\{S_2(g)\} = \frac{nRT}{V} = \frac{8.00\times10^{-6}\text{ mol }S_2 \times \frac{0.08206\,\text{L atm}}{\text{mol K}} \times 1670\,\text{K}}{0.500\,\text{L}} = 2.19\times10^{-3}\text{ atm}$$

Equation:	$2\,H_2(g)$	+ $S_2(g)$	$\rightleftharpoons$ $2\,H_2S(g)$
Initial:	136 atm	0 atm	8.52 atm
Changes:	+0.00438 atm	0.00219 atm	–0.00438 atm
Equil:	136 atm	0.00219 atm	8.52 atm

$$K_p = \frac{P\{H_2S(g)\}^2}{P\{H_2(g)\}^2\,P\{S_2(g)\}} = \frac{(8.52)^2}{(136)^2\,0.00219} = 1.79$$

<u>19.</u> **(M)**

(a) $$K_c = \frac{\left[\mathrm{PCl_5}\right]}{\left[\mathrm{PCl_3}\right]\left[\mathrm{Cl_2}\right]} = \frac{\dfrac{0.105\ \mathrm{g\ PCl_5}}{2.50\ \mathrm{L}} \times \dfrac{1\ \mathrm{mol\ PCl_5}}{208.2\ \mathrm{g}}}{\left(\dfrac{0.220\ \mathrm{g\ PCl_3}}{2.50\ \mathrm{L}} \times \dfrac{1\ \mathrm{mol\ PCl_3}}{137.3\mathrm{g}}\right) \times \left(\dfrac{2.12\ \mathrm{g\,Cl_2}}{2.50\ \mathrm{L}} \times \dfrac{1\mathrm{mol\,Cl_2}}{70.9\ \mathrm{g}}\right)} = 26.3$$

(b) $$K_p = K_c\left(RT\right)^{\Delta n} = 26.3\left(0.08206 \times 523\right)^{-1} = 0.613$$

20. **(M)**

$$[\mathrm{ICl}]_{\mathrm{initial}} = \frac{0.682\ \mathrm{g\ ICl} \times \dfrac{1\ \mathrm{mol\ ICl}}{162.36\ \mathrm{g\ ICl}}}{0.625\ \mathrm{L}} = 6.72 \times 10^{-3}\ \mathrm{M}$$

Reaction:	$2\ \mathrm{ICl(g)}$	$\rightleftharpoons$	$\mathrm{I_2(g)}$	+	$\mathrm{Cl_2(g)}$
Initial:	6.72×10^{-3} M		0 M		0 M
Change	$-2x$		$+x$		$+x$
Equilibrium	6.72×10^{-3} M $-2x$		x		x

$$[\mathrm{I_2}]_{\mathrm{equil}} = \frac{0.0383\ \mathrm{g\ I_2} \times \dfrac{1\ \mathrm{mol\ I_2}}{253.808\ \mathrm{g\ I_2}}}{0.625\mathrm{L}} = 2.41 \times 10^{-4}\ \mathrm{M} \quad = x$$

$$K_c = \frac{x \cdot x}{(6.72 \times 10^{-3} - 2x)} = \frac{(2.41 \times 10^{-4})^2}{(6.72 \times 10^{-3} - 2(2.41 \times 10^{-4}))} = 9.31 \times 10^{-6}$$

<u>21.</u> **(E)**

$$\mathrm{K} = \frac{\left[\mathrm{Fe^{3+}}\right]}{\left[\mathrm{H^+}\right]^3} \Rightarrow 9.1 \times 10^3 = \frac{\left[\mathrm{Fe^{3+}}\right]}{\left(1.0 \times 10^{-7}\right)^3}$$

$$\left[\mathrm{Fe^{3+}}\right] = 9.1 \times 10^{-18}\ \mathrm{M}$$

22. **(E)**

$$\mathrm{K} = \frac{\left[\mathrm{NH_3(aq)}\right]}{\mathrm{P_{NH_3(g)}}} \Rightarrow 57.5 = \frac{5 \times 10^{-9}}{\mathrm{P_{NH_3(g)}}}$$

$$\mathrm{P_{NH_3(g)}} = 5 \times 10^{-9} / 57.5 = 8.7 \times 10^{-11}$$

Equilibrium Relationships

<u>23.</u> **(M)** $K_c = 281 = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = \dfrac{[SO_3]^2}{[SO_2]^2} \times \dfrac{0.185\text{ L}}{0.00247\text{ mol}} \quad \dfrac{[SO_2]}{[SO_3]} = \sqrt{\dfrac{0.185}{0.00247 \times 281}} = 0.516$

24. **(M)** $K_c = 0.011 = \dfrac{[I]^2}{[I_2]} = \dfrac{\left(\dfrac{0.37\text{ mol I}}{V}\right)^2}{\dfrac{1.00\text{ mol }I_2}{V}} = \dfrac{1}{V} \times 0.14 \quad V = \dfrac{0.14}{0.011} = 13\text{ L}$

<u>25.</u> **(M)**

(a) A possible equation for the oxidation of $NH_3(g)$ to $NO_2(g)$ follows.

$$NH_3(g) + \tfrac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \tfrac{3}{2}H_2O(g)$$

(b) We obtain K_p for the reaction in part (a) by appropriately combining the values of K_p given in the problem.

$NH_3(g) + \tfrac{5}{4}O_2(g) \rightleftharpoons NO(g) + \tfrac{3}{2}H_2O(g) \qquad K_p = 2.11 \times 10^{19}$

$NO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO_2(g) \qquad K_p = \dfrac{1}{0.524}$

net: $NH_3(g) + \tfrac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \tfrac{3}{2}H_2O(g) \qquad K_p = \dfrac{2.11 \times 10^{19}}{0.524} = 4.03 \times 10^{19}$

26. **(D)**

(a) We first determine $[H_2]$ and $[CH_4]$ and then $[C_2H_2]$. $[CH_4] = [H_2] = \dfrac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\text{ M}$

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} \quad [C_2H_2] = \frac{K_c[CH_4]^2}{[H_2]^3} = \frac{0.154 \times 0.10^2}{0.10^3} = 1.54\text{ M}$$

In a 1.00 L container, each concentration numerically equals the molar quantities of the substance.

$$\chi\{C_2H_2\} = \frac{1.54\text{ mol }C_2H_2}{1.54\text{ mol }C_2H_2 + 0.10\text{ mol }CH_4 + 0.10\text{ mol }H_2} = 0.89$$

(b) The conversion of $CH_4(g)$ to $C_2H_2(g)$ is favored at low pressures, since the conversion reaction has a larger sum of the stoichiometric coefficients of gaseous products (4) than of reactants (2).

(c) Initially, all concentrations are halved when the mixture is transferred to a flask that is twice as large. To re-establish equilibrium, the system reacts to the right, forming more moles of gas (to compensate for the drop in pressure). We base our solution on the balanced chemical equation, in the manner we have used before.

Equation:	$2\ \mathrm{CH_4(g)}$	$\rightleftharpoons$	$\mathrm{C_2H_2(g)}$	+	$3\ \mathrm{H_2}$
Initial:	$\dfrac{0.10\,\mathrm{mol}}{2.00\,\mathrm{L}}$		$\dfrac{1.5\,\mathrm{mol}}{2.00\,\mathrm{L}}$		$\dfrac{0.10\,\mathrm{mol}}{2.00\,\mathrm{L}}$
	$= 0.050\ \mathrm{M}$		$= 0.75\ \mathrm{M}$		$= 0.050\ \mathrm{M}$
Changes:	$-2x\ \mathrm{M}$		$+x\ \mathrm{M}$		$+3x\ \mathrm{M}$
Equil:	$(0.050-2x)\ \mathrm{M}$		$(0.0750+x)\ \mathrm{M}$		$(0.050+3x)\ \mathrm{M}$

$$K_c = \frac{[\mathrm{C_2H_2}][\mathrm{H_2}]^3}{[\mathrm{CH_4}]^2} = \frac{(0.050+3x)^3(0.750+x)}{(0.050-2x)^2} = 0.154$$

We can solve this 4th-order equation by successive approximations.
First guess: $x = 0.010\ \mathrm{M}$.

$$x = 0.010 \qquad Q_c = \frac{(0.050+3(0.010))^3(0.750+0.010)}{(0.050-2(0.010))^2} = \frac{(0.080)^3(0.760)}{(0.030)^2} = 0.433 > 0.154$$

$$x = 0.020 \qquad Q_c = \frac{(0.050+3(0.020))^3(0.750+0.020)}{(0.050-2(0.020))^2} = \frac{(0.110)^3(0.770)}{(0.010)^2} = 10.2 > 0.154$$

$$x = 0.005 \qquad Q_c = \frac{(0.050+3(0.005))^3(0.750+0.005)}{(0.050-2(0.005))^2} = \frac{(0.065)^3(0.755)}{(0.040)^2} = 0.129 < 0.154$$

$$x = 0.006 \qquad Q_c = \frac{(0.050+3(0.006))^3(0.750+0.006)}{(0.050-2(0.006))^2} = \frac{(0.068)^3(0.756)}{(0.038)^2} = 0.165 > 0.154$$

This is the maximum number of significant figures our system permits. We have $x = 0.006\ \mathrm{M}$. $[\mathrm{CH_4}] = 0.038\ \mathrm{M}$; $[\mathrm{C_2H_2}] = 0.756\ \mathrm{M}$; $[\mathrm{H_2}] = 0.068\ \mathrm{M}$

Because the container volume is 2.00 L, the molar amounts are double the values of molarities.

$$2.00\ \mathrm{L} \times \frac{0.756\ \mathrm{mol\ C_2H_2}}{1\ \mathrm{L}} = 1.51\ \mathrm{mol\ C_2H_2} \qquad 2.00\ \mathrm{L} \times \frac{0.038\ \mathrm{mol\ CH_4}}{1\ \mathrm{L}} = 0.076\ \mathrm{mol\ CH_4}$$

$$2.00\ \mathrm{L} \times \frac{0.068\ \mathrm{mol\ H_2}}{1\ \mathrm{L}} = 0.14\ \mathrm{mol\ H_2}$$

Thus, the increase in volume results in the production of some additional $\mathrm{C_2H_2}$.

27. **(M)**

(a) $$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{\frac{n\{CO\}}{V} \times \frac{n\{H_2O\}}{V}}{\frac{n\{CO_2\}}{V} \times \frac{n\{H_2\}}{V}}$$

Since V is present in both the denominator and the numerator, it can be stricken from the expression. This happens here because $\Delta n_g = 0$. Therefore, K_c is independent of V.

(b) Note that $K_p = K_c$ for this reaction, since $\Delta n_{gas} = 0$.

$$K_c = K_p = \frac{0.224 \text{ mol CO} \times 0.224 \text{ mol } H_2O}{0.276 \text{ mol } CO_2 \times 0.276 \text{ mol } H_2} = 0.659$$

28. **(M)** For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ the value of $K_p = 23.2$

The expression for Q_p is $\frac{[CO_2][H_2]}{[CO][H_2O]}$. Consider each of the provided situations

(a) $P_{CO} = P_{H_2O} = P_{H_2} = P_{CO_2}$; $Q_p = 1$ Not an equilibrium position

(b) $\frac{P_{H_2}}{P_{H_2O}} = \frac{P_{CO_2}}{P_{CO}} = x$; $Q_p = x^2$ If $x = \sqrt{23.2}$, this is an equilibrium position.

(c) $(P_{CO} \times P_{H_2O}) = (P_{CO_2} \times P_{H_2})$; $Q_p = 1$ Not an equilibrium position

(d) $\frac{P_{H_2}}{P_{CO}} = \frac{P_{CO_2}}{P_{H_2O}} = x$; $Q_p = x^2$ If $x = \sqrt{23.2}$, this is an equilibrium position.

Direction and Extent of Chemical Change

29. **(M)** We compute the value of Q_c for the given amounts of product and reactants.

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{1.8 \text{ mol } SO_3}{7.2 \text{ L}}\right)^2}{\left(\frac{3.6 \text{ mol } SO_2}{7.2 \text{ L}}\right)^2 \frac{2.2 \text{ mol } O_2}{7.2 \text{ L}}} = 0.82 < K_c = 100$$

The mixture described cannot be maintained indefinitely. In fact, because $Q_c < K_c$, the reaction will proceed to the right, that is, toward products, until equilibrium is established. We do not know how long it will take to reach equilibrium.

30. **(M)** We compute the value of Q_c for the given amounts of product and reactants.

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\dfrac{0.0205\,\text{mol}\,NO_2}{5.25\,\text{L}}\right)^2}{\dfrac{0.750\,\text{mol}\,N_2O_4}{5.25\,\text{L}}} = 1.07\times10^{-4} < K_c = 4.61\times10^{-3}$$

The mixture described cannot be maintained indefinitely. In fact, because $Q_c < K_c$, the reaction will proceed to the right, that is, toward products, until equilibrium is established. If E_a is large, however, it may take some time to reach equilibrium.

31. **(M)**

(a) We determine the concentration of each species in the gaseous mixture, use these concentrations to determine the value of the reaction quotient, and compare this value of Q_c with the value of K_c.

$$[SO_2] = \frac{0.455\text{ mol }SO_2}{1.90\text{ L}} = 0.239\text{ M} \qquad [O_2] = \frac{0.183\text{ mol }O_2}{1.90\text{ L}} = 0.0963\text{ M}$$

$$[SO_3] = \frac{0.568\text{ mol }SO_3}{1.90\text{ L}} = 0.299\text{ M} \qquad Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.299)^2}{(0.239)^2\,0.0963} = 16.3$$

Since $Q_c = 16.3 \neq 2.8\times10^2 = K_c$, this mixture is not at equilibrium.

(b) Since the value of Q_c is smaller than that of K_c, the reaction will proceed to the right, forming product and consuming reactants to reach equilibrium.

32. **(M)** We compute the value of Q_c. Each concentration equals the mass (m) of the substance divided by its molar mass and further divided by the volume of the container.

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\dfrac{m\times\dfrac{1\text{ mol }CO_2}{44.0\text{ g }CO_2}}{V}\times\dfrac{m\times\dfrac{1\text{ mol }H_2}{2.0\text{ g }H_2}}{V}}{\dfrac{m\times\dfrac{1\text{ mol CO}}{28.0\text{ g CO}}}{V}\times\dfrac{m\times\dfrac{1\text{ mol }H_2O}{18.0\text{ g }H_2O}}{V}} = \frac{\dfrac{1}{44.0\times2.0}}{\dfrac{1}{28.0\times18.0}} = \frac{28.0\times18.0}{44.0\times2.0} = 5.7 < 31.4(\text{value of }K_c)$$

(In evaluating the expression above, we cancelled the equal values of V, along with, the equal values of m.) Because the value of Q_c is smaller than the value of K_c, (a) the reaction is not at equilibrium and (b) the reaction will proceed to the right (formation of products) to reach a state of equilibrium.

33. **(M)** The information for the calculation is organized around the chemical equation. Let $x =$ mol H_2 (or I_2) that reacts. Then use stoichiometry to determine the amount of HI formed, in terms of x, and finally solve for x.

Equation:	$H_2(g)$	+	$I_2(g) \rightleftharpoons$	$2\ HI(g)$
Initial:	0.150 mol		0.150 mol	0.000 mol
Changes:	$-x$ mol		$-x$ mol	$+2x$ mol
Equil:	$0.150-x$		$0.150-x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\dfrac{2x}{3.25\text{ L}}\right)^2}{\dfrac{0.150-x}{3.25\text{ L}} \times \dfrac{0.150-x}{3.25\text{ L}}}$$

Then take the square root of both sides: $\sqrt{K_c} = \sqrt{50.2} = \dfrac{2x}{0.150-x} = 7.09$

$2x = 1.06 - 7.09x \qquad x = \dfrac{1.06}{9.09} = 0.117$ mol, amount HI = $2x = 2 \times 0.117$ mol = 0.234 mol HI

amount H_2 = amount I_2 = $(0.150 - x)$ mol = $(0.150 - 0.117)$ mol = 0.033 mol H_2 (or I_2)

34. **(M)** We use the balanced chemical equation as a basis to organize the information

Equation:	$SbCl_5(g) \rightleftharpoons$	$SbCl_3(g)$	+	$Cl_2(g)$
Initial:	$\dfrac{0.00\text{ mol}}{2.50\text{ L}}$	$\dfrac{0.280\text{ mol}}{2.50\text{ L}}$		$\dfrac{0.160\text{ mol}}{2.50\text{ L}}$
Initial:	0.000 M	0.112 M		0.0640 M
Changes:	$+x$ M	$-x$ M		$-x$ M
Equil:	x M	$(0.112-x)$ M		$(0.0640-x)$ M

$$K_c = 0.025 = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{(0.112-x)(0.0640-x)}{x} = \frac{0.00717 - 0.176x + x^2}{x}$$

$0.025x = 0.00717 - 0.176x + x^2 \qquad x^2 - 0.201x + 0.00717 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{0.201 \pm \sqrt{0.0404 - 0.0287}}{2} = 0.0464 \text{ or } 0.155$$

The second of the two values for x gives a negative value of $[Cl_2]$ $(= -0.091\text{ M})$, and thus is physically meaningless in our universe. Thus, concentrations and amounts follow.

$[SbCl_5] = x = 0.0464$ M $\qquad$ amount $SbCl_5$ = 2.50 L × 0.0464 M = 0.116 mol $SbCl_5$

$[SbCl_3] = 0.112 - x = 0.066$ M $\qquad$ amount $SbCl_3$ = 2.50 L × 0.066 M = 0.17 mol $SbCl_3$

$[Cl_2] = 0.0640 - x = 0.0176$ M $\qquad$ amount Cl_2 = 2.50 L × 0.0176 M = 0.0440 mol Cl_2

35. **(M)** We use the chemical equation as a basis to organize the information provided about the reaction, and then determine the final number of moles of $Cl_2(g)$ present.

Equation:	$CO(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$
Initial:	0.3500 mol		0.0000 mol		0.05500 mol
Changes:	$+x$ mol		$+x$ mol		$-x$ mol
Equil.:	$(0.3500+x)$ mol		x mol		$(0.05500-x)$ mol

$$K_c = 1.2\times10^3 = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{\dfrac{(0.0550-x)\text{ mol}}{3.050\text{ L}}}{\dfrac{(0.3500+x)\text{mol}}{3.050\text{ L}}\times\dfrac{x\text{ mol}}{3.050\text{ L}}}$$

$$\frac{1.2\times10^3}{3.050} = \frac{0.05500-x}{(0.3500+x)\,x}$$ Assume $x << 0.0550$ This produces the following expression.

$$\frac{1.2\times10^3}{3.050} = \frac{0.05500}{0.3500\,x} \qquad x = \frac{3.050\times0.05500}{0.3500\times1.2\times10^3} = 4.0\times10^{-4}\text{ mol }Cl_2$$

We use the first value we obtained, 4.0×10^{-4} (= 0.00040), to arrive at a second value.

$$x = \frac{3.050\times(0.0550-0.00040)}{(0.3500+0.00040)\times1.2\times10^3} = 4.0\times10^{-4}\text{ mol }Cl_2$$

Because the value did not change on the second iteration, we have arrived at a solution.

36. **(M)** Compute the initial concentration of each species present. Then determine the equilibrium concentrations of all species. Finally, compute the mass of CO_2 present at equilibrium.

$$[CO]_{\text{int}} = \frac{1.00\text{ g}}{1.41\text{ L}}\times\frac{1\text{ mol CO}}{28.01\text{ g CO}} = 0.0253\text{ M} \qquad [H_2O]_{\text{int}} = \frac{1.00\text{ g}}{1.41\text{ L}}\times\frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O} = 0.0394\text{ M}$$

$$[H_2]_{\text{int}} = \frac{1.00\text{ g}}{1.41\text{ L}}\times\frac{1\text{ mol }H_2}{2.016\text{ g }H_2} = 0.352\text{ M}$$

Equation :	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial :	0.0253 M		0.0394 M		0.0000 M		0.352 M
Changes :	$-x$ M		$-x$ M		$+x$ M		$+x$ M
Equil :	$(0.0253-x)$ M		$(0.0394-x)$ M		x M		$(0.352+x)$ M

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 23.2 = \frac{x(0.352+x)}{(0.0253-x)(0.0394-x)} = \frac{0.352x+x^2}{0.000997-0.0647x+x^2}$$

$$0.0231-1.50x+23.2x^2 = 0.352x+x^2 \qquad 22.2x^2-1.852x+0.0231=0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{1.852 \pm \sqrt{3.430 - 2.051}}{44.4} = 0.0682\text{ M},\quad 0.0153\text{ M}$$

The first value of x gives negative concentrations for reactants ([CO] = -0.0429 M and [H_2O] = -0.0288 M). Thus, $x = 0.0153\text{ M} = \left[\text{CO}_2\right]$. Now we can find the mass of CO_2.

$$1.41\text{ L} \times \frac{0.0153\text{ mol CO}_2}{1\text{ L mixture}} \times \frac{44.01\text{ g CO}_2}{1\text{ mol CO}_2} = 0.949\text{ g CO}_2$$

37. **(D)** We base each of our solutions on the balanced chemical equation.

(a)

$$\begin{array}{lcccccc}
\text{Equation:} & \text{PCl}_5(\text{g}) & \rightleftharpoons & \text{PCl}_3(\text{g}) & + & \text{Cl}_2(\text{g}) \\
\text{Initial:} & \dfrac{0.550\text{ mol}}{2.50\text{ L}} & & \dfrac{0.550\text{ mol}}{2.50\text{ L}} & & \dfrac{0\text{ mol}}{2.50\text{ L}} \\
\text{Changes:} & \dfrac{-x\text{ mol}}{2.50\text{ L}} & & \dfrac{+x\text{ mol}}{2.50\text{ L}} & & \dfrac{+x\text{ mol}}{2.50\text{ L}} \\
\text{Equil:} & \dfrac{(0.550-x)\text{ mol}}{2.50\text{ L}} & & \dfrac{(0.550+x)\text{ mol}}{2.50\text{ L}} & & \dfrac{x\text{ mol}}{2.50\text{ L}}
\end{array}$$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 3.8\times10^{-2} = \frac{\dfrac{(0.550+x)\text{mol}}{2.50\text{L}} \times \dfrac{x\text{mol}}{2.50\text{L}}}{\dfrac{(0.550-x)\text{mol}}{2.50\text{L}}} \qquad \frac{x(0.550+x)}{2.50(0.550-x)} = 3.8\times10^{-2}$$

$$x^2 + 0.550x = 0.052 - 0.095x \qquad x^2 + 0.645x - 0.052 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.645 \pm \sqrt{0.416 + 0.208}}{2} = 0.0725\text{ mol},\quad -0.717\text{ mol}$$

The second answer gives a negative quantity. of Cl_2, which makes no physical sense.

$n_{\text{PCl}_5} = (0.550 - 0.0725) = 0.478$ mol PCl_5 $\qquad n_{\text{PCl}_3} = (0.550 + 0.0725) = 0.623$ mol PCl_3

$n_{\text{Cl}_2} = x = 0.0725$ mol Cl_2

(b)

$$\begin{array}{lcccccc}
\text{Equation:} & \text{PCl}_5(\text{g}) & \rightleftharpoons & \text{PCl}_3(\text{g}) & + & \text{Cl}_2(\text{g}) \\
\text{Initial:} & \dfrac{0.610\text{ mol}}{2.50\text{ L}} & & 0\text{ M} & & 0\text{ M} \\
\text{Changes:} & \dfrac{-x\text{ mol}}{2.50\text{ L}} & & \dfrac{+x\text{ mol}}{2.50\text{ L}} & & \dfrac{+x\text{ mol}}{2.50\text{ L}} \\
\text{Equil:} & \dfrac{0.610 - x\text{ mol}}{2.50\text{ L}} & & \dfrac{(x\text{ mol})}{2.50\text{ L}} & & \dfrac{(x\text{ mol})}{2.50\text{ L}}
\end{array}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 3.8\times10^{-2} = \frac{\frac{(x\,\text{mol})}{2.50\,\text{L}}\times\frac{(x\text{ mol})}{2.50\text{ L}}}{\frac{0.610-x\,\text{mol}}{2.50\text{ L}}}$$

$$2.50\times3.8\times10^{-2} = \frac{x^2}{0.610-x} = 0.095 \qquad 0.058-0.095x = x^2 \qquad x^2+0.095x-0.058=0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.095\pm\sqrt{0.0090+0.23}}{2} = 0.20\text{ mol},\ -0.29\text{ mol}$$

amount $PCl_3 = 0.20$ mol = amount Cl_2; amount $PCl_5 = 0.610 - 0.20 = 0.41$ mol

38. **(D)**

(a) We use the balanced chemical equation as a basis to organize the information we have about the reactants and products.

Equation:	$2\ COF_2(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$CF_4(g)$
Initial:	$\frac{0.145\text{ mol}}{5.00\text{ L}}$		$\frac{0.262\text{ mol}}{5.00\text{ L}}$		$\frac{0.074\text{ mol}}{5.00\text{ L}}$
Initial:	0.0290 M		0.0524 M		0.0148 M

And we now compute a value of Q_c and compare it to the given value of K_c.

$$Q_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{(0.0524)(0.0148)}{(0.0290)^2} = 0.922 < 2.00 = K_c$$

Because Q_c is not equal to K_c, the mixture is not at equilibrium.

(b) Because Q_c is smaller than K_c, the reaction will shift right, that is, products will be formed at the expense of COF_2, to reach a state of equilibrium.

(c) We continue the organization of information about reactants and products.

Equation:	$2\ COF_2(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$CF_4(g)$
Initial:	0.0290 M		0.0524 M		0.0148 M
Changes:	$-2x$ M		$+x$ M		$+x$ M
Equil:	$(0.0290-2x)$M		$(0.0524+x)$M		$(0.0148+x)$M

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{(0.0524+x)(0.0148+x)}{(0.0290-2x)^2} = 2.00 = \frac{0.000776+0.0672x+x^2}{0.000841-0.1160x+4x^2}$$

$$0.00168-0.232x+8x^2 = 0.000776+0.0672x+x^2 \quad 7x^2-0.299x+0.000904=0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{0.299\pm\sqrt{0.0894-0.0253}}{14} = 0.0033\text{ M}, 0.0394\text{ M}$$

The second of these values for x (0.0394) gives a negative $[COF_2](=-0.0498\text{ M})$, clearly a nonsensical result. We now compute the concentration of each species at equilibrium, and check to ensure that the equilibrium constant is satisfied.

$$[COF_2] = 0.0290-2x = 0.0290-2(0.0033) = 0.0224\text{ M}$$

$$[CO_2] = 0.0524+x = 0.0524+0.0033 = 0.0557\text{ M}$$

$$[CF_4] = 0.0148+x = 0.0148+0.0033 = 0.0181\text{ M}$$

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{0.0557\text{ M}\times 0.0181\text{ M}}{(0.0224\text{ M})^2} = 2.01$$

The agreement of this value of K_c with the cited value (2.00) indicates that this solution is correct. Now we determine the number of moles of each species at equilibrium.

$$\text{mol } COF_2 = 5.00\text{ L}\times 0.0224\text{ M} = 0.112\text{ mol } COF_2$$

$$\text{mol } CO_2 = 5.00\text{ L}\times 0.0557\text{ M} = 0.279\text{ mol } CO_2$$

$$\text{mol } CF_4 = 5.00\text{ L}\times 0.0181\text{ M} = 0.0905\text{ mol } CF_4$$

But suppose we had incorrectly concluded, in part (b), that reactants would be formed in reaching equilibrium. What result would we obtain? The set-up follows.

Equation:	$2\ COF_2(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$CF_4(g)$
Initial:	0.0290 M		0.0524 M		0.0148 M
Changes:	$+2y$ M		$-y$ M		$-y$ M
Equil:	$(0.0290+2y)$M		$(0.0524-y)$M		$(0.0148-y)$ M

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{(0.0524-y)(0.0148-y)}{(0.0290+2y)^2} = 2.00 = \frac{0.000776-0.0672y+y^2}{0.000841+0.1160y+4y^2}$$

$$0.00168+0.232y+8y^2 = 0.000776-0.0672y+y^2 \quad 7y^2+0.299y+0.000904=0$$

$$y = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.299\pm\sqrt{0.0894-0.0253}}{14} = -0.0033\text{ M}, -0.0394\text{ M}$$

The second of these values for $x(-0.0394)$ gives a negative $[\text{COF}_2](= -0.0498\text{ M})$, clearly a nonsensical result. We now compute the concentration of each species at equilibrium, and check to ensure that the equilibrium constant is satisfied.

$$[\text{COF}_2] = 0.0290 + 2y = 0.0290 + 2(-0.0033) = 0.0224\text{ M}$$

$$[\text{CO}_2] = 0.0524 - y = 0.0524 + 0.0033 = 0.0557\text{ M}$$

$$[\text{CF}_4] = 0.0148 - y = 0.0148 + 0.0033 = 0.0181\text{ M}$$

These are the same equilibrium concentrations that we obtained by making the correct decision regarding the direction that the reaction would take. Thus, you can be assured that, if you perform the algebra correctly, it will guide you even if you make the incorrect decision about the direction of the reaction.

39. **(D)**
(a) We calculate the initial amount of each substance.

$$n\{\text{C}_2\text{H}_5\text{OH}\} = 17.2\text{ g C}_2\text{H}_5\text{OH} \times \frac{1\text{ mol C}_2\text{H}_5\text{OH}}{46.07\text{ g C}_2\text{H}_5\text{OH}} = 0.373\text{ mol C}_2\text{H}_5\text{OH}$$

$$n\{\text{CH}_3\text{CO}_2\text{H}\} = 23.8\text{ g CH}_3\text{CO}_2\text{H} \times \frac{1\text{ mol CH}_3\text{CO}_2\text{H}}{60.05\text{ g CH}_3\text{CO}_2\text{H}} = 0.396\text{ mol CH}_3\text{CO}_2\text{H}$$

$$n\{\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5\} = 48.6\text{ g CH}_3\text{CO}_2\text{C}_2\text{H}_5 \times \frac{1\text{ mol CH}_3\text{CO}_2\text{C}_2\text{H}_5}{88.11\text{ g CH}_3\text{CO}_2\text{C}_2\text{H}_5}$$

$$n\{\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5\} = 0.552\text{ mol CH}_3\text{CO}_2\text{C}_2\text{H}_5$$

$$n\{\text{H}_2\text{O}\} = 71.2\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} = 3.95\text{ mol H}_2\text{O}$$

Since we would divide each amount by the total volume, and since there are the same numbers of product and reactant stoichiometric coefficients, we can use moles rather than concentrations in the Q_c expression.

$$Q_c = \frac{n\{\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5\}\,n\{\text{H}_2\text{O}\}}{n\{\text{C}_2\text{H}_5\text{OH}\}\,n\{\text{CH}_3\text{CO}_2\text{H}\}} = \frac{0.552\text{ mol} \times 3.95\text{ mol}}{0.373\text{ mol} \times 0.396\text{ mol}} = 14.8 > K_c = 4.0$$

Since $Q_c > K_c$ the reaction will shift to the left, forming reactants, as it attains equilibrium.

(b)

Equation:	$\text{C}_2\text{H}_5\text{OH}$	+	$\text{CH}_3\text{CO}_2\text{H}$	$\rightleftharpoons$	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	+	H_2O
Initial	0.373 mol		0.396 mol		0.552 mol		3.95 mol
Changes	$+x$ mol		$+x$ mol		$-x$ mol		$-x$ mol
Equil	$(0.373+x)$ mol		$(0.396+x)$ mol		$(0.552-x)$ mol		$(3.95-x)$ mol

$$K_c = \frac{(0.552-x)(3.95-x)}{(0.373+x)(0.396+x)} = \frac{2.18-4.50x+x^2}{0.148+0.769\,x+x^2} = 4.0$$

$$x^2 - 4.50x + 2.18 = 4x^2 + 3.08x + 0.59 \qquad 3x^2 + 7.58x - 1.59 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-7.58 \pm \sqrt{57+19}}{6} = 0.19 \text{ moles}, -2.72 \text{ moles}$$

Negative amounts do not make physical sense. We compute the equilibrium amount of each substance with $x = 0.19$ moles.

$$n\{C_2H_5OH\} = 0.373 \text{ mol} + 0.19 \text{ mol} = 0.56 \text{ mol } C_2H_5OH$$

$$\text{mass } C_2H_5OH = 0.56 \text{ mol } C_2H_5OH \times \frac{46.07 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH} = 26 \text{ g } C_2H_5OH$$

$$n\{CH_3CO_2H\} = 0.396 \text{ mol} + 0.19 \text{ mol} = 0.59 \text{ mol } CH_3CO_2H$$

$$\text{mass } CH_3CO_2H = 0.59 \text{ mol } CH_3CO_2H \times \frac{60.05 \text{ g } CH_3CO_2H}{1 \text{ mol } CH_3CO_2H} = 35 \text{ g } CH_3CO_2H$$

$$n\{CH_3CO_2C_2H_5\} = 0.552 \text{ mol} - 0.19 \text{ mol} = 0.36 \; CH_3CO_2C_2H_5$$

$$\text{mass } CH_3CO_2C_2H_5 = 0.36 \text{ mol } CH_3CO_2C_2H_5 \times \frac{88.10 \text{ g } CH_3CO_2C_2H_5}{1 \text{ mol } CH_3CO_2C_2H_5} = 32 \text{ g } CH_3CO_2C_2H_5$$

$$n\{H_2O\} = 3.95 \text{ mol} - 0.19 \text{ mol} = 3.76 \text{ mol } H_2O$$

$$\text{mass } H_2O = 3.76 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} = 68 \text{ g } H_2O$$

$$\text{To check } K_c = \frac{n\{CH_3CO_2C_2H_5\}\, n\{H_2O\}}{n\{C_2H_5OH\}\, n\{CH_3CO_2H\}} = \frac{0.36 \text{ mol} \times 3.76 \text{ mol}}{0.56 \text{ mol} \times 0.59 \text{ mol}} = 4.1$$

40. **(M)** The final volume of the mixture is $0.750 \text{ L} + 2.25 \text{ L} = 3.00 \text{ L}$. Then use the balanced chemical equation to organize the data we have concerning the reaction. The reaction should shift to the right, that is, form products in reaching a new equilibrium, since the volume is greater.

Equation:	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
Initial:	$\frac{0.971 \text{ mol}}{3.00 \text{ L}}$		$\frac{0.0580 \text{ mol}}{3.00 \text{ L}}$
Initial:	0.324M		0.0193M
Changes:	$-x\text{M}$		$+2x\text{M}$
Equil :	$(0.324-x)\text{M}$		$(0.0193+2x)\text{M}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0193 + 2x)^2}{0.324 - x} = \frac{0.000372 + 0.0772x + 4x^2}{0.324 - x} = 4.61 \times 10^{-3}$$

$$0.000372 + 0.0772x + 4x^2 = 0.00149 - 0.00461x \qquad 4x^2 + 0.0818x - 0.00112 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0818 \pm \sqrt{0.00669 + 0.0179}}{8} = 0.00938 \text{ M}, \ -0.0298 \text{ M}$$

$[NO_2] = 0.0193 + (2 \times 0.00938) = 0.0381 \text{ M}$
amount $NO_2 = 0.0381 \text{ M} \times 3.00 \text{ L} = 0.114 \text{ mol } NO_2$

$[N_2O_4] = 0.324 - 0.00938 = 0.3146 \text{ M}$
amount $N_2O_4 = 0.3146 \text{ M} \times 3.00 \text{ L} = 0.944 \text{ mol } N_2O_4$

41. **(M)** $[HCONH_2]_{init} = \dfrac{0.186 \text{ mol}}{2.16 \text{ L}} = 0.0861 \text{ M}$

Equation:	$HCONH_2(g) \rightleftharpoons$	$NH_3(g)$	+	$CO(g)$
Initial:	0.0861 M	0 M		0 M
Changes:	$-x$ M	$+x$ M		$+x$ M
Equil :	(0.0861-x) M	x M		x M

$$K_c = \frac{[NH_3][CO]}{[HCONH_2]} = \frac{x \cdot x}{0.0861 - x} = 4.84 \qquad x^2 = 0.417 - 4.84x \qquad 0 = x^2 + 4.84x - 0.417$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.84 \pm \sqrt{23.4 + 1.67}}{2} = 0.084 \text{ M}, \ -4.92 \text{ M}$$

The negative concentration obviously is physically meaningless. We determine the total concentration of all species, and then the total pressure with $x = 0.084$.

$$[\text{total}] = [NH_3] + [CO] + [HCONH_2] = x + x + 0.0861 - x = 0.0861 + 0.084 = 0.170 \text{ M}$$

$$P_{tot} = 0.170 \text{ mol L}^{-1} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 400. \text{ K} = 5.58 \text{ atm}$$

42. **(E) C**ompare Q_p to K_p. We assume that the added solids are of negligible volume so that the initial partial pressures of CO_2(g) and H_2O(g) do not significantly change.

$$P\{H_2O\} = \left(715 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) = 0.941 \text{ atm } H_2O$$

$$Q_p = P\{CO_2\}P\{H_2O\} = 2.10 \text{ atm } CO_2 \times 0.941 \text{ atm } H_2O = 1.98 > 0.23 = K_p$$

Because Q_p is larger than K_p, the reaction will proceed left toward reactants to reach equilibrium. Thus, the partial pressures of the two gases will decrease.

43. **(M)**

We organize the solution around the balanced chemical equation.

Equation:	$2\ \mathrm{Cr^{3+}(aq)}$	$+$	$\mathrm{Cd(s)}$	$\rightleftharpoons$	$2\ \mathrm{Cr^{2+}(aq)}$	$+$	$\mathrm{Cd^{2+}(aq)}$
Initial:	$1.00\ \mathrm{M}$				$0\ \mathrm{M}$		$0\ \mathrm{M}$
Changes:	$-2x\,\mathrm{M}$				$+2x$		$+x$
Equil:	$(1.00-2x)\,\mathrm{M}$				$2x$		x

$$K_c = \frac{[\mathrm{Cr^{2+}}]^2[\mathrm{Cd^{2+}}]}{[\mathrm{Cr^{3+}}]^2} = \frac{(2x)^2(x)}{(1.00-2x)^2} = 0.288$$

Via successive approximations, one obtains $x = 0.257\,\mathrm{M}$

Therefore, at equilibrium, $[\mathrm{Cd^{2+}}]$ = 0.257 M, $[\mathrm{Cr^{2+}}]$ = 0.514 M and $[\mathrm{Cr^{3+}}]$ = 0.486 M

Minimum mass of Cd(s) = 0.350L × 0.257 M × 112.41 g/mol = 10.1 g of Cd metal

44. **(M)** Again we base the set-up of the problem around the balanced chemical equation.

Equation:	$\mathrm{Pb(s)} +$	$2\ \mathrm{Cr^{3+}(aq)}$	$\xrightleftharpoons{K_c=3.2\times10^{-10}}$	$\mathrm{Pb^{2+}(aq)}$	$+$	$2\ \mathrm{Cr^{2+}(aq)}$
Initial:	$-$	$0.100\,\mathrm{M}$		$0\,\mathrm{M}$		$0\,\mathrm{M}$
Changes:	$-$	$-2x\,\mathrm{M}$		$+x\mathrm{M}$		$+2x\,\mathrm{M}$
Equil :	$-$	$(0.100-2x)\mathrm{M}$		$x\mathrm{M}$		$2x\,\mathrm{M}$

$$K_c = \frac{x(2x)^2}{(0.100)^2} = 3.2\times10^{-10} \qquad 4x^3 = (0.100)^2 \times 3.2\times10^{-10} = 3.2\times10^{-12}$$

$x = \sqrt[3]{\dfrac{3.2\times10^{-12}}{4}} = 9.3\times10^{-5}\ \mathrm{M}$ Assumption that $2x << 0.100$, is valid and thus

$[\mathrm{Pb^{2+}}] = x = 9.3\times10^{-5}\ \mathrm{M}$, $[\mathrm{Cr^{2+}}]$ = 1.9×10^{-4} M and $[\mathrm{Cr^{3+}}]$ = 0.100 M

<u>**45.**</u> **(M)** We are told in this question that the reaction $SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$ has

K_c = 4.0 at a certain temperature *T*. This means that at the temperature *T*, $[SO_2Cl_2] = 4.0 \times [Cl_2] \times [SO_2]$. Careful scrutiny of the three diagrams reveals that sketch (b) is the best representation because it contains numbers of SO_2Cl_2, SO_2, and Cl_2 molecules that are consistent with the K_c for the reaction. In other words, sketch (b) is the best choice because it contains 12 SO_2Cl_2 molecules (per unit volume), 1 Cl_2 molecule (per unit volume) and 3 SO_2 molecules (per unit volume), which is the requisite number of each type of molecule needed to generate the expected K_c value for the reaction at temperature *T*.

46. **(M)** In this question we are told that the reaction $2\ NO(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g)$ has

K_c = 3.0 at a certain temperature *T*. This means that at the temperature *T*, $[NOBr]^2 = 3.0 \times [Br_2][NO]^{2.}$ Sketch (c) is the most accurate representation because it contains 18 NOBr molecules (per unit volume), 6 NO molecules (per unit volume), and 3 Br_2 molecules (per unit volume), which is the requisite number of each type of molecule needed to generate the expected K_c value for the reaction at temperature *T*.

47. **(E)**

$$K = \frac{[\text{aconitate}]}{[\text{citrate}]}$$

$$Q = \frac{4.0 \times 10^{-5}}{(0.00128)} = 0.031$$

Since Q = K, the reaction is at equilibrium,

48. **(E)**

$$K = \frac{[\text{CO}_2][\text{NAD}_{\text{red}}][\text{oxoglut.}]}{[\text{citrate}][\text{NAD}_{\text{ox}}]}$$

$$Q = \frac{(0.00868)(0.00132)(0.00868)}{(0.00128)(0.00868)} = 0.00895$$

Since Q < K, the reaction needs to proceed to the right (products).

Partial Pressure Equilibrium Constant, *K*$_p$

49. **(M)** The $I_2(s)$ maintains the presence of I_2 in the flask until it has all vaporized. Thus, if enough HI(g) is produced to completely consume the $I_2\ (s)$, equilibrium will not be achieved.

$$P\{H_2S\} = 747.6 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.9837 \text{ atm}$$

Equation:	$H_2S(g) +$	$I_2(s)$	$\rightleftharpoons$	$2\ HI(g) +$	$S(s)$
Initial:	0.9837 atm			0 atm	
Changes:	$-x$ atm			$+2x$ atm	
Equil:	$(0.9837 - x)$ atm			$2x$ atm	

$$K_p = \frac{P\{HI\}^2}{P\{H_2S\}} = \frac{(2x)^2}{(0.9837 - x)} = 1.34 \times 10^{-5} = \frac{4x^2}{0.9837}$$

$$x = \sqrt{\frac{1.34 \times 10^{-5} \times 0.9837}{4}} = 1.82 \times 10^{-3} \text{ atm}$$

The assumption that $0.9837 >> x$ is valid. Now we verify that sufficient $I_2(s)$ is present by computing the mass of I_2 needed to produce the predicted pressure of HI(g). Initially, 1.85 g I_2 is present (given).

$$\text{mass } I_2 = \frac{1.82 \times 10^{-3} \text{ atm} \times 0.725 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 333 \text{ K}} \times \frac{1 \text{ mol } I_2}{2 \text{ mol HI}} \times \frac{253.8 \text{ g } I_2}{1 \text{ mol } I_2} = 0.00613 \text{ g } I_2$$

$$P_{\text{tot}} = P\{H_2S\} + P\{HI\} = (0.9837 - x) + 2x = 0.9837 + x = 0.9837 + 0.00182 = 0.9855 \text{ atm}$$

$$P_{\text{tot}} = 749.0 \text{ mmHg}$$

50. **(M)** We first determine the initial pressure of NH_3.

$$P\{NH_3(g)\} = \frac{nRT}{V} = \frac{0.100\text{ mol }NH_3 \times 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1} \times 298\text{ K}}{2.58\text{ L}} = 0.948\text{ atm}$$

Equation:	$NH_4HS(s) \rightleftharpoons$	$NH_3(g)$	$+$	$H_2S(g)$
Initial:		0.948 atm		0 atm
Changes:		$+x$ atm		$+x$ atm
Equil:		$(0.948+x)$ atm		x atm

$$K_p = P\{NH_3\}P\{H_2S\} = 0.108 = (0.948+x)x = 0.948x + x^2 \quad 0 = x^2 + 0.948x - 0.108$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.948 \pm \sqrt{0.899+0.432}}{2} = 0.103\text{ atm},\ -1.05\text{ atm}$$

The negative root makes no physical sense. The total gas pressure is obtained as follows.

$$P_{tot} = P\{NH_3\} + P\{H_2\text{ S}\} = (0.948+x) + x = 0.948 + 2x = 0.948 + 2 \times 0.103 = 1.154\text{ atm}$$

51. **(M)** We substitute the given equilibrium pressure into the equilibrium constant expression and solve for the other equilibrium pressure. $K_p = \frac{P\{O_2\}^3}{P\{CO_2\}^2} = 28.5 = \frac{P\{O_2\}^3}{(0.0721\text{ atm }CO_2)^2}$

$$P\{O_2\} = \sqrt[3]{P\{O_2\}^3} = \sqrt[3]{28.5(0.0712\text{ atm})^2} = 0.529\text{ atm }O_2$$

$$P_{total} = P\{CO_2\} + P\{O_2\} = 0.0721\text{ atm }CO_2 + 0.529\text{ atm }O_2 = 0.601\text{ atm total}$$

52. **(M)** The composition of dry air is given in volume percent. Division of these percentages by 100 gives the volume fraction, which equals the mole fraction and also the partial pressure in atmospheres, if the total pressure is 1.00 atm. Thus, we have $P\{O_2\} = 0.20946$ atm and $P\{CO_2\} = 0.00036$ atm. We substitute these two values into the expression for Q_p.

$$Q_p = \frac{P\{O_2\}^3}{P\{CO_2\}^2} = \frac{(0.20946\text{ atm }O_2)^3}{(0.00036\text{ atm }CO_2)^2} = 6.4\times10^4 > 28.5 = K_p$$

The value of Q_p is much larger than the value of K_p. Thus this reaction should be spontaneous in the reverse direction until equilibrium is achieved. It will only be spontaneous in the forward direction when the pressure of O_2 drops or that of CO_2 rises (as would be the case in self-contained breathing devices).

53. **(M)**

(a) We first determine the initial pressure of each gas.

$$P\{\mathrm{CO}\} = P\{\mathrm{Cl_2}\} = \frac{nRT}{V} = \frac{1.00\ \mathrm{mol} \times 0.08206\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}} \times 668\ \mathrm{K}}{1.75\ \mathrm{L}} = 31.3\ \mathrm{atm}$$

Then we calculate equilibrium partial pressures, organizing our calculation around the balanced chemical equation. We see that the equilibrium constant is not very large, meaning that we must solve the polynomial exactly (or by successive approximations).

Equation	$\mathrm{CO(g)}$	$+\ \mathrm{Cl_2(g)}$	$\rightleftharpoons\ \mathrm{COCl_2(g)}$	$K_\mathrm{p} = 22.5$
Initial:	31.3 atm	31.3 atm	0 atm	
Changes:	$-x$ atm	$-x$ atm	$+x$ atm	
Equil:	$31.3-x$ atm	$31.3-x$ atm	x atm	

$$K_\mathrm{p} = \frac{P\{\mathrm{COCl_2}\}}{P\{\mathrm{CO}\}P\{\mathrm{Cl_2}\}} = 22.5 = \frac{x}{(31.3-x)^2} = \frac{x}{(979.\underline{7} - 62.6x + x^2)}$$

$$22.5(979.\underline{7} - 62.6x + x^2) = x = 220\underline{43} - 140\underline{8.5}x + 22.5x^2 = x$$

$$220\underline{43} - 140\underline{9.5}x + 22.5x^2 = 0 \quad \text{(Solve by using the quadratic equation)}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-1409.5) \pm \sqrt{(-140\underline{9.5})^2 - 4(22.5)(220\underline{43})}}{2(22.5)}$$

$$x = \frac{1409.5 \pm \sqrt{2818}}{45} = 30.1\underline{4},\ 32.5\ \text{(too large)}$$

$P\{\mathrm{CO}\} = P\{\mathrm{Cl_2}\} = 31.3\ \mathrm{atm} - 30.1\underline{4}\ \mathrm{atm} = 1.16\ \mathrm{atm}$ $\qquad P\{\mathrm{COCl_2}\} = 30.1\underline{4}\ \mathrm{atm}$

(b) $P_\mathrm{total} = P\{\mathrm{CO}\} + P\{\mathrm{Cl_2}\} + P\{\mathrm{COCl_2}\} = 1.1\underline{6}\ \mathrm{atm} + 1.1\underline{6}\ \mathrm{atm} + 30.1\underline{4}\ \mathrm{atm} = 32.46\ \mathrm{atm}$

54. **(M)** We first find the value of K_p for the reaction.

$$2\ \mathrm{NO_2(g)} \rightleftharpoons 2\ \mathrm{NO(g)} + \mathrm{O_2(g)}, \quad K_\mathrm{c} = 1.8 \times 10^{-6} \text{ at } 184\ ^\circ\mathrm{C} = 457\ \mathrm{K}\ .$$

For this reaction $\Delta n_\mathrm{gas} = 2 + 1 - 2 = +1$.

$$K_p = K_c(\mathrm{RT})^{\Delta n_g} = 1.8 \times 10^{-6}\ (0.08206 \times 457)^{+1} = 6.8 \times 10^{-5}$$

To obtain the required reaction $\mathrm{NO(g)} + \frac{1}{2}\mathrm{O_2(g)} \rightleftharpoons \mathrm{NO_2(g)}$ from the initial reaction, that initial reaction must be reversed and then divided by two. Thus, in order to determine the value of the equilibrium constant for the final reaction, the value of K_p for the initial reaction must be inverted, and the square root taken of the result.

$$K_\mathrm{p,\ final} = \sqrt{\frac{1}{6.8 \times 10^{-5}}} = 1.2 \times 10^2$$

Le Châtelier's Principle

55. **(E)** Continuous removal of the product, of course, has the effect of decreasing the concentration of the products below their equilibrium values. Thus, the equilibrium system is disturbed by removing the products and the system will attempt (in vain, as it turns out) to re-establish the equilibrium by shifting toward the right, that is, to generate more products.

56. **(E)** We notice that the density of the solid ice is smaller than is that of liquid water. This means that the same mass of liquid water is present in a smaller volume than an equal mass of ice. Thus, if pressure is placed on ice, attempting to force it into a smaller volume, the ice will be transformed into the less-space-occupying water at 0°C. Thus, at 0°C under pressure, $H_2O(s)$ will melt to form $H_2O(l)$. This behavior is *not* expected in most cases because generally a solid is *more* dense than its liquid phase.

57. **(M)**

(a) This reaction is exothermic with $\Delta H^\circ = -150.$ kJ. Thus, high temperatures favor the reverse reaction (endothermic reaction). The amount of $H_2(g)$ present at high temperatures will be less than that present at low temperatures.

(b) $H_2O(g)$ is one of the reactants involved. Introducing more will cause the equilibrium position to shift to the right, favoring products. The amount of $H_2(g)$ will increase.

(c) Doubling the volume of the container will favor the side of the reaction with the largest sum of gaseous stoichiometric coefficients. The sum of the stoichiometric coefficients of gaseous species is the same (4) on both sides of this reaction. Therefore, increasing the volume of the container will have no effect on the amount of $H_2(g)$ present at equilibrium.

(d) A catalyst merely speeds up the rate at which a reaction reaches the equilibrium position. The addition of a catalyst has no effect on the amount of $H_2(g)$ present at equilibrium.

58. **(M)**

(a) This reaction is endothermic, with $\Delta H^o = +92.5$ kJ. Thus, a higher temperature will favor the forward reaction and increase the amount of HI(g) present at equilibrium.

(b) The introduction of more product will favor the reverse reaction and decrease the amount of HI(g) present at equilibrium.

(c) The sum of the stoichiometric coefficients of gaseous products is larger than that for gaseous reactants. Increasing the volume of the container will favor the forward reaction and increase the amount of HI(g) present at equilibrium.

(d) A catalyst merely speeds up the rate at which a reaction reaches the equilibrium position. The addition of a catalyst has no effect on the amount of HI(g) present at equilibrium.

(e) The addition of an inert gas to the constant-volume reaction mixture will not change any partial pressures. It will have no effect on the amount of HI(g) present at equilibrium.

59. **(M)**

(a) The formation of NO(g) from its elements is an endothermic reaction (ΔH° = +181 kJ/mol). Since the equilibrium position of endothermic reactions is shifted toward products at higher temperatures, we expect more NO(g) to be formed from the elements at higher temperatures.

(b) Reaction rates always are enhanced by higher temperatures, since a larger fraction of the collisions will have an energy that surmounts the activation energy. This enhancement of rates affects both the forward and the reverse reactions. Thus, the position of equilibrium is reached more rapidly at higher temperatures than at lower temperatures.

60. **(M)** If the reaction is endothermic (ΔH° > 0), the forward reaction is favored at high temperatures. If the reaction is exothermic (ΔH° < 0), the forward reaction is favored at low temperatures.

(a) $\Delta H^\circ = \Delta H_f^\circ\left[\mathrm{PCl_5(g)}\right] - \Delta H_f^\circ\left[\mathrm{PCl_3(g)}\right] - \Delta H_f^\circ\left[\mathrm{Cl_2(g)}\right]$

$\Delta H^\circ = -374.9\text{ kJ} - (-287.0\text{ kJ}) - 0.00\text{ kJ} = -87.9\text{ kJ/mol}$ (favored at low temperatures)

(b) $\Delta H^\circ = 2\Delta H_f^\circ[\mathrm{H_2O(g)}] + 3\Delta H_f^\circ[\mathrm{S(rhombic)}] - \Delta H_f^\circ[\mathrm{SO_2(g)}] - 2\,\Delta H_f^\circ[\mathrm{H_2S(g)}]$

$\Delta H^\circ = 2(-241.8\text{ kJ}) + 3(0.00\text{ kJ}) - (-296.8\text{ kJ}) - 2(-20.63\text{ kJ})$

$\Delta H^\circ = -145.5\text{ kJ/mol}$ (favored at low temperatures)

(c) $\Delta H^\circ = 4\Delta H_f^\circ\left[\mathrm{NOCl(g)}\right] + 2\Delta H_f^\circ\left[\mathrm{H_2O(g)}\right]$

$-2\Delta H_f^\circ\left[\mathrm{N_2(g)}\right] - 3\Delta H_f^\circ\left[\mathrm{O_2(g)}\right] - 4\Delta H_f^\circ\left[\mathrm{HCl(g)}\right]$

$\Delta H^\circ = 4(51.71\text{ kJ}) + 2(-241.8\text{ kJ}) - 2(0.00\text{ kJ}) - 3(0.00\text{ kJ}) - 4(-92.31\text{ kJ})$

$\Delta H^\circ = +92.5\text{ kJ/mol}$ (favored at higher temperatures)

61. **(E)** If the total pressure of a mixture of gases at equilibrium is doubled by compression, the equilibrium will shift to the side with fewer moles of gas to counteract the increase in pressure. Thus, if the pressure of an equilibrium mixture of N_2(g), H_2(g), and NH_3(g) is doubled, the reaction involving these three gases, i.e., $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, will proceed in the forward direction to produce a new equilibrium mixture that contains additional ammonia and less molecular nitrogen and molecular hydrogen. In other words, $P\{N_2(g)\}$ will have decreased when equilibrium is re-established. It is important to note, however, that the final equilibrium partial pressure for the N_2 will, nevertheless, be higher than its original partial pressure prior to the doubling of the total pressure.

62. **(M)**

(a) Because $\Delta H^o = 0$, the position of the equilibrium for this reaction will not be affected by temperature. Since the equilibrium position is expressed by the value of the equilibrium constant, we expect K_p to be unaffected by, or to remain constant with, temperature.

(b) From part (a), we know that the value of K_p will not change when the temperature is changed. The pressures of the gases, however, will change with temperature. (Recall the ideal gas law: $P = nRT/V$.) In fact, all pressures will increase. The stoichiometric coefficients in the reaction are such that at higher pressures the formation of more reactant will be favored (the reactant side has fewer moles of gas). Thus, the amount of D(g) will be smaller when equilibrium is reestablished at the higher temperature for the cited reaction.

$$\mathrm{A(s)} \rightleftharpoons \mathrm{B(s)} + 2\ \mathrm{C(g)} + \frac{1}{2}\ \mathrm{D(g)}$$

63. **(M)** Increasing the volume of an equilibrium mixture causes that mixture to shift toward the side (reactants or products) where the sum of the stoichiometric coefficients of the gaseous species is the larger. That is: shifts to the right if $\Delta n_{gas} > 0$, shifts to the left if $\Delta n_{gas} < 0$, and does not shift if $\Delta n_{gas} = 0$.

(a) $\mathrm{C(s)} + \mathrm{H_2O(g)} \rightleftharpoons \mathrm{CO(g)} + \mathrm{H_2(g)}, \Delta n_{gas} > 0,$ shift right, toward products

(b) $\mathrm{Ca(OH)_2(s)} + \mathrm{CO_2(g)} \rightleftharpoons \mathrm{CaCO_3(s)} + \mathrm{H_2O(g)},\ \Delta n_{gas} = 0,$ no shift, no change in equilibrium position.

(c) $4\ \mathrm{NH_3(g)} + 5\ \mathrm{O_2(g)} \rightleftharpoons 4\ \mathrm{NO(g)} + 6\ \mathrm{H_2O(g)},\ \Delta n_{gas} > 0,$ shifts right, towards products

64. **(M)** The equilibrium position for a reaction that is exothermic shifts to the left (reactants are favored) when the temperature is raised. For one that is endothermic, it shifts right (products are favored) when the temperature is raised.

(a) $\mathrm{NO(g)} \rightleftharpoons \frac{1}{2}\ \mathrm{N_2(g)} + \frac{1}{2}\ \mathrm{O_2(g)}$ $\Delta H^o = -90.2$ kJ shifts left, % dissociation ↓

(b) $\mathrm{SO_3(g)} \rightleftharpoons \mathrm{SO_2(g)} + \frac{1}{2}\ \mathrm{O_2(g)}$ $\Delta H^o = +98.9$ kJ shifts right, % dissociation ↑

(c) $\mathrm{N_2H_4(g)} \rightleftharpoons \mathrm{N_2(g)} + 2\ \mathrm{H_2(g)}$ $\Delta H^o = -95.4$ kJ shifts left, % dissociation ↓

(d) $\mathrm{COCl_2(g)} \rightleftharpoons \mathrm{CO(g)} + \mathrm{Cl_2(g)}$ $\Delta H^o = +108.3$ kJ shifts right, % dissociation ↑

65. **(E)**

(a) Hb:O_2 is reduced, because the reaction is exothermic and heat is like a product.

(b) No effect, because the equilibrium involves O_2 (aq). Eventually it will reduce the Hb:O_2 level because removing O_2(g) from the atmosphere also reduces O_2 (aq) in the blood.

(c) Hb:O_2 level increases to use up the extra Hb.

66. **(E)**

(a) CO_2 (g) increases as the equilibrium is pushed toward the reactant side
(b) Increase CO_2 (aq) levels, which then pushes the equilibrium to the product side
(c) It has no effect, but it helps establish the final equilibrium more quickly
(d) CO_2 increases, as the equilibrium shifts to the reactants

67. **(E)** The pressure on N_2O_4 will initially increase as the crystal melts and then vaporizes, but over time the new concentration decreases as the equilibrium is shifted toward NO_2.

68. **(E)** If the equilibrium is shifted to the product side by increasing temperature, that means that heat is a "reactant" (or being consumed). Therefore, HI decomposition is endothermic.

69. **(E)** Since ΔH is >0, the reaction is endothermic. If we increase the temperature of the reaction, we are adding heat to the reaction, which shifts the reaction toward the decomposition of calcium carbonate. While the amount of calcium carbonate will decrease, its concentration will remain the same because it is a solid.

70. **(E)** The amount of N_2 increases in the body. As the pressure on the body increases, the equilibrium shifts from N_2 gas to N_2 (aq).

Integrative and Advanced Exercises

71. **(E)** In a reaction of the type $I_2(g) \rightarrow 2\ I(g)$ the bond between two iodine atoms, the I—I bond, must be broken. Since $I_2(g)$ is a stable molecule, this bond breaking process must be endothermic. Hence, the reaction cited is an endothermic reaction. The equilibrium position of endothermic reactions will be shifted toward products when the temperature is raised.

72. **(M)**

(a) In order to determine a value of K_c, we first must find the CO_2 concentration in the gas phase. Note, the total volume for the gas is 1.00 L (moles and molarity are numerically equal)

$$[CO_2] = \frac{n}{V} = \frac{P}{RT} = \frac{1.00 \text{ atm}}{0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 298 \text{ K}} = 0.0409 \text{ M} \qquad K_c = \frac{[CO_2(aq)]}{[CO_2(g)]} = \frac{3.29\times10^{-2} \text{ M}}{0.0409 \text{ M}} = 0.804$$

(b) It does not matter to which phase the radioactive $^{14}CO_2$ is added. This is an example of a Le Châtelier's principle problem in which the stress is a change in concentration of the reactant $CO_2(g)$. To find the new equilibrium concentrations, we must solve and I.C.E. table. Since $Q_c < K_c$, the reaction shifts to the product, CO_2 (aq) side.

Reaction:	$CO_2(g)$	$\rightleftharpoons$	$CO_2(aq)$
Initial:	0.0409 mol		3.29×10^{-3} mol
Stress	+0.01000 mol		–
Changes:	$-x$ mol		$+x$ mol
Equilibrium:	$(0.05090 - x)$ mol		$3.29\times10^{-3} + x$ mol

$$K_C = \frac{[CO_2(aq)]}{[CO_2(g)]} = \frac{\dfrac{3.29\times10^{-3} + x \text{ mol}}{0.1000 \text{ L}}}{\dfrac{(0.05090\ -\ x) \text{ mol}}{1.000 \text{ L}}} = 0.804 = \frac{3.29\times10^{-2} + 10x}{0.05090\ -\ x} \qquad x = 7.43\times10^{-4} \text{ mol } CO_2$$

Total moles of CO_2 in the aqueous phase (0.1000 L)($3.29\times10^{-2} + 7.43\times10^{-3}$) = 4.03×10^{-3} moles

Total moles of CO_2 in the gaseous phase (1.000 L)($5.090\times10^{-2} - 7.43\times10^{-4}$) = 5.02×10^{-2} moles
Total moles of CO_2 = 5.02×10^{-2} moles + 4.03×10^{-3} moles = 5.42×10^{-2} moles
There is continuous mixing of the ^{12}C and ^{14}C such that the isotopic ratios in the two phases is the same. This ratio is given by the mole fraction of the two isotopes.
For $^{14}CO_2$ in either phase its mole fraction is $\dfrac{0.01000 \text{ mol}}{5.41\underline{9}\times10^{-2} \text{ mol}}\times100 = 18.4\underline{5}\ \%$

Moles of $^{14}CO_2$ in the gaseous phase = 5.02×10^{-2} moles×0.1845 = 0.00926 moles

Moles of $^{14}CO_2$ in the aqueous phase = 4.03×10^{-3} moles×0.1845 = 0.000744 moles

73. **(M)** Dilution makes Q_c larger than K_c. Thus, the reaction mixture will shift left in order to regain equilibrium. We organize our calculation around the balanced chemical equation.

Equation:	$Ag^+(aq)$	+	$Fe^{2+}(aq)$	$\rightleftharpoons$	$Fe^{3+}(aq)\ +\ Ag(s)$		$K_c = 2.98$
Equil:	0.31 M		0.21 M		0.19 M	–	
Dilution:	0.12 M		0.084 M		0.076 M	–	
Changes:	$+x$ M		$+x$ M		$-x$ M	–	
New equil:	$(0.12\ +\ x)$ M		$(0.084\ +\ x)$ M		$(0.076\ -\ x)$ M	–	

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = 2.98 = \frac{0.076 - x}{(0.12 + x)\ (0.084 + x)} \qquad 2.98\ (0.12\ +\ x)\ (0.084\ +\ x) = 0.076 - x$$

$$0.076 - x = 0.030 + 0.61x\ +\ 2.98\ x^2 \qquad 2.98\ x^2 + 1.61\quad x - 0.046 = 0$$

$$x = \frac{-1.61 \pm \sqrt{2.59 + 0.55}}{5.96} = 0.027, -0.57$$

Note that the negative root makes no physical sense; it gives $[Fe^{2+}] = 0.084 - 0.57 = -0.49$ M.
Thus, the new equilibrium concentrations are

$[Fe^{2+}]\ =\ 0.084\ +\ 0.027\ =\ 0.111$ M $\qquad [Ag^+]\ =\ 0.12\ +\ 0.027\ =\ 0.15$ M

$[Fe^{3+}]\ =\ 0.076-\ 0.027\ =\ 0.049$ M We can check our answer by substitution.

$$Kc = \frac{0.049 \text{ M}}{0.111 \text{ M} \times 0.15 \text{ M}} = 2.94\ \approx 2.98 \text{ (within precision limits)}$$

74. **(M)** The percent dissociation should increase as the pressure is lowered, according to Le Châtelier's principle. Thus the total pressure in this instance should be more than in Example 15-12, where the percent dissociation is 12.5%. The total pressure in Example 15-12 was computed starting from the total number of moles at equilibrium.
The total amount = (0.0240 – 0.00300) moles N_2O_4 + 2 × 0.00300 mol NO_2 = 0.027 mol gas.

$$P_{total} = \frac{nRT}{V} = \frac{0.0270\text{mol} \times 0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1} \times 298\text{ K}}{0.372\text{ L}} = 1.77\,\text{atm (Example 15-12)}$$

We base our solution on the balanced chemical equation. We designate the initial pressure of N_2O_4 as P. The change in P{N_2O_4}is given as –0.10 P atm. to represent the 10.0 % dissociation.

Equation:	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
Initial:	P atm		0 atm
Changes:	$-0.10\,P$ atm		$+2(0.10\,P$ atm)
Equil:	0.90 P atm		$0.20\,P$ atm

$$K_p = \frac{P\{NO_2\}^2}{P\{N_2O_4\}} = \frac{(0.20\,P)^2}{0.90\,P} = \frac{0.040\,P}{0.90} = 0.113 \qquad P = \frac{0.113 \times 0.90}{0.040} = 2.54\,\text{atm.}$$

Thus, the total pressure at equilibrium is 0.90 P + 0.20 P and 1.10 P (where P = 2.54 atm) Therefore, total pressure at equilibrium = 2.79 atm.

75. **(M)**

Equation:	$2\ SO_3(g)$	$\rightleftharpoons$	$2\ SO_2(g)$	+	$O_2(g)$
Initial:	1.00 atm		0 atm		0 atm
Changes:	$-2x$ atm		$+2x$ atm		$+x$ atm
Equil:	$(1.00 - 2x)$atm		$2x$ atm		x atm

Because of the small value of the equilibrium constant, the reaction does not proceed very far toward products in reaching equilibrium. Hence, we assume that $x << 1.00$ atm and calculate an approximate value of x (small K problem).

$$K_P = \frac{P\{SO_2\}^2\ P\{O_2\}}{P\{SO_3\}^2} = \frac{(2x)^2\ x}{(1.00-2x)^2} = 1.6\times10^{-5} \approx \frac{4x^3}{(1.00)^2} \qquad x = 0.016\text{ atm}$$

A second cycle may get closer to the true value of x.

$$1.6\times10^{-5} \approx \frac{4x^3}{(1.00-0.032)^2} = \ x = 0.016\,\text{atm}$$

Our initial value was sufficiently close. We now compute the total pressure at equilibrium.

$$P_{total} = P\{SO_3\} + P\{SO_2\} + P\{O_2\} = (1.00-2x) + 2x + x = 1.00 + x = 1.00 + 0.016 = 1.02\,\text{atm}$$

76. **(M)** Let us start with one mole of air, and let $2x$ be the amount in moles of NO formed.

Equation:	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\ NO(g)$
Initial:	0.79 mol		0.21 mol		0 mol
Changes:	$-x$ mol		$-x$ mol		$+2x$ mol
Equil:	$(0.79 - x)$mol		$(0.21 - x)$mol		$2x$ mol

$$\chi_{\text{NO}} = \frac{n\{\text{NO}\}}{n\{\text{N}_2\} + n\{\text{O}_2\} + n\{\text{NO}\}} = \frac{2x}{(0.79 - x) + (0.21 - x) + 2x} = 0.018 = \frac{2x}{1.00}$$

$x = 0.0090$ mol $\qquad 0.79 - x = 0.78 \text{ mol N}_2 \qquad 0.21 - x = 0.20 \text{ mol O}_2$

$2x = 0.018$ mol NO

$$K_{\text{p}} = \frac{P\{\text{NO}\}^2}{P(\text{N}_2\}\, P\{\text{O}_2\}} = \frac{\left(\dfrac{n\{\text{NO}\}\, RT}{V_{\text{total}}}\right)^2}{\dfrac{n\{\text{N}_2)\, RT}{V_{\text{total}}}\, \dfrac{n\{\text{O}_2\}\, RT}{V_{\text{total}}}} = \frac{n\{\text{NO}\}^2}{n\{\text{N}_2\}\, n\{\text{O}_2\}} = \frac{(0.018)^2}{0.78 \times 0.20} = 2.1 \times 10^{-3}$$

77. **(D)** We organize the data around the balanced chemical equation. Note that the reaction is stoichimoetrically balanced.

(a) Equation:	$2\,\text{SO}_2(\text{g})$ +	$\text{O}_2(\text{g}) \rightleftharpoons$	$2\,\text{SO}_3(\text{g})$
Equil:	0.32 mol	0.16 mol	0.68 mol
Add SO_3	0.32 mol	0.16 mol	1.68 mol
Initial:	$\frac{0.32\text{ mol}}{10.0\text{ L}}$	$\frac{0.16\text{ mol}}{10.0\text{ L}}$	$\frac{1.68\text{ mol}}{10.0\text{ L}}$
Initial:	0.032 M	0.016 M	0.168 M
To right:	0.000 M	0.000 M	0.200 M
Changes:	$+2x$ M	$+x$ M	$-2x$ M
Equil:	$2x$ M	x M	$(0.200 - 2x)$M

In setting up this problem, we note that solving this question exactly involves finding the roots for a cubic equation. Thus, we assumed that all of the reactants have been converted to products. This gives the results in the line labeled "To right." We then reach equilibrium from this position by converting some of the product back into reactants. Now, we substitute these expressions into the equilibrium constant expression, and we solve this expression approximately by assuming that $2x << 0.200$.

$$K_{\text{c}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.200 - 2x)^2}{(2x)^2 x} = 2.8 \times 10^2 \approx \frac{(0.200)^2}{4x^3} \text{ or } x = 0.033$$

We then substitute this approximate value into the expression for K_{c}.

$$K_{\text{c}} = \frac{(0.200 - 0.066)^2}{4x^3} = 2.8 \times 10^2 \; or \; x = 0.025$$

Let us try one more cycle. $K_{\text{c}} = \dfrac{(0.200 - 0.050)^2}{4x^3} = 2.8 \times 10^2$ or $x = 0.027$

This gives the following concentrations and amounts of each species.

$[SO_3] = 0.200 - (2 \times 0.027) = 0.146\text{ M}$ amount $SO_3 = 10.0\text{ L} \times 0.146\text{ M} = 1.46\text{ mol } SO_3$

$[SO_2] = 2 \times 0.027 = 0.054\text{ M}$ amount $SO_2 = 10.0\text{ L} \times 0.054\text{ M} = 0.54\text{ mol } SO_2$

$[O_2] = 0.027\text{ M}$ amount $O_2 = 10.0\text{ L} \times 0.027\text{ M} = 0.27\text{ mol } O_2$

(b)

Equation:	$2\ SO_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\ SO_3(g)$
Equil:	0.32 mol		0.16 mol		0.68 mol
Equil:	$\frac{0.32\text{ mol}}{10.0\text{ L}}$		$\frac{0.16\text{ mol}}{10.0\text{ L}}$		$\frac{0.68\text{ mol}}{10.0\text{ L}}$
Equil:	0.032 M		0.016 M		0.068 M
0.10 V:	0.32 M		0.16 M		0.68 M
To right:	0.00 M		0.00 M		1.00 M
Changes:	$+2x$ M		$+x$ M		$-2x$ M
Equil:	$2x$ M		x M		$(1.00-2x)$M

Again, notice that an exact solution involves finding the roots of a cubic. So we have taken the reaction 100% in the forward direction and then sent it back in the reverse direction to a small extent to reach equilibrium. We now solve the K_c expression for x, obtaining first an approximate value by assuming $2x << 1.00$.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.00-2x)^2}{(2x)^2 x} = 2.8 \times 10^2 \approx \frac{(1.00)^2}{4x^3} \text{ or } x = 0.096$$

We then use this approximate value of x to find a second approximation for x.

$$K_c = \frac{(1.00-0.19)^2}{4x^3} = 2.8 \times 10^2 \qquad \text{or} \qquad x = 0.084$$

Another cycle gives $K_c = \frac{(1.00-0.17)^2}{4x^3} = 2.8 \times 10^2$ or $x = 0.085$

Then we compute the equilibrium concentrations and amounts.

$[SO_3] = 1.00 - (2 \times 0.085) = 0.83\text{ M}$ amount $SO_3 = 1.00\text{ L} \times 0.83\text{ M} = 0.83\text{ mol } SO_3$

$[SO_2] = 2 \times 0.085 = 0.17\text{ M}$ amount $SO_2 = 1.00\text{ L} \times 0.17\text{ M} = 0.17\text{ mol } SO_2$

$[O_2] = 0.085\text{ M}$ amount $O_2 = 1.00\text{ L} \times 0.085\text{ M} = 0.085\text{ mol } O_2$

78. (M)

Equation: $HOC_6H_4COOH(g) \rightleftharpoons C_6H_5OH(g) + CO_2(g)$

$$n_{co_2} = \frac{PV}{RT} = \left(\frac{\frac{730\text{mmHg}}{760\text{mmHg/atm}}}{0.0821\text{L}-\text{atm/mol}-\text{K}}\right)\left(\frac{\left(\frac{48.2+48.5}{2}\right) \times \frac{1\text{ L}}{1000\text{ mL}}}{(293\text{K})}\right) = 1.93 \times 10^{-3}\text{ mol } CO_2$$

Note that moles of CO_2 = moles phenol

$$n_{\text{salicylic acid}} = \frac{0.300g}{138g/mol} = 2.17\times10^{-3} \text{ mol salicylic acid}$$

$$K_c = \frac{[C_6H_5OH]\,[CO_2(g)]}{[HOC_6H_4COOH]} = \frac{\left(\dfrac{1.93 \text{ mmol}}{50.0 \text{ mL}}\right)^2}{\dfrac{(2.17-1.93)\text{ mmol}}{50.0 \text{ mL}}} = 0.310$$

$$K_p = K_c(RT)^{(2-1)} = (0.310)\times\left(0.08206\ \frac{\text{L atm}}{\text{mol K}}\right)\times(473\text{ K}) = 12.0$$

79. (D)

(a) This reaction is exothermic and thus, conversion of synthesis gas to methane is favored at lower temperatures. Since $\Delta n_{\text{gas}} = (1+1)-(1+3) = -2$, high pressure favors the products.

(b) The value of K_c is a large number, meaning that almost all of the reactants are converted to products (note that the reaction is stoichiometrically balanced). Thus, after we set up the initial conditions we force the reaction to products and then allow the system to reach equilibrium.

Equation:	$3\,H_2(g)$	+	$CO(g)$	$\rightleftharpoons$	$CH_4(g)$	+	$H_2O(g)$
Initial:	$\frac{3.00\text{ mol}}{15.0\text{ L}}$		$\frac{1.00\text{ mol}}{15.0\text{ L}}$		0 M		0 M
Initial:	0.200 M		0.0667 M		0 M		0 M
To right:	0.000 M		0.000 M		0.0667 M		0.0667 M
Changes:	$+3x$ M		$+x$ M		$-x$ M		$-x$ M
Equil:	$3x$ M		x M		$(0.0667-x)$M		$(0.0667-x)$M

$$K_c = \frac{[CH_4][H_2O]}{[H_2]^3[CO]} = \frac{(0.0667-x)^2}{(3x)^3x} = 190. \qquad \sqrt{190.} = \frac{0.0667-x}{\sqrt{27}\ x^2}$$

$$\sqrt{190\times27}\ x^2 = 0.0667 - x = 71.6\ x^2 \qquad 71.6\,x^2 + x - 0.0667 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-1.00\pm\sqrt{1.00+19.1}}{143} = 0.0244\text{ M}$$

$[CH_4] = [H_2O] = 0.0667 - 0.0244 = 0.0423$ M

$[H_2] = 3\times0.0244 = 0.0732$ M

$[CO] = 0.0244$ M

We check our calculation by computing the value of the equilibrium constant.

$$K_c = \frac{[CH_4]\,[H_2O]}{[H_2]^3\,[CO]} = \frac{(0.0423)^2}{(0.0732)^3\ 0.0244} = 187$$

Now we compute the amount in moles of each component present at equilibrium, and finally the mole fraction of CH_4.

$$\text{amount } CH_4 = \text{amount } H_2O = 0.0423\text{ M} \times 15.0\text{ L} = 0.635\text{ mol}$$

$$\text{amount } H_2 = 0.0732\text{ M} \times 15.0\text{ L} = 1.10\text{ mol}$$

$$\text{amount CO} = 0.0244\text{ M } \times 15.0\text{ L} = 0.366\text{ mol}$$

$$\chi_{CH_4} = \frac{0.635\text{ mol}}{0.635\text{ mol } + \text{ } 0.635\text{ mol } + \text{ } 1.10\text{ mol } + 0.366\text{ mol}} = 0.232$$

80. **(M)** We base our calculation on 1.00 mole of PCl_5 being present initially.

Equation:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial:	1.00 mol		0 M		0 M
Changes:	$-\alpha$ mol		$+\alpha$ mol		$+\alpha$ mol
Equil:	$(1.00-\alpha)$ mol		α mol		α mol

$$n_{total} = 1.00 - \alpha \; + \; \alpha \; + \; \alpha \; = 1.00 + \alpha$$

Equation:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Mol fract.	$\frac{1.00-\alpha}{1.00+\alpha}$		$\frac{\alpha}{1.00 + \alpha}$		$\frac{\alpha}{1.00 + \alpha}$

$$K_p = \frac{P\{Cl_2\}\;P\{PCl_3\}}{P\{PCl_5\}} = \frac{[\chi\{Cl_2\}P_{total}]\;[\chi\{PCl_3\}P_{total}]}{[\chi\{PCl_5\}P_{total}]} = \frac{\left(\frac{\alpha}{1.00+\alpha}P_{total}\right)^2}{\frac{1.00-\alpha}{1.00+\alpha}\,\mathrm{P}_{total}} = \frac{\alpha^2\;P_{total}}{(1.00+\alpha)(1.00-\alpha)} = \frac{\alpha^2\;P_{total}}{1-\alpha^2}$$

81. **(M)** We assume that the entire 5.00 g is N_2O_4 and reach equilibrium from this starting point.

$$[N_2O_4]_i = \frac{5.00\text{ g}}{0.500\text{ L}} \times \frac{1\text{ mol } N_2O_4}{92.01\text{ g } N_2O_4} = 0.109\text{ M}$$

Equation:	N_2O_4 (g)	$\rightleftharpoons$	2 NO_2 (g)
Initial:	0.109		0 M
Changes:	– x M		+ 2x M
Equil:	(0.0109 – x) M		2x M

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = 4.61\times10^{-3} = \frac{(2x)^2}{0.109-x} \qquad 4x^2 = 5.02\times10^{-4} - 4.61\times10^{-3}\;x$$

$$4x^2 + 0.00461\,x - 0.000502 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.00461 \pm \sqrt{2.13\times10^{-5} + 8.03\times10^{-3}}}{8} = 0.0106\text{ M}, \; -0.0118\text{ M}$$

(The method of successive approximations yields 0.0106 after two iterations)

$$\text{amount } N_2O_4 = 0.500\text{ L }(0.109 - 0.0106)\text{ M} = 0.0492\text{ mol } N_2O_4$$

$$\text{amount } NO_2 = 0.500\text{ L } \times 2 \times 0.0106\text{ M } = 0.0106\text{ mol } NO_2$$

$$\text{mol fraction } NO_2 = \frac{0.0106\text{ mol } NO_2}{0.0106\text{ mol } NO_2 + 0.0492\text{ mol } N_2O_4} = 0.177$$

82. **(M)** We let *P* be the initial pressure in atmospheres of $COCl_2(g)$.

Equation:	$COCl_2(g)$	$\rightleftharpoons$	CO(g)	+	$Cl_2(g)$
Initial:	P		0 M		0 M
Changes:	$-x$		$+x$		$+x$
Equil:	$P-x$		x		x

Total pressure = 3.00 atm $= P - x + x + x = P + x \qquad P = 3.00 - x$

$$P\{COCl_2\} = P - x = 3.00 - x - x = 3.00 - 2x$$

$$K_p = \frac{P\{CO\}P\{Cl_2\}}{P(COCl_2\}} = 0.0444 = \frac{x \cdot x}{3.00 - 2x}$$

$$x^2 = 0.133 - 0.0888\,x \quad x^2 + 0.0888\,x - 0.133 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0888 \pm \sqrt{0.00789 + 0.532}}{2} = 0.323, \;\; -0.421$$

Since a negative pressure is physically meaningless, *x* = 0.323 atm.
(The method of successive approximations yields *x* = 0.323 after four iterations.)

$$P\{CO\} = P\{Cl_2\} = 0.323\text{ atm}$$

$$P\{COCl_2\} = 3.00 - 2 \times 0.323 = 2.35\text{ atm}$$

The mole fraction of each gas is its partial pressure divided by the total pressure. And the contribution of each gas to the apparent molar mass of the mixture is the mole fraction of that gas multiplied by the molar mass of that gas.

$$M_{\text{avg}} = \frac{P\{CO\}}{P_{\text{tot}}}M\{CO\} + \frac{P\{Cl_2\}}{P_{\text{tot}}}M\{Cl_2\} + \frac{P\{COCl_2\}}{P_{\text{tot}}}M\{COCl_2\}$$

$$= \left(\frac{0.323\text{ atm}}{3.00\text{ atm}} \times 28.01\text{ g/mol}\right) + \left(\frac{0.323\text{ atm}}{3.00\text{ atm}} \times 70.91\text{ g/mol}\right) + \left(\frac{2.32\text{ atm}}{3.00\text{ atm}} \times 98.92\text{ g/mol}\right)$$

$$= 87.1\text{ g/mol}$$

83. **(M)** Each mole fraction equals the partial pressure of the substance divided by the total pressure. Thus $\chi\{NH_3\} = P\{NH_3\}/P_{tot}$ or $P\{NH_3\} = \chi\{NH_3\}\,P_{tot}$

$$K_p = \frac{P\{NH_3\}^2}{P\{N_2\}\,P\{H_2\}^3} = \frac{(\chi\{NH_3\}P_{tot})^2}{(\chi\{N_2\}P_{tot})\,(\chi\{H_2\}P_{tot})^3} = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,\chi\{H_2\}^3}\,\frac{(P_{tot})^2}{(P_{tot})^4}$$

$$= \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,\chi\{H_2\}^3}\,\frac{1}{(P_{tot})^2}$$

This is the expression we were asked to derive.

84. **(D)** Since the mole ratio of N_2 to H_2 is 1:3, $\chi\{H_2\} = 3\chi\{N_2\}$. Since P_{tot} = 1.00 atm, it follows.

$$K_p = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,(3\chi\{N_2\})^3}\,\frac{1}{(1.00)^2} = 9.06\times10^{-2} = 0.0906$$

$$3^3\times0.0906 = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,\chi\{N_2\}^3} = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}^4} \qquad \frac{\chi\{NH_3\}}{\chi\{N_2\}^2} = \sqrt{3^3\times0.0906} = 1.56$$

We realize that $\chi\{NH_3\} + \chi\{N_2\} + \chi\{H_2\} = 1.00 = \chi\{NH_3\} + \chi\{N_2\} + 3\chi\{N_2\}$

This gives $\chi\{NH_3\} = 1.00 - 4\chi\{N_2\}$ And we have

$$1.56 = \frac{1.00 - 4\chi\{N_2\}}{\chi\{N_2\}^2} \qquad \text{For ease of solving, we let } x = \chi\{N_2\}$$

$$1.56 = \frac{1.00 - 4x}{x^2} \qquad 1.56\,x^2 = 1.00 - 4x \qquad 1.56\,x^2 + 4x - 1.00 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.00 \pm \sqrt{16.00 + 6.24}}{3.12} = 0.229,\ -2.794$$

Thus $\chi\{N_2\} = 0.229$ Mole % NH_3 = (1.000 mol –(4 × 0.229 mol)) × 100% = 8.4%

<u>85.</u> **(M)** Since the initial mole ratio is 2 $H_2S(g)$ to 1 $CH_4(g)$, the reactants remain in their stoichiometric ratio when equilibrium is reached. Also, the products are formed in their stoichiometric ratio.

$$\text{amount } CH_4 = 9.54\times10^{-3}\text{ mol } H_2S \times \frac{1\text{ mol } CH_4}{2\text{ mol } H_2S} = 4.77\times10^{-3}\text{ mol } CH_4$$

$$\text{amount } CS_2 = 1.42\times10^{-3}\text{ mol } BaSO_4 \times \frac{1\text{ mol S}}{1\text{ mol } BaSO_4} \times \frac{1\text{ mol } CS_2}{2\text{ mol S}} = 7.10\times10^{-4}\text{ mol } CS_2$$

$$\text{amount } H_2 = 7.10\times10^{-4}\text{ mol } CS_2 \times \frac{4\text{ mol } H_2}{1\text{ mol } CS_2} = 2.84\times10^{-3}\text{ mol } H_2$$

$$\text{total amount } = 9.54\times10^{-3}\text{mol } H_2S + 4.77\times10^{-3}\text{ mol } CH_4 + 7.10\times10^{-4}\text{mol } CS_2 + 2.84\times10^{-3}\text{ mol } H_2$$
$$= 17.86\times10^{-3}\text{ mol}$$

The partial pressure of each gas equals its mole fraction times the total pressure.

$$P\{H_2S\} = 1.00 \text{ atm } \times \frac{9.54\times10^{-3} \text{ mol } H_2S}{17.86\times10^{-3} \text{ mol total}} = 0.534 \text{ atm}$$

$$P\{CH_4\} = 1.00 \text{ atm} \times \frac{4.77\times10^{-3} \text{ mol } CH_4}{17.86\times10^{-3} \text{ mol total}} = 0.267 \text{ atm}$$

$$P\{CS_2\} = 1.00 \text{ atm} \times \frac{7.10\times10^{-4} \text{ mol } CS_2}{17.86\times10^{-3} \text{ mol total}} = 0.0398 \text{ atm}$$

$$P\{H_2\} = 1.00 \text{ atm } \times \frac{2.84\times10^{-3} \text{ mol } H_2}{17.86\times10^{-3} \text{ mol total}} = 0.159 \text{ atm}$$

$$K_p = \frac{P\{H_2\}^4 \; P\{CS_2\}}{P\{H_2S\}^2 \; P\{CH_4\}} = \frac{0.159^4 \times 0.0398}{0.534^2 \times 0.267} = 3.34\times10^{-4}$$

86. **(D)**

81. We base our calculation on an I.C.E. table, after we first determine the direction of the reaction by computing :

$$Q_c = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]} = \frac{(0.03000)^2\,(0.03000)^2}{(0.5000)^2\,(0.5000)} = 6.48\times10^{-6}$$

Because this value is smaller than K_c, the reaction will shift to the right to reach equilibrium. Since the value of the equilibrium constant for the forward reaction is quite small, let us assume that the reaction initially shifts all the way to the left (line labeled "to left:"), and then reacts back in the forward direction to reach a position of equilibrium.

Equation:	$2\,Fe^{3+}(aq)$	+	$Hg_2{}^{2+}(aq)$	$\rightleftharpoons$	$2\,Fe^{2+}(aq)$	+	$2\,Hg^{2+}(aq)$
Initial:	0.5000 M		0.5000 M		0.03000 M		0.03000 M
$\longleftarrow$	$+0.03000$ M		$+0.0150$ M		-0.03000 M		-0.03000 M
To left:	0.5300 M		0.5150 M		0 M		0 M
Changes:	$-2x$ M		$-x$ M		$+2x$ M		$+2x$ M
Equil:	$(0.5300-2x)$M		$(0.5150-x)$M		$2x$ M		$2x$ M

$$K_c = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]} = 9.14\times10^{-6} = \frac{(2x)^2(2x)^2}{(0.5300-2x)^2(0.5150-x)} \approx \frac{4x^2 \; 4x^2}{(0.5300)^2 \; 0.5150}$$

Note that we have assumed that $2x << 0.5300$ and $x < 0.5150$

$$x^4 = \frac{9.14\times10^{-6} \; (0.5300)^2 \; (0.5150)}{4\times4} = 8.26\times10^{-8} \qquad x = 0.0170$$

Our assumption, that $2x\,(=0.0340) << 0.5300$, is reasonably good.

$[Fe^{3+}] = 0.5300 - 2\times0.0170 = 0.4960$ M $\qquad [Hg_2{}^{2+}] = 0.5150 - 0.0170 = 0.4980$

$[Fe^{2+}] = [Hg^{2+}] = 2\times0.0170 = 0.0340$ M

We check by substituting into the K_c expression.

$$9.14\times10^{-6}=K_c=\frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]}=\frac{(0.0340)^2(0.0340)^2}{(0.4960)^2\ 0.4980}=11\times10^{-6}\quad\text{Not a substantial difference.}$$

M*athematica* (version 4.0, Wolfram Research, Champaign, IL) gives a root of 0.0163.

87. **(D)** Again we base our calculation on an I.C.E. table. In the course of solving the Integrative Example, we found that we could obtain the desired equation by reversing equation (2) and adding the result to equation (1)

$$-(2)\quad H_2O(g)\ +\ CH_4(g)\ \rightleftharpoons\ CO(g)\ +\ 3\,H_2(g)\qquad K=1/190$$

$$+(1)\quad \underline{CO(g)\ +\ H_2O(g)\ \rightleftharpoons\ CO_2(g)\ +\ H_2(g)\qquad K=1.4}$$

$$\text{Equation:}CH_4(g)\ +\ 2\,H_2O(g)\ \rightleftharpoons\ CO_2(g)\ +\ 4\,H_2(g)\qquad K=1.4/190=0.0074$$

$$-(2)\quad H_2O(g)\ +\ CH_4(g)\ \rightleftharpoons\ CO(g)\ +\ 3\,H_2(g)\qquad K=1/190$$

$$+(1)\quad \underline{CO(g)\ +\ H_2O(g)\ \rightleftharpoons\ CO_2(g)\ +\ H_2(g)\qquad K=1.4}$$

Equation:	$CH_4(g)$ +	$2\,H_2O(g)$ ⇌	$CO_2(g)$ +	$4\,H_2(g)$	$K=1.4/190=0.0074$
Initial:	0.100 mol	0.100 mol	0.100 mol	0.100 mol	
⟵	$+0.025$ mol	$+0.050$ mol	-0.025 mol	-0.100 mol	
To left:	0.125 mol	0.150 mol	0.075 mol	0.000 mol	
Concns:	0.0250 M	0.0300 M	0.015 M	0.000 M	
Changes:	$-x$ M	$-2x$ mol	$+x$ mol	$+4x$ mol	
Equil:	$(0.0250-x)$ M	$(0.0300-2x)$	$(0.015+x)$ M	$4x$ mol	

Notice that we have a fifth order polynomial to solve. Hence, we need to try to approximate its final solution as closely as possible. The reaction favors the reactants because of the small size of the equilibrium constant. Thus, we approach equilibrium from as far to the left as possible.

$$K_c=0.0074=\frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}=\frac{(0.0150+x)(4x)^4}{(0.0250-x)\ (0.0300-2x)^2}\approx\frac{0.0150\ (4x)^4}{0.0250\ (0.0300)^2}$$

$$x\approx\sqrt[4]{\frac{0.0250\,(0.0300)^2\ 0.0074}{0.0150\times256}}=0.014\,\text{M}$$

Our assumption is terrible. We substitute to continue successive approximations.

$$0.0074=\frac{(0.0150\ +\ 0.014)\ (4x)^4}{(0.0250-0.014)\ \ (0.0300-2\times0.014)^2}=\frac{(0.029)(4x)^4}{(0.011)(0.002)^2}$$

Next, try x_2 = 0.0026

$$0.074=\frac{(0.0150+0.0026)(4x)^4}{(0.0250-\ 0.0026)\ \ (0.0300-2\times0.0026)^2}$$

then, try $x_3 = 0.0123$.

After 18 iterations, the x value converges to 0.0080.

Considering that the equilibrium constant is known to only two significant figures, this is a pretty good result. Recall that the total volume is 5.00 L. We calculate amounts in moles.

$CH_4(g)$	$(0.0250-0.0080)\times 5.00\text{ L} = 0.017\text{ M}\times 5.00\text{ L} = 0.085\text{ moles }CH_4(g)$
$H_2O(g)$	$(0.0300-2\times 0.0080)\text{ M}\times 5.00\text{ L} = 0.014\text{ M}\times 5.00\text{ L} = 0.070\text{ moles }H_2O(g)$
$CO_2(g)$	$(0.015 + 0.0080)\text{ M}\times 5.00\text{ L} = 0.023\text{ M}\times 5.00\text{ L} = 0.12\text{ mol }CO_2$
$H_2(g)$	$(4\times 0.0080)\text{ M}\times 5.00\text{ L} = 0.032\text{ M}\times 5.00\text{ L} = 0.16\text{ mol }H_2$

88. **(M)** The initial mole fraction of C_2H_2 is $\chi_i = 0.88$. We use molar amounts at equilibrium to compute the equilibrium mole fraction of C_2H_2, χ_{eq}. Because we have a 2.00-L container, molar amounts are double the molar concentrations.

$$\chi_{eq} = \frac{(2\times 0.756)\text{ mol }C_2H_2}{(2\times 0.756)\text{ mol }C_2H_2 + (2\times 0.038)\text{ mol }CH_4 + (2\times 0.068)\text{ mol }H_2} = 0.87\underline{7}$$

Thus, there has been only a slight decrease in mole fraction.

89. **(M)**

(a) $K_{eq} = 4.6\times 10^4 \quad \frac{P\{NOCl\}^2}{P\{NO\}^2\,P\{Cl_2\}} = \frac{(4.125)^2}{P\{NO\}^2(0.1125)}$

$$P\{NO\} = \sqrt{\frac{(4.125)^2}{4.6\times 10^4(0.1125)}} = 0.057\underline{3}\text{ atm}$$

(b) $P_{total} = P_{NO} + P_{Cl_2} + P_{NOCl} = 0.057\underline{3}\text{ atm} + 0.1125\text{ atm} + 4.125\text{ atm} = 4.295\text{ atm}$

90. **(M)** We base our calculation on an I.C.E. table.

Reaction:	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial:	$\frac{0.424\text{ mol}}{10.0\text{ L}}$		$\frac{1.272\text{ mol}}{10.0\text{ L}}$		$\frac{0\text{ mol}}{10.0\text{ L}}$
Change	$\frac{-x\text{ mol}}{10.0\text{ L}}$		$\frac{-3x\text{ mol}}{10.0\text{ L}}$		$\frac{+2x\text{ mol}}{10.0\text{ L}}$
Equilibrium	$\frac{(0.424-x)\text{ mol}}{10.0\text{ L}}$		$\frac{(1.272-3x)\text{ mol}}{10.0\text{ L}}$		$\frac{2x\text{ mol}}{10.0\text{ L}}$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 152 = \frac{\left(\dfrac{2x\,\text{mol}}{10.0\,\text{L}}\right)^2}{\left(\dfrac{(0.424\text{-}x)\ \text{mol}}{10.0\,\text{L}}\right)\left(\dfrac{(1.272\text{-}3x)\,\text{mol}}{10.0\,\text{L}}\right)^3}$$

$$K_c = \frac{100\left(2x\,\text{mol}\right)^2}{\left((0.424\text{-}x)\ \text{mol}\right)\left(3\left(0.424\text{-}x)\ \text{mol}\right)\right)^3}$$

$$K_c = \frac{100\left(2x\,\text{mol}\right)^2}{3^3\left(0.424\text{-}x)\ \text{mol}\right)^4} = 152 \qquad \frac{\left(2x\,\text{mol}\right)^2}{\left(0.424\text{-}x)\ \text{mol}\right)^4} = 41.0\underline{4}$$

Take root of both sides

$$\frac{\left(2x\,\text{mol}\right)}{\left(0.424\text{-}x)\ \text{mol}\right)^2} = 6.41 \qquad 6.41(0.424\text{-}x)^2 = 2x$$

$$3.20(0.180 - 0.848x + x^2) = x = 3.20x^2 - 2.71x + 0.576 \qquad 3.20x^2 - 3.71x + 0.576 = 0$$

Now solve using the quadratic equation: $x = 0.184\underline{6}$ mol or $0.975\underline{6}$ mol (too large)

amount of $NH_3 = 2x = 2(0.1846\,\text{mol}) = 0.369\,\text{mol}$ in 10.0 L or 0.0369 M

$([H_2] = 0.0718\,M \text{ and } [N_2] = 0.0239\,M)$

91. **(D)**

Equation: $2\ H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$ $K_c = 14.5$ at 483 K

$$K_p = K_c(RT)^{\Delta n} = 14.5\left(0.08206\ \frac{\text{L-atm}}{\text{mol-K}} \times 483\text{K}\right)^{-2} = 9.23\times10^{-3}$$

We know that mole percents equal pressure percents for ideal gases.

$P_{CO} = 0.350 \times 100$ atm = 35.0 atm

$P_{H_2} = 0.650 \times 100$ atm = 65.0 atm

Equation:	$2\ H_2(g)$ +	$CO(g)$ $\rightleftharpoons$	$CH_3OH(g)$
Initial:	65 atm	35 atm	
Changes:	$-2P$ atm	$-P$ atm	$+P$ atm
Equil:	65-2P	35-P	P

$$K_p = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}{}^2} = \frac{P}{(35.0 - P)(65.0 - 2P)^2} = 9.23\times10^{-3}$$

By successive approximations, P = 24.6 atm = P_{CH_3OH} at equilibrium.

Mathematica (version 4.0, Wolfram Research, Champaign, IL) gives a root of 24.5.

FEATURE PROBLEMS

92. **(M)** We first determine the amount in moles of acetic acid in the equilibrium mixture.

$$\text{amount } CH_3CO_2H = 28.85\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{0.1000\text{ mol Ba}(OH)_2}{1\text{ L}} \times \frac{2\text{ mol } CH_3CO_2H}{1\text{ mol Ba}(OH)_2}$$

$$\times \frac{\text{complete equilibrium mixture}}{0.01\text{ of equilibrium mixture}} = 0.5770\text{ mol } CH_3CO_2H$$

$$K_c = \frac{[CH_3CO_2C_2H_5][H_2O]}{[C_2H_5OH][CH_3CO_2H]} = \frac{\dfrac{0.423\,\text{mol}}{V} \times \dfrac{0.423\,\text{mol}}{V}}{\dfrac{0.077\,\text{mol}}{V} \times \dfrac{0.577\,\text{mol}}{V}} = \frac{0.423 \times 0.423}{0.077 \times 0.577} = 4.0$$

93. **(D)** In order to determine whether or not equilibrium has been established in each bulb, we need to calculate the concentrations for all three species at the time of opening. The results from these calculations are tabulated below and a typical calculation is given beneath this table.

Bulb No.	Time Bulb Opened (hours)	Initial Amount HI(g) (in mmol)	Amount of I_2(g) and H_2(g) at Time of Opening (in mmol)	Amount HI(g) at Time of Opening (in mmol)	[HI] (mM)	[I_2] & [H_2] (mM)	$\frac{[H_2][I_2]}{[HI]^2}$
1	2	$2.34\underline{5}$	0.1572	2.03	5.08	0.393	0.00599
2	4	$2.51\underline{8}$	0.2093	2.10	5.25	0.523	0.00992
3	12	$2.46\underline{3}$	0.2423	1.98	4.95	0.606	0.0150
4	20	$3.17\underline{4}$	0.3113	2.55	6.38	0.778	0.0149
5	40	$2.18\underline{9}$	0.2151	1.76	4.40	0.538	0.0150

Consider, for instance, bulb #4 (opened after 20 hours).

Initial moles of HI(g) = 0.406 g HI(g) $\times \frac{1\text{ mole HI}}{127.9\text{ g HI}}$ = $0.00317\underline{4}$ mol HI(g) or $3.17\underline{4}$ mmol

moles of I_2(g) present in bulb when opened.

$$= 0.04150\text{ L } Na_2S_2O_3 \times \frac{0.0150\text{ mol } Na_2S_2O_3}{1\text{ L } Na_2S_2O_3} \times \frac{1\text{ mol } I_2}{2\text{ mol } Na_2S_2O_3} = 3.113 \times 10^{-4}\text{ mol } I_2$$

millimoles of I_2(g) present in bulb when opened = 3.113×10^{-4} mol I_2

moles of H_2 present in bulb when opened = moles of I_2(g) present in bulb when opened.

HI reacted = 3.113×10^{-4} mol $I_2 \times \frac{2\text{ mole HI}}{1\,\text{mol } I_2}$ = 6.226×10^{-4} mol HI (0.6226 mmol HI)

moles of HI(g) in bulb when opened= $3.17\underline{4}$ mmol HI − 0.6226 mmol HI = 2.55 mmol HI

Concentrations of HI, I_2, and H_2

[HI] = 2.55 mmol HI ÷ 0.400 L = 6.38 mM

$[I_2] = [H_2] = 0.3113\text{ mmol} \div 0.400\text{ L} = 0.778\text{ mM}$

Ratio: $\dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{(0.778\text{ mM})(0.778\text{ mM})}{(6.38\text{ mM})^2} = 0.0149$

As the time increases, the ratio $\dfrac{[H_2][I_2]}{[HI]^2}$ initially climbs sharply, but then plateaus at

0.0150 somewhere between 4 and 12 hours. Consequently, it seems quite reasonable to conclude that the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ has a $K_c \sim 0.015$ at 623 K.

94. **(D)** We first need to determine the number of moles of ammonia that were present in the sample of gas that left the reactor. This will be accomplished by using the data from the titrations involving HCl(aq).

Original number of moles of HCl(aq) in the 20.00 mL sample

$= 0.01872\text{ L of KOH} \times \dfrac{0.0523\text{ mol KOH}}{1\text{ L KOH}} \times \dfrac{1\text{ mol HCl}}{1\text{ mol KOH}}$

$= 9.79\underline{06} \times 10^{-4}$ moles of $HCl_{(\text{initially})}$

Moles of unreacted HCl(aq)

$= 0.01542\text{ L of KOH} \times \dfrac{0.0523\text{ mol KOH}}{1\text{ L KOH}} \times \dfrac{1\text{ mol HCl}}{1\text{ mol KOH}} =$
$8.06\underline{47} \times 10^{-4}$ moles of $HCl_{(\text{unreacted})}$

Moles of HCl that reacted and /or moles of NH_3 present in the sample of reactor gas
$= 9.79\underline{06} \times 10^{-4}$ moles $-$ $8.06\underline{47} \times 10^{-4}$ moles $= 1.73 \times 10^{-4}$ mole of NH_3 (or HCl).

The remaining gas, which is a mixture of $N_2(g)$ and $H_2(g)$ gases, was found to occupy 1.82 L at 273.2 K and 1.00 atm. Thus, the total number of moles of N_2 and H_2 can be found via the

ideal gas law: $n_{H_2+N_2} = \dfrac{PV}{RT} = \dfrac{(1.00\text{ atm})(1.82\text{ L})}{(0.08206\ \frac{\text{L atm}}{\text{K mol}})(273.2\text{ K})} = 0.0811\underline{8}$ moles of $(N_2 + H_2)$

According to the stoichiometry for the reaction, 2 parts NH_3 decompose to give 3 parts H_2 and 1 part N_2. Thus the non-reacting mixture must be 75% H_2 and 25% N_2.

So, the number of moles of $N_2 = 0.25 \times 0.0811\underline{8}$ moles $= 0.0203$ moles N_2 and the number of moles of $H_2 = 0.75 \times 0.0811\underline{8}$ moles $= 0.0609$ moles H_2.

Before we can calculate K_c, we need to determine the volume that the NH_3, N_2, and H_2 molecules occupied in the reactor. Once again, the ideal gas law ($PV = nRT$) will be employed. $n_{gas} = 0.0811\underline{8}$ moles ($N_2 + H_2$) + 1.73×10^{-4} moles $NH_3 = 0.0813\underline{5}$ moles

$$V_{gases} = \frac{nRT}{P} = \frac{(0.08135\text{ mol})(0.08206\ \frac{\text{L atm}}{\text{K mol}})(1174.2\text{ K})}{30.0\text{ atm}} = 0.261\underline{3}\text{ L}$$

$$\text{So, } K_c = \frac{\left[\frac{1.73\times 10^{-4}\text{ moles}}{0.2613\text{ L}}\right]^2}{\left[\frac{0.0609\text{ moles}}{0.2613\text{ L}}\right]^3\left[\frac{0.0203\text{ moles}}{0.2613\text{ L}}\right]^1} = 4.46\times 10^{-4}$$

To calculate K_p at 901 °C, we need to employ the equation $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$; $\Delta n_{gas} = -2$

$K_p = 4.46 \times 10^{-4}\ [(0.08206\text{ L atm K}^{-1}\text{mol}^{-1})] \times (1174.2\text{ K})]^{-2} = 4.80 \times 10^{-8}$ at 901°C for the reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

95. **(M)** For step 1, rate of the forward reaction = rate of the reverse reaction, so,

$k_1[I_2] = k_{-1}[I]^2$ or $\frac{k_1}{k_{-1}} = \frac{[I]^2}{[I_2]} = K_c$ (step 1)

Like the first step, the rates for the forward and reverse reactions are equal in the second step and thus,

$k_2[I]^2[H_2] = k_{-2}[HI]^2$ or $\frac{k_2}{k_{-2}} = \frac{[HI]^2}{[I]^2[H_2]} = K_c$ (step 2)

Now we combine the two elementary steps to obtain the overall equation and its associated equilibrium constant.

$I_2(g) \rightleftharpoons 2\ I(g)$ $\quad K_c = \frac{k_1}{k_{-1}} = \frac{[I]^2}{[I_2]}$ (STEP 1)

and

$H_2(g) + 2\ I(g) \rightleftharpoons 2\ HI(g)$ $\quad K_c = \frac{k_2}{k_{-2}} = \frac{[HI]^2}{[I]^2[H_2]}$ (STEP 2)

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$ $\quad K_{c(\text{overall})} = K_{c(\text{step 1})} \times K_{c(\text{step 2})}$

$$K_{c(\text{overall})} = \frac{k_1}{k_{-1}} \times \frac{k_2}{k_{-2}} = \frac{[I]^2}{[I_2]} \times \frac{[HI]^2}{[I]^2[H_2]}$$

$$K_{c(\text{overall})} = \frac{k_1 k_2}{k_{-1}k_{-2}} = \frac{[I]^2[HI]^2}{[I]^2[I_2][H_2]} = \frac{[HI]^2}{[I_2][H_2]}$$

96. **(M)** The equilibrium expressions for the two reactions are:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]};\ K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

First, start with $[H^+] = 0.1$ and $[HCO_3^-] = 1$. This means that $[H^+]/[HCO_3^-] = 0.1$, which means that $[CO_3^{2-}] = 10K_2$. By adding a small amount of H_2CO_3 we shift $[H^+]$ by 0.1 and $[HCO_3^-]$ by 0.1. This leads to $[H^+]/[HCO_3^-] \approx 0.2$, which means that $[CO_3^{2-}] = 5K_2$. Note that $[CO_3^{2-}]$ has *decreased* as a result of adding H_2CO_3 to the solution.

97. **(D)** First, it is most important to get a general feel for the direction of the reaction by determining the reaction quotient:

$$Q = \frac{[C(aq)]}{[A(aq)]\cdot[B(aq)]} = \frac{0.1}{0.1\times 0.1} = 10$$

Since Q>>K, the reaction proceeds toward the reactants. Looking at the reaction in the aqueous phase only, the equilibrium can be expressed as follows:

	A(aq)	+	B(aq)	$\rightleftharpoons$	C(aq)
Initial	0.1		0.1		0.1
Change	-x		-x		+x
Equil.	0.1 - x		0.1 - x		0.1 + x

We will do part (b) first, which assumes the absence of an organic layer for extraction:

$$K = \frac{(0.1 + x)}{(0.1 - x)(0.1 - x)} = 0.01$$

Expanding the above equation and using the quadratic formula, x = -0.0996. Therefore, the concentration of C(aq) and equilibrium is 0.1 + (-0.0996) = 4×10^{-4} M.

If the organic layer is present for extraction, we can add the two equations together, as shown below:

$$\begin{array}{lcl} A(aq) + B(aq) & \rightleftharpoons & C(aq) \\ C(aq) & \rightleftharpoons & C(or) \\ \hline A(aq) + B(aq) & \rightleftharpoons & C(or) \end{array}$$

$K = K_1 \times K_2 = 0.1 \times 15 = 0.15$.

Since the organic layer is present with the aqueous layer, and K_2 is large, we can expect that the vast portion of C initially placed in the aqueous phase will go into the organic phase.

Therefore, the initial [C] = 0.1 can be assumed to be for C(or). The equilibrium can be expressed as follows

	A(aq)	+	B(aq)	$\rightleftharpoons$	C(or)
Initial	0.1		0.1		0.1
Change	-x		-x		+x
Equil.	0.1 - x		0.1 - x		0.1 + x

We will do part (b) first, which assumes the absence of an organic layer for extraction:

$$K=\frac{(0.1+x)}{(0.1-x)(0.1-x)}=0.15$$

Expanding the above equation and using the quadratic formula, x = -0.0943. Therefore, the concentration of C(or) and equilibrium is 0.1 + (-0.0943) = 6×10^{-4} M. This makes sense because the K for the overall reaction is < 1, which means that the reaction favors the reactants.

SELF-ASSESSMENT EXERCISES

98. **(E)**

(a) K_p: The equilibrium constant of a reaction where the pressures of gaseous reactants and products are used instead of their concentrations

(b) Q_c: The reaction quotient using the molarities of the reactants and products

(c) Δn_{gas}: The difference between the number of moles (as determined from a balanced reaction) of product and reactant gases

99. **(E)**

(a) Dynamic equilibrium: In a dynamic equilibrium (which is to say, real equilibrium), the forward and reverse reactions happen, but at a constant rate

(b) Direction of net chemical change: In a reversible reaction, if the reaction quotient $Q_c > K_c$, then the net reaction will go toward the reactants, and vice versa

(c) Le Châtelier’s principle: When a system at equilibrium is subjected to external change (change in partial pressure of reactants/products, temperature or concentration), the equilibrium shifts to a side to diminish the effects of that external change

(d) Effect of catalyst on equilibrium: A catalyst does not affect the final concentrations of the reactants and products. However, since it speeds up the reaction, it allows for the equilibrium concentrations to be established more quickly

100. **(E)**

(a) Reaction that goes to completion and reversible reaction: In a reversible reaction, the products can revert back to the reactants in a dynamic equilibrium. In a reaction that goes to completion, the formation of products is so highly favored that there is practically no reverse reaction (or the reverse is practically impossible, such as a combustion reaction).

(b) K_p and K_c: K_p is the equilibrium constant using pressures of products and reactants, while K_c is the constant for reaction using concentrations.

(c) Reaction quotient (Q) and equilibrium constant expression (K): The reaction quotient Q is the ratio of the concentrations of the reactants and products expressed in the same format as the equilibrium expression. The equilibrium constant expression is the ratio of concentrations at equilibrium.

(d) Homogeneous and heterogeneous reaction: In a homogeneous reaction, the reaction happens within a single phase (either aqueous or gas). In a heterogeneous reaction, there is more than one phase present in the reaction.

101. **(E)** The answer is (c). Because the limiting reagent is I_2 at one mole, the theoretical yield of HI is 2 moles. However, because there is an established equilibrium, there is a small amount of HI which will decompose to yield H_2 and I_2. Therefore the total moles of HI created is close, but less than 2.

102. **(E)** The answer is (d). The equilibrium expression is:

$$K = \frac{P(SO_3)^2}{P(SO_2)^2 P(O_2)} = 100$$

If equilibrium is established, moles of SO_3 and SO_2 cancel out of the equilibrium expression. Therefore, if K = 100, the moles of O_2 have to be 0.01 to make K = 100.

103. **(E)** The answer is (a). As the volume of the vessel is expanded (i.e., pressure is reduced), the equilibrium shifts $_{\text{toward}}$ the side with more moles of gas.

104. **(E)** The answer is (b). At half the stoichiometric values, the equilibrium constant is $K^{1/2}$. If the equation is reversed, it is K^{-1}. Therefore, the $K' = K^{-1/2} = (1.8\times10^{-6})^{-1/2} = 7.5\times10^{-2}$.

105. **(E)** The answer is (a). We know that $K_p = K_c (RT)^{\Delta n}$. Since $\Delta n = (3–2) = 1$, $K_p = K_c (RT)$. Therefore, $K_p > K_c$.

106. **(E)** The answer is (c). Since the number of moles of gas of products is more than the reactants, increasing the vessel volume will drive the equilibrium more toward the product side. The other options: (a) has no effect, and (b) drives the equilibrium to the reactant side.

107. **(E)** The equilibrium expression is:

$$K = \frac{[C]^2}{[B]^2[A]} = \frac{(0.43)^2}{(0.55)^2(0.33)} = 1.9$$

108. **(E)**

(a) As more O_2 (a reactant) is added, more Cl_2 is produced.

(b) As HCl (a reactant) is removed, equilibrium shifts to the left and less Cl_2 is made.

(c) Since there are more moles of reactants, equilibrium shifts to the left and less Cl_2 is made.

(d) No change. However, the equilibrium is reached faster.

(e) Since the reaction is exothermic, increasing the temperature causes less Cl_2 to be made.

109. **(E)** SO_2 (g) will be less than SO_2 (aq), because K > 1, so the equilibrium lies to the product side, SO_2 (aq).

110. **(E)** Since K >>1, there will be much more product than reactant

111. **(M)** The equilibrium expression for this reaction is:

$$K=\frac{[SO_3]^2}{[SO_2]^2[O_2]}=35.5$$

(a) If $[SO_3]_{eq} = [SO_2]_{eq}$, then $[O_2] = 1/35.5 = 0.0282$ M.
moles of $O_2 = 0.0282 \times 2.05$ L = 0.0578 moles

(b) Plugging in the new concentration values into the equilibrium expression:

$$K=\frac{[SO_3]^2}{[SO_2]^2[O_2]}=\frac{[2\times SO_2]^2}{[SO_2]^2[O_2]}=\frac{4}{[O_2]}=35.5$$

$[O_2] = 0.113$ M

moles of $O_2 = 0.113 \times 2.05$ L = 0.232 moles

112. **(M)** This concept map involves the various conditions that affect equilibrium of a reaction, and those that don't. Under the category of conditions that do cause a change, there is changing the partial pressure of gaseous products and reactants, which includes pressure and vessel volume. The changes that do not affect partial pressure are changing the concentration of reactants or products in an aqueous solution, through dilution or concentration. Changing the temperature can affect both aqueous and gaseous reactions. Under the category of major changes that don't affect anything is the addition of a non-reactive gas.

CHAPTER 16
ACIDS AND BASES

PRACTICE EXAMPLES

1A **(E)**

(a) In the forward direction, HF is the acid (proton donor; forms F^-), and H_2O is the base (proton acceptor; forms H_3O^+). In the reverse direction, F^- is the base (forms HF), accepting a proton from H_3O^+, which is the acid (forms H_2O).

(b) In the forward direction, HSO_4^- is the acid (proton donor; forms SO_4^{2-}), and NH_3 is the base (proton acceptor; forms NH_4^+). In the reverse direction, SO_4^{2-} is the base (forms HSO_4^-), accepting a proton from NH_4^+, which is the acid (forms NH_3).

(c) In the forward direction, HCl is the acid (proton donor; forms Cl^-), and $C_2H_3O_2^-$ is the base (proton acceptor; forms $HC_2H_3O_2$). In the reverse direction, Cl^- is the base (forms HCl), accepting a proton from $HC_2H_3O_2$, which is the acid (forms $C_2H_3O_2^-$).

1B **(E)** We know that the formulas of most acids begin with H. Thus, we identify HNO_2 and HCO_3^- as acids.

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq);$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

A negatively charged species will attract a positively charged proton and act as a base. Thus PO_4^{3-} and HCO_3^- can act as bases. We also know that PO_4^{3-} must be a base because it cannot act as an acid—it has no protons to donate—and we know that all three species have acid-base properties.

$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq);$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightarrow CO_2 \cdot H_2O(aq) + OH^-(aq)$$

Notice that HCO_3^- is the amphiprotic species, acting as both an acid and a base.

2A **(M)** $\left[H_3O^+\right]$ is readily computed from pH: $\left[H_3O^+\right] = 10^{-pH}$ $\quad\left[H_3O^+\right] = 10^{-2.85} = 1.4 \times 10^{-3}$ M.

$\left[OH^-\right]$ can be found in two ways: (1) from $K_w = \left[H_3O^+\right]\left[OH^-\right]$, giving

$\left[OH^-\right] = \dfrac{K_w}{\left[H_3O^+\right]} = \dfrac{1.0\times10^{-14}}{1.4\times10^{-3}} = 7.1\times10^{-12}$ M, or (2) from $pH + pOH = 14.00$, giving

$pOH = 14.00 - pH = 14.00 - 2.85 = 11.15$, and then $\left[OH^-\right] = 10^{-pOH} = 10^{-11.15} = 7.1\times10^{-12}$ M.

2B **(M)** $\left[H_3O^+\right]$ is computed from pH in each case: $\left[H_3O^+\right]=10^{-pH}$

$\left[H_3O^+\right]_{conc.}=10^{-2.50}=3.2\times10^{-3}\,M \qquad \left[H_3O^+\right]_{dil.}=10^{-3.10}=7.9\times10^{-4}\,M$

All of the H_3O^+ in the dilute solution comes from the concentrated solution.

$$\text{amount } H_3O^+ = 1.00\ \text{L conc. soln}\times\frac{3.2\times10^{-3}\,\text{mol } H_3O^+}{1\ \text{L conc. soln}} = 3.2\times10^{-3}\,\text{mol } H_3O^+$$

Next we calculate the volume of the dilute solution.

$$\text{volume of dilute solution} = 3.2\times10^{-3}\,\text{mol } H_3O^+\times\frac{1\ \text{L dilute soln}}{7.9\times10^{-4}\,\text{mol } H_3O^+} = 4.1\ \text{L dilute soln}$$

Thus, the volume of water to be added is = 3.1 L.

Infinite dilution does not lead to infinitely small hydrogen ion concentrations. Since dilution is done with water, the pH of an infinitely dilute solution will approach that of pure water, namely pH = 7.

3A **(E)** pH is computed directly from the equation below.

$\left[H_3O^+\right]$, $pH = -\log\left[H_3O^+\right] = -\log(0.0025) = 2.60$.

We know that HI is a strong acid and, thus, is completely dissociated into H_3O^+ and I^-. The consequence is that $\left[I^-\right]=\left[H_3O^+\right]=0.0025$ M. $\left[OH^-\right]$ is most readily computed from pH: $pOH = 14.00 - pH = 14.00 - 2.60 = 11.40$; $\left[OH^-\right]=10^{-pOH}=10^{-11.40}=4.0\times10^{-12}\,M$

3B **(M)** The number of moles of HCl(g) is calculated from the ideal gas law. Then $\left[H_3O^+\right]$ is calculated, based on the fact that HCl(aq) is a strong acid (1 mol H_3O^+ is produced from each mole of HCl).

$$\text{moles HCl(g)} = \frac{\left(747\,\text{mmHg}\times\dfrac{1\,\text{atm}}{760\,\text{mmHg}}\right)\times0.535\,\text{L}}{\dfrac{0.08206\,\text{L atm}}{\text{mol K}}\times(26.5+273.2)\,\text{K}}$$

moles HCl(g) = 0.0214 mol HCl(g) = 0.0214 mol H_3O^+ when dissolved in water

$[H_3O^+] = 0.0214\,\text{mol}$ $\qquad$ pH = -log(0.0214) = 1.670

4A **(E)** pH is most readily determined from $pOH = -\log\left[OH^-\right]$. Assume $Mg(OH)_2$ is a strong base.

$$\left[OH^-\right]=\frac{9.63\ \text{mg } Mg(OH)_2}{100.0\ \text{mL soln}}\times\frac{1000\ \text{mL}}{1\ \text{L}}\times\frac{1\text{g}}{1000\ \text{mg}}\times\frac{1\ \text{mol } Mg(OH)_2}{58.32\,\text{g } Mg(OH)_2}\times\frac{2\,\text{mol } OH^-}{1\ \text{mol } Mg(OH)_2}$$

$\left[OH^-\right] = 0.00330\,M$; $pOH = -\log(0.00330) = 2.481$

$pH = 14.000 - pOH = 14.000 - 2.481 = 11.519$

<u>4B</u> **(E)** KOH is a strong base, which means that each mole of KOH that dissolves produces one mole of dissolved $\mathrm{OH^-(aq)}$. First we calculate $\left[\mathrm{OH^-}\right]$ and the pOH. We then use $\mathrm{pH + pOH = 14.00}$ to determine pH.

$$\left[\mathrm{OH^-}\right] = \frac{3.00\,\mathrm{g\ KOH}}{100.00\,\mathrm{g\ soln}} \times \frac{1\ \mathrm{mol\ KOH}}{56.11\ \mathrm{g\ KOH}} \times \frac{1\,\mathrm{mol\ OH^-}}{1\,\mathrm{mol\ KOH}} \times \frac{1.0242\,\mathrm{g\ soln}}{1\,\mathrm{mL\ soln}} \times \frac{1000\,\mathrm{mL}}{1\,\mathrm{L}} = 0.548\,\mathrm{M}$$

$$\mathrm{pOH} = -\log(0.548) = 0.261 \qquad \mathrm{pH} = 14.000 - \mathrm{pOH} = 14.000 - 0.261 = 13.739$$

<u>5A</u> **(M)** $\left[\mathrm{H_3O^+}\right] = 10^{-\mathrm{pH}} = 10^{-4.18} = 6.6 \times 10^{-5}\ \mathrm{M}$.

Organize the solution using the balanced chemical equation.

Equation:	$\mathrm{HOCl(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{H_3O^+(aq)}$	+	$\mathrm{OCl^-(aq)}$
Initial:	0.150 M		—		≈ 0 M		0 M
Changes:	-6.6×10^{-5} M		—		$+6.6\times10^{-5}$ M		$+6.6\times10^{-5}$ M
Equil:	≈ 0.150 M		—		6.6×10^{-5} M		6.6×10^{-5} M

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{OCl^-}\right]}{\left[\mathrm{HOCl}\right]} = \frac{\left(6.6\times10^{-5}\right)\left(6.6\times10^{-5}\right)}{0.150} = 2.9\times10^{-8}$$

<u>5B</u> **(M)** First, we use pH to determine $\left[\mathrm{OH^-}\right]$. $\mathrm{pOH} = 14.00 - \mathrm{pH} = 14.00 - 10.08 = 3.92$.

$\left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}} = 10^{-3.92} = 1.2\times10^{-4}$ M. We determine the initial concentration of cocaine and then organize the solution around the balanced equation in the manner we have used before.

$$[\mathrm{C_{17}H_{21}O_4N}] = \frac{0.17\,\mathrm{g\ C_{17}H_{21}O_4N}}{100\,\mathrm{mL\ soln}} \times \frac{1000\,\mathrm{mL}}{1\,\mathrm{L}} \times \frac{1\,\mathrm{mol\ C_{17}H_{21}O_4N}}{303.36\,\mathrm{g\ C_{17}H_{21}O_4N}} = 0.0056\,\mathrm{M}$$

Equation:	$\mathrm{C_{17}H_{21}O_4N(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{C_{17}H_{21}O_4NH^+(aq)}$	+	$\mathrm{OH^-(aq)}$
Initial:	0.0056 M		—		0 M		≈ 0 M
Changes:	-1.2×10^{-4} M		—		$+1.2\times10^{-4}$ M		$+1.2\times10^{-4}$ M
Equil:	≈ 0.0055 M		—		1.2×10^{-4} M		1.2×10^{-4} M

$$K_b = \frac{\left[\mathrm{C_{17}H_{21}O_4NH^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{C_{17}H_{21}O_4N}\right]} = \frac{\left(1.2\times10^{-4}\right)\left(1.2\times10^{-4}\right)}{0.0055} = 2.6\times10^{-6}$$

6A **(M)** Again we organize our solution around the balanced chemical equation.

Equation:	$HC_2H_2FO_2(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$ +	$C_2H_2FO_2^-(aq)$
Initial:	0.100 M	—		$\approx$ 0M	0 M
Changes:	$-x$ M	—		$+x$ M	$+x$ M
Equil:	$(0.100-x)$ M	—		x M	x M

$$K_a=\frac{[H_3O^+][C_2H_2FO_2^-]}{[HC_2H_2FO_2^-]}\text{; therefore, } 2.6\times10^{-3}=\frac{x\cdot x}{(0.100-x)}$$

We can use the 5% rule to ignore x in the denominator. Therefore, $x = [H_3O^+] = 0.016$ M, and pH = –log (0.016) = 1.8. Thus, the calculated pH is considerably lower than 2.89 (Example 16-6).

6B **(M)** We first determine the concentration of undissociated acid. We then use this value in a set-up that is based on the balanced chemical equation.

$$2\,\text{aspirin tablets}\times\frac{0.500\text{ g }HC_9H_7O_4}{\text{tablet}}\times\frac{1\text{ mol }HC_9H_7O_4}{180.155\text{ g }HC_9H_7O_4}\times\frac{1}{0.325\text{ L}}=0.0171\text{M}$$

Equation:	$HC_9H_7O_4(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$ +	$C_9H_7O_4^-(aq)$
Initial:	0.0171 M	—		0 M	0 M
Changes:	$-x$ M	—		$+x$ M	$+x$ M
Equil:	$(0.0171-x)$ M	—		x M	x M

$$K_a=\frac{[H_3O^+][C_9H_7O_4^-]}{[HC_9H_7O_4]}=3.3\times10^{-4}=\frac{x\cdot x}{0.0171-x}$$

$x^2+3.3\times10^{-4}-5.6\underline{4}\times10^{-6}=0$ (find the physically reasonable roots of the quadratic equation)

$$x=\frac{-3.3\times10^{-4}\pm\sqrt{1.1\times10^{-7}+2.3\times10^{-5}}}{2}=0.0022\,\text{M};\quad \text{pH}=-\log(0.0022)=2.66$$

7A **(M)** Again we organize our solution around the balanced chemical equation.

Equation:	$HC_2H_2FO_2(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$ +	$C_2H_2FO_2^-(aq)$
Initial:	0.015 M	—		≈ 0M	0 M
Changes	$-x$ M	—		$+x$ M	$+x$ M
Equil:	$(0.015-x)$ M	—		x M	x M

$$K_a=\frac{[H_3O^+][C_2H_2FO_2^-]}{[HC_2H_2FO_2]}=2.6\times10^{-3}=\frac{(x)(x)}{0.015-x}\approx\frac{x^2}{0.015}$$

$x=\sqrt{x^2}=\sqrt{0.015\times2.6\times10^{-3}}=0.0062\,\text{M}=[H_3O^+]$ Our assumption is invalid:

0.0062 is not quite small enough compared to 0.015 for the 5% rule to hold. Thus we use another cycle of successive approximations.

$$K_a = \frac{(x)(x)}{0.015-0.0062} = 2.6\times10^{-3} \quad x = \sqrt{(0.015-0.0062)\times2.6\times10^{-3}} = 0.0048\ \text{M} = [H_3O^+]$$

$$K_a = \frac{(x)(x)}{0.015-0.0048} = 2.6\times10^{-3} \quad x = \sqrt{(0.015-0.0048)\times2.6\times10^{-3}} = 0.0051\ \text{M} = [H_3O^+]$$

$$K_a = \frac{(x)(x)}{0.015-0.0051} = 2.6\times10^{-3} \quad x = \sqrt{(0.015-0.0051)\times2.6\times10^{-3}} = 0.0051\ \text{M} = [H_3O^+]$$

Two successive identical results indicate that we have the solution.

$\text{pH} = -\log\left[H_3O^+\right] = -\log(0.0051) = 2.29$. The quadratic equation gives the same result (0.0051 M) as this method of successive approximations.

7B **(M)** First we find [$C_5H_{11}N$]. We then use this value as the starting base concentration in a set-up based on the balanced chemical equation.

$$\left[C_5H_{11}N\right] = \frac{114\,\text{mg } C_5H_{11}N}{315\,\text{mL soln}} \times \frac{1\,\text{mmol } C_5H_{11}N}{85.15\,\text{mg } C_5H_{11}N} = 0.00425\,\text{M}$$

Equation:	$C_5H_{11}N(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$C_5H_{11}NH^+(aq)$	+	$OH^-(aq)$
Initial:	0.00425 M		—		0 M		≈ 0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.00425-x)$ M		—		x M		x M

$$K_b = \frac{\left[C_5H_{11}NH^+\right]\left[OH^-\right]}{\left[C_5H_{11}N\right]} = 1.6\times10^{-3} = \frac{x\cdot x}{0.00425-x} \approx \frac{x\cdot x}{0.00425} \quad \text{We assumed that } x \ll 0.00425$$

$x = \sqrt{0.0016\times0.00425} = 0.0026\,\text{M}$ The assumption is not valid. Let's assume $x \approx 0.0026$

$x = \sqrt{0.0016(0.00425-0.0026)} = 0.0016$ Let's try again, with $x \approx 0.0016$

$x = \sqrt{0.0016(0.00425-0.0016)} = 0.0021$ Yet another try, with $x \approx 0.0021$

$x = \sqrt{0.0016(0.00425-0.0021)} = 0.0019$ The last time, with $x \approx 0.0019$

$x = \sqrt{0.0016(0.00425-0.0019)} = 0.0019\,\text{M} = [OH^-]$

$\text{pOH} = -\log[H_3O^+] = -\log(0.0019) = 2.72 \quad \text{pH} = 14.00 - \text{pOH} = 14.00 - 2.72 = 11.28$

We could have solved the problem with the quadratic formula roots equation rather than by successive approximations. The same answer is obtained. In fact, if we substitute $x = 0.0019$ into the K_b expression, we obtain $(0.0019)^2/(0.00425-0.0019) = 1.5\times10^{-3}$ compared to $K_b = 1.6\times10^{-3}$. The error is due to rounding, not to an incorrect value. Using $x = 0.0020$ gives a value of 1.8×10^{-3}, while using $x = 0.0018$ gives 1.3×10^{-3}.

8A **(M)** We organize the solution around the balanced chemical equation; a M is $[\text{HF}]_{\text{initial}}$.

Equation:	HF(aq)	+	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+\text{(aq)}$	+	$\text{F}^-\text{(aq)}$
Initial:	a M		—		≈ 0 M		0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(a-x)$ M		—		x M		x M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{a-x} \approx \frac{x^2}{a} = 6.6\times10^{-4} \qquad x = \sqrt{a\times 6.6\times10^{-4}}$$

For 0.20 M HF, a = 0.20 M $\qquad x = \sqrt{0.20\times6.6\times10^{-4}} = 0.011\ \text{M}$

$$\%\ \text{dissoc} = \frac{0.011\ \text{M}}{0.20\ \text{M}}\times100\% = 5.5\%$$

For 0.020 M HF, a = 0.020 M $\qquad x = \sqrt{0.020\times6.6\times10^{-4}} = 0.0036\ \text{M}$

We need another cycle of approximation: $x = \sqrt{(0.020-0.0036)\times6.6\times10^{-4}} = 0.0033\ \text{M}$

Yet another cycle with $x \approx 0.0033$ M : $x = \sqrt{(0.020-0.0033)\times6.6\times10^{-4}} = 0.0033\ \text{M}$

$$\%\ \text{dissoc} = \frac{0.0033\text{M}}{0.020\text{M}}\times100\% = 17\%$$

As expected, the weak acid is more dissociated.

8B **(E)** Since both H_3O^+ and $\text{C}_3\text{H}_5\text{O}_3{}^-$ come from the same source in equimolar amounts, their concentrations are equal. $[\text{H}_3\text{O}^+] = [\text{C}_3\text{H}_5\text{O}_3{}^-] = 0.067\times0.0284\text{M} = 0.0019\text{M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_3{}^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{(0.0019)(0.0019)}{0.0284-0.0019} = 1.4\times10^{-4}$$

9A **(M)** For an aqueous solution of a diprotic acid, the concentration of the divalent anion is very close to the second ionization constant: $[{}^-\text{OOCCH}_2\text{COO}^-] \approx K_{a_2} = 2.0\times10^{-6}\text{M}$. We organize around the chemical equation.

Equation:	$\text{CH}_2(\text{COOH})_2\text{(aq)}$	+	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+\text{(aq)}$	+	$\text{HCH}_2(\text{COO})_2{}^-\text{(aq)}$
Initial:	1.0 M		—		≈ 0 M		0 M
Change:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(1.0-x)$ M		—		x M		x M

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCH}_2(\text{COO})_2{}^-]}{[\text{CH}_2(\text{COOH})_2]} = \frac{(x)(x)}{1.0-x} \approx \frac{x^2}{1.0} = 1.4\times10^{-3}$$

$x = \sqrt{1.4\times10^{-3}} = 3.7\times10^{-2}\ \text{M} = [\text{H}_3\text{O}^+] = [\text{HOOCCH}_2\text{COO}^-]$ $\quad x \ll 1.0\text{M}$ is a valid assumption.

9B **(M)** We know $K_{a_2} \approx [\text{doubly charged anion}]$ for a polyprotic acid. Thus, $K_{a_2} = 5.3\times10^{-5} \approx [C_2O_4{}^{2-}]$. From the pH, $[H_3O^+] = 10^{-pH} = 10^{-0.67} = 0.21\text{ M}$. We also recognize that $[HC_2O_4{}^-] = [H_3O^+]$, since the second ionization occurs to only a very small extent. We note as well that $HC_2O_4{}^-$ is produced by the ionization of $H_2C_2O_4$. Each mole of $HC_2O_4{}^-$ present results from the ionization of 1 mole of $H_2C_2O_4$. Now we have sufficient information to determine the K_{a_1}.

$$K_{a_1} = \frac{[H_3O^+][HC_2O_4{}^-]}{[H_2C_2O_4]} = \frac{0.21\times0.21}{1.05-0.21} = 5.3\times10^{-2}$$

10A **(M)** H_2SO_4 is a strong acid in its first ionization, and somewhat weak in its second, with $K_{a_2} = 1.1\times10^{-2} = 0.011$. Because of the strong first ionization step, this problem involves determining concentrations in a solution that initially is 0.20 M H_3O^+ and 0.20 M $HSO_4{}^-$. We base the set-up on the balanced chemical equation.

Equation:	$HSO_4{}^-(aq) + H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$SO_4{}^{2-}(aq)$
Initial:	0.20 M	—	0.20 M		0 M
Changes:	$-x$ M	—	$+x$ M		$+x$ M
Equil:	$(0.20-x)$ M	—	$(0.20+x)$ M		x M

$$K_{a_2} = \frac{[H_3O^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = \frac{(0.20+x)x}{0.20-x} = 0.011 \approx \frac{0.20\times x}{0.20}\text{, assuming that } x \ll 0.20\text{M.}$$

$x = 0.011$M Try one cycle of approximation:

$$0.011 \approx \frac{(0.20+0.011)x}{(0.20-0.011)} = \frac{0.21x}{0.19} \qquad x = \frac{0.19\times0.011}{0.21} = 0.010\text{ M}$$

The next cycle of approximation produces the same answer $0.010\text{M} = [SO_4{}^{2-}]$,

$[H_3O^+] = 0.010 + 0.20\text{ M} = 0.21\text{ M}$, $[HSO_4{}^-] = 0.20 - 0.010\text{ M} = 0.19\text{ M}$

10B **(M)** We know that H_2SO_4 is a strong acid in its first ionization, and a somewhat weak acid in its second, with $K_{a_2} = 1.1\times10^{-2} = 0.011$. Because of the strong first ionization step, the problem essentially reduces to determining concentrations in a solution that initially is 0.020 M H_3O^+ and 0.020 M $HSO_4{}^-$. We base the set-up on the balanced chemical equation. The result is solved using the quadratic equation.

Equation:	$HSO_4^-(aq) + H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$SO_4^{2-}(aq)$
Initial:	0.020 M	—	0.020 M		0 M
Changes:	$-x$ M	—	$+x$ M		$+x$ M
Equil:	$(0.020-x)$ M	—	$(0.020+x)$ M		x M

$$K_{a_2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.020+x)x}{0.020-x} = 0.011 \qquad 0.020x + x^2 = 2.2\times10^{-4} - 0.011x$$

$$x^2 + 0.031x - 0.00022 = 0 \qquad x = \frac{-0.031 \pm \sqrt{0.00096+0.00088}}{2} = 0.0060 \text{ M} = [SO_4^{2-}]$$

$$[HSO_4^-] = 0.020 - 0.0060 = 0.014 \text{ M} \qquad [H_3O^+] = 0.020 + 0.0060 = 0.026 \text{ M}$$

(The method of successive approximations converges to $x = 0.006$ M in 8 cycles.)

11A **(E)**

(a) $CH_3NH_3^+NO_3^-$ is the salt of the cation of a weak base. The cation, $CH_3NH_3^+$, will hydrolyze to form an acidic solution $\left(CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+\right)$, while NO_3^-, by virtue of being the conjugate base of a strong acid will not hydrolyze to a detectable extent. The aqueous solutions of this compound will thus be acidic.

(b) NaI is the salt composed of the cation of a strong base and the anion of a strong acid, neither of which hydrolyzes in water. Solutions of this compound will be pH neutral.

(c) $NaNO_2$ is the salt composed of the cation of a strong base that will not hydrolyze in water and the anion of a weak acid that will hydrolyze to form an alkaline solution $\left(NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-\right)$. Thus aqueous solutions of this compound will be basic (alkaline).

11B **(E)** Even without referring to the *K* values for acids and bases, we can predict that the reaction that produces H_3O^+ occurs to the greater extent. This, of course, is because the pH is less than 7, thus acid hydrolysis must predominate.

We write the two reactions of $H_2PO_4^-$ with water, along with the values of their equilibrium constants.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a_2} = 6.3\times10^{-8}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3PO_4(aq) \qquad K_b = \frac{K_w}{K_{a_1}} = \frac{1.0\times10^{-14}}{7.1\times10^{-3}} = 1.4\times10^{-12}$$

As predicted, the acid ionization occurs to the greater extent.

12A **(M)** From the value of $\mathrm{p}K_\mathrm{b}$ we determine the value of K_b and then K_a for the cation.

cocaine: $K_\mathrm{b} = 10^{-\mathrm{p}K} = 10^{-8.41} = 3.9 \times 10^{-9}$ $\quad K_\mathrm{a} = \dfrac{K_\mathrm{w}}{K_\mathrm{b}} = \dfrac{1.0 \times 10^{-14}}{3.9 \times 10^{-9}} = 2.6 \times 10^{-6}$

codeine: $K_\mathrm{b} = 10^{-\mathrm{p}K} = 10^{-7.95} = 1.1 \times 10^{-8}$ $\quad K_\mathrm{a} = \dfrac{K_\mathrm{w}}{K_\mathrm{b}} = \dfrac{1.0 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.1 \times 10^{-7}$

(This method may be a bit easier: $\mathrm{p}K_\mathrm{a} = 14.00 - \mathrm{p}K_\mathrm{b} = 14.00 - 8.41 = 5.59, K_\mathrm{a} = 10^{-5.59} = 2.6 \times 10^{-6}$) The acid with the larger K_a will produce the higher $[\mathrm{H}^+]$, and that solution will have the lower pH. Thus, the solution of codeine hydrochloride will have the higher pH (i.e., codeine hydrochloride is the weaker acid).

12B **(E)** Both of the ions of $\mathrm{NH_4CN(aq)}$ react with water in hydrolysis reactions.

$\mathrm{NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)}$ $\quad K_\mathrm{a} = \dfrac{K_\mathrm{w}}{K_\mathrm{b}} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

$\mathrm{CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)}$ $\quad K_\mathrm{b} = \dfrac{K_\mathrm{w}}{K_\mathrm{a}} = \dfrac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$

Since the value of the equilibrium constant for the hydrolysis reaction of cyanide ion is larger than that for the hydrolysis of ammonium ion, the cyanide ion hydrolysis reaction will proceed to a greater extent and thus the solution of $\mathrm{NH_4CN(aq)}$ will be basic (alkaline).

13A **(M)** NaF dissociates completely into sodium ions and fluoride ions. The released fluoride ion hydrolyzes in aqueous solution to form hydroxide ion. The determination of the equilibrium pH is organized around the balanced equation.

Equation:	$\mathrm{F^-(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{HF(aq)}$	+	$\mathrm{OH^-(aq)}$
Initial:	0.10 M		—		0 M		0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.10-x)$ M		—		x M		x M

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{6.6\times10^{-4}} = 1.5\times10^{-11} = \frac{[\mathrm{HF}][\mathrm{OH^-}]}{[\mathrm{F^-}]} = \frac{(x)(x)}{(0.10-x)} = \frac{x^2}{0.10}$$

$x = \sqrt{0.10\times1.5\times10^{-11}} = 1.2\times10^{-6}$ M=[OH$^-$]; pOH=$-\log(1.2\times10^{-6}) = 5.92$

pH = 14.00 $-$ pOH = 14.00 $-$ 5.92 = 8.08 (As expected, pH > 7)

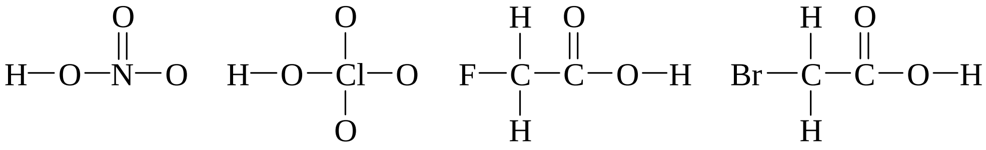
13B **(M)** The cyanide ion hydrolyzes in solution, as indicated in Practice Example 16-12B. As a consequence of the hydrolysis, $[\text{OH}^-]=[\text{HCN}]$. $[\text{OH}^-]$ can be found from the pH of the solution, and then values are substituted into the K_b expression for CN^-, which is then solved for $[\text{CN}^-]$.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.38 = 3.62$$

$$[\text{OH}^-] = 10^{\text{-pOH}} = 10^{-3.62} = 2.4\times10^{-4}\,\text{M} = [\text{HCN}]$$

$$K_\text{b} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = 1.6\times10^{-5} = \frac{(2.4\times10^{-4})^2}{[\text{CN}^-]} \qquad [\text{CN}^-] = \frac{(2.4\times10^{-4})^2}{1.6\times10^{-5}} = 3.6\times10^{-3}\,\text{M}$$

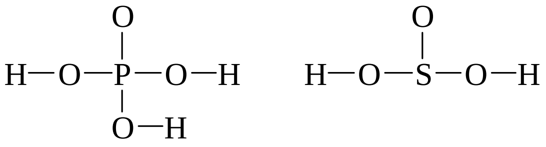
14A **(M)** First we draw the Lewis structures of the four acids. Lone pairs have been omitted since we are interested only in the arrangements of atoms.



$H{-}O{-}\overset{O}{\overset{\|}{N}}{-}O \quad H{-}O{-}\underset{O}{\overset{O}{Cl}}{-}O \quad F{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H \quad Br{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H$

HClO_4 should be stronger than HNO_3. Although Cl and N have similar electronegativities, there are more terminal oxygen atoms attached to the chlorine in perchloric acid than to the nitrogen in nitric acid. By virtue of having more terminal oxygens, perchloric acid, when ionized, affords a more stable conjugate base. The more stable the anion, the more easily it is formed and hence the stronger is the conjugate acid from which it is derived. CH_2FCOOH will be a stronger acid than CH_2BrCOOH because F is a more electronegative atom than Br. The F atom withdraws additional electron density from the O—H bond, making the bond easier to break, which leads to increased acidity.

14B **(M)** First we draw the Lewis structures of the first two acids. Lone pairs are not depicted since we are interested in the arrangements of atoms.

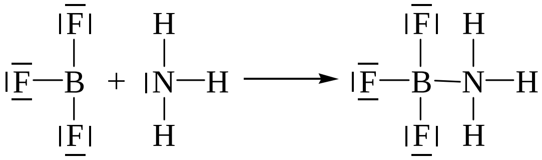


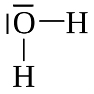
$H{-}O{-}\underset{O-H}{\overset{O}{P}}{-}O{-}H \qquad H{-}O{-}\overset{O}{S}{-}O{-}H$

H_3PO_4 and H_2SO_3 both have one terminal oxygen atom, but S is more electronegative than P. This suggests that H_2SO_3 $(K_{\text{a}_1} = 1.3\times10^{-2})$ should be a stronger acid than H_3PO_4 $(K_{\text{a}_1} = 7.1\times10^{-3})$, and it is. The only difference between $\text{CCl}_3\text{CH}_2\text{COOH}$ and $\text{CCl}_2\text{FCH}_2\text{COOH}$ is the replacement of Cl by F. Since F is more electronegative than Cl, $\text{CCl}_3\text{CH}_2\text{COOH}$ should be a weaker acid than $\text{CCl}_2\text{FCH}_2\text{COOH}$.

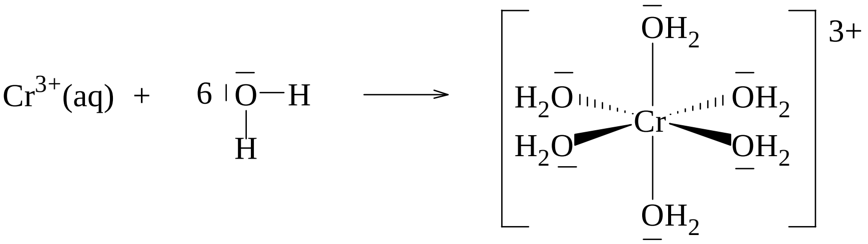
15A **(M)** We draw Lewis structures to help us decide.

(a) Clearly, BF_3 is an electron pair acceptor, a Lewis acid, and NH_3 is an electron pair donor, a Lewis base.

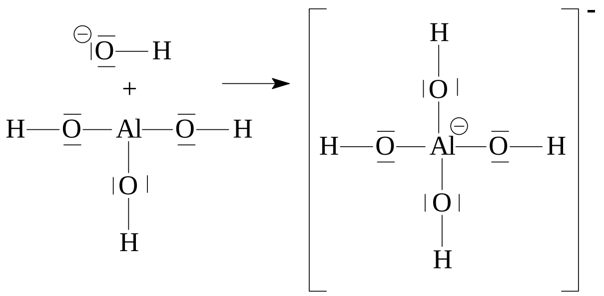


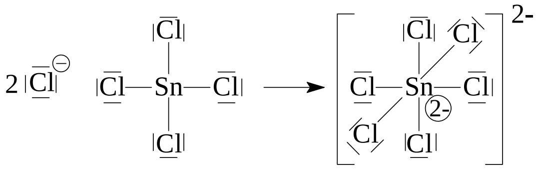


(b) H_2O certainly has electron pairs (lone pairs) to donate and thus it can be a Lewis base. It is unlikely that the cation Cr^{3+} has any accessible valence electrons that can be donated to another atom, thus, it is the Lewis acid. The product of the reaction, $[Cr(H_2O)_6]^{3+}$, is described as a water adduct of Cr^{3+}.



15B **(M)** The Lewis structures of the six species follow.





Both the hydroxide ion and the chloride ion have lone pairs of electrons that can be donated to electron-poor centers. These two are the electron pair donors, or the Lewis bases. $Al(OH)_3$ and $SnCl_4$ have additional spaces in their structures to accept pairs of electrons, which is what occurs when they form the complex anions $[Al(OH)_4]^-$ and $[SnCl_6]^{2-}$. Thus, $Al(OH)_3$ and $SnCl_4$ are the Lewis acids in these reactions.

INTEGRATIVE EXAMPLE

A. **(D)** To confirm the pH of rainwater, we have to calculate the concentration of $CO_2(aq)$ in water and then use simple acid-base equilibrium to calculate pH.

Concentration of CO_2 in water at 1 atm pressure and 298 K is 1.45 g/L, or

$$\frac{1.45\text{ g CO}_2}{\text{L}} \times \frac{1\text{ mol CO}_2}{44.0\text{ g CO}_2} = 0.0329\text{ M CO}_2$$

Furthermore, if the atmosphere is 0.037% by volume CO_2, then the mole fraction of CO_2 is 0.00037, and the partial pressure of CO_2 also becomes 0.00037 atm (because $P_{CO_2} = \chi_{CO_2} \cdot P_{atm}$)

From Henry's law, we know that concentration of a gas in a liquid is proportional to its partial pressure.
$C(\text{mol}/\text{L}) = H \cdot P_{CO_2}$, which can rearrange to solve for H:

$$H = \frac{0.0329\text{ M}}{1\text{ atm}} = 0.0329\text{ mol}\cdot\text{L}^{-1}\cdot\text{atm}^{-1}$$

Therefore, concentration of $CO_2(aq)$ in water under atmospheric pressures at 298 K is:

$$C_{CO_2}\ (\text{mol}/\text{L}) = 0.0329\text{ mol}\cdot\text{L}^{-1}\cdot\text{atm}^{-1}\cdot 0.00037\text{ atm} = 1.217\times10^{-5}\text{ M}$$

Using the equation for reaction of CO_2 with water:

CO_2 (aq)	+	2 H_2O (l)	$\rightleftharpoons$	H_3O^+ (aq)	+	HCO_3^- (aq)
1.217×10^{-5}				0		0
-x				+x		+x
1.217×10^{-5}–x				x		X

$$K_{a1} = \frac{x^2}{\left(1.217\times10^{-5} - x\right)} = 4.4\times10^{-7}$$

Using the quadratic formula, $x = 2.104\times10^{-6}$M

$$pH = -\log\left[H_3O^+\right] = -\log\left(2.104\times10^{-6}\right) = 5.68 \approx 5.7$$

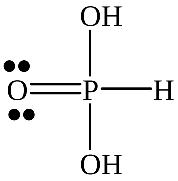
We can, of course, continue to refine the value of $[H_3O^+]$ further by considering the dissociation of HCO_3^-, but the change is too small to matter.

B. **(D)**

(a) For the acids given, we determine values of m and n in the formula $EO_m(OH)_n$. HOCl or Cl(OH) has $m = 0$ and $n = 1$. We expect $K_a \approx 10^{-7}$ or $pK_a \approx 7$, which is in good agreement with the accepted $pK_a = 7.52$. HOClO or ClO(OH) has $m = 1$ and $n = 1$. We expect $K_a \approx 10^{-2}$ or $pK_a \approx 2$, in good agreement with the $pK_a = 1.92$. $HOClO_2$ or $ClO_2(OH)$ has $m = 2$ and $n = 1$. We expect K_a to be large and in good agreement with the accepted value of $pK_a = -3$, $K_a = 10^{-pKa} = 10^3$. $HOClO_3$ or $ClO_3(OH)$ has $m = 3$ and $n = 1$. We expect K_a to be very large and in good agreement with the accepted $K_a = -8$, $pK_a = -8$, $K_a = 10^{-pKa} = 10^8$ which turns out to be the case.

(**b**) The formula H_3AsO_4 can be rewritten as $AsO(OH)_3$, which has $m = 1$ and $n = 3$. The expected value is $K_a = 10^{-2}$.

(**c**) The value of $pK_a = 1.1$ corresponds to $K_a = 10^{-pKa} = 10^{-1.1} = 0.08$, which indicates that $m = 1$. The following Lewis structure is consistent with this value of m.



EXERCISES

Brønsted-Lowry Theory of Acids and Bases

1. **(E)**

(a) HNO_2 is an acid, a proton donor. Its conjugate base is NO_2^-.

(b) OCl^- is a base, a proton acceptor. Its conjugate acid is HOCl.

(c) NH_2^- is a base, a proton acceptor. Its conjugate acid is NH_3.

(d) NH_4^+ is an acid, a proton donor. It's conjugate base is NH_3.

(e) $CH_3NH_3^+$ is an acid, a proton donor. It's conjugate base is CH_3NH_2.

2. **(E)** We write the conjugate base as the first product of the equilibrium for which the acid is the first reactant.

(a) $HIO_3(aq) + H_2O(l) \rightleftharpoons IO_3^-(aq) + H_3O^+(aq)$

(b) $C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$

(c) $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$

(d) $C_2H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_2H_5NH_2(aq) + H_3O^+(aq)$

3. **(E)** The acids (proton donors) and bases (proton acceptors) are labeled below their formulas. Remember that a proton, in Brønsted-Lowry acid-base theory, is H^+.

(a) $HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OBr^-(aq)$

acid base acid base

(b) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

acid base acid base

(c) $HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$

base acid acid base

(d) $C_6H_5NH_3^+(aq) + OH^-(aq) \rightleftharpoons C_6H_5NH_2(aq) + H_2O(l)$

acid base base acid

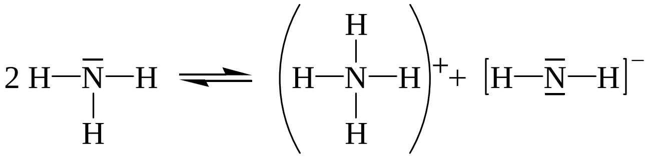
4. **(E)** For each amphiprotic substance, we write both its acid and base hydrolysis reaction. Even for the substances that are not usually considered amphiprotic, both reactions are written, but one of them is labeled as unlikely. In some instances we have written an oxygen as $\varnothing$ to keep track of it through the reaction.

$\varnothing H^- + H_2O \rightleftharpoons \varnothing^{2-} + H_3O^+$ (unlikely)	$\varnothing H^- + H_2O \rightleftharpoons H_2\varnothing + OH^-$
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	NH_4^+ has no e^- pairs that can be donated
$H_2\varnothing + H_2O \rightleftharpoons \varnothing H^- + H_3O^+$	$H_2\varnothing + H_2O \rightleftharpoons H_3\varnothing^+ + OH^-$
$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+$	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$
NO_2^- cannot act as an acid, (no protons)	$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$
$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$	$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$
$HBr + H_2O \rightleftharpoons H_3O^+ + Br^-$	$HBr + H_2O \rightleftharpoons H_2Br^+ + OH^-$ (unlikely)

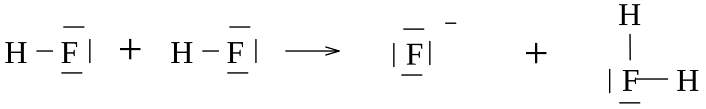
5. **(E)** Answer (b), NH_3, is correct. $HC_2H_3O_2$ will react most completely with the strongest base. NO_3^- and Cl^- are very weak bases. H_2O is a weak base, but it is amphiprotic, acting as an acid (donating protons), as in the presence of NH_3. Thus, NH_3 must be the strongest base and the most effective in deprotonating $HC_2H_3O_2$.

6. **(M)** Lewis structures are given below each equation.

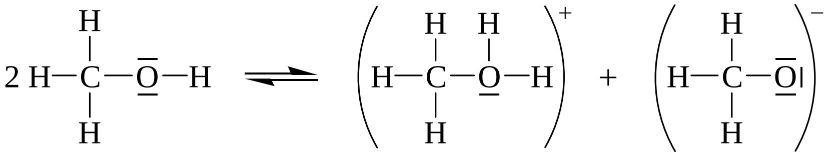
(a) $2NH_3(l) \rightleftharpoons NH_4^+ + NH_2^-$



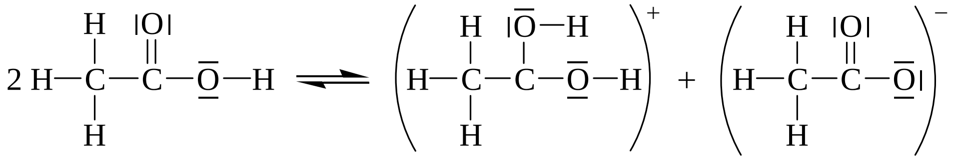
(b) $2HF(l) \rightleftharpoons H_2F^+ + F^-$



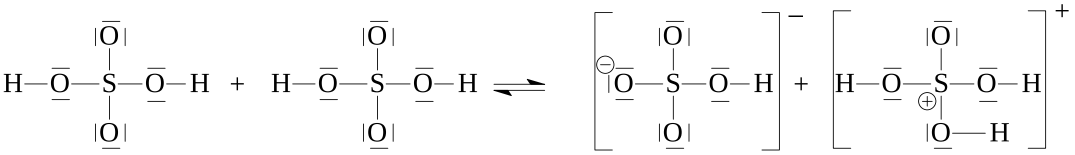
(c) $2CH_3OH(l) \rightleftharpoons CH_3OH_2^+ + CH_3O^-$



(d) $2HC_2H_3O_2(l) \rightleftharpoons H_2C_2H_3O_2^+ + C_2H_3O_2^-$



(e) $2\,H_2SO_4(l) \rightleftharpoons 2\,H_3SO_4^+ + HSO_4^-$



7. **(E)** The principle we will follow here is that, in terms of their concentrations, the weaker acid and the weaker base will predominate at equilibrium. The reason for this is that a strong acid will do a good job of donating its protons and, having done so, its conjugate base will be left behind. The preferred direction is:

strong acid + strong base → weak (conjugate) base + weak (conjugate) acid

(a) The reaction will favor the forward direction because OH^- (a strong base) $> NH_3$ (a weak base) and NH_4^+ (relatively strong weak acid) $> H_2O$ (very weak acid).

(b) The reaction will favor the reverse direction because $HNO_3 > HSO_4^-$ (a weak acid in the second ionization) (acting as acids), and $SO_4^{2-} > NO_3^-$ (acting as bases).

(c) The reaction will favor the reverse direction because $HC_2H_3O_2 > CH_3OH$ (not usually thought of as an acid) (acting as acids), and $CH_3O^- > C_2H_3O_2^-$ (acting as bases).

8. **(M)** The principle we follow here is that, in terms of their concentrations, the weaker acid and the weaker base predominate at equilibrium. This is because a strong acid will do a good job of donating its protons and, having done so, its conjugate base will remain in solution. The preferred direction is:

strong acid + strong base → weak (conjugate) base + weak (conjugate) acid

(a) The reaction will favor the forward direction because $HC_2H_3O_2$ (a moderate acid) $> HCO_3^-$ (a rather weak acid) (acting as acids) and $CO_3^{2-} > C_2H_3O_2^-$ (acting as bases).

(b) The reaction will favor the reverse direction because $HClO_4$ (a strong acid) $> HNO_2$ (acting as acids), and $NO_2^- > ClO_4^-$ (acting as bases).

(c) The reaction will favor the forward direction, because $H_2CO_3 > HCO_3^-$ (acting as acids) (because $K_1 > K_2$) and $CO_3^{2-} > HCO_3^-$ (acting as bases).

Strong Acids, Strong Bases, and pH

9. **(M)** All of the solutes are strong acids or strong bases.

(a)
$$\left[H_3O^+\right] = 0.00165\text{ M HNO}_3 \times \frac{1\text{ mol H}_3\text{O}^+}{1\text{ mol HNO}_3} = 0.00165\text{ M}$$
$$\left[OH^-\right] = \frac{K_w}{\left[H_3O^+\right]} = \frac{1.0\times10^{-14}}{0.00165\text{M}} = 6.1\times10^{-12}\text{ M}$$

(b)
$$\left[OH^-\right] = 0.0087\text{ M KOH}\times\frac{1\text{ mol OH}^-}{1\text{ mol KOH}} = 0.0087\text{ M}$$
$$\left[H_3O^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.0\times10^{-14}}{0.0087\text{M}} = 1.1\times10^{-12}\text{ M}$$

(c)
$$\left[OH^-\right] = 0.00213\text{ M Sr}\left(OH\right)_2\times\frac{2\text{ mol OH}^-}{1\text{mol Sr}\left(OH\right)_2} = 0.00426\text{ M}$$
$$\left[H_3O^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.0\times10^{-14}}{0.00426\text{ M}} = 2.3\times10^{-12}\text{ M}$$

(d)
$$\left[H_3O^+\right] = 5.8\times10^{-4}\text{M HI}\times\frac{1\text{mol H}_3\text{O}^+}{1\text{mol HI}} = 5.8\times10^{-4}\text{ M}$$
$$\left[OH^-\right] = \frac{K_w}{\left[H_3O^+\right]} = \frac{1.0\times10^{-14}}{5.8\times10^{-4}\text{M}} = 1.7\times10^{-11}\text{ M}$$

10. **(M)** Again, all of the solutes are strong acids or strong bases.

(a) $\left[H_3O^+\right] = 0.0045 \text{ M HCl} \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol HCl}} = 0.0045 \text{ M}$

$\text{pH} = -\log(0.0045) = 2.35$

(b) $\left[H_3O^+\right] = 6.14\times10^{-4}\text{M HNO}_3 \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol HNO}_3} = 6.14\times10^{-4}\text{M}$

$\text{pH} = -\log\left(6.14\times10^{-4}\right) = 3.21$

(c) $\left[OH^-\right] = 0.00683 \text{ M NaOH} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.00683\text{M}$

$\text{pOH} = -\log(0.00683) = 2.166$ and $\text{pH} = 14.000 - \text{pOH} = 14.000 - 2.166 = 11.83$

(d) $\left[OH^-\right] = 4.8\times10^{-3}\text{M Ba}(OH)_2 \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(OH)_2} = 9.6\times10^{-3}\text{M}$

$\text{pOH} = -\log\left(9.6\times10^{-3}\right) = 2.02$ $\quad$ $\text{pH} = 14.00 - 2.02 = 11.98$

<u>**11.**</u> **(E)**

$$\left[OH^-\right] = \frac{3.9 \text{ g Ba}(OH)_2\cdot 8H_2O}{100 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ mol Ba}(OH)_2\cdot 8H_2O}{315.5 \text{ g Ba}(OH)_2\cdot 8H_2O} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(OH)_2\cdot 8H_2O}$$

$= 0.25 \text{ M}$

$\left[H_3O^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.0\times10^{-14}}{0.25 \text{ M OH}^-} = 4.0\times10^{-14}\text{M}$ $\qquad$ $\text{pH} = -\log\left(4.0\times10^{-14}\right) = 13.40$

12. **(M)** The dissolved $Ca(OH)_2$ is completely dissociated into ions.

$\text{pOH} = 14.00 - \text{pH} = 14.00 - 12.35 = 1.65$

$\left[OH^-\right] = 10^{-\text{pOH}} = 10^{-1.65} = 2.2\times10^{-2} \text{ M OH}^- = 0.022 \text{ M OH}^-$

$$\text{solubility} = \frac{0.022 \text{ mol OH}^-}{1 \text{ L soln}} \times \frac{1 \text{ mol Ca}(OH)_2}{2 \text{ mol OH}^-} \times \frac{74.09 \text{ g Ca}(OH)_2}{1 \text{ mol Ca}(OH)_2} \times \frac{1000 \text{ mg Ca}(OH)_2}{1 \text{ g Ca}(OH)_2}$$

$$= \frac{8.1\times10^2 \text{mg Ca}(OH)_2}{1 \text{ L soln}}$$

In 100 mL the solubility is $100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{8.1\times10^2 \text{mg Ca}(OH)_2}{1 \text{ L soln}} = 81 \text{ mg Ca}(OH)_2$

13. **(M)** First we determine the moles of HCl, and then its concentration.

$$\text{moles HCl} = \frac{PV}{RT} = \frac{\left(751\ \text{mmHg} \times \dfrac{1\ \text{atm}}{760\ \text{mmHg}}\right) \times 0.205\ \text{L}}{0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 296\ \text{K}} = 8.34 \times 10^{-3}\ \text{mol HCl}$$

$$\left[\text{H}_3\text{O}^+\right] = \frac{8.34 \times 10^{-3}\ \text{mol HCl}}{4.25\ \text{L soln}} \times \frac{1\ \text{mol H}_3\text{O}^+}{1\ \text{mol HCl}} = 1.96 \times 10^{-3}\ \text{M}$$

14. **(E)** First determine the concentration of NaOH, then of OH^-.

$$\left[\text{OH}^-\right] = \frac{0.125\ \text{L} \times \dfrac{0.606\ \text{mol NaOH}}{1\ \text{L}} \times \dfrac{1\ \text{mol OH}^-}{1\ \text{mol NaOH}}}{15.0\ \text{L final solution}} = 0.00505\ \text{M}$$

$$\text{pOH} = -\log\left(0.00505\ \text{M}\right) = 2.297 \qquad \text{pH} = 14.00 - 2.297 = 11.703$$

15. **(E)** First determine the amount of HCl, and then the volume of the concentrated solution required.

$$\text{amount HCl} = 12.5\ \text{L} \times \frac{10^{-2.10}\ \text{mol H}_3\text{O}^+}{1\ \text{L soln}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol H}_3\text{O}^+} = 0.099\ \text{mol HCl}$$

$$V_{\text{solution}} = 0.099\ \text{mol HCl} \times \frac{36.46\ \text{g HCl}}{1\ \text{mol HCl}} \times \frac{100.0\ \text{g soln}}{36.0\ \text{g HCl}} \times \frac{1\ \text{mL soln}}{1.18\ \text{g soln}} = 8.5\ \text{mL soln}$$

16. **(E)** First we determine the amount of KOH, and then the volume of the concentrated solution required.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 11.55 = 2.45 \qquad \left[\text{OH}^-\right] = 10^{-\text{pOH}} = 10^{-2.45} = 0.0035\ \text{M}$$

$$\text{amount KOH} = 25.0\ \text{L} \times \frac{0.0035\ \text{M mol OH}^-}{1\ \text{L soln}} \times \frac{1\ \text{mol KOH}}{1\ \text{mol OH}^-} = 0.088\ \text{mol KOH}$$

$$V_{\text{solution}} = 0.088\ \text{mol KOH} \times \frac{56.11\ \text{g KOH}}{1\ \text{mol KOH}} \times \frac{100.0\ \text{g soln}}{15.0\ \text{g KOH}} \times \frac{1\ \text{mL soln}}{1.14\ \text{g soln}} = 29\ \text{mL soln}$$

17. **(E)** The volume of HCl(aq) needed is determined by first finding the amount of $\text{NH}_3(\text{aq})$ present, and then realizing that acid and base react in a 1:1 molar ratio.

$$V_{\text{HCl}} = 1.25\ \text{L base} \times \frac{0.265\ \text{mol NH}_3}{1\ \text{L base}} \times \frac{1\ \text{mol H}_3\text{O}^+}{1\ \text{mol NH}_3} \times \frac{1\ \text{mol HCl}}{1\ \text{mol H}_3\text{O}^+} \times \frac{1\ \text{L acid}}{6.15\ \text{mol HCl}}$$

$$= 0.0539\ \text{L acid} \text{ or } 53.9\ \text{mL acid.}$$

18. **(M)** NH_3 and HCl react in a 1:1 molar ratio. According to Avogadro's hypothesis, equal volumes of gases at the same temperature and pressure contain equal numbers of moles. Thus, the volume of $H_2(g)$ at 762 mmHg and $21.0^\circ C$ that is equivalent to 28.2 L of $H_2(g)$ at 742 mmHg and $25.0^\circ C$ will be equal to the volume of $NH_3(g)$ needed for stoichiometric neutralization.

$$V_{NH_3(g)} = 28.2 \text{ L HCl}(g) \times \frac{742 \text{ mmHg}}{762 \text{ mmHg}} \times \frac{(273.2+21.0) \text{ K}}{(273.2+25.0) \text{ K}} \times \frac{1 \text{ L NH}_3(g)}{1 \text{ L HCl}(g)} = 27.1 \text{ L NH}_3(g)$$

Alternatively, we can solve the ideal gas equation for the amount of each gas, and then, by equating these two expressions, we can find the volume of NH_3 needed.

$$n\{\text{HCl}\} = \frac{742 \text{ mmHg} \cdot 28.2 \text{ L}}{R \cdot 298.2\ K} \qquad n\{\text{NH}_3\} = \frac{762 \text{ mmHg} \cdot V\{\text{NH}_3\}}{R \cdot 294.2\ K}$$

$$\frac{742 \text{ mmHg} \cdot 28.2 \text{ L}}{R \cdot 298.2\ K} = \frac{762 \text{ mmHg} \cdot V\{\text{NH}_3\}}{R \cdot 294.2\ K} \quad \text{This yields } V\{\text{NH}_3\} = 27.1 \text{ L NH}_3(g)$$

<u>19.</u> **(M)** Here we determine the amounts of H_3O^+ and OH^- and then the amount of the one that is in excess. We express molar concentration in millimoles/milliliter, equivalent to mol/L.

$$50.00 \text{ mL} \times \frac{0.0155 \text{ mmol HI}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HI}} = 0.775 \text{ mmol H}_3\text{O}^+$$

$$75.00 \text{ mL} \times \frac{0.0106 \text{ mmol KOH}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 0.795 \text{ mmol OH}^-$$

The net reaction is $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$.

There is an excess of OH^- of $(0.795 - 0.775 =)$ 0.020 mmol OH^-.
Thus, this is a basic solution. The total solution volume is $(50.00 + 75.00 =)$ 125.00 mL.

$$[\text{OH}^-] = \frac{0.020 \text{ mmol OH}^-}{125.00 \text{ mL}} = 1.6 \times 10^{-4} \text{ M}, \quad \text{pOH} = -\log(1.6 \times 10^{-4}) = 3.80, \quad \text{pH} = 10.20$$

20. **(M)** In each case, we need to determine the $[H_3O^+]$ or $[OH^-]$ of each solution being mixed, and then the amount of H_3O^+ or OH^-, so that we can determine the amount in excess. We express molar concentration in millimoles/milliliter, equivalent to mol/L.

$$[\text{H}_3\text{O}^+] = 10^{-2.12} = 7.6 \times 10^{-3} \text{ M} \qquad \text{moles H}_3\text{O}^+ = 25.00 \text{ mL} \times 7.6 \times 10^{-3} \text{ M} = 0.19 \text{ mmol H}_3\text{O}^+$$

$$\text{pOH} = 14.00 - 12.65 = 1.35 \qquad [\text{OH}^-] = 10^{-1.35} = 4.5 \times 10^{-2} \text{ M}$$

$$\text{amount OH}^- = 25.00 \text{ mL} \times 4.5 \times 10^{-2} \text{ M} = 1.13 \text{ mmol OH}^-$$

There is excess OH^- in the amount of 0.94 mmol (=1.13 mmol OH^- – 0.19 mmol H_3O^+).

$$\left[OH^-\right] = \frac{0.94 \text{ mmol } OH^-}{25.00 \text{ mL} + 25.00 \text{ mL}} = 1.8\underline{8}\times10^{-2} \text{ M} \qquad pOH = -\log\left(1.8\underline{8}\times10^{-2}\right) = 1.73 \quad pH=12.27$$

Weak Acids, Weak Bases, and pH

21. **(M)** We organize the solution around the balanced chemical equation.

Equation:	$HNO_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$NO_2^-(aq)$
Initial:	0.143 M		—		≈ 0 M		0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.143-x)$ M		—		x M		x M

$$K_a = \frac{\left[H_3O^+\right]\left[NO_2^-\right]}{\left[HNO_2\right]} = \frac{x^2}{0.143-x} = 7.2\times10^{-4} \gg \frac{x^2}{0.143} \quad (\text{if } x \ll 0.143)$$

$$x = \sqrt{0.143\times7.2\times10^{-4}} = 0.010 \text{ M}$$

We have assumed that $x \ll 0.143$ M, an almost acceptable assumption. Another cycle of approximations yields:

$$x = \sqrt{(0.143-0.010)\times7.2\times10^{-4}} = 0.0098 \text{ M} = [H_3O^+] \qquad pH = -\log(0.0098) = 2.01$$

This is the same result as is determined with the quadratic formula roots equation.

22. **(M)** We organize the solution around the balanced chemical equation, and solve first for $\left[OH^-\right]$

Equation :	$C_2H_5NH_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$OH^-(aq)$	+	$C_2H_5NH_3^+(aq)$
Initial :	0.085 M		–		≈ 0 M		0 M
Changes :	$-x$ M		–		$+x$ M		$+x$ M
Equil :	$(0.085-x)$ M		–		x M		x M

$$K_b = \frac{\left[OH^-\right]\left[C_2H_5NH_3^+\right]}{\left[C_2H_5NH_2\right]} = \frac{x^2}{0.085-x} = 4.3\times10^{-4} \approx \frac{x^2}{0.085} \text{assuming } x \ll 0.085$$

$$x = \sqrt{0.085\times4.3\times10^{-4}} = 0.0060 \text{ M}$$

We have assumed that $x \ll 0.085$ M, an almost acceptable assumption. Another cycle of approximations yields:

$$x = \sqrt{(0.085-0.0060)\times4.3\times10^{-4}} = 0.0058 \text{ M} = [OH^-]$$ Yet another cycle produces:

$$x=\sqrt{(0.085-0.0058)\times 4.3\times 10^{-4}}=0.0058\text{ M}=[\text{OH}^-] \qquad \text{pOH}=-\log(0.0058)=2.24$$

$$\text{pH}=14.00-2.24=11.76 \qquad \left[\text{H}_3\text{O}^+\right]=10^{-\text{pH}}=10^{-11.76}=1.7\times 10^{-12}\text{ M}$$

This is the same result as determined with the quadratic formula roots equation.

23. **(M)**

(a) The set-up is based on the balanced chemical equation.

Equation:	$HC_8H_7O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$ +	$C_8H_7O_2^-(aq)$
Initial:	0.186 M		—		≈ 0 M	0 M
Changes:	$-x$ M		—		$+x$ M	$+x$ M
Equil:	$(0.186-x)$ M		—		x M	x M

$$K_a=4.9\times 10^{-5}=\frac{[H_3O^+][C_8H_7O_2^-]}{[HC_8H_7O_2]}=\frac{x\cdot x}{0.186-x}\approx\frac{x^2}{0.186}$$

$$x=\sqrt{0.186\times 4.9\times 10^{-5}}=0.0030\text{ M}=[H_3O^+]=[C_8H_7O_2^-]$$

0.0030 M is less than 5 % OF 0.186 M, thus, the approximation is valid.

(b) The set-up is based on the balanced chemical equation.

Equation:	$HC_8H_7O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$C_8H_7O_2(aq)$
Initial:	0.121 M		—		≈ 0 M		0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.121-x)$ M		—		x M		x M

$$K_a=4.9\times 10^{-5}=\frac{\left[H_3O^+\right]\left[C_8H_7O_2^-\right]}{\left[HC_8H_7O_2\right]}=\frac{x^2}{0.121-x}\approx\frac{x^2}{0.121} \qquad x=0.0024\text{ M}=\left[H_3O^+\right]$$

Assumption $x \ll 0.121$, is correct. $\text{pH}=-\log(0.0024)=2.62$

24. **(E)**

$$\left[HC_3H_5O_2\right]_{\text{initial}}=\left(\frac{0.275\text{ mol}}{625\text{ mL}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right)=0.440\text{ M}$$

$$\left[HC_3H_5O_2\right]_{\text{equilibrium}}=0.440\text{ M}-0.00239\text{ M}=0.438\text{ M}$$

$$K_a=\frac{\left[H_3O^+\right]\left[C_3H_5O_2^-\right]}{\left[HC_3H_5O_2\right]}=\frac{(0.00239)^2}{0.438}=1.30\times 10^{-5}$$

25. **(M)** We base our solution on the balanced chemical equation.

$$\left[H_3O^+\right] = 10^{-1.56} = 2.8\times10^{-2}\,\text{M}$$

$$\begin{array}{llcllcl}
\text{Equation:} & CH_2FCOOH(aq) & + & H_2O(l) & \rightleftharpoons & CH_2FCOO^-(aq) & + & H_3O^+(aq) \\
\text{Initial:} & 0.318\ \text{M} & & - & & 0\ \text{M} & & \approx 0\ \text{M} \\
\text{Changes:} & -0.028\ \text{M} & & - & & +0.028\ \text{M} & & +0.028\ \text{M} \\
\text{Equil:} & 0.290\ \text{M} & & - & & 0.028\ \text{M} & & \approx 0.028\ \text{M}
\end{array}$$

$$K_a = \frac{\left[H_3O^+\right]\left[CH_2FCOO^-\right]}{\left[CH_2FCOOH\right]} = \frac{(0.028)(0.028)}{0.290} = 2.7\times10^{-3}$$

26. **(M)** $\left[HC_6H_{11}O_2\right] = \dfrac{11\ \text{g}}{1\ \text{L}} \times \dfrac{1\ \text{mol}\ HC_6H_{11}O_2}{116.2\ \text{g}\ HC_6H_{11}O_2} = 9.5\times10^{-2}\ \text{M} = 0.095\ \text{M}$

$$\left[H_3O^+\right]_{\text{equil}} = 10^{-2.94} = 1.1\times10^{-3}\,\text{M} = 0.0011\ \text{M}$$

The stoichiometry of the reaction, written below, indicates that $\left[H_3O^+\right] = \left[C_6H_{11}O_2^{\ -}\right]$

$$\begin{array}{llcllcl}
\text{Equation:} & HC_6H_{11}O_2(aq) & + & H_2O(l) & \rightleftharpoons & C_6H_{11}O_2^{\ -}(aq) & + & H_3O^+(aq) \\
\text{Initial:} & 0.095\ \text{M} & & - & & 0\ \text{M} & & \approx 0\ \text{M} \\
\text{Changes:} & -0.0011\ \text{M} & & - & & +0.0011\ \text{M} & & +0.0011\ \text{M} \\
\text{Equil:} & 0.094\ \text{M} & & - & & 0.0011\ \text{M} & & 0.0011\ \text{M}
\end{array}$$

$$K_a = \frac{\left[C_6H_{11}O_2^{\ -}\right]\left[H_3O^+\right]}{\left[HC_6H_{11}O_2\right]} = \frac{(0.0011)^2}{0.094} = 1.3\times10^{-5}$$

27. **(M)** Here we need to find the molarity S of the acid needed that yields $\left[H_3O^+\right] = 10^{-2.85} = 1.4\times10^{-3}\,\text{M}$

$$\begin{array}{llcllcl}
\text{Equation:} & HC_7H_5O_2(aq) & + & H_2O(l) & \rightleftharpoons & H_3O^+(aq) & + & C_7H_5O_2^{\ -}(aq) \\
\text{Initial:} & S & & \text{—} & & 0\ \text{M} & & 0\ \text{M} \\
\text{Changes:} & -0.0014\ \text{M} & & \text{—} & & +0.0014\text{M} & & +0.0014\text{M} \\
\text{Equil:} & S-0.0014\text{M} & & \text{—} & & 0.0014\ \text{M} & & 0.0014\ \text{M}
\end{array}$$

$$K_a = \frac{\left[H_3O^+\right]\left[C_7H_5O_2^{\ -}\right]}{\left[HC_7H_5O_2\right]} = \frac{(0.0014)^2}{S-0.0014} = 6.3\times10^{-5} \qquad S-0.0014 = \frac{(0.0014)^2}{6.3\times10^{-5}} = 0.031$$

$$S = 0.031 + 0.0014 = 0.032\ \text{M} = \left[HC_7H_5O_2\right]$$

$$350.0\ \text{mL}\times\frac{1\ \text{L}}{1000\ \text{mL}}\times\frac{0.032\ \text{mol}\ HC_7H_5O_2}{1\ \text{L soln}}\times\frac{122.1\ \text{g}\ HC_7H_5O_2}{1\ \text{mol}\ HC_7H_5O_2} = 1.4\ \text{g}\ HC_7H_5O_2$$

28. **(M)** First we find $\left[\mathrm{OH^-}\right]$ and then use the K_b expression to find $\left[\mathrm{(CH_3)_3N}\right]$

$$\mathrm{pOH} = 14.00 - \mathrm{pH} = 14.00 - 11.12 = 2.88 \qquad \left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}} = 10^{-2.88} = 0.0013\ \mathrm{M}$$

$$K_\mathrm{b} = 6.3\times10^{-5} = \frac{\left[\mathrm{(CH_3)_3NH^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{(CH_3)_3N}\right]_\mathrm{equil}} = \frac{(0.0013)^2}{\left[\mathrm{(CH_3)_3N}\right]_\mathrm{equil}} \qquad \left[\mathrm{(CH_3)_3N}\right]_\mathrm{equil} = 0.027\ \mathrm{M\ (CH_3)_3N}$$

$$\left[\mathrm{(CH_3)_3\,N}\right]_\mathrm{initial} = 0.027\ \mathrm{M(equil.\ concentration)} + 0.0013\ \mathrm{M(concentration\ ionized)}$$

$$\left[\mathrm{(CH_3)_3\,N}\right]_\mathrm{initial} = 0.028\ \mathrm{M}$$

29. **(M)** We use the balanced chemical equation, then solve using the quadratic formula.

Equation:	$\mathrm{HClO_2(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{H_3O^+(aq)}$	+	$\mathrm{ClO_2^-(aq)}$
Initial:	0.55 M		–		≈ 0M		0M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.55-x)$ M		–		x M		x M

$$K_\mathrm{a} = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{ClO_2^-}\right]}{\left[\mathrm{HClO_2}\right]} = \frac{x^2}{0.55-x} = 1.1\times10^{-2} = 0.011 \qquad x^2 = 0.0061 - 0.011x$$

$$x^2 + 0.011x - 0.0061 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.011\pm\sqrt{0.000121+0.0244}}{2} = 0.073\ \mathrm{M} = \left[\mathrm{H_3O^+}\right]$$

The method of successive approximations converges to the same answer in four cycles.

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] = -\log(0.073) = 1.14 \qquad \mathrm{pOH} = 14.00 - \mathrm{pH} = 14.00 - 1.14 = 12.86$$

$$\left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}} = 10^{-12.86} = 1.4\times10^{-13}\ \mathrm{M}$$

30. **(M)** Organize the solution around the balanced chemical equation, and solve first for $\left[\mathrm{OH^-}\right]$.

Equation:	$\mathrm{CH_3NH_2(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{OH^-(aq)}$	+	$\mathrm{CH_3NH_3^+(aq)}$
Initial:	0.386 M		–		≈ 0 M		0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.386-x)$ M		–		x M		x M

$$K_\mathrm{b} = \frac{\left[\mathrm{OH^-}\right]\left[\mathrm{CH_3NH_3^+}\right]}{\left[\mathrm{CH_3NH_2}\right]} = \frac{x^2}{0.386-x} = 4.2\times10^{-4} \approx \frac{x^2}{0.386} \quad \text{assuming } x \ll 0.386$$

$$x = \sqrt{0.386\times4.2\times10^{-4}} = 0.013\ \mathrm{M} = [\mathrm{OH^-}] \qquad \mathrm{pOH} = -\log(0.013) = 1.89$$

$pH = 14.00 - 1.89 = 12.11 \qquad \left[H_3O^+\right] = 10^{-pH} = 10^{-12.11} = 7.8\times10^{-13}\text{ M}$

This is the same result as is determined with the quadratic equation roots formula.

31. **(M)**

$$\left[C_{10}H_7NH_2\right] = \frac{1\text{ g }C_{10}H_7NH_2}{590\text{ g }H_2O}\times\frac{1.00\text{ g }H_2O}{1\text{ mL}}\times\frac{1000\text{ mL}}{1\text{ L}}\times\frac{1\text{ mol }C_{10}H_7NH_2}{143.2\text{ g }C_{10}H_7NH_2}$$
$$= 0.012\text{ M }C_{10}H_7NH_2$$

$K_b = 10^{-pK_b} = 10^{-3.92} = 1.2\times10^{-4}$

Equation:	$C_{10}H_7NH_2(aq)$	+ $H_2O(l)$	$\rightleftharpoons$ $OH^-(aq)$	+ $C_{10}H_7NH_3^+(aq)$
Initial:	0.012 M	—	≈ 0 M	0 M
Changes:	$-x$ M	—	$+x$ M	$+x$ M
Equil:	$(0.012 - x)$ M	—	x M	x M

$$K_b = \frac{\left[OH^-\right]\left[C_{10}H_7NH_3^+\right]}{\left[C_{10}H_7NH_2\right]} = \frac{x^2}{0.012 - x} = 1.2\times10^{-4} \approx \frac{x^2}{0.012} \qquad \text{assuming } x \ll 0.012$$

$x = \sqrt{0.012\times1.2\times10^{-4}} = 0.0012$ This is an almost acceptable assumption. Another approximation cycle gives:

$x = \sqrt{(0.012 - 0.0012)\times1.2\times10^{-4}} = 0.0011$ Yet another cycle seems necessary.

$x = \sqrt{(0.012 - 0.0011)\times1.2\times10^{-4}} = 0.0011\text{M} = [OH^-]$

The quadratic equation roots formula provides the same answer.

$pOH = -\log\left[OH^-\right] = -\log(0.0011) = 2.96 \qquad pH = 14.00 - pOH = 11.04$

$H_3O^+ = 10^{-pH} = 10^{-11.04} = 9.1\times10^{-12}\text{ M}$

32. **(M)** The stoichiometry of the ionization reaction indicates that

$\left[H_3O^+\right] = \left[OC_6H_4NO_2^-\right], K_a = 10^{-pK_b} = 10^{-7.23} = 5.9\times10^{-8}$ and

$\left[H_3O^+\right] = 10^{-4.53} = 3.0\times10^{-5}\text{M}$. We let S = the molar solubility of o-nitrophenol.

Equation:	$HOC_6H_4NO_2(aq) + H_2O(l)$		$\rightleftharpoons$ $OC_6H_4NO_2^-(aq)$ +	$H_3O^+(aq)$
Initial:	S	—	0 M	≈ 0 M
Changes:	-3.0×10^{-5} M	—	$+3.0\times10^{-5}$ M	$+3.0\times10^{-5}$ M
Equil:	$(S - 3.0\times10^{-5})$ M	—	3.0×10^{-5} M	3.0×10^{-5} M

$$K_a = 5.9\times10^{-8} = \frac{\left[\mathrm{OC_6H_4NO_2}^-\right]\left[\mathrm{H_3O^+}\right]}{\left[\mathrm{HOC_6H_5NO_2}\right]} = \frac{\left(3.0\times10^{-5}\right)^2}{S-3.0\times10^{-5}}$$

$$S-3.0\times10^{-5} = \frac{\left(3.0\times10^{-5}\right)^2}{5.9\times10^{-8}} = 1.5\times10^{-2}\,\mathrm{M} \qquad S = 1.5\times10^{-2}\,\mathrm{M} + 3.0\times10^{-5}\,\mathrm{M} = 1.5\times10^{-2}\,\mathrm{M}$$

Hence,

$$\text{solubility} = \frac{1.5\times10^{-2}\,\mathrm{mol\ HOC_6H_4NO_2}}{1\,\mathrm{L\ soln}}\times\frac{139.1\,\mathrm{g\ HOC_6H_4NO_2}}{1\,\mathrm{mol\ HOC_6H_4NO_2}} = 2.1\,\mathrm{g\ HOC_6H_4NO_2\,/\,L\ soln}$$

33. **(M)** Here we determine $\left[\mathrm{H_3O^+}\right]$ which, because of the stoichiometry of the reaction, equals $\left[\mathrm{C_2H_3O_2}^-\right]$. $\left[\mathrm{H_3O^+}\right] = 10^{-\mathrm{pH}} = 10^{-4.52} = 3.0\times10^{-5}\,\mathrm{M} = \left[\mathrm{C_2H_3O_2}^-\right]$

We solve for S, the concentration of $\mathrm{HC_2H_3O_2}$ in the 0.750 L solution before it dissociates.

Equation:	$\mathrm{HC_2H_3O_2(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{C_2H_3O_2^-(aq)}$	+	$\mathrm{H_3O^+(aq)}$
Initial:	S M		—		0 M		≈ 0M
Changes:	-3.0×10^{-5}M		—		$+3.0\times10^{-5}$M		$+3.0\times10^{-5}$M
Equil:	$\left(S-3.0\times10^{-5}\right)$ M		—		3.0×10^{-5}M		3.0×10^{-5}M

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{C_2H_3O_2}^-]}{[\mathrm{HC_2H_3O_2}]} = 1.8\times10^{-5} = \frac{(3.0\times10^{-5})^2}{(S-3.0\times10^{-5})}$$

$$\left(3.0\times10^{-5}\right)^2 = 1.8\times10^{-5}\left(S-3.0\times10^{-5}\right) = 9.0\times10^{-10} = 1.8\times10^{-5}S - 5.4\times10^{-10}$$

$$S = \frac{9.0\times10^{-10}+5.4\times10^{-10}}{1.8\times10^{-5}} = 8.0\times10^{-5}\,\mathrm{M}$$ Now we determine the mass of vinegar needed.

$$\text{mass vinegar} = 0.750\ \mathrm{L}\times\frac{8.0\times10^{-5}\,\mathrm{mol\ HC_2H_3O_2}}{1\,\mathrm{L\ soln}}\times\frac{60.05\,\mathrm{g\ HC_2H_3O_2}}{1\,\mathrm{mol\ HC_2H_3O_2}}\times\frac{100.0\,\mathrm{g\ vinegar}}{5.7\,\mathrm{g\ HC_2H_3O_2}}$$
$$= 0.063\ \mathrm{g\ vinegar}$$

34. **(M)** First we determine $\left[\mathrm{OH^-}\right]$ which, because of the stoichiometry of the reaction, equals $\left[\mathrm{NH_4}^+\right]$.

$$\mathrm{pOH} = 14.00 - \mathrm{pH} = 14.00 - 11.55 = 2.45 \qquad \left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}} = 10^{-2.45} = 3.5\times10^{-3}\,\mathrm{M} = \left[\mathrm{NH_4}^+\right]$$

We solve for S, the concentration of $\mathrm{NH_3}$ in the 0.625 L solution prior to dissociation.

Equation:	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	S M		—		0 M		≈ 0 M
Changes:	–0.0035 M		—		+0.0035 M		+0.0035 M
Equil:	$(S-0.0035)$ M		—		0.0035 M		0.0035 M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5} = \frac{(0.0035)^2}{(S-0.0035)}$$

$$(0.0035)^2 = 1.8\times10^{-5}(S-0.0035) = 1.225\times10^{-5} = 1.8\times10^{-5}S - 6.3\times10^{-8}$$

$$S = \frac{1.225\times10^{-5} + 6.3\times10^{-8}}{1.8\times10^{-5}} = 0.68 \text{ M}$$

Now we determine the volume of household ammonia needed

$$V_{\text{ammonia}} = 0.625 \text{ L soln} \times \frac{0.68 \text{ mol NH}_3}{1 \text{ L soln}} \times \frac{17.03 \text{ g NH}_3}{1 \text{ mol NH}_3} \times \frac{100.0 \text{ g soln}}{6.8 \text{ g NH}_3} \times \frac{1 \text{ mL soln}}{0.97 \text{ g soln}}$$

$$= 1.1\times10^2 \text{ mL household ammonia solution}$$

35. **(D)**

(a) $$n_{\text{proplyamine}} = \frac{PV}{RT} = \frac{\left(316 \text{ Torr} \times \frac{1 \text{ atm}}{760 \text{ Torr}}\right)(0.275 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})} = 4.67\times10^{-3} \text{ mol propylamine}$$

$$[\text{propylamine}] = \frac{n}{V} = \frac{4.67\times10^{-3} \text{ moles}}{0.500 \text{ L}} = 9.35\times10^{-3} \text{ M}$$

$K_b = 10^{-pK_b} = 10^{-3.43} = 3.7\times10^{-4}$

	$CH_3CH_2CH_2NH_2(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$CH_3CH_2CH_2NH_3^+(aq)$	+	$OH^-(aq)$
Initial	9.35×10^{-3} M	—		0 M		≈ 0 M
Change	$-x$ M	—		$+x$ M		$+x$ M
Equil.	$(9.35\times10^{-3} - x)$ M	—		x M		x M

$$K_b = 3.7\times10^{-4} = \frac{x^2}{9.35\times10^{-3} - x} \quad \text{or} \quad 3.5\times10^{-6} - 3.\ 7\times10^{-4}(x) = x^2$$

$$x^2 + 3.7\times10^{-4}x - 3.5\times10^{-6} = 0$$

Find x with the roots formula:

$$x = \frac{-3.7 \times 10^{-4} \pm \sqrt{(3.7 \times 10^{-4})^2 - 4(1)(-3.5 \times 10^{-6})}}{2(1)}$$

Therefore $x = 1.6\underline{95} \times 10^{-3}$ M = $[\mathrm{OH}^-]$ pOH = 2.77 and pH = 11.23

(b) $[\mathrm{OH}^-] = 1.7 \times 10^{-3}$ M = [NaOH] $(\mathrm{MM_{NaOH}} = 39.997\ \mathrm{g\ mol^{-1}})$

$n_{\mathrm{NaOH}} = (C)(V) = 1.7 \times 10^{-3}\ \mathrm{M} \times 0.500\ \mathrm{L} = 8.5 \times 10^{-4}$ moles NaOH

mass of NaOH = $(n)(\mathrm{MM_{NaOH}}) = 8.5 \times 10^{-4}$ mol NaOH × 39.997 g NaOH/mol NaOH

mass of NaOH = 0.034 g NaOH(34 mg of NaOH)

36. **(M)** $K_b = 10^{-pK_b} = 10^{-9.5} = 3.\underline{2} \times 10^{-10}$ $\mathrm{MM_{quinoline}} = 129.16\ \mathrm{g\ mol^{-1}}$

$$\text{Solubility}(25\ °\text{C}) = \frac{0.6\ \text{g}}{100\ \text{mL}}$$

$$\text{Molar solubility}(25\ °\text{C}) = \frac{0.6\ \text{g}}{100\ \text{mL}} \times \frac{1\ \text{mol}}{129.16\ \text{g}} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 0.04\underline{6}\ \text{M}$$ (note: only 1 sig fig)

	$C_9H_7N(aq)$	$+\ H_2O(l)$ $\rightleftharpoons$	$C_9H_7NH^+(aq)$	$+\ OH^-(aq)$
Initial	0.046 M	—	0 M	≈ 0 M
Change	$-x$ M	—	$+x$ M	$+x$ M
Equil.	$(0.046 - x)$ M	—	x M	x M

$$3.\underline{2} \times 10^{-10} = \frac{x^2}{0.046 - x} \approx \frac{x^2}{0.046}, \qquad x = 3.\underline{8} \times 10^{-6}\ \text{M} \quad (x \ll 0.04\underline{6}, \text{ valid assumption})$$

Therefore, $[\mathrm{OH}^-] = 4 \times 10^{-6}$ M pOH = 5.4 and pH = 8.6

<u>37.</u> **(M)** If the molarity of acetic acid is doubled, we expect a lower initial pH (more $H_3O^+(aq)$ in solution) and a lower percent ionization as a result of the increase in concentration. The ratio between $[H_3O^+]$ of concentration "M" and concentration 2 M is $\sqrt{2} \approx 1.4$. Therefore, (b), containing 14 H_3O^+ symbols best represents the conditions (~$(2)^{1/2}$ times greater).

38. **(M)** If NH_3 is diluted to half its original molarity, we expect a lower pH (a lower $[OH^-]$) and a higher percent ionization in the diluted sample. The ratio between $[OH^-]$ of concentration "M" and concentration 0.5 M is $\sqrt{0.5} \approx 0.71$. Since the diagram represent M has 24 OH^- symbols, then diagram (c), containing 17 OH^- symbols would be the correct choice.

Percent Ionization

39. **(M)** Let us first compute the $[H_3O^+]$ in this solution.

Equation:	$HC_3H_5O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$C_3H_5O_2^-(aq)$
Initial:	0.45 M		—		≈ 0 M		≈ 0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.45-x)$ M		—		x M		x M

$$K_a = \frac{[H_3O^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{x^2}{0.45-x} = 10^{-4.89} = 1.3\times10^{-5} \approx \frac{x^2}{0.45}$$

$x = 2.4\times10^{-3}$ M; We have assumed that $x \ll 0.45$ M, an assumption that clearly is correct.

(a) $$\alpha = \frac{[H_3O^+]_{\text{equil}}}{[HC_3H_5O_2]_{\text{initial}}} = \frac{2.4\times10^{-3}\,\text{M}}{0.45\ \text{M}} = 0.0053 = \text{degree of ionization}$$

(b) $\%\ \text{ionization} = \alpha\times100\% = 0.0053\times100\% = 0.53\%$

40. **(M)** For $C_2H_5NH_2$ (ethylamine), $K_b = 4.3\times10^{-4}$

	$C_2H_5NH_2(aq)$	$+ H_2O(l)$	$\rightleftharpoons$	$C_2H_5NH_3^+(aq)$	+	$OH^-(aq)$
Initial	0.85 M	—		0 M		≈ 0 M
Change	$-x$ M	—		$+x$ M		$+x$ M
Equil.	$(0.85-x)$ M	—		x M		x M

$$4.3\times10^{-4} = \frac{x^2}{(0.85-x)\ \text{M}} \approx \frac{x^2}{0.85\ \text{M}}$$ $x = 0.019$ M ($x << 0.85$, thus a valid assumption)

Degree of ionization $\alpha = \frac{0.019\,\text{M}}{0.85\ \text{M}} = 0.022$ Percent ionization = $\alpha\times100\% = 2.2\ \%$

41. **(M)** Let x be the initial concentration of NH_3, hence, the amount dissociated is $0.042\,x$

	$NH_3(aq)$	$+ H_2O(l)$	$\xrightleftharpoons{K_a = 1.8\times10^{-5}}$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial	x M	—		0 M		≈ 0 M
Change	$-0.042x$ M	—		$+0.042x$ M		$+0.042x$ M
Equil.	$(1x-0.042x)$ M $= 0.958\,x$	—		$0.042x$ M		$0.042x$ M

$$K_b = 1.8\times10^{-5} = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]_{equil}} = \frac{[0.042x]^2}{[0.958x]} = 0.0018\underline{4}x$$

$$\left[NH_3\right]_{initial} = x = \frac{1.8\times10^{-5}}{0.0018\underline{4}} = 0.0097\underline{8}\,M = 0.0098\,M$$

42. **(M)**

	$HC_3H_5O_2(aq)$	$+\ H_2O(l)$	$\overset{K_a\,=\,1.3\,\times\,10^{-5}}{\rightleftharpoons}$	$C_3H_5O_2^-(aq)$	+	$H_3O^+(aq)$
Initial	0.100 M	—		0 M		≈ 0 M
Change	$-x$ M	—		$+x$ M		$+x$ M
Equil.	$(0.100 - x)$ M	—		x M		x M

$$1.3\times10^{-5} = \frac{x^2}{0.100\ \text{M} - x} \approx \frac{x^2}{0.100} \qquad x = 1.1\times10^{-3}$$ ($x << 0.100$, thus a valid assumption)

Percent ionization = $\frac{0.0011}{0.100}\times 100\% = 1.1\underline{4}\ \%$

Next we need to find molarity of acetic acid that is 1.1% ionized

	$HC_2H_3O_2(aq)$	+	$H_2O(l)$	$\overset{K_a\,=1.8\,\times\,10^{-5}}{\rightleftharpoons}$	$C_2H_3O_2^-(aq)$	+	$H_3O^+(aq)$
Initial	X M		—		0 M		≈ 0 M
Change	$-\frac{1.1\underline{4}}{100}X$ M		—		$+\frac{1.1\underline{4}}{100}X$ M		$+\frac{1.1\underline{4}}{100}X$ M
Equil.	$X - \frac{1.1\underline{4}}{100}X$ $= 0.98\underline{86}\,X$ M		—		$\frac{1.1\underline{4}}{100}X$ M $= 0.011\underline{4}$ M		$\frac{1.1\underline{4}}{100}X$ M $= 0.011\underline{4}$ M

$$1.8\times10^{-5} = \frac{\left(\frac{1.1\underline{4}}{100}X\right)^2}{0.9886\ \ X} = 1.3\times10^{-4}(X); \qquad X = 0.13\underline{8}\ \text{M}$$

Consequently, approximately 0.14 moles of acetic acid must be dissolved in one liter of water in order to have the same percent ionization as 0.100 M propionic acid.

43. **(E)** We would not expect these ionizations to be correct because the calculated degree of ionization is based on the assumption that the $[HC_2H_3O_2]_{initial} \approx [HC_2H_3O_2]_{initial} - [HC_2H_3O_2]_{equil.,}$ which is invalid at the 13 and 42 percent levels of ionization seen here.

44. **(M)** $HC_2Cl_3O_2$ (trichloroacetic acid) pK_a = 0.52 $K_a = 10^{-0.52} = 0.30$
For a 0.035 M solution, the assumption will not work (the concentration is too small and K_a is too large) Thus, we must solve the problem using the quadratic equation.

	$HC_2Cl_3O_2(aq)$	$+\ H_2O(l)$	$\rightleftharpoons$	$C_2Cl_3O_2^-(aq)$	+	$H_3O^+(aq)$
Initial	0.035 M	—		0 M		≈ 0 M
Change	$-x$ M	—		$+x$ M		$+x$ M
Equil.	$(0.035 - x)$ M	—		x M		x M

$0.30 = \dfrac{x^2}{0.035 - x}$ or $0.010\underline{5} - 0.30(x) = x^2$ or $x^2 + 0.30x - 0.010\underline{5} = 0$; solve quadratic:

$x = \dfrac{-0.30 \pm \sqrt{(0.30)^2 - 4(1)(0.010\underline{5})}}{2(1)}$ Therefore $x = 0.032$ M = $[H_3O^+]$

Degree of ionization $\alpha = \dfrac{0.032\text{ M}}{0.035\text{ M}} = 0.91$ Percent ionization = $\alpha \times 100\% = 91.$ %

Polyprotic Acids

45. **(E)** Because H_3PO_4 is a weak acid, there is little HPO_4^{2-} (produced in the 2nd ionization) compared to the H_3O^+ (produced in the 1st ionization). In turn, there is little PO_4^{3-} (produced in the 3rd ionization) compared to the HPO_4^{2-}, and very little compared to the H_3O^+.

46. **(E)** The main estimate involves assuming that the mass percents can be expressed as 0.057 g of 75% H_3PO_4 per 100. mL of solution and 0.084 g of 75% H_3PO_4 per 100. mL of solution. That is, that the density of the aqueous solution is essentially 1.00 g/mL. Based on this assumption, the initial minimum and maximum concentrations of H_3PO_4 is:

$$[H_3PO_4] = \frac{0.057\,\text{g impure}\,H_3PO_4 \times \dfrac{75\,\text{g}\,H_3PO_4}{100\,\text{g impure}\,H_3PO_4} \times \dfrac{1\,\text{mol}\,H_3PO_4}{98.00\ \text{g}\,H_3PO_4}}{100\,\text{mL soln} \times \dfrac{1\text{L}}{1000\,\text{mL}}} = 0.0044\,\text{M}$$

$$[H_3PO_4] = \frac{0.084\,\text{g impure}\,H_3PO_4 \times \dfrac{75\,\text{g}\,H_3PO_4}{100\,\text{g impure}\,H_3PO_4} \times \dfrac{1\,\text{mol}\,H_3PO_4}{98.00\ \text{g}\,H_3PO_4}}{100\,\text{mL soln} \times \dfrac{1\text{L}}{1000\,\text{mL}}} = 0.0064\,\text{M}$$

$$\begin{array}{llccccccc}
\text{Equation:} & H_3PO_4(aq) & + & H_2O(l) & \rightleftharpoons & H_2PO_4^-(aq) & + & H_3O^+(aq) \\
\text{Initial:} & 0.0044\text{ M} & & - & & 0\text{ M} & & \approx 0\text{ M} \\
\text{Changes:} & -x\,\text{M} & & - & & +x\ \text{M} & & +x\ \text{M} \\
\text{Equil:} & (0.0044 - x)\text{ M} & & - & & x\ \text{M} & & x\ \text{M}
\end{array}$$

$$K_{a_1} = \frac{\left[H_2PO_4^-\right]\left[H_3O^+\right]}{\left[H_3PO_4\right]} = \frac{x^2}{0.0044 - x} = 7.1\times10^{-3} \qquad x^2 + 0.0071x - 3.1\times10^{-5} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0071 \pm \sqrt{5.0\times10^{-5} + 1.2\times10^{-4}}}{2} = 3.0\times10^{-3}\text{M} = \left[H_3O^+\right]$$

The set-up for the second concentration is the same as for the first, with the exception that 0.0044 M is replaced by 0.0064 M.

$$K_{a_1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = \frac{x^2}{0.0064 - x} = 7.1\times10^{-3} \qquad x^2 + 0.0071x - 4.5\times10^{-5} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0071 \pm \sqrt{5.0\times10^{-5} + 1.8\times10^{-4}}}{2} = 4.0\times10^{-3}\,\text{M} = [H_3O^+]$$

The two values of pH now are determined, representing the pH range in a cola drink.

$$\text{pH} = -\log\left(3.0\times10^{-3}\right) = 2.52 \qquad \text{pH} = -\log\left(4.\times10^{-3}\right) = 2.40$$

47. **(D)**

(a)

Equation:	$H_2S(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HS^-(aq)$	+	$H_3O^+(aq)$
Initial:	0.075 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.075 - x)$ M		–		x M		$+x$ M

$$K_{a_1} = \frac{[HS^-][H_3O^+]}{[H_2S]} = 1.0\times10^{-7} = \frac{x^2}{0.075 - x} \approx \frac{x^2}{0.075} \qquad x = 8.7\times10^{-5}\,\text{M} = [H_3O^+]$$

$$[HS^-] = 8.7\times10^{-5}\,\text{M} \text{ and } [S^{2-}] = K_{a_2} = 1\times10^{-19}\,\text{M}$$

(b) The set-up for this problem is the same as for part (a), with 0.0050 M replacing 0.075 M as the initial value of $[H_2S]$.

$$K_{a_1} = \frac{[HS^-][H_3O^+]}{[H_2S]} = 1.0\times10^{-7} = \frac{x^2}{0.0050 - x} \approx \frac{x^2}{0.0050} \qquad x = 2.2\times10^{-5}\,\text{M} = [H_3O^+]$$

$$[HS^-] = 2.2\times10^{-5}\,\text{M} \text{ and } [S^{2-}] = K_{a_2} = 1\times10^{-19}\,\text{M}$$

(c) The set-up for this part is the same as for part (a), with 1.0×10^{-5} M replacing 0.075 M as the initial value of $[H_2S]$. The solution differs in that we cannot assume $x << 1.0\times10^{-5}$. Solve the quadratic equation to find the desired equilibrium concentrations.

$$K_{a_1} = \frac{[HS^-][H_3O^+]}{[H_2S]} = 1.0\times10^{-7} = \frac{x^2}{1.0\times10^{-5} - x}$$

$$x^2 + 1.0\times10^{-7}x - 1.0\times10^{-12} = 0$$

$$x = \frac{-1.0\times10^{-7} \pm \sqrt{1.0\times10^{-14} + \left(4\times 1.0\times10^{-12}\right)}}{2\times(1)}$$

$$x = 9.5\times10^{-7}\,\text{M} = \left[H_3O^+\right] \qquad \left[HS^-\right] = 9.5\times10^{-7}\,\text{M} \qquad \left[S^{2-}\right] = K_{a_2} = 1\times10^{-19}\,\text{M}$$

48. **(M)** For H_2CO_3, $K_1 = 4.4\times10^{-7}$ and $K_2 = 4.7\times10^{-11}$

(a) The first acid ionization proceeds to a far greater extent than does the second and determines the value of $\left[H_3O^+\right]$.

Equation:	$H_2CO_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$HCO_3^-(aq)$
Initial:	0.045 M		—		≈ 0 M		0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.045-x)$ M		—		x M		x M

$$K_1 = \frac{\left[H_3O^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = \frac{x^2}{0.045-x} = 4.4\times10^{-7} \approx \frac{x^2}{0.045} \qquad x = 1.4\times10^{-4}\,\text{M} = \left[H_3O^+\right]$$

(b) Since the second ionization occurs to only a limited extent,
$\left[HCO_3^-\right] = 1.4\times10^{-4}$ M = 0.00014 M

(c) We use the second ionization to determine $\left[CO_3^{2-}\right]$.

Equation:	$HCO_3^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$CO_3^{2-}(aq)$
Initial:	0.00014 M		—		0.00014 M		0 M
Changes:	$-x$ M		—		$+x$ M		$+x$ M
Equil:	$(0.00014-x)$ M		—		$(0.00014+x)$ M		x M

$$K_2 = \frac{\left[H_3O^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = \frac{(0.00014+x)x}{0.00014-x} = 4.7\times10^{-11} \approx \frac{(0.00014)\,x}{0.00014}$$

$$x = 4.7\times10^{-11}\,\text{M} = \left[CO_3^{2-}\right]$$

Again we assumed that $x \ll 0.00014$ M, which clearly is the case. We also note that our original assumption, that the second ionization is much less significant than the first, also is a valid one. As an alternative to all of this, we could have recognized that the concentration of the divalent anion equals the second ionization constant: $\left[CO_3^{2-}\right] = K_2$.

49. **(D)** In all cases, of course, the first ionization of H_2SO_4 is complete, and establishes the initial values of $\left[H_3O^+\right]$ and $\left[HSO_4^-\right]$. Thus, we need only deal with the second ionization in each case.

(a)

Equation:	$HSO_4^-(aq)$ +	$H_2O(l) \rightleftharpoons$	$SO_4^{2-}(aq)$ +	$H_3O^+(aq)$
Initial:	0.75 M	–	0 M	0.75 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.75-x)$ M	–	x M	$(0.75+x)$ M

$$K_{a_2} = \frac{\left[SO_4^{2-}\right]\left[H_3O^+\right]}{\left[HSO_4^-\right]} = 0.011 = \frac{x(0.75+x)}{0.75-x} \approx \frac{0.75x}{0.75} \qquad x = 0.011\,\text{M} = \left[SO_4^{2-}\right]$$

We have assumed that $x \ll 0.75$ M, an assumption that clearly is correct.

$$\left[HSO_4^-\right] = 0.75 - 0.011 = 0.74\,\text{M} \qquad \left[H_3O^+\right] = 0.75 + 0.011 = 0.76\,\text{M}$$

(b) The set-up for this part is similar to part (a), with the exception that 0.75 M is replaced by 0.075 M.

$$K_{a_2} = \frac{\left[SO_4^{2-}\right]\left[H_3O^+\right]}{\left[HSO_4^-\right]} = 0.011 = \frac{x(0.075+x)}{0.075-x} \qquad 0.011(0.075-x) = 0.075x + x^2$$

$$x^2 + 0.086x - 8.3\times10^{-4} = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.086 \pm \sqrt{0.0074 + 0.0033}}{2} = 0.0087\,\text{M}$$

$$x = 0.0087\,\text{M} = \left[SO_4^{2-}\right]$$

$$\left[HSO_4^-\right] = 0.075 - 0.0087 = 0.066\text{M} \qquad \left[H_3O^+\right] = 0.075 + 0.0088\text{M} = 0.084\,\text{M}$$

(c) Again, the set-up is the same as for part (a), with the exception that 0.75 M is replaced by 0.00075 M

$$K_{a_2} = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = 0.011 = \frac{x(0.00075+x)}{0.00075-x} \qquad \begin{array}{c} 0.011(0.00075-x) = 0.00075x + x^2 \\ x^2 + 0.0118x - 8.3\times10^{-6} = 0 \end{array}$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.0118 \pm \sqrt{1.39\times10^{-4} + 3.3\times10^{-5}}}{2} = 6.6\times10^{-4}$$

$$x = 6.6\times10^{-4}\,\text{M} = \left[SO_4^{2-}\right] \qquad \left[HSO_4^-\right] = 0.00075 - 0.00066 = 9\times10^{-5}\,\text{M}$$

$\left[H_3O^+\right] = 0.00075 + 0.00066\text{M} = 1.41\times10^{-3}\,\text{M}$ $\left[H_3O^+\right]$ is almost twice the initial value of $\left[H_2SO_4\right]$. Thus, the second ionization of H_2SO_4 is nearly complete in this dilute solution.

50. **(D)** First we determine $\left[H_3O^+\right]$, with the calculation based on the balanced chemical equation.

Equation:	$HOOC(CH_2)_4COOH(aq)$ +	$H_2O(l) \rightleftharpoons$	$HOOC(CH_2)_4COO^-(aq)$ +	$H_3O^+(aq)$
Initial:	$0.10\ M$	−	$0\ M$	$\approx 0\ M$
Changes:	$-x\ M$	−	$+x\ M$	$+x\ M$
Equil:	$(0.10-x)\ M$	−	$x\ M$	$x\ M$

$$K_{a_1}=\frac{\left[H_3O^+\right]\left[HOOC(CH_2)_4COO^-\right]}{\left[HOOC(CH_2)_4COOH\right]}=3.9\times10^{-5}=\frac{x\cdot x}{0.10-x}\approx\frac{x^2}{0.10}$$

$$x=\sqrt{0.10\times3.9\times10^{-5}}=2.0\times10^{-3}\,M=[H_3O^+]$$

We see that our simplifying assumption, that $x \ll 0.10$ M, is indeed valid. Now we consider the second ionization. We shall see that very little H_3O^+ is produced in this ionization because of the small size of two numbers: K_{a_2} and $\left[HOOC(CH_2)_4COO^-\right]$. Again we base our calculation on the balanced chemical equation.

Equation:	$HOOC(CH_2)_4COO^-(aq)$ +	$H_2O(l) \rightleftharpoons$	$^-OOC(CH_2)_4COO^-(aq)$ +	$H_3O^+(aq)$
Initial:	$2.0\times10^{-3}\ M$	−	$0\ M$	$2.0\times10^{-3}\ M$
Changes:	$-y\ M$	−	$+y\ M$	$+y\ M$
Equil:	$(0.0020-y)\ M$	−	$y\ M$	$(0.0020+y)\ M$

$$K_{a_2}=\frac{\left[H_3O^+\right]\left[^-OOC(CH_2)_4COO^-\right]}{\left[HOOC(CH_2)_4COO^-\right]}=3.9\times10^{-6}=\frac{y(0.0020+y)}{0.0020-y}\approx\frac{0.0020y}{0.0020}$$

$$y=3.9\times10^{-6}\,M=[^-OOC(CH_2)_4COO^-]$$

Again, we see that our assumption, that $y \ll 0.0020$ M, is valid. In addition, we also note that virtually no H_3O^+ is created in this second ionization. The concentrations of all species have been calculated above, with the exception of $\left[OH^-\right]$.

$$\left[OH^-\right]=\frac{K_w}{\left[H_3O^+\right]}=\frac{1.0\times10^{-14}}{2.0\times10^{-3}}=5.0\times10^{-12}\,M; \qquad \left[HOOC(CH_2)_4COOH\right]=0.10\,M$$

$$\left[H_3O^+\right]=\left[HOOC(CH_2)_4COO^-\right]=2.0\times10^{-3}\,M; \qquad \left[^-OOC(CH_2)_4COO^-\right]=3.9\times10^{-6}\,M$$

51. (M)

(a) Recall that a base is a proton acceptor, in this case, accepting H^+ from H_2O.

First ionization: $C_{20}H_{24}O_2N_2 + H_2O \rightleftharpoons C_{20}H_{24}O_2N_2H^+ + OH^-$ $\quad pK_{b_1} = 6.0$

Second ionization: $C_{20}H_{24}O_2N_2H^+ + H_2O \rightleftharpoons C_{20}H_{24}O_2N_2H_2{}^{2+} + OH^-$ $\quad pK_{b_2} = 9.8$

(b)

$$[C_{20}H_{24}O_2N_2] = \frac{1.00\text{ g quinine} \times \dfrac{1\text{ mol quinine}}{324.4\text{ g quinine}}}{1900\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ mL}}} = 1.62 \times 10^{-3}\text{ M}$$

$$K_{b_1} = 10^{-6.0} = 1 \times 10^{-6}$$

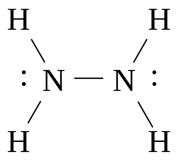
Because the OH^- produced in (a) suppresses the reaction in (b) and since $K_{b1} >> K_{b2}$, the solution's pH is determined almost entirely by the first base hydrolysis of the first reaction. Once again, we set-up the I.C.E. table and solve for the $[OH^-]$ in this case:

Equation:	$C_{20}H_{24}O_2N_2(aq)$	+ $H_2O(l)$ $\rightleftharpoons$	$C_{20}H_{24}O_2N_2H^+(aq)$	+ $OH^-(aq)$
Initial:	0.00162 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.00162 - x)$ M	–	x M	x M

$$K_{b_1} = \frac{\left[C_{20}H_{24}O_2N_2H^+\right]\left[OH^-\right]}{\left[C_{20}H_{24}O_2N_2\right]} = 1 \times 10^{-6} = \frac{x^2}{0.00162 - x} \approx \frac{x^2}{0.00162} \qquad x \approx 4 \times 10^{-5}\text{ M}$$

The assumption $x \ll 0.00162$, is valid. pOH = $-\log\left(4 \times 10^{-5}\right) = 4.4$ $\quad$ pH = 9.6

52. (M) Hydrazine is made up of two NH_2 units held together by a nitrogen–nitrogen single bond:



(a) $N_2H_4(aq) + H_2O(l) \rightleftharpoons N_2H_5{}^+(aq) + OH^-(aq)$ $\qquad K_{b1} = 10^{-6.07} = 8.5 \times 10^{-7}$

(b) $N_2H_5{}^+(aq) + H_2O(l) \rightleftharpoons N_2H_6{}^{2+}(aq) + OH^-(aq)$ $\qquad K_{b2} = 10^{-15.05} = 8.9 \times 10^{-16}$

Because the OH^- produced in (a) suppresses the reaction in (b) and since $K_{b1} >> K_{b2}$, the solution's pH is determined almost entirely by the first base hydrolysis reaction (a). Thus we need only solve the I.C.E. table for the hydrolysis of N_2H_4 in order to find the $[OH^-]_{equil}$, which will ultimately provide us with the pH via the relationship $[OH^-] \times [H_3O^+] = 1.00 \times 10^{-14}$.

Reaction:	$N_2H_4(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$N_2H_5^+(aq)$	+	$OH^-(aq)$
Initial:	0.245 M		$-$		0 M		≈ 0 M
Changes:	$-x$ M		$-$		$+x$ M		$+x$ M
Equil:	$(0.245\ -x)$ M		$-$		x M		x M

$$K_{b_1} = \frac{\left[N_2H_5^+\right]\left[OH^-\right]}{\left[N_2H_4\right]} = 8.5\times10^{-7} = \frac{x^2}{0.245-x} = \frac{x^2}{0.245} \qquad x = 4.56\times10^{-4}\text{ M} = [OH^-]_{\text{equil}}$$

$$\text{Thus, } [H_3O^+] = \frac{1.0\times10^{-14}}{4.56\times10^{-4}} = 2.19\times10^{-11}\text{M} \qquad \text{pH} = -\log(2.19\times10^{-11}) = 10.66$$

53. **(E)** Protonated codeine hydrolyzes water according to the following reaction:

$$C_{18}H_{21}O_3NH^+ + H_2O \rightleftharpoons C_{18}H_{21}O_3N + H_3O^+$$

$$pK_a = 6.05$$

$$pK_b = 14 - pK_a = 7.95$$

54. **(E)** Protonated quinoline is, of course, an acid, which hydrolyzes water to give a hydronium ion. The reaction is as follows:

$$C_9H_7NH^+ + H_2O \rightleftharpoons C_9H_7N + H_3O^+$$

$$K_b = \frac{K_W}{K_a} = \frac{1\times10^{-14}}{6.3\times10^{-10}} = 1.6\times10^{-5}$$

$$pK_b = -\log\left(1.6\times10^{-5}\right) = 4.8$$

55. **(E)** The species that hydrolyze are the cations of weak bases, namely, NH_4^+ and $C_6H_5NH_3^+$, and the anions of weak acids, namely, NO_2^- and $C_7H_5O_2^-$.

(a) $NH_4^+(aq) + NO_3^-(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + NO_3^-(aq) + H_3O^+(aq)$

(b) $Na^+(aq) + NO_2^-(aq) + H_2O(l) \rightleftharpoons Na^+(aq) + HNO_2(aq) + OH^-(aq)$

(c) $K^+(aq) + C_7H_5O_2^-(aq) + H_2O(l) \rightleftharpoons K^+(aq) + HC_7H_5O_2(aq) + OH^-(aq)$

(d) $K^+(aq) + Cl^-(aq) + Na^+(aq) + I^-(aq) + H_2O(l) \rightarrow \text{no reaction}$

(e) $C_6H_5NH_3^+(aq) + Cl^-(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + Cl^-(aq) + H_3O^+(aq)$

56. (E) Recall that, for a conjugate weak acid–weak base pair, $K_a \times K_b = K_w$

(a) $K_a = \dfrac{K_w}{K_b} = \dfrac{1.0\times10^{-14}}{1.5\times10^{-9}} = 6.7\times10^{-6}$ for $C_5H_5NH^+$

(b) $K_b = \dfrac{K_w}{K_a} = \dfrac{1.0\times10^{-14}}{1.8\times10^{-4}} = 5.6\times10^{-11}$ for CHO_2^-

(c) $K_b = \dfrac{K_w}{K_a} = \dfrac{1.0\times10^{-14}}{1.0\times10^{-10}} = 1.0\times10^{-4}$ for $C_6H_5O^-$

57. (E)

(a) Because it is composed of the cation of a strong base, and the anion of a strong acid, KCl forms a neutral solution (i.e., no hydrolysis occurs).

(b) KF forms an alkaline (basic) solution. The fluoride ion, being the conjugate base of a relatively strong weak acid, undergoes hydrolysis, while potassium ion, the weakly polarizing cation of a strong base, does not react with water.

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

(c) $NaNO_3$ forms a neutral solution, being composed of a weakly polarizing cation and anionic conjugate base of a strong acid. No hydrolysis occurs.

(d) $Ca(OCl)_2$ forms an alkaline (basic) solution, being composed of a weakly polarizing cation and the anion of a weak acid Thus, only the hypochlorite ion hydrolyzes.

$$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$$

(e) NH_4NO_2 forms an acidic solution. The salt is composed of the cation of a weak base and the anion of a weak acid. The ammonium ion hydrolyzes:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad K_a = 5.6\times10^{-10}$$

as does the nitrite ion:

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) \qquad K_b = 1.4\times10^{-11}$$

Since NH_4^+ is a stronger acid than NO_2^- is a base (as shown by the relative sizes of the *K* values), the solution will be acidic. The ionization constants were computed from data in Table 16-3 and with the relationship $K_w = K_a \times K_b$.

For NH_4^+, $K_a = \dfrac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$ For NO_2^-, $K_b = \dfrac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11}$

Where $1.8\times10^{-5} = K_b$ of NH_3 and $7.2\times10^{-4} = K_a$ of HNO_2

58. **(E)** Our list in order of increasing pH is also in order of decreasing acidity. First we look for the strong acids; there is just HNO_3. Next we look for the weak acids; there is only one, $HC_2H_3O_2$. Next in order of decreasing acidity come salts with cations from weak bases and anions from strong acids; NH_4ClO_4 is in this category. Then come salts in which both ions hydrolyze to the same degree; $NH_4C_2H_3O_2$ is an example, forming a pH-neutral solution. Next are salts that have the cation of a strong base and the anion of a weak acid; $NaNO_2$ is in this category. Then come weak bases, of which $NH_3(aq)$ is an example. And finally, we terminate the list with strong bases: NaOH is the only one. Thus, in order of increasing pH of their 0.010 M aqueous solutions, the solutes are:
$HNO_3 < HC_2H_3O_2 < NH_4ClO_4 < NH_4C_2H_3O_2 < NaNO_2 < NH_3 < NaOH$

59. **(M)** NaOCl dissociates completely in aqueous solution into $Na^+(aq)$, which does not hydrolyze, and $OCl^-(aq)$, which undergoes base hydrolysis. We determine $[OH^-]$ in a 0.089 M solution of OCl^-, finding the value of the hydrolysis constant from the ionization constant of HOCl, $K_a = 2.9 \times 10^{-8}$.

Equation:	$OCl^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HOCl(aq)$	+	$OH^-(aq)$
Initial:	0.089 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.089 - x)$ M		–		x M		x M

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7} = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{x^2}{0.089 - x} \approx \frac{x^2}{0.089}$$

1.7×10^{-4} M << 0.089, the assumption is valid.

$$x = 1.7 \times 10^{-4}\,\text{M} = [OH^-]; \quad \text{pOH} = -\log(1.7 \times 10^{-4}) = 3.77, \quad \text{pH} = 14.00 - 3.77 = 10.23$$

60. **(M)** dissociates completely in aqueous solution into $NH_4^+(aq)$, which hydrolyzes, and $Cl^-(aq)$, which does not. We determine $[H_3O^+]$ in a 0.123 M solution of NH_4^+, finding the value of the hydrolysis constant from the ionization constant of NH_3, $K_b = 1.8 \times 10^{-5}$.

Equation:	$NH_4^+(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_3(aq)$	+	$H_3O^+(aq)$
Initial:	0.123 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.123 - x)$ M		–		x M		x M

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.123 - x} \approx \frac{x^2}{0.123}$$

$8.3\times10^{-6}\,\text{M} \ll 0.123$, the assumption is valid

$x = 8.3\times10^{-6}\,\text{M} = \left[\text{H}_3\text{O}^+\right];\quad \text{pH} = -\log\left(8.3\times10^{-6}\right) = 5.08$

61. **(M)** $\text{KC}_6\text{H}_7\text{O}_2$ dissociates completely in aqueous solution into $\text{K}^+(\text{aq})$, which does not hydrolyze, and the ion $\text{C}_6\text{H}_7\text{O}_2{}^-(\text{aq})$, which undergoes base hydrolysis. We determine $\left[\text{OH}^-\right]$ in 0.37 M $\text{KC}_6\text{H}_7\text{O}_2$ solution using an I.C.E. table.

Note: $K_\text{a} = 10^{-\text{p}K} = 10^{-4.77} = 1.7\times10^{-5}$

Equation:	$\text{C}_6\text{H}_7\text{O}_2{}^-(\text{aq})$	+	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{HC}_6\text{H}_7\text{O}_2(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial:	0.37 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.37-x)$ M		–		x M		x M

$$K_\text{b} = \frac{K_\text{w}}{K_\text{a}} = \frac{1.0\times10^{-14}}{1.7\times10^{-5}} = 5.9\times10^{-10} = \frac{[\text{HC}_6\text{H}_7\text{O}_2][\text{OH}^-]}{[\text{C}_6\text{H}_7\text{O}_2{}^-]} = \frac{x^2}{0.37-x} \approx \frac{x^2}{0.37}$$

$x = 1.5\times10^{-5}\,\text{M} = \left[\text{OH}^-\right],\quad \text{pOH} = -\log\left(1.5\times10^{-5}\right) = 4.82,\quad \text{pH} = 14.00 - 4.82 = 9.18$

62. **(M)**

Equation:	$\text{C}_5\text{H}_5\text{NH}^+(\text{aq})$	+	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{C}_5\text{H}_5\text{N(aq)}$	+	$\text{H}_3\text{O}^+(\text{aq})$
Initial:	0.0482 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.0482-x)$ M		–		x M		x M

$$K_\text{a} = \frac{K_\text{w}}{K_\text{b}} = \frac{1.0\times10^{-14}}{1.5\times10^{-9}} = 6.7\times10^{-6} = \frac{\left[\text{C}_5\text{H}_5\text{N}\right]\left[\text{H}_3\text{O}^+\right]}{\left[\text{C}_5\text{H}_5\text{NH}^+\right]} = \frac{x^2}{0.0482-x} \approx \frac{x^2}{0.0482}$$

$5.7\times10^{-4}\,\text{M} \ll 0.0482$ M, the assumption is valid

$x = 5.7\times10^{-4}\,\text{M} = \left[\text{H}_3\text{O}^+\right],\quad \text{pH} = -\log\left(5.7\times10^{-4}\right) = 3.24$

63. **(M)**

(a) $\text{HSO}_3{}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_3{}^{2-}\quad K_\text{a} = K_{\text{a}_2,\text{Sulfurous}} = 6.2\times10^{-8}$

$$\text{HSO}_3{}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_2\text{SO}_3\quad K_\text{b} = \frac{K_\text{w}}{K_{\text{a}_1,\text{Sulfurous}}} = \frac{1.0\times10^{-14}}{1.3\times10^{-2}} = 7.7\times10^{-13}$$

Since $K_\text{a} > K_\text{b}$, solutions of $\text{HSO}_3{}^-$ are acidic.

(b) $HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$ $\quad K_a = K_{a_2,\text{Hydrosulfuric}} = 1\times10^{-19}$

$HS^- + H_2O \rightleftharpoons OH^- + H_2S$ $\quad K_b = \dfrac{K_w}{K_{a_1,\text{Hydrosulfuric}}} = \dfrac{1.0\times10^{-14}}{1.0\times10^{-7}} = 1.0\times10^{-7}$

Since $K_a < K_b$, solutions of HS^- are alkaline, or basic.

(c) $HPO_4^{\ 2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{\ 3-}$ $\quad K_a = K_{a_3,\text{Phosphoric}} = 4.2\times10^{-13}$

$HPO_4^{\ 2-} + H_2O \rightleftharpoons OH^- + H_2PO_4^{\ -}$ $\quad K_b = \dfrac{K_w}{K_{a_2,\text{Phosphoric}}} = \dfrac{1.0\times10^{-14}}{6.3\times10^{-8}} = 1.6\times10^{-7}$

Since $K_a < K_b$, solutions of $HPO_4^{\ 2-}$ are alkaline, or basic.

64. **(M)** $pH = 8.65$ (basic). We need a salt made up of a weakly polarizing cation and an anion of a weak acid, which will hydrolyze to produce a basic solution. The salt (c) KNO_2 satisfies these requirements. (a) NH_4Cl is the salt of the cation of a weak base and the anion of a strong acid, and should form an acidic solution. (b) $KHSO_4$ and (d) $NaNO_3$ have weakly polarizing cations and anions of strong acids; they form pH-neutral solutions.

$pOH = 14.00 - 8.65 = 5.35 \quad [OH^-] = 10^{-5.35} = 4.5\times10^{-6}\,M$

Equation:	$NO_2^{\ -}(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HNO_2(aq)$	+	$OH^-(aq)$
Initial:	S		$-$		$0\ M$		$\approx 0\ M$
Changes:	$-4.5\times10^{-6}M$		$-$		$+4.5\times10^{-6}M$		$+4.5\times10^{-6}M$
Equil:	$(S-4.5\times10^{-6}M)$		$-$		$4.5\times10^{-6}M$		$4.5\times10^{-6}M$

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11} = \frac{[HNO_2][OH^-]}{[NO_2^{\ -}]} = \frac{(4.5\times10^{-6})^2}{S-4.5\times10^{-6}}$$

$$S-4.5\times10^{-6} = \frac{(4.5\times10^{-6})^2}{1.4\times10^{-11}} = 1.4\,M \qquad S = 1.4\,M + 4.5\times10^{-6} = 1.4\,M = [KNO_2]$$

Molecular Structure and Acid-Base Behavior

<u>65.</u> **(M)**

(a) $HClO_3$ should be a stronger acid than is $HClO_2$. In each acid there is an $H-O-Cl$ grouping. The remaining oxygen atoms are bonded directly to Cl as terminal O atoms. Thus, there are two terminal O atoms in $HClO_3$ and only one in $HClO_2$. For oxoacids of the same element, the one with the higher number of terminal oxygen atoms is the stronger. With more oxygen atoms, the negative charge on the conjugate base is more effectively spread out, which affords greater stability. $HClO_3: K_{a_1} = 5\times10^2$ and $HClO_2: K_a = 1.1\times10^{-2}$.

(b) HNO_2 and H_2CO_3 each have one terminal oxygen atom. The difference? N is more electronegative than C, which makes $HNO_2\left(K_a = 7.2\times10^{-4}\right)$, a stronger acid than H_2CO_3 $\left(K_{a_1} = 4.4\times10^{-7}\right)$.

(c) H_3PO_4 and H_2SiO_3 have the same number (one) of terminal oxygen atoms. They differ in P being more electronegative than Si, which makes H_3PO_4 $\left(K_{a_1} = 7.1\times10^{-3}\right)$ a stronger acid than $H_2SiO_3\left(K_{a_1} = 1.7\times10^{-10}\right)$.

66. **(E)** CCl_3COOH is a stronger acid than CH_3COOH because in CCl_3COOH there are electronegative (electro-withdrawing) Cl atoms bonded to the carbon atom adjacent to the COOH group. The electron-withdrawing Cl atoms further polarize the OH bond and enhance the stability of the conjugate base, resulting in a stronger acid.

67. **(E)**

(a) HI is the stronger acid because the $H—I$ bond length is longer than the $H—Br$ bond length and, as a result, $H—I$ is easier to cleave.

(b) HOClO is a stronger acid than HOBr because
(i) there is a terminal O in HOClO but not in HOBr
(ii) Cl is more electronegative than Br.

(c) $H_3CCH_2CCl_2COOH$ is a stronger acid than $I_3CCH_2CH_2COOH$ both because Cl is more electronegative than is I and because the Cl atoms are closer to the acidic hydrogen in the COOH group and thus can exert a stronger e^- withdrawing effect on the O–H bond than can the more distant I atoms.

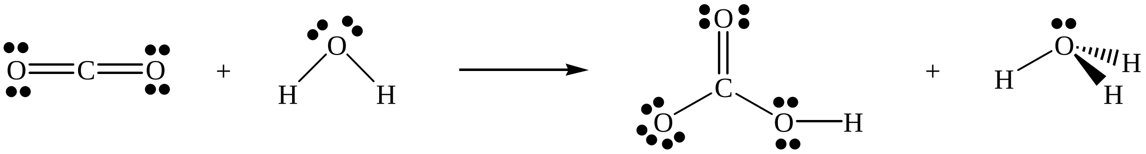
68. **(M)** The weakest of the five acids is CH_3CH_2COOH. The reasoning is as follows. HBr is a strong acid, stronger than the carboxylic acids. A carboxylic acid—such as $CH_2ClCOOH$ and CH_2FCH_2COOH—with a strongly electronegative atom attached to the hydrocarbon chain will be stronger than one in which no such group is present. But the I atom is so weakly electronegative that it barely influences the acid strength. Acid strengths of some of these acids (as values of pK_a) follow. (Larger values of pK_a indicate weaker acids.)
Strength: $CH_3CH_2COOH(4.89) < CI_3COOH < CH_2FCH_2COOH < CH_2ClCOOH < HBr(-8.72)$

69. **(E)** The largest K_b (most basic) belongs to (c) $CH_3CH_2CH_2NH_2$ (hydrocarbon chains have the lowest electronegativity). The smallest K_b (least basic) is that of (a) o-chloroaniline (the nitrogen lone pair is delocalized (spread out over the ring), hence, less available to accept a proton (i.e., it is a poorer Brønsted base)).

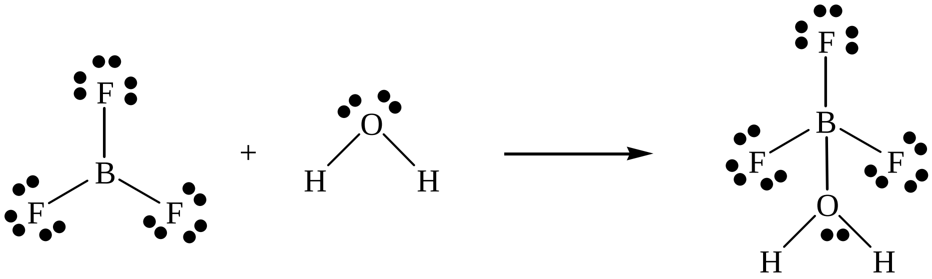
70. **(E)** The most basic species is (c) CH_3O^- (methoxide ion). Methanol is the weakest acid, thus its anion is the strongest base. Most acidic: (b) ortho-chlorophenol. In fact, it is the only acidic compound shown.

Lewis Theory of Acids and Bases

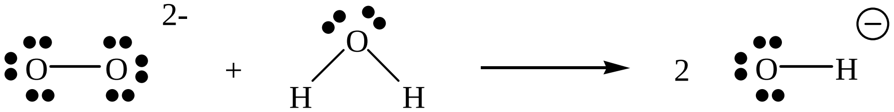
71. **(E)**
(a) acid is CO_2 and base is H_2O



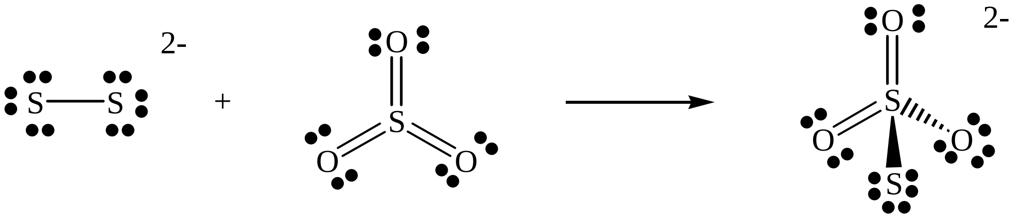
(b) acid is BF_3 and base is H_2O



(c) acid is H_2O and base is O^{2-}



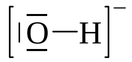
(d) acid is SO_3 and base is S^{2-}



72. **(E)**
(a) SOI_2 is the acid, and $BaSO_3$ the base.
(b) $HgCl_3^-$ is the acid, Cl^- the base.

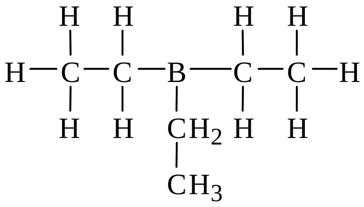
73. **(E)** A Lewis base is an electron pair donor, while a Lewis acid is an electron pair acceptor. We draw Lewis structures to assist our interpretation.

(a)

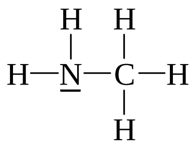


The lone pairs on oxygen can readily be donated; this is a Lewis base.

(b)

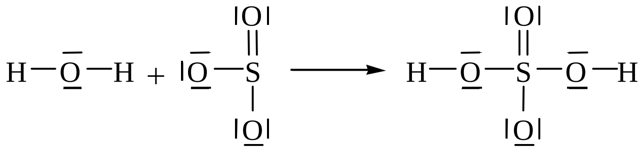


The incomplete octet of B provides a site for acceptance of an electron pair, this is a Lewis acid.

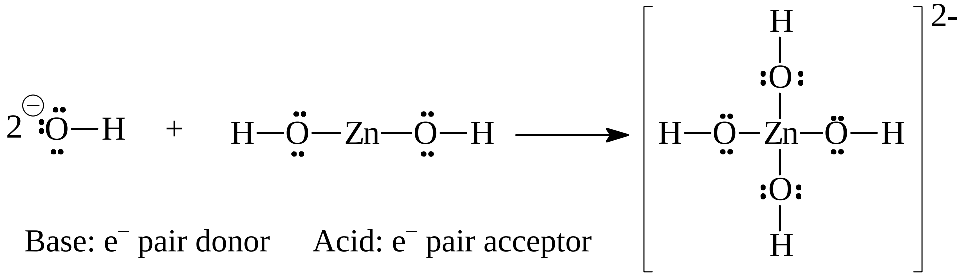
(c)  The incomplete octet of B provides a site for acceptance of an electron pair, this is a Lewis acid.

74. **(M)** A Lewis base is an electron pair donor, while a Lewis acid is an electron pair acceptor. We draw Lewis structures to assist our interpretation.

(a) According to the following Lewis structures, SO_3 appears to be the electron pair acceptor (the Lewis acid), and H_2O is the electron pair donor (the Lewis base). (Note that an additional sulfur-to-oxygen bond is formed upon successful attachment of water to SO_3.)

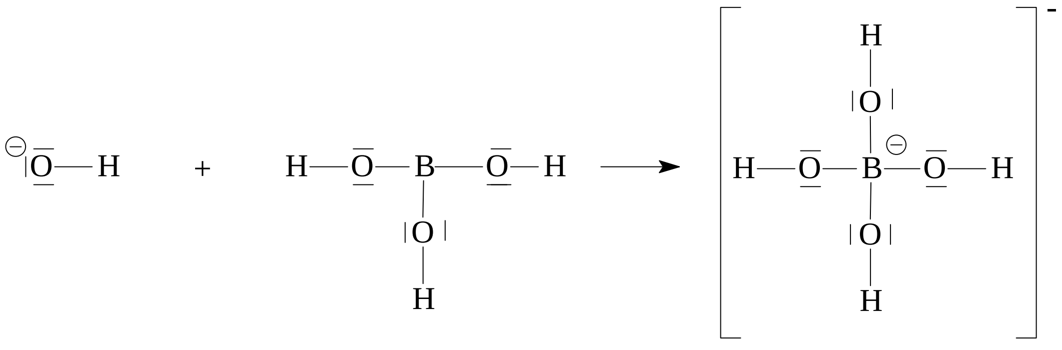


(b) The Zn metal center in $Zn(OH)_2$ accepts a pair of electrons. Thus, $Zn(OH)_2$ is a Lewis acid. OH^- donates the pair of electrons that form the covalent bond. Therefore, OH^- is a Lewis base. We have assumed here that Zn has sufficient covalent character to form coordinate covalent bonds with hydroxide ions.



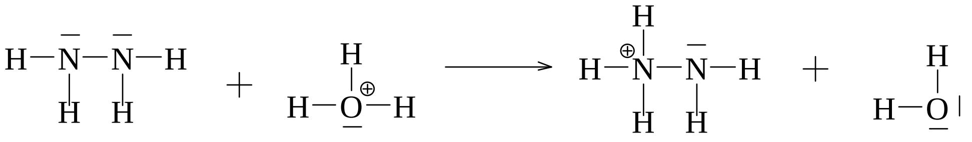
Base: e^- pair donor Acid: e^- pair acceptor

75. **(M) (a)**



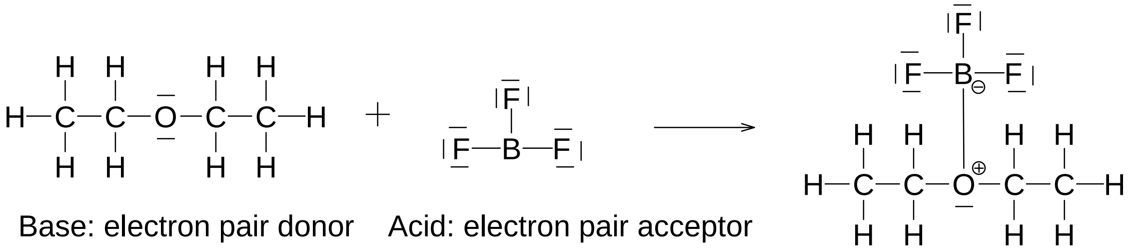
Base: e^- pair donor Acid: e^- pair acceptor

(b)

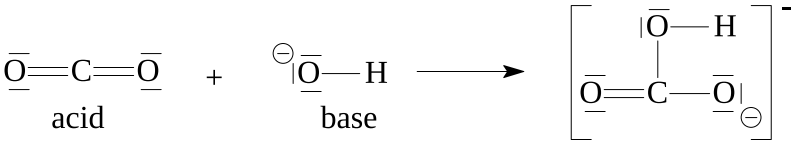


The actual Lewis acid is H^+, which is supplied by H_3O^+

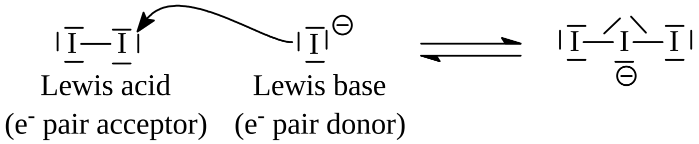
(c)



76. **(E)** The C in a CO_2 molecule can accept a pair of electrons. Thus, CO_2 is the Lewis acid. The hydroxide anion is the Lewis base as it has pairs of electrons it can donate.

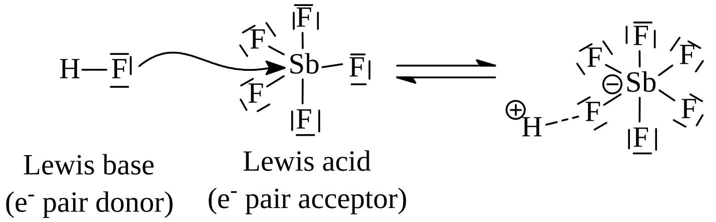


77. **(E)** $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

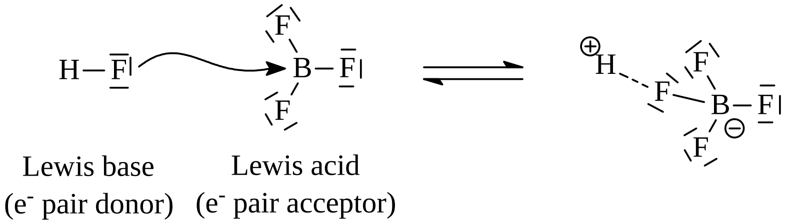


78. **(E)**

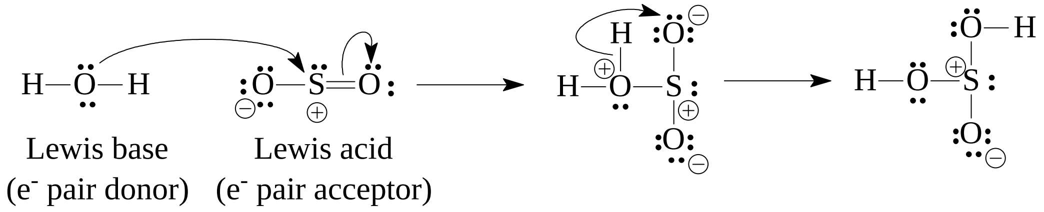
(a)



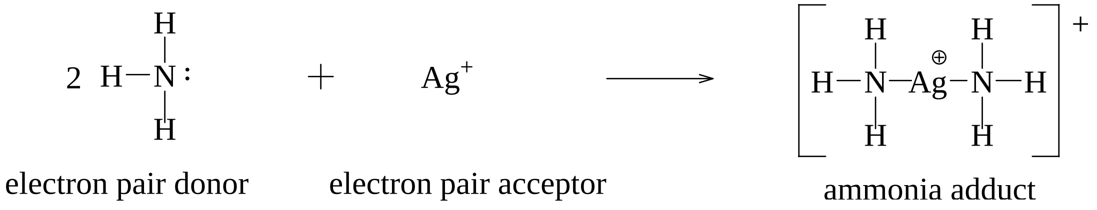
(b)



79. **(E)**



80. **(E)**



INTEGRATIVE AND ADVANCED EXERCISES

81. **(E)** We use (ac) to represent the fact that a species is dissolved in acetic acid.

(a) $C_2H_3O_2^-(ac) + HC_2H_3O_2(l) \rightleftharpoons HC_2H_3O_2(l) + C_2H_3O_2^-(ac)$

$C_2H_3O_2^-$ is a base in acetic acid.

(b) $H_2O(ac) + HC_2H_3O_2(l) \rightleftharpoons H_3O^+(ac) + C_2H_3O_2^-(ac)$

Since H_2O is a weaker acid than $HC_2H_3O_2$ in aqueous solution, it will also be weaker in acetic acid. Thus H_2O will accept a proton from the solvent acetic acid, making H_2O a base in acetic acid.

(c) $HC_2H_3O_2(l) + HC_2H_3O_2(l) \rightleftharpoons H_2C_2H_3O_2^+(ac) + C_2H_3O_2^-(aq)$

Acetic acid can act as an acid or a base in acetic acid.

(d) $HClO_4(ac) + HC_2H_3O_2(l) \rightleftharpoons ClO_4^-(ac) + H_2C_2H_3O_2^-(ac)$

Since $HClO_4$ is a stronger acid than $HC_2H_3O_2$ in aqueous solution, it will also be stronger in acetic acid. Thus, $HClO_4$ will donate a proton to the solvent acetic acid, making $HClO_4$ an acid in acetic acid.

82. **(E)** $Sr(OH)_2$ (sat'd) $\rightleftharpoons Sr^{2+}(aq) + 2\ OH^-(aq)$

$pOH = 14 - pH = 14 - 13.12 = 0.88$

$[OH^-] = 10^{-0.88} = 0.132$ M

$$[\text{OH}^-]_{\text{dilute}} = 0.132\text{M} \times (\frac{10.0 \text{ ml concentrate}}{250.0 \text{ mL total}}) = 5.28 \times 10^{-3}\text{M}$$

$$[\text{HCl}] = \frac{(10.0 \text{ ml}) \times (5.28 \times 10^{-3}\text{M})}{25.1 \text{ mL}} = 2.10 \times 10^{-3}\text{M}$$

83. **(M)**

(a) H_2SO_4 is a diprotic acid. A pH of 2 assumes no second ionization step and the second ionization step alone would produce a pH of less than 2, so it is not matched.

(b) pH 4.6 matched; ammonium salts hydrolyze to form solutions with pH < 7.

(c) KI should be nearly neutral (pH 7.0) in solution since it is the salt of a strong acid (HI) and a strong base (KOH). Thus it is not matched.

(d) pH of this solution is not matched as it's a weak base. A 0.002 M solution of KOH has a pH of about 11.3. A 0.0020 M methylamine solution would be lower (~10.9).

(e) pH of this solution is matched, since a 1.0 M hypochlorite salt hydrolyzes to form a solution of ~ pH 10.8.

(f) pH of this solution is not matched. Phenol is a very weak acid (pH >5).

(g) pH of this solution is 4.3. It is close, but not matched.

(h) pH of this solution is 2.1, matched as it's a strong organic acid.

(i) pH of this solution is 2.5, it is close, but not matched.

84. **(M)** We let $[H_3O^+]_a = 0.500\ [H_3O^+]_i$ $\qquad$ $pH = -\log[H_3O^+]_i$

$pH_a = -\log[H_3O^+]_a = -\log(0.500\ [H_3O^+]_i) = -\log\ [H_3O^+]_i - \log\ (0.500) = pH_i + 0.301$

The truth of the statement has been demonstrated. Remember, however, that the extent of ionization of weak acids and weak bases in water increases as these solutions become more and more dilute. Finally, there are some solutions whose pH doesn't change with dilution, such as NaCl(aq), which has pH = 7.0 at all concentrations.

85. **(M)** Since a strong acid is completely ionized, increasing its concentration has the effect of increasing $[H_3O^+]$ by an equal degree. In the case of a weak acid, however, the solution of the K_a expression gives the following equation (if we can assume that $[H_3O^+]$ is negligible compared to the original concentration of the undissociated acid, [HA]). $x^2 = K_a[HA]$ (where $x = [H_3O^+]$), or $x = \sqrt{K_a[\text{HA}]}$. Thus, if [HA] is doubled, $[H_3O^+]$ increases by $\sqrt{2}$.

86. **(E)** $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $\Delta H^o = (-230.0 \text{ kJ mol}) - (-285.8 \text{ kJ mol}^{-1})$
= 55.8 kJ
Since ΔH^o is positive, the value of K_{eq} is larger at higher temperatures. Therefore, the ionic products increase with increasing temperature. Le Ch âtelier's principle or the Van't Hoff equation would show this to be true.

87. **(M)** First we assume that molarity and molality are numerically equal in this dilute aqueous solution. Then compute the molality that creates the observed freezing point, with $K_f = 1.86$ °C/*m* for water.

$$m = \frac{\Delta T_\mathrm{f}}{K_f} = \frac{0.096\ ^\circ\mathrm{C}}{1.86\ ^\circ\mathrm{C}/m} = 0.052\ m \qquad \text{concentration} = 0.052\ \mathrm{M}$$

This is the total concentration of all species in solution, ions as well as molecules. We base our remaining calculation on the balanced chemical equation.

Equation:	$HC_4H_5O_2(aq) + H_2O \rightleftharpoons$	$C_4H_5O_2^-(aq)$ +	$H_3O^+(aq)$
Initial:	0.0500 M	0 M	0 M
Changes:	$-x$ M	$+x$ M	$+x$ M
Equil:	$(0.0500-x)$ M	x M	x M

$$\text{Total conc.} = 0.051_6\ \mathrm{M} = (0.0500-x)\ \mathrm{M} + x\ \mathrm{M} + x\ \mathrm{M} = 0.0500\ \mathrm{M} + x\mathrm{M} \qquad x = 0.001_6\ \mathrm{M}$$

$$K_\mathrm{a} = \frac{[C_4H_5O_2^-][H_3O^+]}{[HC_4H_5O_2]} = \frac{x \cdot x}{0.0500-x} = \frac{(0.001_6)^2}{0.0500-0.001_6} = 5\times10^{-5}$$

88. **(D)** $[H_3O^+] = 10^{-\mathrm{pH}} = 10^{-5.50} = 3.2 \times 10^{-6}$ M

(a) To produce this acidic solution we could not use 15 M $NH_3(aq)$, because aqueous solutions of NH_3 have pH values greater than 7 owing to the fact that NH_3 is a weak base.

(b)

$$V_{HCl} = 100.0\ \mathrm{mL} \times \frac{3.2\times10^{-6}\mathrm{mol\ H_3O^+}}{1\ \mathrm{L}} \times \frac{1\ \mathrm{mol\ HCl}}{1\ \mathrm{mol\ H_3O^+}} \times \frac{1\ \mathrm{L\ soln}}{12\ \ \mathrm{mol\ HCl}} = 2.7\times10^{-5}\ \ \mathrm{mL\ 12\ M\ HCl\ soln}$$

(very unlikely, since this small a volume is hard to measure)

(c) $K_\mathrm{a} = 5.6 \times 10^{-10}$ for $NH_4^+(aq)$

Equation:	$NH_4^+(aq)$	+	$H_2O(l) \rightleftharpoons$	$NH_3(aq)$	+	$H_3O^+(aq)$
Initial:	c M		–	0 M		≈ 0 M
Changes:	-3.2×10^{-6} M		–	$+3.2\times10^{-6}$ M		$+3.2\times10^{-6}$ M
Equil:	$(c-3.2\times10^{-6})$ M		–	3.2×10^{-6} M		3.2×10^{-6} M

$$K_\mathrm{a} = 5.6\times10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{(3.2\times10^{-6})(3.2\times10^{-6})}{\left(c-3.2\times10^{-6}\right)}$$

$$c - 3.2\times10^{-6} = \frac{(3.2\times10^{-6})^2}{5.6\times10^{-10}} = 1.8\times10^{-2}\ \text{M} \qquad [\text{NH}_4{}^+] = 0.018\,\text{M}$$

$$\text{NH}_4\text{Cl mass} = 100.0\ \text{mL}\times\frac{0.018\ \text{mol NH}_4{}^+}{1000\ \text{mL}}\times\frac{1\ \text{mol NH}_4\text{Cl}}{1\ \text{mol NH}_4{}^+}\times\frac{53.49\ \text{g NH}_4\text{Cl}}{1\ \text{mol NH}_4\text{Cl}} = 0.096\ \text{g NH}_4\text{Cl}$$

This would be an easy mass to measure on a laboratory three decimal place balance.

(**d**) The set-up is similar to that for NH_4Cl.

Equation:	$HC_2H_3O_2\,(aq)$	$+$	$H_2O\ (l) \rightleftharpoons$	$C_2H_3O_2{}^-\,(aq)$	$+$	$H_3O^+\,(aq)$
Initial:	c M		$-$	0 M		≈ 0 M
Changes:	-3.2×10^{-6} M		$-$	$+3.2\times10^{-6}$ M		$+3.2\times10^{-6}$ M
Equil:	$(c-3.2\times10^{-6})$ M		$-$	3.2×10^{-6} M		3.2×10^{-6} M

$$\text{K}_a = 1.8\times10^{-5} = \frac{[\text{C}_2\text{H}_3\text{O}_2{}^-][\text{H}_3\text{O}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(3.2\times10^{-6})(3.2\times10^{-6})}{c-3.2\times10^{-6}}$$

$$c - 3.2\times10^{-6} = \frac{(3.2\times10^{-6})^2}{1.8\times10^{-5}} = 5.7\times10^{-7} \qquad c = [\text{HC}_2\text{H}_3\text{O}_2] = 3.8\times10^{-6}$$

$$\text{HC}_2\text{H}_3\text{O}_2\ \text{mass} = 100.0\ \text{mL}\times\frac{3.8\times10^{-6}\ \text{mol HC}_2\text{H}_3\text{O}_2}{1000\ \text{mL}}\times\frac{60.05\ \text{g HC}_2\text{H}_3\text{O}_2}{1\ \text{mol HC}_2\text{H}_3\text{O}_2}$$

$= 2.3\times10^{-5}$ g $HC_2H_3O_2$ (an almost impossibly small mass to measure using conventional laboratory scales)

89. (M)

(a) 1.0×10^{-5} M HCN:

	$HCN(aq)$	$+$	$H_2O(l)$	$\xrightleftharpoons{K_a = 6.2\times10^{-10}}$	$H_3O^+(aq)$	$+$	$CN^-(aq)$
Initial:	1.0×10^{-5} M		$-$		1.0×10^{-7} M		0 M
Change:	$-x$		$-$		$+x$		$+x$
Equilibrium:	$(1.0\times10^{-5}-x)$ M		$-$		$(1.0\times10^{-7}+x)$ M		x

$$6.2\times10^{-10} = \frac{x(1.0\times10^{-7}+x)}{(1.0\times10^{-5}-x)} \quad\Rightarrow\quad 6.2\times10^{-15} - 6.2\times10^{-10}x = 1.0\times10^{-7}x + x^2$$

$$x^2 + 1.006\times10^{-7} - 6.2\times10^{-15} = 0$$

$$x = \frac{-1.006\times10^{-7} \pm \sqrt{(1.006\times10^{-7})^2 - 4(1)(-6.2\times10^{-15})}}{2(1)} = 1.4\underline{4}\times10^{-7}$$

Final pH = $-\log[H_3O^+] = -\log(1.0\times10^{-7} + 1.4\underline{4}\times10^{-7}) = 6.61$

(b) 1.0×10^{-5} M $C_6H_5NH_2$:

	$C_6H_5NH_2(aq)$	+ $H_2O(l)$ $\xrightleftharpoons{K_a = 7.4\times10^{-10}}$	$OH^-(aq)$	+ $C_6H_5NH_3^+(aq)$
Initial:	1.0×10^{-5} M	–	1.0×10^{-7} M	0 M
Change:	$-x$	–	$+x$	$+x$
Equilibrium:	$(1.0 \times 10^{-5} - x)$ M	–	$(1.0 \times 10^{-7} + x)$ M	x

$$7.4\times10^{-10} = \frac{x(1.0\times10^{-7} + x)}{(1.0\times10^{-5} - x)} \quad \Rightarrow \quad 7.4\times10^{-15} - 7.4\times10^{-10}\,x = 1.0\times10^{-7}\,x + x^2$$

$$x^2 + 1.0074\times10^{-7} - 7.4\times10^{-15} = 0$$

$$x = \frac{-1.0074\times10^{-7} \pm \sqrt{(1.0074\times10^{-7})^2 - 4(1)(-7.4\times10^{-15})}}{2(1)} = 4.9\underline{3}\times10^{-8}\ \text{M}$$

Final pOH = $-\log[OH^-] = -\log(1.0 \times 10^{-8} + 4.9\underline{3} \times 10^{-7}) = 6.83$ Final pH = 7.17

90. **(D)**

(a) For a weak acid, we begin with the ionization constant expression for the weak acid, HA.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]} = \frac{[H^+]^2}{M - [H^+]} \approx \frac{[H^+]^2}{M}$$

The first modification results from realizing that $[H^+] = [A^-]$. The second modification is based on the fact that the equilibrium [HA] equals the initial [HA] minus the amount that dissociates. And the third modification is an approximation, assuming that the amount of dissociated weak acid is small compared to the original amount of HA in solution. Now we take the logarithm of both sides of the equation.

$$\log K_a = \log\frac{[H^+]^2}{c} = \log[H^+]^2 - \log M = 2\log[H^+] - \log M$$

$$-2\ \log[H^+] = -\log K_a - \log\ M \qquad 2\ \text{pH}\ =\ \text{p}K_a - \log M \qquad \text{pH} = \tfrac{1}{2}\text{p}K_a - \tfrac{1}{2}\ \log M$$

For a weak base, we begin with the ionization constant expression for a weak base, B.

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{[OH^-]^2}{[B]} = \frac{[OH^-]^2}{M - [OH^-]} \approx \frac{[OH^-]^2}{M}$$

The first modification results from realizing that $[OH^-] = [BH^+]$. The second modification is based on the fact that the equilibrium [B] equals the initial [B] minus the amount that dissociates. And the third modification is an approximation, assuming that the amount of dissociated weak base is small compared to the original amount of B in solution. Now we take the logarithm of both sides of the equation.

$$\log K_b = \log\frac{[OH^-]^2}{M} = \log\,[OH^-]^2 - \ \log M = 2\ \log\ [OH^-] - \log M$$

$$-2\log[OH^-] = -\log K_b - \log\ M \qquad 2\ \text{pOH} = \text{p}K_b - \log\ M \qquad \text{pOH} = \tfrac{1}{2}\ \text{p}K_b\ - \tfrac{1}{2}\ \log M$$

$$\text{pH} = 14.00\ -\ \text{pOH} = 14.00 - \tfrac{1}{2}\text{p}K_b + \tfrac{1}{2}\ \log\ M$$

The anion of a relatively strong weak acid is a weak base. Thus, the derivation is the same as that for a weak base, immediately above, with the exception of the value for K_b. We now obtain an expression for pK_b.

$$K_b = \frac{K_w}{K_a} \qquad \log K_b = \log \frac{K_w}{K_a} = \log K_w - \log K_a$$

$$-\log K_b = -\log K_w + \log K_a = pK_b = pK_w - pK_a$$

Substitution of this expression for pK_b into the expression above gives the following result.

$$pH = 14.00 - \tfrac{1}{2} pK_w + \tfrac{1}{2} pK_a + \tfrac{1}{2} \log M$$

(**b**) **0.10 M $HC_2H_3O_2$** pH = 0.500 × 4.74 – 0.500 log 0.10 = 2.87

Equation:	$HC_2H_3O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$C_2H_3O_2^-(aq)$	+	$H_3O^+(aq)$
Initial:	0.10 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.10-x)$ M		–		x M		x M

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5} = \frac{x \cdot x}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = \sqrt{0.10 \times 1.8 \times 10^{-5}} = 1.3 \times 10^{-3}\ \text{M}, \ \ pH = -\log(1.3 \times 10^{-3}) = 2.89$$

0.10 M NH_3 $pH = 14.00 - 0.500 \times 4.74 + 0.500 \log 0.10 = 11.13$

Equation:	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	0.10 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.10-x)$ M		–		x M		x M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{x \cdot x}{0.10 - x} \approx \frac{x^2}{0.10} \quad x = \sqrt{0.10 \times 1.8 \times 10^{-5}} = 1.3 \times 10^{-3}\ \text{M}$$

$$pOH = -\log(1.3 \times 10^{-3}) = 2.89 \qquad pH = 14.00 - 2.89 = 11.11$$

0.10 M $NaC_2H_3O_2$ $pH = 14.00 - 0.500 \times 14.00 + 0.500 \times 4.74 + 0.500 \log 0.10 = 8.87$

Equation:	$C_2H_3O_2^-(aq) + H_2O(l)$	$\rightleftharpoons$	$HC_2H_3O_2(aq)$	+	$OH^-(aq)$
Initial:	0.10 M	–	0 M		≈ 0 M
Changes:	$-x$ M	–	$+x$ M		$+x$ M
Equil:	$(0.10-x)$ M	–	x M		x M

$$K_a = \frac{[OH^-][HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x \cdot x}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x = \sqrt{\frac{0.10 \times 1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 7.5 \times 10^{-6}\ \text{M} \qquad pOH = -\log(7.5 \times 10^{-6}) = 5.12$$

$$pH = 14.00 - 5.12 = 8.88$$

91. (D)

(a) We know $K_a = \dfrac{[H_3O^+]_{eq}[A^-]_{eq}}{[HA]_{eq}}$, $\alpha = \dfrac{[A^-]_{eq}}{[HA]_i}$ and finally % ionized = α × 100%.

Let us see how far we can get with no assumptions. Recall first what we mean by $[HA]_{eq}$.

$[HA]_{eq} = [HA]_i - [A^-]_{eq}$ or $[HA]_i = [HA]_{eq} + [A^-]_{eq}$

We substitute this expression into the expression for α. $\alpha = \dfrac{[A^-]_{eq}}{[HA]_{eq} + [A^-]_{eq}}$

We solve both the α and the K_{eq} expressions for $[HA]_{eq}$, equate the results, and solve for α.

$$[HA]_{eq} = \frac{[H_3O^+][A^-]}{K_a} \quad [A^-] = \alpha[HA]_{eq} + \alpha[A^-] \qquad [HA]_{eq} = \frac{[A^-] - \alpha[A^-]}{\alpha}$$

$$\frac{[H_3O^+][A^-]}{K_a} = \frac{[A^-](1-\alpha)}{\alpha} = R$$

$$R\alpha = 1 - \alpha \qquad R\alpha + \alpha = 1 = \alpha(1+R) \qquad \alpha = \frac{1}{1+R}$$

Momentarily, for ease in writing, we have let $R = \dfrac{[H_3O]^+}{K_a} = \dfrac{10^{-pH}}{10^{-pK}} = 10^{(pK-pH)}$

Once we realize that 100α = % ionized, we note that we have proven the cited formula. Notice that no approximations were made during the course of this derivation.

(b) Formic acid has $pK_a = 3.74$. Thus $10^{(pK-pH)} = 10^{(3.74-2.50)} = 10^{1.24} = 17.4$

$$\%\,\text{ionization} = \frac{100}{1+17.4} = 5.43\%$$

(c) $[H_3O^+] = 10^{-2.85} = 1.4 \times 10^{-3}$ M $\qquad \%\,\text{ionization} = \dfrac{1.4\times10^{-3}\text{ M}}{0.150\text{ M}} \times 100\% = 0.93\%$

$$0.93 = \frac{100}{1+10^{(pK-pH)}} \qquad 1+10^{(pK-pH)} = \frac{100}{0.93} = 108 \qquad 10^{(pK-pH)} = 107$$

$$2.03 = pK - pH \qquad pK = pH + 2.03 = 2.85 + 2.03 = 4.88 \quad K_a = 10^{-4.88} = 1.3\times10^{-5}$$

92. (M) We note that, as the hydrocarbon chain between the two COOH groups increases in length, the two values of pK_a get closer together. The reason for this is that the ionized COOH group, COO^-, is negatively charged. When the two COOH groups are close together, the negative charge on the molecule, arising from the first ionization, inhibits the second ionization, producing a large difference between the two ionization constants. But as the hydrocarbon chain lengthens, the effect of this negative $—COO^-$ group on the second ionization becomes less pronounced, due to the increasing separation between the two carbonyl groups, and the values of the two ionization constants are more alike.

93. **(M)** Consider only the 1st dissociation.

Equation:	$H_2C_4H_4O_4(aq) + H_2O(l)$	$\xrightleftharpoons{6.2\times10^{-5}}$	$H_3O^+(aq)$	+	$HC_4H_4O_4^-(aq)$
Initial:	0.100 M	–	≈ 0 M		0 M
Changes:	$-x$ M	–	$+x$ M		$+x$ M
Equil:	$(0.100 - x)$ M	–	x M		x M

$$K_a = \frac{x^2}{0.100 - x} = 6.2\times10^{-5} \qquad x = 0.0024\underline{6}\text{ M}$$

Solve using the quadratic equation. Hence pH = $-\log(0.00246) = 2.61$

Consider only the 2nd dissociation.

Equation:	$HC_4H_4O_4^-(aq)$	+	$H_2O(l)$	$\xrightleftharpoons{2.3\times10^{-5}}$	$H_3O^+(aq)$	+	$C_4H_4O_4^{2-}(aq)$
Initial:	0.0975 M		–		$0.0024\underline{6}$ M		0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.0975 - x)$ M		–		$0.0024\underline{6} + x$ M		x M

$$K_a = \frac{x(0.00246 + x)}{0.0975 - x} = 2.3\times10^{-6} = \frac{x(0.00246)}{0.0975}$$

$x = 0.000091$ M or $x = 0.000088$ M (solve quadratic) Hence pH ≈ 2.59

Thus, the pH is virually identical, hence, we need only consider the 1st ionization.

<u>94.</u> **(M)** To have the same freezing point, the two solutions must have the same total concentration of all particles of solute—ions and molecules. We first determine the concentrations of all solute species in 0.150 M $HC_2H_2ClO_2$, $K_a = 1.4 \times 10^{-3}$

Equation:	$HC_2H_2ClO_2(aq) + H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$C_2H_2ClO_2^-(aq)$
Initial:	0.150 M	–	≈ 0 M		0 M
Changes:	$-x$ M	–	$+x$ M		$+x$ M
Equil:	$(0.150 - x)$ M	–	$+x$ M		x M

$$K_a = \frac{[H_3O^+][C_2H_2ClO_2^-]}{[HC_2H_2ClO_2]} = \frac{x \cdot x}{0.150 - x} = 1.4\times10^{-3}$$

$$x^2 = 2.1\times10^{-4} - 1.4\times10^{-3}\,x \qquad x^2 + 1.4\times10^{-3}\,x - 2.1\times10^{-4} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.4\times10^{-3} \pm \sqrt{2.0\times10^{-6} + 8.4\times10^{-4}}}{2} = 0.014\text{ M}$$

total concentration = $(0.150 - x) + x + x = 0.150 + x = 0.150 + 0.014 = 0.164$ M

Now we determine the $[HC_2H_3O_2]$ that has this total concentration.

Equation:	$HC_2H_3O_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial:	z M		–		≈ 0 M		0 M
Changes:	$-y$ M		–		$+y$ M		$+y$ M
Equil:	$(z-y)$ M		–		y M		y M

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8\times10^{-5} = \frac{y \cdot y}{z - y}$$

We also know that the total concentration of all solute species is 0.164 M.

$$z - y + y + y = z + y = 0.164 \qquad z = 0.164 - y \qquad \frac{y^2}{0.164 - 2y} = 1.8\times10^{-5}$$

We assume that $2y << 0.164$ $\quad y^2 = 0.164\times1.8\times10^{-5} = 3.0\times10^{-6} \quad y = 1.7\times10^{-3}$

The assumption is valid: $2y = 0.0034 << 0.164$

Thus, $[HC_2H_3O_2] = z = 0.164 - y = 0.164 - 0.0017 = 0.162$ M

$$\text{mass } HC_2H_3O_2 = 1.000\text{ L}\times\frac{0.162\text{ mol } HC_2H_3O_2}{1\text{ L soln}}\times\frac{60.05\text{ g } HC_2H_3O_2}{1\text{ mol } HC_2H_3O_2} = 9.73\text{ g } HC_2H_3O_2$$

95. **(M)** The first ionization of H_2SO_4 makes the major contribution to the acidity of the solution.

Then the following two ionizations, both of which are repressed because of the presence of H_3O^+ in the solution, must be solved simultaneously.

Equation:	$HSO_4^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$SO_4^{2-}(aq)$	+	$H_3O^+(aq)$
Initial:	0.68 M		–		0 M		0.68 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.68 - x)$ M		–		x M		$(0.68 + x)$M

$$K_2 = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = 0.011 = \frac{x(0.68+x)}{0.68-x}$$

Let us solve this expression for x. $0.011\,(0.68 - x) = 0.68x + x^2 = 0.0075 - 0.011x$

$$x^2 + 0.69\,x - 0.0075 = 0 \qquad x = \frac{-b \pm\sqrt{b^2-4ac}}{2a} = \frac{-0.69 \pm\sqrt{0.48+0.030}}{2} = 0.01\text{ M}$$

This gives $[H_3O^+]$ = 0.68 + 0.01 = 0.69 M. Now we solve the second equilibrium.

Equation:	$HCHO_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CHO_2^-(aq)$	+	$H_3O^+(aq)$
Initial:	1.5 M		–		0 M		0.69 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(1.5-x)$ M		–		x M		$(0.69+x)$ M

$$K_a = \frac{[H_3O^+][CHO_2-]}{[HCHO_2]} = 1.8\times10^{-4} = \frac{x(0.69\ +\ x)}{1.5-x} \approx \frac{0.69x}{1.5} \qquad x = 3.9\times10^{-4}\ \text{M}$$

We see that the second acid does not significantly affect the $[H_3O^+]$, for which a final value is now obtained. $[H_3O^+]$ = 0.69 M, pH = –log(0.69) = 0.16

96. (D)

$$\text{Let } [HA_1]=M \qquad K_{HA_1} = \frac{[H^+][A_1^-]}{[HA_1]-[H^+]} \approx \frac{[H^+]^2}{[HA_1]} = \frac{[H^+]^2}{M}$$

$$\text{Let } [HA_2]=M \qquad K_{HA_2} = 2K_{HA_1} = \frac{[H^+][A_2^-]}{[HA_2]-[H^+]} \approx \frac{[H^+]^2}{[HA_2]} = \frac{[H^+]^2}{M}$$

$$K_{HA_1} = \frac{[H^+]^2}{M} \qquad [H^+]^2 = K_{HA_1}\times M \qquad [H^+] = \sqrt{K_{HA_1}\times M} = \left(K_{HA_1}\times M\right)^{1/2}$$

$$2K_{HA_1} = \frac{[H^+]^2}{M} \qquad [H^+]^2 = 2K_{HA_1}\times M \qquad [H^+] = \sqrt{2K_{HA_1}\times M} = \left(2K_{HA_1}\times M\right)^{1/2}$$

$$[H^+]_{overall} = \left(K_{HA_1}\times M\right)^{1/2} + \left(2K_{HA_1}\times M\right)^{1/2} \text{(take the negative } \log_{10} \text{of both sides)}$$

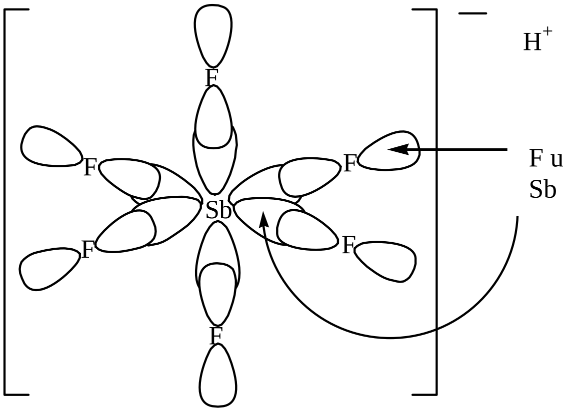
$$-\log([H^+]_{overall}) = -\log\left(\left(K_{HA_1}\times M\right)^{1/2}\right) + -\log\left(\left(2K_{HA_1}\times M\right)^{1/2}\right)$$

$$\text{pH} = -\log\left(\left(K_{HA_1}\times M\right)^{1/2}\right) - \log\left(\left(K_{HA_1}\times M\right)^{1/2}\right) = -\frac{1}{2}\log K_{HA_1}\times M - \frac{1}{2}\log 2K_{HA_1}\times M$$

$$\text{pH} = -\frac{1}{2}\left(\log K_{HA_1}\times M + \log 2K_{HA_1}\times M\right) = -\frac{1}{2}\left(\log\left(K_{HA_1}\times M + 2K_{HA_1}\times M\right)\right)$$

$$\text{pH} = -\frac{1}{2}\left(3K_{HA_1}\times M\right) = -\frac{1}{2}\left(3MK_{HA_1}\right)$$

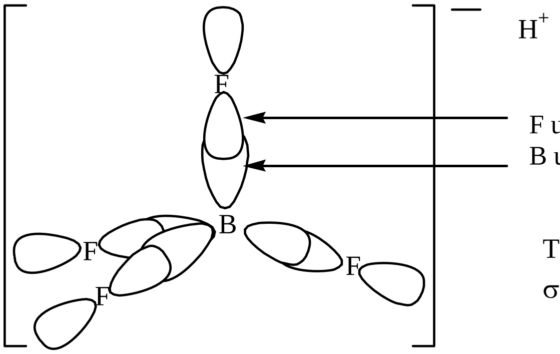
97. **(M)** $HSbF_6 \rightarrow H^+ + SbF_6^-$



F uses one of its 2p orbitals
Sb uses all six of its sp^3d^2 hybrid orbitals

The six bonds are all sigma bonds
σ (Sb_{sp3d2} - F_{2p})

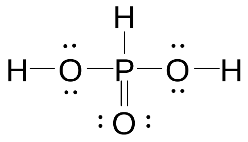
$HBF_4 \rightarrow H^+ + BF_4^-$



F uses one of its 2p orbitals
B uses all four of its sp^3 hybrid orbitals

The four bonds are all sigma bonds
σ (B_{sp3} - F_{2p})

98. **(M)** The structure of H_3PO_3 is shown on the right. The two ionizable protons are bound to oxygen.



99. **(M)**

(a) $H_2SO_3 > HF > N_2H_5^+ > CH_3NH_3^+ > H_2O$
(b) $OH^- > CH_3NH_2 > N_2H_4 > F^- > HSO_3^-$
(c) **(i)** to the right and **(ii)** to the left.

FEATURE PROBLEMS

100. **(D)**

(a) From the combustion analysis we can determine the empirical formula. Note that the mass of oxygen is determined by difference.

$$\text{amount C} = 1.599\text{ g CO}_2 \times \frac{1\text{ mol CO}_2}{44.01\text{ g CO}_2} \times \frac{1\text{ mol C}}{1\text{ mol CO}_2} = 0.03633\text{ mol C}$$

$$\text{mass of C} = 0.03633\text{ mol C} \times \frac{12.011\text{ g C}}{1\text{ mol C}} = 0.4364\text{ g C}$$

$$\text{amount H} = 0.327\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} \times \frac{2\text{ mol H}}{1\text{ mol H}_2\text{O}} = 0.03629\text{ mol H}$$

$$\text{mass of H} = 0.03629\text{ mol H} \times \frac{1.008\text{ g H}}{1\text{ mol H}} = 0.03658\text{ g H}$$

$$\text{amount O} = \left(1.054\text{ g sample} - 0.4364\text{ g C} - 0.03568\text{ g H}\right) \times \frac{1\text{ mol O}}{16.00\text{ g O}} = 0.0364\text{ mol O}$$

There are equal moles of the three elements. The empirical formula is CHO.
The freezing-point depression data are used to determine the molar mass.

$$\Delta T_\text{f} = -K_\text{f} m \quad m = \frac{\Delta T_\text{f}}{-K_\text{f}} = \frac{-0.82\ ^\circ\text{C}}{-3.90\ ^\circ\text{C}/m} = 0.21\ m$$

$$\text{amount of solute} = 25.10\text{ g solvent} \times \frac{1\text{ kg}}{1000\text{ g}} \times \frac{0.21\text{ mol solute}}{1\text{ kg solvent}} = 0.0053\text{ mol}$$

$$M = \frac{0.615\text{ g solute}}{0.0053\text{ mol solute}} = 1.2 \times 10^2\text{ g/mol}$$

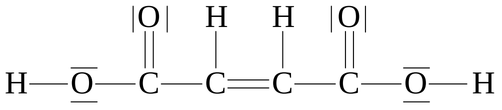
The formula mass of the empirical formula is: $12.0\text{g C} + 1.0\text{g H} + 16.0\text{g O} = 29.0\text{g/mol}$
Thus, there are four empirical units in a molecule, the molecular formula is $C_4H_4O_4$, and the molar mass is 116.1 g/mol.

(b) Here we determine the mass of maleic acid that reacts with one mol OH^-,

$$\frac{\text{mass}}{\text{mol OH}^-} = \frac{0.4250\text{ g maleic acid}}{34.03\text{ mL base} \times \frac{1\text{L}}{1000\text{ mL}} \times \frac{0.2152\text{ mol KOH}}{1\text{L base}}} = 58.03\text{ g/mol OH}^-$$

This means that one mole of maleic acid (116.1 g/mol) reacts with two moles of hydroxide ion. Maleic acid is a diprotic acid: $H_2C_4H_2O_4$.

(c) Maleic acid has two—COOH groups joined together by a bridging C_2H_2 group. A plausible Lewis structure is shown below:



$$\text{H—}\overline{\underline{\text{O}}}\text{—}\overset{\overset{|\text{O}|}{\|}}{\text{C}}\text{—}\overset{\overset{\text{H}}{|}}{\text{C}}\text{=}\overset{\overset{\text{H}}{|}}{\text{C}}\text{—}\overset{\overset{|\text{O}|}{\|}}{\text{C}}\text{—}\overline{\underline{\text{O}}}\text{—H}$$

(d) We first determine $\left[H_3O^+\right] = 10^{-pH} = 10^{-1.80} = 0.016\ M$ and then the initial concentration of acid.

$$\left[(CHCOOH)_2\right]_{initial} = \frac{0.215\,g}{50.00\ mL} \times \frac{1000\ mL}{1L} \times \frac{1\ mol}{116.1\ g} = 0.0370\ M$$

We use the first ionization to determine the value of K_{a_1}

Equation:	$(CHCOOH)_2\,(aq)$	$+\ H_2O(l) \rightleftharpoons$	$H(CHCOO)_2^-\,(aq)\ +$	$H_3O^+\,(aq)$
Initial:	$0.0370\,M$	–	$0\,M$	$\approx 0\ M$
Changes:	$-0.016\,M$	–	$+0.016\,M$	$+0.016\,M$
Equil:	$0.021\,M$	–	$0.016\,M$	$0.016\,M$

$$K_a = \frac{\left[H(CHCOO)_2^-\right]\left[H_3O^+\right]}{\left[(CHCOOH)_2\right]} = \frac{(0.016)(0.016)}{0.021} = 1.2\times10^{-2}$$

K_{a_2} could be determined if we had some way to measure the total concentration of all ions in solution, or if we could determine $\left[(CHCOO)_2^{\ 2-}\right] = K_{a_2}$

(e) Practically all the $\left[H_3O^+\right]$ arises from the first ionization.

Equation:	$(CHCOOH)_2\,(aq)\ +$	$H_2O(l) \rightleftharpoons$	$H(CHCOO)_2^-\,(aq)\ +$	$H_3O^+\,(aq)$
Initial:	$0.0500\,M$	–	$0\ M$	$\approx 0\ M$
Changes:	$-x\,M$	–	$+x\,M$	$+x\,M$
Equil:	$(0.0500 - x)\ M$	–	$x\,M$	$x\,M$

$$K_a = \frac{[H(CHCOO)_2^-][H_3O^+]}{[(CHCOOH)_2]} = \frac{x^2}{0.0500 - x} = 1.2\times10^{-2}$$

$$x^2 = 0.00060 - 0.012\ x \qquad x^2 + 0.012\ x - 0.00060 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.012 \pm \sqrt{0.00014 + 0.0024}}{2} = 0.019\ M = \left[H_3O^+\right]$$

$$pH = -\log(0.019) = 1.72$$

101. (D)

(a)

$$\frac{x^2}{0.00250-x} \simeq \frac{x^2}{0.00250} \simeq 4.2\times10^{-4} \qquad x_1 \simeq 0.00102$$

$$\frac{x^2}{0.00250-0.00102} = \frac{x^2}{0.00148} \simeq 4.2\times10^{-4} \qquad x_2 \simeq 0.000788$$

$$\frac{x^2}{0.00250-0.000788} = \frac{x^2}{0.00171} \simeq 4.2\times10^{-4} \qquad x_3 \simeq 0.000848$$

$$\frac{x^2}{0.00250-0.000848} = \frac{x^2}{0.00165} \simeq 4.2\times10^{-4} \qquad x_4 \simeq 0.000833$$

$$\frac{x^2}{0.00250-0.000833} = \frac{x^2}{0.00167} \simeq 4.2\times10^{-4} \qquad x_5 \simeq 0.000837$$

$$\frac{x^2}{0.00250-0.000837} = \frac{x^2}{0.00166} \simeq 4.2\times10^{-4} \qquad x_6 \simeq 0.000836$$

$x_6 \simeq 0.000836$ or $\simeq 8.4\times10^{-4}$,
which is the same as the value obtained using the quadratic equation.

(b) We organize the solution around the balanced chemical equation, as we have done before.

Equation:	$HClO_2(aq) + H_2O(l)$	$\rightleftharpoons$	$ClO_2^-(aq)$ +	$H_3O^+(aq)$
Initial:	$0.500\,M$	–	$0\,M$	$\approx 0\,M$
Changes:	$-x\,M$	–	$+x\,M$	$+x\,M$
Equil:	$x\,M$	–	$x\,M$	$x\,M$

$$K_a = \frac{[ClO_2^-][H_3O^+]}{[HClO_2]} = \frac{x^2}{0.500-x} = 1.1\times10^{-2} \approx \frac{x^2}{0.500} \qquad \text{Assuming } x \ll 0.500\text{ M},$$

$x = \sqrt{x^2} = \sqrt{0.500\times1.1\times10^{-2}} = 0.074\,M$ Not significantly smaller than 0.500 M.

Assume $x = 0.074$ $x = \sqrt{(0.500-0.0774)\times1.1\times10^{-2}} = 0.068\,M$ Try once more.

Assume $x = 0.068$ $x = \sqrt{(0.500-0.068)\times1.1\times10^{-2}} = 0.069\,M$ One more time.

Assume $x = 0.069$ $x = \sqrt{(0.500-0.069)\times1.1\times10^{-2}} = 0.069\,M$ Final result!

$[H_3O^+] = 0.069$ M, $\text{pH} = -\log[H_3O^+] = -\log(0.069) = 1.16$

102. **(D)**

(a) Here, two equilibria must be satisfied simultaneously. The common variable, $\left[H_3O^+\right] = z$.

Equation:	$HC_2H_3O_2(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$C_2H_3O_2^-(aq)$	+	$H_3O^+(aq)$
Initial:	0.315 M	–		0 M		≈ 0 M
Changes:	$+x$ M	–		$+x$ M		$+z$ M
Equil:	$(0.315-x)$ M	–		x M		z M

$$K_a = \frac{\left[H_3O^+\right]\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = \frac{xz}{0.315-x} = 1.8\times10^{-5}$$

Equation:	$HCHO_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CHO_2^-(aq)$	+	$H_3O^+(aq)$
Initial:	0.250 M		–		0 M		0 M
Changes:	$-y$ M		–		$+y$ M		$+z$ M
Equil:	$(0.250-y)$ M		–		y M		z M

$$K_a = \frac{\left[H_3O^+\right]\left[CHO_2^-\right]}{\left[HCHO_2\right]} = \frac{yz}{0.250-y} = 1.8\times10^{-4}$$

In this system, there are three variables, $x = \left[C_2H_3O_2^-\right], y = \left[CHO_2^-\right]$, and $z = \left[H_3O^+\right]$. These three variables also represent the concentrations of the only charged species in the reaction, and thus $x + y = z$. We solve the two K_a expressions for x and y. (Before we do so, however, we take advantage of the fact that x and y are quite small: $x << 0.315$ and $y << 0.250$.) Then we substitute these results into the expression for z, and solve to obtain a value of that variable.

$$xz = 1.8\times10^{-5}(0.315) = 5.7\times10^{-6} \qquad yz = 1.8\times10^{-4}(0.250) = 4.5\times10^{-5}$$

$$x = \frac{5.7\times10^{-6}}{z} \qquad y = \frac{4.5\times10^{-5}}{z}$$

$$z = x + y = \frac{5.7\times10^{-6}}{z} + \frac{4.5\times10^{-5}}{z} = \frac{5.07\times10^{-5}}{z} \qquad z = \sqrt{5.07\times10^{-5}} = 7.1\times10^{-3}\text{M} = [H_3O^+]$$

$\text{pH} = -\log\left(7.1\times10^{-3}\right) = 2.15$ We see that our assumptions about the sizes of x and y must be valid, since each of them is smaller than z. (Remember that $x + y = z$.)

(b) We first determine the initial concentration of each solute.

$$\left[NH_3\right] = \frac{12.5\text{g } NH_2}{0.375\text{L soln}} \times \frac{1 \text{ mol } NH_3}{17.03\text{g } NH_3} = 1.96\text{M} \qquad K_b = 1.8\times10^{-5}$$

$$\left[CH_3NH_2\right] = \frac{1.55 \text{ g } CH_3NH_2}{0.375\text{L soln}} \times \frac{1 \text{ mol } CH_3NH_2}{31.06 \text{ g } CH_3NH_2} = 0.133\text{M} \qquad K_b = 4.2\times10^{-4}$$

Now we solve simultaneously two equilibria, which have a common variable, $\left[OH^-\right] = z$.

Equation:	$NH_3(aq)$	+	H_2O	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	1.96 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+z$ M
Equil:	$(1.96-x)$ M		–		x M		z M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5} = \frac{xz}{1.96-x} \approx \frac{xz}{1.96}$$

Eqn:	$CH_3NH_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$	+	$OH^-(aq)$
Initial:	0.133 M		–		0 M		≈ 0 M
Changes:	$-y$ M		–		$+y$ M		$+z$ M
Equil:	$(0.133-y)$ M		–		y M		z M

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.2\times10^{-4} = \frac{yz}{0.133-y} = \frac{yz}{0.133}$$

In this system, there are three variables, $x = [NH_4^+], y = [CH_3NH_3^+]$, and $z = [OH^-]$. These three variables also represent the concentrations of the only charged species in solution in substantial concentration, and thus $x + y = z$. We solve the two K_b expressions for x and y. Then we substitute these results into the expression for z, and solve to obtain the value of that variable.

$$xz = 1.96\times1.8\times10^{-5} = 3.53\times10^{-5} \qquad yz = 0.133\times4.2\times10^{-5} = 5.59\times10^{-5}$$

$$x = \frac{3.53\times10^{-5}}{z} \qquad y = \frac{5.59\times10^{-5}}{z}$$

$$z = x + y = \frac{3.53\times10^{-5}}{z} + \frac{5.59\times10^{-5}}{z} = \frac{9.12\times10^{-5}}{z} \qquad z^2 = 9.12\times10^{-5}$$

$$z = 9.5\times10^{-3}\,\text{M} = [OH^-] \quad pOH = -\log(9.5\times10^{-3}) = 2.02 \quad pH = 14.00 - 2.02 = 11.98$$

We see that our assumptions about x and y (that $x << 1.96$ M and $y << 0.133$ M) must be valid, since each of them is smaller than z. (Remember that $x + y = z$.)

(c) In 1.0 M NH_4CN there are the following species: $NH_4^+(aq), NH_3(aq), CN^-(aq)$, HCN(aq), $H_3O^+(aq)$, and $OH^-(aq)$. These species are related by the following six equations.

$$(1)\ K_w = 1.0\times10^{-14} = [H_3O^+][OH^-] \qquad [OH^-] = \frac{1.0\times10^{-14}}{[H_3O^+]}$$

$$(2)\ K_a = 6.2\times10^{-10} = \frac{[H_3O^+][CN^-]}{[HCN]} \qquad (3)\ K_b = 1.8\times10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$(4)\ \left[\mathrm{NH_3}\right]+\left[\mathrm{NH_4}^+\right]=1.0\ \mathrm{M} \qquad \left[\mathrm{NH_3}\right]=1.0-\left[\mathrm{NH_4}^+\right]$$

$$(5)\ \left[\mathrm{HCN}\right]+\left[\mathrm{CN}^-\right]=1.0\ \mathrm{M} \qquad \left[\mathrm{HCN}\right]=1.0-\left[\mathrm{CN}^-\right]$$

$$(6)\ \left[\mathrm{NH_4}^+\right]+\left[\mathrm{H_3O}^+\right]=\left[\mathrm{CN}^-\right]+\left[\mathrm{OH}^-\right]\ \text{or}\left[\mathrm{NH_4}^+\right]\approx\left[\mathrm{CN}^-\right]$$

Equation (6) is the result of charge balance, that there must be the same quantity of positive and negative charge in the solution. The approximation is the result of remembering that not much $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$ will be formed as the result of hydrolysis of ions. Substitute equation (4) into equation (3), and equation (5) into equation (2).

$$(3')K_\mathrm{b}=1.8\times10^{-5}=\frac{\left[\mathrm{NH_4}^+\right]\left[\mathrm{OH}^-\right]}{1.0-\left[\mathrm{NH_4}^+\right]} \qquad (2')K_\mathrm{a}=4.0\times10^{-10}=\frac{\left[\mathrm{H_3O}^+\right]\left[\mathrm{CN}^-\right]}{1.0-\left[\mathrm{CN}^-\right]}$$

Now substitute equation (6) into equation $(2')$, and equation (1) into equation $(3')$.

$$(2'')K_\mathrm{a}=6.2\times10^{-10}=\frac{\left[\mathrm{H_3O}^+\right]\left[\mathrm{NH_4}^+\right]}{1.0-\left[\mathrm{NH_4}^+\right]} \qquad (3'')\frac{1.8\times10^{-5}}{1.0\times10^{-14}}=\frac{\left[\mathrm{NH_4}^+\right]}{\left[\mathrm{H_3O}^+\right]\left(1.0-\left[\mathrm{NH_4}^+\right]\right)}$$

Now we solve both of these equations for $\left[\mathrm{NH_4}^+\right]$.

$$('2):6.2\times10^{-10}-6.2\times10^{-10}\left[\mathrm{NH_4}^+\right]=\left[\mathrm{H_3O}^+\right]\left[\mathrm{NH_4}^+\right] \qquad \left[\mathrm{NH_4}^+\right]=\frac{6.2\times10^{-10}}{6.2\times10^{-10}+\left[\mathrm{H_3O}^+\right]}$$

$$('3):1.8\times10^{9}\left[\mathrm{H_3O}^+\right]-1.8\times10^{9}\left[\mathrm{H_3O}^+\right]\left[\mathrm{NH_4}^+\right]=\left[\mathrm{NH_4}^+\right] \qquad \left[\mathrm{NH_4}^+\right]=\frac{1.8\times10^{9}\left[\mathrm{H_3O}^+\right]}{1.00+1.8\times10^{9}\left[\mathrm{H_3O}^+\right]}$$

We equate the two results and solve for

$$\left[\mathrm{H_3O}^+\right].\frac{6.2\times10^{-10}}{6.2\times10^{-10}+\left[\mathrm{H_3O}^+\right]}=\frac{1.8\times10^{9}\left[\mathrm{H_3O}^+\right]}{1.00+1.8\times10^{9}\left[\mathrm{H_3O}^+\right]}$$

$$6.2\times10^{-10}+1.1\left[\mathrm{H_3O}^+\right]=1.1\left[\mathrm{H_3O}^+\right]+1.8\times10^{9}\left[\mathrm{H_3O}^+\right]^2 \qquad 6.2\times10^{-10}=1.8\times10^{9}\left[\mathrm{H_3O}^+\right]^2$$

$$\left[\mathrm{H_3O}^+\right]=\sqrt{\frac{6.2\times10^{-10}}{1.8\times10^{9}}}=5.9\times10^{-10}\,\mathrm{M} \quad \mathrm{pH}=-\log\left(5.9\times10^{-10}\right)=9.23$$

Note that $\left[\mathrm{H_3O}^+\right]=\sqrt{\dfrac{K_\mathrm{a}\times K_\mathrm{w}}{K_\mathrm{b}}}$ or $\mathrm{pH}=0.500\ (\mathrm{p}K_\mathrm{a}+\mathrm{p}K_\mathrm{w}-\mathrm{p}K_\mathrm{b})$

SELF-ASSESSMENT EXERCISES

103. (E)

(a) K_W: Dissociation constant of water, which is defined as $[H_3O^+][OH^-]$

(b) pH: A logarithmic scale of expressing acidity of a solution (H_3O^+); it is defined as -log $[H_3O^+]$

(c) pKa: A logarithmic scale expressing the strength of an acid (which is how much an acid dissociates in water at equilibrium); it is defined as –log K_a

(d) Hydrolysis: A reaction involving ionization of water

(e) Lewis acid: A compound or species that accepts electrons

104. (E)

(a) Conjugate base: A base that is derived by removing an abstractable proton from the acid

(b) Percent ionization of acid/base: The ratio between the conjugate of the acid or base under study and the acid/base itself times 100

(c) Self-ionization: A reaction involving ionization of two molecules of water to give $[H_3O^+]$ and $[OH^-]$

(d) Amphiprotic behavior: A substance acting as either an acid or a base

105. (E)

(a) Brønstead–Lowry acid and base: A Brønsted–Lowry acid is a substance that when placed in water will cause the formation of hydronium ion by donating a proton to water. The base is one that abstracts a proton from water and results in a hydroxyl ion.

(b) $[H_3O^+]$ and pH: $[H_3O^+]$ is the molar concentration of hydronium ion in water, whereas pH is the –log $[H_3O^+]$

(c) K_a for NH_4^+ and K_b for NH_3: K_b of NH_3 is the equilibrium constant for hydrolysis of water with NH_3 to generate NH_4^+ and OH^-. K_a of NH_4^+ is for deprotonation of NH_4^+ with water to give NH_3 and OH^-.

(d) Leveling effect and electron-withdrawing effect: The leveling effect is the result of reaction of water with any acid or base such that no acid or base can exist in water that are more acidic than H_3O^+ or more basic than OH^-. The electron-withdrawing effect is the tendency for a central atom with high electronegativity in an oxoacid to withdraw electrons from the O–H bond.

106. (E) The answer is (a), HCO_3^-, because it can donate a proton to water to become CO_3^{2-}, or it can be protonated to give H_2CO_3 (i.e., $CO_2(aq)$).

107. (E) The answer is (c). CH_3CH_2COOH is a weak acid, so the concentration of H_3O^+ ions it will generate upon dissociation in water will be significantly less than 0.1 M. Therefore, its pH will be higher the 0.10 M HBr, which dissociates completely in water to give 0.10 M H_3O^+.

108. (E) The answer is (d). CH_3NH_2 is a weak base.

109. **(M)** The answer is (e) because CO_3^{2-} is the strongest base and it drives the dissociation of acetic acid furthest.

110. **(M)** The answer is (c). H_2SO_4 dissociation is nearly complete for the first proton, giving a $[H_3O^+] = 0.10$ M (pH = 1). The second dissociation is not complete. Therefore, (c) is the only choice that makes sense.

111. **(M)** The answer is (b). You can write down the stepwise equations for dissociation of H_2SO_3 and then the dissociation of HSO_3^- and calculate the equilibrium concentration of each species. However, you can determine the answer without detailed calculations. The two dissociation equations are given below:

Eq.1 $H_2SO_3 + H_2O \rightleftharpoons HSO_3^- + H_3O^+$ $K_{a1} = 1.3\times10^{-2}$

Eq.2 $HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$ $K_{a2} = 6.3\times10^{-8}$

For the first equation, the equilibrium concentrations, of HSO_3^- and H_3O^+ are the same. They become the initial concentration values for the second dissociation reaction. Since K_{a2} is 6.3×10^{-8} (which is small), the equilibrium concentrations of HSO_3^- and H_3O^+ won't change significantly. So, the equation simplifies as follows:

$$K_{a2} = 6.8\times10^{-8} = \frac{\left[SO_3^{2-}\right]\left(\left[H_3O^+\right]+\cancel{x}\right)}{\left[HSO_3^-\right]-\cancel{x}} = \frac{\left[SO_3^{2-}\right]\cancel{\left[H_3O^+\right]}}{\cancel{\left[HSO_3^-\right]}}$$

$$K_{a2}=6.8\times10^{-8} = \left[SO_3^{2-}\right]$$

112. **(E)** Since both the acid and the base in this reaction are strong, they dissociate completely. The pH is determined as follows:

mol H_3O^+: 0.248 M HNO_3 × 0.02480 L = 0.00615 mol
mol OH^-: 0.394 M KOH × 0.01540 L = 0.00607 mol

Final: 0.00615 – 0.00607 = 8.00×10^{-5} mol H_3O^+

$$\left[H_3O^+\right] = \frac{8.00\times10^{-5}\,\text{mol}}{(0.02480\text{ L} + 0.01540\text{ L})} = 0.00200\text{ M}$$

$$\text{pH} = -\log(0.00200) = 2.70$$

113. **(M)** Since pH = 3.25, the $[H_3O^+] = 10^{-3.25} = 5.62\times10^{-4}$ M. Using the reaction below, we can determine the equilibrium concentrations of other species

	$HC_2H_3O_2$	+	H_2O	$\rightleftharpoons$	$C_2H_3O_2^-$	+	H_3O^+
Initial	C				0		0
Change	$-x$				$+x$		$+x$
Equil.	$C - x$				x		x

Since x = 5.62×10^{-4} M, the equilibrium expression becomes

$$K_a = \frac{\left[H_3O^+\right]\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = \frac{\left(5.62\times10^{-4}\,M\right)\left(5.62\times10^{-4}\,M\right)}{\left(C-5.62\times10^{-4}\,M\right)} = 1.8\times10^{-5}$$

Solving C gives a concentration of 0.0181 M.

Since concentrated acetic acid is 35% by weight and the density is 1.044 g/mL, the concentration of acetic acid is:

$$\frac{35\text{ g HAc}}{100\text{ g Conc. HAc sol'n}}\times\frac{1.044\text{ g Conc. HAc}}{0.001\text{ L sol'n}}\times\frac{1\text{ mol HAc}}{60.06\text{ g HAc}} = 6.084\text{ M HAc}$$

Therefore, volume of concentrated solution required to make 12.5 L of 0.0181 M HAc solution is:

$$\left(M\cdot V\right)_{\text{dilute}} = \left(M\cdot V\right)_{\text{conc.}}$$

$$V_{\text{conc}} = \frac{\left(0.0181\text{ M}\right)\left(12500\text{ mL}\right)}{6.084\text{ M}} = 37.2\text{ mL}$$

114. **(M)** Table 16.3 has the K_a value for chloroacetic acid, $HC_2H_2ClO_2$. $K_a = 1.4\times10^{-3}$. The solution is made of the chloroacetate salt, which hydrolyzes water according to the following reaction:

	$C_2H_2ClO_2^-$	+	H_2O	$\rightleftharpoons$	$HC_2H_2ClO_2$	+	OH^-
Initial	2.05				0		0
Change	$-x$				$+x$		$+x$
Equil.	$2.05-x$				x		x

$$K_b = \frac{K_W}{K_a} = \frac{1.0\times10^{-14}}{1.4\times10^{-3}} = 7.14\times10^{-12}$$

$$K_b = \frac{\left[HC_2H_2ClO_2\right]\left[OH^-\right]}{\left[C_2H_2ClO_2^-\right]}$$

$$7.14\times10^{-12} = \frac{x\cdot x}{2.05-\cancel{x}}$$

Solving the above simplified expression for x, we get x = $\left[OH^-\right]=3.826\times10^{-6}$

$$pH=14-pOH=14-\left[-\log\left(3.826\times10^{-6}\right)\right]=8.58$$

<u>115.</u> **(M)** 0.10 M HI < 0.05 M H_2SO_4 < 0.05 M $HC_2H_2ClO_2$ < 0.50 M $HC_2H_3O_2$ < 0.50 M NH_4Cl < 1.0 M NaBr < 0.05 M $KC_2H_3O_2$ < 0.05 M NH_3 < 0.06 M NaOH < 0.05 M $Ba(OH)_2$

<u>116.</u> **(M)** Since pH = 5 pOH, pH must be significantly larger than pOH, which means that the solution is basic. The pH can be determined by solving two simultaneous equations:

$$\text{pH} - 5\ \text{pOH} = 0$$

$$\text{pH} + \text{pOH} = 14$$

pOH = 2.333
pH = 14 – 2.33 = 11.67.
Therefore, $[H_3O^+] = 2.14\times10^{-12}$ M (and $[OH^-] = 4.67\times10^{-3}$ M)

The solute must be NH_3, because it is the only basic species (the other two are acidic and neutral, respectively). Since the K_b of NH_3 is 1.8×10^{-5}, the concentration of NH_3 can be determined as follows:

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} = \frac{(4.67\times10^{-3})(4.67\times10^{-3})}{x} = 1.8\times10^{-5}$$

x = 1.2 M

<u>117.</u> **(M)** The answer is (a). If $HC_3H_5O_2$ is 0.42% ionized for a 0.80 M solution, then the concentration of the acid at equilibrium is (0.80×0.0042) = 0.00336. The equilibrium expression for the dissociation of $HC_3H_5O_2$ is:

$$K_a = \frac{[H_3O^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{(0.00336)(0.00336)}{(0.800 - 0.00336)} = 1.42\times10^{-5}$$

<u>118.</u> **(E)** The answer is (b), because $H_2PO_4^-$ is a result of addition of one proton to the base HPO_4^{2-}.

<u>119.</u> **(M)** The answer is (d). This is because, in the second equation, HNO_2 will give its proton to ClO^- (rather than HClO giving its proton to NO_2^-), which means that HNO_2 is a stronger acid than HClO. Also, in the first equation, ClO^- is not a strong enough base to abstract a proton from water, which means that HClO is in turn a stronger acid than H_2O.

<u>120.</u> **(M)** The dominant species in the solution is ClO_2^-. Therefore, determine its concentration and ionization constant first:

$$[ClO_2^-] = \frac{3.00\text{ mol CaClO}_2}{2.50\text{ L}} \times \frac{2\text{ mol ClO}_2^-}{1\text{ mol CaClO}_2} = 2.40\text{ M}$$

$$K_b = \frac{K_W}{K_a} = \frac{1.0\times10^{-14}}{1.1\times10^{-2}} = 9.1\times10^{-13}$$

The reaction and the dissociation of ClO_2^- is as follows:

	ClO_2^-	+	H_2O	$\rightleftharpoons$	$HClO_2$	+	OH^-
Initial	2.40				0		0
Change	-x				+x		+x
Equil.	2.40 – x				x		x

$$K_b = \frac{\left[HClO_2\right]\left[OH^-\right]}{\left[ClO_2^-\right]}$$

$$9.1\times10^{-13} = \frac{x \cdot x}{2.40 - \cancel{x}}$$

Solving the above simplified expression for x, we get x = $\left[OH^-\right]=1.478\times10^{-6}$.

$$pH=14-pOH=14-\left[-\log\left(1.478\times10^{-6}\right)\right]=8.2$$

121. **(M)** Section 16-8 discusses the effects of structure on acid/base behavior. The major subtopics are effects of structure on binary acids, oxo acids, organic acids, and amine bases. For binary acids, acidity can be discussed in terms of electronegativity of the main atom, bond length, and heterolytic bond dissociation energy. For oxo acids, the main things affecting acidity are the electronegativity of the central atom and number of oxygen atoms surrounding the central atom. For organic acids, the main topic is the electron-withdrawing capability of constituent groups attached to the carboxyl unit. For amines, the basicity is discussed in terms of electron withdrawing or donating groups attached to the nitrogen in the amine, and the number of resonance structures possible for the base molecule.

CHAPTER 17

ADDITIONAL ASPECTS OF ACID–BASE EQUILIBRIA

PRACTICE EXAMPLES

1A **(D)** Organize the solution around the balanced chemical equation, as we have done before.

Equation:	$HF(aq)$	$+\ H_2O(l)\ \rightleftharpoons$	$H_3O^+(aq)$	$+\ F^-(aq)$
Initial:	$0.500\,M$	$-$	$\approx 0\,M$	$0\,M$
Changes:	$-x\,M$	$-$	$+x\,M$	$+x\,M$
Equil:	$(0.500-x)\,M$	$-$	$x\,M$	$x\,M$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)\,(x)}{0.500-x} = 6.6\times10^{-4} \approx \frac{x^2}{0.500} \qquad \text{assuming } x \ll 0.500$$

$$x = \sqrt{0.500\times6.6\times10^{-4}} = 0.018\,M \qquad \text{One further cycle of approximations gives:}$$

$$x = \sqrt{(0.500-0.018)\times6.6\times10^{-4}} = 0.018\,M = [H_3O^+]$$

Thus, $[HF] = 0.500\,M - 0.018\,M = 0.482\,M$

Recognize that 0.100 M HCl means $\left[H_3O^+\right]_{\text{initial}} = 0.100\,M$, since HCl is a strong acid.

Equation:	$HF(aq)$	$+\ H_2O(l)\ \rightleftharpoons$	$H_3O^+(aq)$	$+\ F^-(aq)$
Initial:	$0.500\,M$	$-$	$0.100\,M$	$0\,M$
Changes:	$-x\,M$	$-$	$+x\,M$	$+x\,M$
Equil:	$(0.500-x)\,M$	$-$	$(0.100+x)\,M$	$x\,M$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.100+x)}{0.500-x} = 6.6\times10^{-4} \approx \frac{0.100\,x}{0.500} \quad \text{assuming } x \ll 0.100$$

$$x = \frac{6.6\times10^{-4}\times0.500}{0.100} = 3.3\times10^{-3}\ M = \left[F^-\right] \qquad \text{The assumption is valid.}$$

$\left[HF\right] = 0.500\,M - 0.003\,M = 0.497\,M$

$[H_3O^+] = 0.100\ M + x = 0.100\ M + 0.003\ M = 0.103\ M$

1B **(M)** From Example 17-6 *in the text*, we know that $[H_3O^+] = [C_2H_3O_2^-] = 1.3\times10^{-3}$ M in 0.100 M $HC_2H_3O_2$. We base our calculation, as usual, on the balanced chemical equation. The concentration of H_3O^+ from the added HCl is represented by *x*.

Equation:	$HC_2H_3O_2(aq)$ +	$H_2O(l) \rightleftharpoons$	$H_3O^+(aq)$ +	$C_2H_3O_2^-(aq)$
Initial:	$0.100\,M$	–	$\approx 0\,M$	$0\,M$
Changes:	$-0.00010\,M$	–	$+0.00010\,M$	$+0.00010\,M$
From HCl:			$+x\ M$	
Equil:	$0.100\ M$	–	$(0.00010 + x)\,M$	$0.00010\,M$

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(0.00010 + x)\,0.00010}{0.100} = 1.8\times10^{-5}$$

$$0.00010 + x = \frac{1.8\times10^{-5}\times0.100}{0.00010} = 0.018\,M \qquad x = 0.018\ M - 0.00010\,M = 0.018\,M$$

$$V_{12\ M\ HCl} = 1.00\,L\times\frac{0.018\ mol\ H_3O^+}{1L}\times\frac{1\,mol\,HCl}{1\,mol\,H_3O^+}\times\frac{1\ L\,soln}{12\ mol\ HCl}\times\frac{1000\ mL}{1L}\times\frac{1\ drop}{0.050\ mL} = 30.\,drops$$

Since 30. drops corresponds to 1.5 mL of 12 M solution, we see that the volume of solution does indeed remain approximately 1.00 L after addition of the 12 M HCl.

2A **(M)** We again organize the solution around the balanced chemical equation.

Equation:	$HCHO_2(aq)$ +	$H_2O(l) \rightleftharpoons$	$CHO_2^-(aq)$ +	$H_3O^+(aq)$
Initial:	$0.100\,M$	–	$0.150\,M$	$\approx 0\,M$
Changes:	$-x\,M$	–	$+x\,M$	$+x\,M$
Equil:	$(0.100 - x)\,M$	–	$(0.150 + x)\ M$	$x\,M$

$$K_a = \frac{[CHO_2^-][H_3O^+]}{[HCHO_2]} = \frac{(0.150 + x)(x)}{0.100 - x} = 1.8\times10^{-4} \approx \frac{0.150\,x}{0.100} \qquad \text{assuming } x \ll 0.100$$

$$x = \frac{0.100\times1.8\times10^{-4}}{0.150} = 1.2\times10^{-4}\,M = \left[H_3O^+\right],\ x << 0.100, \text{ thus our assumption is valid}$$

$$\left[CHO_2^-\right] = 0.150\ M + 0.00012\ M = 0.150\,M$$

2B **(M)** This time, a solid sample of a weak base is being added to a solution of its conjugate acid. We let x represent the concentration of acetate ion from the added sodium acetate. Notice that sodium acetate is a strong electrolyte, thus, it completely dissociates in aqueous solution. $\left[H_3O^+\right] = 10^{-pH} = 10^{-5.00} = 1.0 \times 10^{-5}\,M = 0.000010\ M$

Equation:	$HC_2H_3O_2(aq)$	$+\ H_2O(l) \rightleftharpoons$	$C_2H_3O_2^-(aq)$	$+\ H_3O^+(aq)$
Initial:	$0.100\ M$	$-$	$0\,M$	$\approx 0\,M$
Changes:	$-0.000010\ M$	$-$	$+0.000010\,M$	$+0.000010\,M$
From NaAc:			$+x\,M$	
Equil:	$0.100\,M$	$-$	$(0.000010 + x)\,M$	$0.000010\,M$

$$K_a = \frac{\left[H_3O^+\right]\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = \frac{0.000010\left(0.000010 + x\right)}{0.100} = 1.8 \times 10^{-5}$$

$$0.000010 + x = \frac{1.8 \times 10^{-5} \times 0.100}{0.000010} = 0.18\ M \qquad x = 0.18\ M - 0.000010\ M = 0.18\ M$$

$$\text{mass of } NaC_2H_3O_2 = 1.00\,L \times \frac{0.18\ mol\ C_2H_3O_2^-}{1L} \times \frac{1mol\ NaC_2H_3O_2}{1mol\ C_2H_3O_2^-} \times \frac{82.03\,g\ NaC_2H_3O_2}{1mol\ NaC_2H_3O_2}$$
$$= 15\,g\ NaC_2H_3O_2$$

3A **(M)** A strong acid dissociates essentially completely, and effectively is a source of H_3O^+. $NaC_2H_3O_2$ also dissociates completely in solution. The hydronium ion and the acetate ion react to form acetic acid: $H_3O^+(aq) + C_2H_3O_2^-(aq) \rightleftharpoons HC_2H_3O_2(aq) + H_2O(l)$

All that is necessary to form a buffer is to have approximately equal amounts of a weak acid and its conjugate base together in solution. This will be achieved if we add an amount of HCl equal to approximately half the original amount of acetate ion.

3B **(M)** HCl dissociates essentially completely in water and serves as a source of hydronium ion. This reacts with ammonia to form ammonium ion:

$NH_3(aq) + H_3O^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l)$.

Because a buffer contains approximately equal amounts of a weak base (NH_3) and its conjugate acid (NH_4^+), to prepare a buffer we simply add an amount of HCl equal to approximately half the amount of $NH_3(aq)$ initially present.

4A **(M)** We first find the formate ion concentration, remembering that $NaCHO_2$ is a strong electrolyte, existing in solution as $Na^+(aq)$ and $CHO_2^-(aq)$.

$$[CHO_2^-] = \frac{23.1\text{g } NaCHO_2}{500.0 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1\text{L}} \times \frac{1 \text{ mol } NaCHO_2}{68.01\text{g } NaCHO_2} \times \frac{1 \text{ mol } CHO_2^-}{1 \text{ mol } NaCHO_2} = 0.679\,\text{M}$$

As usual, the solution to the problem is organized around the balanced chemical equation.

Equation:	$HCHO_2(aq)$	$+ H_2O(l) \rightleftharpoons$	$CHO_2^-(aq)$	$+ H_3O^+(aq)$
Initial:	$0.432\,\text{M}$	–	$0.679\,\text{M}$	$\approx 0\,\text{M}$
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.432-x)$ M	–	$(0.679+x)$ M	x M

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = \frac{x(0.679+x)}{0.432-x} = 1.8\times10^{-4} \approx \frac{0.679x}{0.432} \qquad x = \frac{0.432\times1.8\times10^{-4}}{0.679}$$

This gives $[H_3O^+] = 1.14\times10^{-4}$ M. The assumption that $x \ll 0.432$ is clearly correct.

$$\text{pH} = -\log[H_3O^+] = -\log(1.14\times10^{-4}) = 3.94 \approx 3.9$$

4B **(M)** The concentrations of the components in the 100.0 mL of buffer solution are found via the dilution factor. Remember that $NaC_2H_3O_2$ is a strong electrolyte, existing in solution as

$Na^+(aq)$ and $C_2H_3O_2^-(aq)$.

$$[HC_2H_3O_2] = 0.200 \text{ M} \times \frac{63.0 \text{ mL}}{100.0 \text{ mL}} = 0.126 \text{ M} \quad [C_2H_3O_2^-] = 0.200 \text{ M} \times \frac{37.0\,\text{mL}}{100.0\,\text{mL}} = 0.0740\,\text{M}$$

As usual, the solution to the problem is organized around the balanced chemical equation.

Equation:	$HC_2H_3O_2(aq)$	$+ H_2O(l) \rightleftharpoons$	$C_2H_3O_2^-(aq)$	$+ H_3O^+(aq)$
Initial:	0.126 M	–	0.0740 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.126-x)$ M	–	$(0.0740+x)$ M	x M

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x(0.0740+x)}{0.126-x} = 1.8\times10^{-5} \approx \frac{0.0740\,x}{0.126}$$

$$x = \frac{1.8\times10^{-5}\times0.126}{0.0740} = 3.1\times10^{-5}\text{M} = [H_3O^+]; \;\; \text{pH} = -\log\,[H_3O^+] = -\log\,3.1\times10^{-5} = 4.51$$

Note that the assumption is valid: $x \ll 0.0740 < 0.126$.
Thus, x is neglected when added or subtracted

<u>**5A**</u> **(M)** We know the initial concentration of NH_3 in the buffer solution and can use the pH to find the equilibrium [OH$^-$]. The rest of the solution is organized around the balanced chemical equation. Our first goal is to determine the initial concentration of NH_4^+.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.00 = 5.00 \qquad [\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.00} = 1.0 \times 10^{-5}\ \text{M}$$

Equation:	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	0.35 M		–		x M		≈ 0 M
Changes:	-1.0×10^{-5} M		–		$+1.0\times10^{-5}$ M		$+1.0\times10^{-5}$ M
Equil:	$(0.35-1.0\times10^{-5})$ M		–		$(x+1.0\times10^{-5})$ M		1.0×10^{-5} M

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8\times10^{-5} = \frac{(x+1.0\times10^{-5})(1.0\times10^{-5})}{0.35-1.0\times10^{-5}} = \frac{1.0\times10^{-5}\times x}{0.35}$$

$$\text{Assume } x \gg 1.0\times10^{-5} \quad x = \frac{0.35\times1.8\times10^{-5}}{1.0\times10^{-5}} = 0.63\ \text{M} = \text{initial NH}_4^+ \text{ concentration}$$

$$\text{mass}\left(\text{NH}_4\right)_2\text{SO}_4 = 0.500\,\text{L}\times\frac{0.63\ \text{mol NH}_4^+}{1\ \text{L soln}}\times\frac{1\ \text{mol}\left(\text{NH}_4\right)_2\text{SO}_4}{2\ \text{mol NH}_4^+}\times\frac{132.1\ \text{g}\left(\text{NH}_4\right)_2\text{SO}_4}{1\ \text{mol}\left(\text{NH}_4\right)_2\text{SO}_4}$$

Mass of $(NH_4)_2SO_4$ = 21 g

<u>**5B**</u> **(M)** The solution is composed of 33.05 g $NaC_2H_3O_2 \cdot 3\,H_2O$ dissolved in 300.0 mL of 0.250 M HCl. $NaC_2H_3O_2 \cdot 3\,H_2O$, a strong electrolyte, exists in solution as Na^+(aq) and $C_2H_3O_2^-$(aq) ions. First we calculate the number of moles of $NaC_2H_3O_2 \cdot 3\,H_2O$, which, based on the 1:1 stoichiometry, is also equal to the number of moles of C_2HO^- that are released into solution. From this we can calculate the initial [$C_2H_3O_2^-$] assuming the solution's volume remains at 300. mL.

moles of $NaC_2H_3O_2 \cdot 3\,H_2O$ (and moles of $C_2H_3O_2^-$)

$$= \frac{33.05\ \text{g NaC}_2\text{H}_3\text{O}_2 \bullet 3\text{H}_2\text{O}}{\dfrac{1\ \text{mole NaC}_2\text{H}_3\text{O}_2 \bullet 3\text{H}_2\text{O}}{136.08\ \text{g NaC}_2\text{H}_3\text{O}_2 \bullet 3\text{H}_2\text{O}}} = 0.243\,\text{moles NaC}_2\text{H}_3\text{O}_2 \bullet 3\text{H}_2\text{O} = \text{moles C}_2\text{H}_3\text{O}_2^-$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{0.243\ \text{mol C}_2\text{H}_3\text{O}_2^-}{0.300\ \text{L soln}} = 0.810\,M$$

(Note: [HCl] is assumed to remain unchanged at 0.250 M)

We organize this information around the balanced chemical equation, as before. We recognize that virtually all of the HCl has been hydrolyzed and that hydronium ion will react to produce the much weaker acetic acid.

Equation:	$HC_2H_3O_2(aq) + H_2O(l)$	$\rightleftharpoons$	$C_2H_3O_2^-(aq)$	+	$H_3O^+(aq)$
Initial:	0 M	–	0.810 M		0.250 M
Form HAc:	+0.250 M	–	–0.250 M		–0.250 M
	0.250 M	–	0.560 M		≈ 0 M
Changes:	$-x$ M	–	$+x$ M		$+x$ M
Equil:	$(0.250-x)$ M	–	$(0.560+x)$ M		$+x$ M

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x(0.560+x)}{0.250-x} = 1.8\times10^{-5} \approx \frac{0.560\,x}{0.250}$$

$$x = \frac{1.8\times10^{-5}\times0.250}{0.560} = 8.0\times10^{-6}\ \text{M} = [H_3O^+]$$

(The approximation was valid since $x \ll$ both 0.250 and 0.560)

$$\text{pH} = -\log\,[H_3O^+] = -\log\,8.0\times10^{-6} = 5.09 \approx 5.1$$

6A **(D)**

(a) For formic acid, $\text{p}K_a = -\log(1.8\times10^{-4}) = 3.74.$ The Henderson-Hasselbalch equation provides the pH of the original buffer solution:

$$\text{pH} = \text{p}K_a + \log\frac{[CHO_2^-]}{[HCHO_2]} = 3.74 + \log\frac{0.350}{0.550} = 3.54$$

(b) The added acid can be considered completely reacted with the formate ion to produce formic acid. Each mole/L of added acid consumes 1 M of formate ion and forms 1 M of formic acid: $CHO_2^-(aq) + H_3O^+(aq) \longrightarrow HCHO_2(aq) + H_2O(l)$. $K_{neut} = K_b/K_w \approx$ 5600. Thus, $\left[CHO_2^-\right] = 0.350\ \text{M} - 0.0050\ \text{M} = 0.345\ \text{M}$ and $\left[HCHO_2\right] = 0.550\ \text{M} + 0.0050\ \text{M} = 0.555\ \text{M}$. By using the Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a + \log\frac{[CHO_2^-]}{[HCHO_2]} = 3.74 + \log\frac{0.345}{0.555} = 3.53$$

(c) Added base reacts completely with formic acid producing, an equivalent amount of formate ion. This continues until all of the formic acid is consumed.
Each 1 mole of added base consumes 1 mol of formic acid and forms 1 mol of formate ion: $HCHO_2 + OH^- \longrightarrow CHO_2^- + H_2O$. $K_{neut} = K_a/K_w \approx 1.8\times10^{10}$. Thus,
$\left[CHO_2^-\right] = 0.350\,\text{M} + 0.0050\ \text{M} = 0.355\ \text{M}$
$\left[HCHO_2\right] = \left(0.550 - 0.0050\right)\text{M} = 0.545\ \text{M}$. With the Henderson-Hasselbalch equation we find $\text{pH} = \text{p}K_a + \log\dfrac{\left[CHO_2^-\right]}{\left[HCHO_2\right]} = 3.74 + \log\dfrac{0.355}{0.545} = 3.55$

6B **(D)** The buffer cited has the same concentration as weak acid and its anion, as does the buffer of Example 17-6. Our goal is to reach $\text{pH} = 5.03$ or

$\left[H_3O^+\right] = 10^{-\text{pH}} = 10^{-5.03} = 9.3\times10^{-6}\ \text{M}$. Adding strong acid $\left(H_3O^+\right)$, of course, produces $HC_2H_3O_2$ at the expense of $C_2H_3O_2^-$. Thus, adding H^+ drives the reaction to the left. Again, we use the data around the balanced chemical equation.

Equation:	$HC_2H_3O_2(\text{aq})$	$+\ H_2O(\text{l})$ $\rightleftharpoons$	$C_2H_3O_2^-(\text{aq})$	$+$	$H_3O^+(\text{aq})$
Initial:	0.250 M	–	0.560 M		8.0×10^{-6} M
Add acid:					$+y$ M
Form HAc:	$+y$ M	–	$-y$ M		$-y$ M
	$(0.250+y)$ M	–	$(0.560-y)$ M		≈ 0 M
Changes:	$-x$ M	–	$+x$ M		$+x$ M
Equil:	$(0.250+y-x)$ M	–	$(0.560-y+x)$ M		9.3×10^{-6} M

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{9.3\times10^{-6}(0.560-y+x)}{0.250+y-x} = 1.8\times10^{-5} \approx \frac{9.3\times10^{-6}(0.560-y)}{0.250+y}$$

(Assume that x is negligible compared to y)

$$\frac{1.8\times10^{-5}\times(0.250+y)}{9.3\times10^{-6}} = 0.484+1.94\ y = 0.560-y \qquad y = \frac{0.560-0.484}{1.94+1.00} = 0.026\ \text{M}$$

Notice that our assumption is valid: $x \ll 0.250+y\ (=0.276) < 0.560-y\ (=0.534)$.

$$V_{HNO_3} = 300.0\ \text{mL buffer}\times\frac{0.026\ \text{mmol}\ H_3O^+}{1\ \text{mL buffer}}\times\frac{1\ \text{mL}\ HNO_3(\text{aq})}{6.0\ \text{mmol}\ H_3O^+} = 1.3\ \text{mL of } 6.0\ \text{M}\ HNO_3$$

Instead of the algebraic solution, we could have used the Henderson-Hasselbalch equation, since the final pH falls within one pH unit of the pK_a of acetic acid. We let z indicate the increase in $\left[HC_2H_3O_2\right]$, and also the decrease in $\left[C_2H_3O_2^-\right]$

$$\text{pH} = pK_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 4.74 + \log\frac{0.560-z}{0.250+z} = 5.03 \qquad \frac{0.560-z}{0.250+z} = 10^{5.03-4.74} = 1.95$$

$$0.560 - z = 1.95\,(0.250+z) = 0.488 + 1.95\ z \qquad z = \frac{0.560-0.488}{1.95+1.00} = 0.024\ \text{M}$$

This is, and should be, almost exactly the same as the value of y we obtained by the I.C.E. table method. The slight difference is due to imprecision arising from rounding errors.

7A **(D)**

(a) The initial pH is the pH of 0.150 M HCl, which we obtain from $\left[H_3O^+\right]$ of that strong acid solution.

$$[H_3O^+] = \frac{0.150\ \text{mol HCl}}{1\ \text{L soln}}\times\frac{1\ \text{mol}\ H_3O^+}{1\ \text{mol HCl}} = 0.150\ \text{M},$$

$$\text{pH} = -\log\,[H_3O^+] = -\log\,(0.150) = 0.824$$

(b) To determine $\left[H_3O^+\right]$ and then pH at the 50.0% point, we need the volume of the solution and the amount of H_3O^+ left unreacted. First we calculate the amount of hydronium ion present and then the volume of base solution needed for its complete neutralization.

$$\text{amount } H_3O^+ = 25.00 \text{ mL} \times \frac{0.150 \text{ mmol HCl}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol } H_3O^+}{1 \text{ mmol HCl}} = 3.75 \text{ mmol } H_3O^+$$

$$V_{\text{acid}} = 3.75 \text{ mmol } H_3O^+ \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol } H_3O^+} \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol OH}^-} \times \frac{1 \text{ mL titrant}}{0.250 \text{ mmol NaOH}}$$
$$= 15.0 \text{ mL titrant}$$

At the 50.0% point, half of the H_3O^+ (1.88 mmol H_3O^+) will remain unreacted and only half (7.50 mL titrant) of the titrant solution will be added. From this information, and the original 25.00-mL volume of the solution, we calculate $\left[H_3O^+\right]$ and then pH.

$$\left[H_3O^+\right] = \frac{1.88 \text{ mmol } H_3O^+ \text{ left}}{25.00 \text{ mL original} + 7.50 \text{ mL titrant}} = 0.0578 \text{ M}$$

$$\text{pH} = -\log(0.0578) = 1.238$$

(c) Since this is the titration of a strong acid by a strong base, at the equivalence point, the $\text{pH} = 7.00$. This is because the only ions of appreciable concentration in the equivalence point solution are Na^+(aq) and Cl^-(aq), and neither of these species undergoes detectable hydrolysis reactions.

(d) Beyond the equivalence point, the solution pH is determined almost entirely by the concentration of excess OH^-(aq) ions. The volume of the solution is $40.00\,\text{mL} + 1.00\,\text{mL} = 41.00$ mL. The amount of hydroxide ion in the excess titrant is calculated and used to determine $\left[OH^-\right]$, from which pH is computed.

$$\text{amount of OH}^- = 1.00 \text{ mL} \times \frac{0.250 \text{ mmol NaOH}}{1 \text{ mL}} = 0.250 \text{ mmol OH}^-$$

$$\left[OH^-\right] = \frac{0.250 \text{ mmol OH}^-}{41.00 \text{ mL}} = 0.00609\underline{8}\,\text{M}$$

$$\text{pOH} = -\log(0.00609\underline{8}) = 2.215; \ \text{pH} = 14.00 - 2.215 = 11.785$$

<u>7B</u> **(D)**

(a) The initial pH is simply the pH of 0.00812 M $Ba(OH)_2$, which we obtain from $\left[OH^-\right]$ for the solution.

$$\left[OH^-\right] = \frac{0.00812 \text{ mol Ba(OH)}_2}{1 \text{L soln}} \times \frac{2 \text{ mol OH}^-}{1 \text{mol Ba(OH)}_2} = 0.01624\,\text{M}$$

$$\text{pOH} = -\log\left[OH^-\right] = -\log(0.0162) = 1.790; \ \text{pH} = 14.00 - \text{pOH} = 14.00 - 1.790 = 12.21$$

(b) To determine $\left[OH^-\right]$ and then pH at the 50.0% point, we need the volume of the solution and the amount of OH^- unreacted. First we calculate the amount of hydroxide ion present and then the volume of acid solution needed for its complete neutralization.

$$\text{amount } OH^- = 50.00\,\text{mL} \times \frac{0.00812\,\text{mmol Ba}(OH)_2}{1\,\text{mL soln}} \times \frac{2\,\text{mmol } OH^-}{1\,\text{mmol Ba}(OH)_2} = 0.812\,\text{mmol } OH^-$$

$$V_{\text{acid}} = 0.812\,\text{mmol } OH^- \times \frac{1\,\text{mmol } H_3O^+}{1\,\text{mmol } OH^-} \times \frac{1\,\text{mmol HCl}}{1\,\text{mmol } H_3O^+} \times \frac{1\,\text{mL titrant}}{0.0250\,\text{mmol HCl}} = 32.48\,\text{mL titrant}$$

At the 50.0 % point, half (0.406 mmol OH^-) will remain unreacted and only half (16.24 mL titrant) of the titrant solution will be added. From this information, and the original 50.00-mL volume of the solution, we calculate $\left[OH^-\right]$ and then pH.

$$\left[OH^-\right] = \frac{0.406\,\text{mmol } OH^- \text{ left}}{50.00\,\text{mL original} + 16.24\,\text{mL titrant}} = 0.00613\text{ M}$$

$$\text{pOH} = -\log(0.00613) = 2.213; \quad \text{pH} = 14.00 - \text{pOH} = 11.79$$

(c) Since this is the titration of a strong base by a strong acid, at the equivalence point,pH = 7.00. The solution at this point is neutral because the dominant ionic species in solution, namely Ba^{2+}(aq) and Cl^-(aq), do not react with water to a detectable extent.

<u>8A</u> (D)

(a) Initial pH is just that of 0.150 M HF ($pK_a = -\log(6.6 \times 10^{-4}) = 3.18$).

[Initial solution contains $20.00\text{ mL} \times \frac{0.150\,\text{mmol HF}}{1\text{ mL}}$ =3.00 mmol HF]

Equation:	HF(aq)	+ H_2O(l)	$\rightleftharpoons$ H_3O^+(aq)	+ F^-(aq)
Initial:	0.150 M	–	≈ 0 M	0 M
Changes:	– x M	–	+ x M	+ x M
Equil:	(0.150 – x) M	–	x M	x M

$$K_a = \frac{\left[H_3O^+\right]\left[F^-\right]}{[HF]} = \frac{x \cdot x}{0.150 - x} \approx \frac{x^2}{0.150} = 6.6 \times 10^{-4}$$

$$x = \sqrt{0.150 \times 6.6 \times 10^{-4}} = 9.9 \times 10^{-3}\text{ M}$$

$x > 0.05(0.150)$. The assumption is invalid. After a second cycle of approximation, $\left[H_3O^+\right] = 9.6 \times 10^{-3}\,\text{M}$; $\text{pH} = -\log(9.6 \times 10^{-3}) = 2.02$

(b) When the titration is 25.0% complete, there are (0.25×3.00=) 0.75 mmol F^- for every 3.00 mmol HF that were present initially. Therefore, (3.00-0.75=) 2.25 mmol HF remain untitrated. We designate the solution volume (the volume holding these 3.00 mmol total) as V and use the Henderson-Hasselbalch equation to find the pH.

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{F}^-]}{[\text{HF}]} = 3.18 + \log\frac{0.75\ \text{mmol}/V}{2.25\ \text{mmol}/V} = 2.70$$

(c) At the midpoint of the titration of a weak base, pH = pK_a = 3.18.

(d) At the endpoint of the titration, the pH of the solution is determined by the conjugate base hydrolysis reaction. We calculate the amount of anion and the volume of solution in order to calculate its initial concentration.

$$\text{amount F}^- = 20.00\ \text{mL} \times \frac{0.150\ \text{mmol HF}}{1\ \text{mL soln}} \times \frac{1\ \text{mmol F}^-}{1\ \text{mmol HF}} = 3.00\ \text{mmol F}^-$$

$$\text{volume titrant} = 3.00\ \text{mmol HF} \times \frac{1\text{mmol OH}^-}{1\text{mmol HF}} \times \frac{1\ \text{mL titrant}}{0.250\ \text{mmol OH}^-} = 12.0\ \text{mL titrant}$$

$$[\text{F}^-] = \frac{3.00\,\text{mmol F}^-}{20.00\,\text{mL original volume} + 12.0\,\text{mL titrant}} = 0.0938\,\text{M}$$

We organize the solution of the hydrolysis problem around its balanced equation.

Equation:	$\text{F}^-(\text{aq})$	+	$H_2O(l)$	$\rightleftharpoons$	$\text{HF}(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial:	0.0938M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.0938-x)$ M		–		x M		x M

$$K_\text{b} = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{K_\text{w}}{K_\text{a}} = \frac{1.0\times10^{-14}}{6.6\times10^{-4}} = 1.5\times10^{-11} = \frac{x\cdot x}{0.0938-x} \approx \frac{x^2}{0.0938}$$

$$x = \sqrt{0.0934\times1.5\times10^{-11}} = 1.2\times10^{-6}\ \text{M} = [\text{OH}^-]$$

The assumption is valid ($x \ll 0.0934$).

$$\text{pOH} = -\log(1.2\times10^{-6}) = 5.92; \quad \text{pH} = 14.00 - \text{pOH} = 14.00 - 5.92 = 8.08$$

8B **(D)**

(a) The initial pH is simply that of 0.106 M NH_3.

Equation:	$NH_3(\text{aq})$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial:	0.106 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.106-x)$ M		–		x M		x M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x \cdot x}{0.106 - x} \approx \frac{x^2}{0.106} = 1.8 \times 10^{-5}$$

$x = \sqrt{0.106 \times 1.8 \times 10^{-4}} = 1.4 \times 10^{-3}$ M = $[OH^-]$

The assumption is valid ($x << 0.106$).

pOH = $-\log(0.0014)$ = 2.85   pH = 14.00 – pOH = 14.00 – 2.85 = 11.15

(b) When the titration is 25.0% complete, there are 25.0 mmol NH_4^+ for every 100.0 mmol of NH_3 that were present initially (i.e., there are 1.33 mmol of NH_4^+ in solution), 3.98 mmol NH_3 remain untitrated. We designate the solution volume (the volume holding these 5.30 mmol total) as V and use the basic version of the Henderson-Hasselbalch equation to find the pH.

$$\text{pOH} = \text{p}K_b + \log\frac{[NH_4^+]}{[NH_3]} = 4.74 + \log\frac{\dfrac{1.33\text{ mmol}}{V}}{\dfrac{3.98\text{ mmol}}{V}} = 4.26$$

pH = 14.00 – 4.26 = 9.74

(c) At the midpoint of the titration of a weak base, pOH = pK_b = 4.74 and pH = 9.26

(d) At the endpoint of the titration, the pH is determined by the conjugate acid hydrolysis reaction. We calculate the amount of that cation and the volume of the solution in order to determine its initial concentration.

$$\text{amount } NH_4^+ = 50.00\text{ mL} \times \frac{0.106\text{ mmol }NH_3}{1\text{ mL soln}} \times \frac{1\text{ mmol }NH_4^+}{1\text{ mmol }NH_3}$$

$$\text{amount } NH_4^+ = 5.30\text{ mmol }NH_4^+$$

$$V_{\text{titrant}} = 5.30\text{ mmol }NH_3 \times \frac{1\text{ mmol }H_3O^+}{1\text{ mmol }NH_3} \times \frac{1\text{ mL titrant}}{0.225\text{ mmol }H_3O^+} = 23.6\text{ mL titrant}$$

$$[NH_4^+] = \frac{5.30\text{ mmol }NH_4^+}{50.00\text{ mL original volume} + 23.6\text{ mL titrant}} = 0.0720\text{ M}$$

We organize the solution of the hydrolysis problem around its balanced chemical equation.

Equation:	$NH_4^+(aq)$	+ $H_2O(l)$ $\rightleftharpoons$	$NH_3(aq)$	+ $H_3O^+(aq)$
Initial:	0.0720 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.0720 - x)$ M	–	x M	x M

$$K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10} = \frac{x\cdot x}{0.0720-x} \approx \frac{x^2}{0.0720}$$

$$x = \sqrt{0.0720\times5.6\times10^{-10}} = 6.3\times10^{-6}\ M=[H_3O^+]$$

The assumption is valid (x << 0.0720).

$$pH = -\log\left(6.3\times10^{-6}\right) = 5.20$$

<u>**9A**</u> **(M)** The acidity of the solution is principally the result of the hydrolysis of the carbonate ion, which is considered first.

Equation:	$CO_3^{2-}(aq)$ +	$H_2O(l) \rightleftharpoons$	$HCO_3^-(aq)$ +	$OH^-(aq)$
Initial:	1.0 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(1.0-x)$ M	–	x M	x M

$$K_b = \frac{K_w}{K_a(HCO_3^-)} = \frac{1.0\times10^{-14}}{4.7\times10^{-11}} = 2.1\times10^{-4} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x\cdot x}{1.0-x} \approx \frac{x^2}{1.0}$$

$x = \sqrt{1.0\times2.1\times10^{-4}} = 1.5\times10^{-2}$ M = 0.015 M = $[OH^-]$ The assumption is valid ($x << 1.0M$).

Now we consider the hydrolysis of the bicarbonate ion.

Equation:	$HCO_3^-(aq)$ +	$H_2O(l) \rightleftharpoons$	$H_2CO_3(aq)$ +	$OH^-(aq)$
Initial:	0.015 M	–	0 M	0.015 M
Changes:	$-y$ M	–	$+y$ M	$+y$ M
Equil:	$(0.015-y)$ M	–	y M	$(0.015+y)$ M

$$K_b = \frac{K_w}{K_a(H_2CO_3)} = \frac{1.0\times10^{-14}}{4.4\times10^{-7}} = 2.3\times10^{-8} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = \frac{y(0.015+y)}{0.015-x} \approx \frac{0.015y}{0.015} = y$$

The assumption is valid (y << 0.015) and $y = [H_2CO_3] = 2.3\times10^{-8}$ M. Clearly, the second hydrolysis makes a negligible contribution to the acidity of the solution. For the entire solution, then

$$pOH = -\log[OH^-] = -\log(0.015) = 1.82 \qquad pH = 14.00-1.82 = 12.18$$

<u>**9B**</u> **(M)** The acidity of the solution is principally the result of hydrolysis of the sulfite ion.

Equation:	$SO_3^{2-}(aq)$ +	$H_2O(l) \rightleftharpoons$	$HSO_3^-(aq)$ +	$OH^-(aq)$
Initial:	0.500 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.500-x)$ M	–	x M	x M

$$K_b = \frac{K_w}{K_a \mathrm{HSO_3^-}} = \frac{1.0\times10^{-14}}{6.2\times10^{-8}} = 1.6\times10^{-7} = \frac{\left[\mathrm{HSO_3^-}\right]\left[\mathrm{OH^-}\right]}{[\mathrm{SO_3^{2-}}]} = \frac{x\cdot x}{0.500-x} \approx \frac{x^2}{0.500}$$

$x = \sqrt{0.500\times1.6\times10^{-7}} = 2.8\times10^{-4}$ M = 0.00028 M = $[\mathrm{OH^-}]$

The assumption is valid ($x << 0.500$).

Next we consider the hydrolysis of the bisulfite ion.

Equation:	$\mathrm{HSO_3^-(aq)}$ +	$\mathrm{H_2O(l)} \rightleftharpoons$	$\mathrm{H_2SO_3(aq)}$ +	$\mathrm{OH^-(aq)}$
Initial:	0.00028 M	–	0 M	0.00028 M
Changes:	$-y$ M	–	$+y$ M	$+y$ M
Equil:	$(0.00028-y)$ M	–	y M	$(0.00028+y)$ M

$$K_b = \frac{K_w}{K_a \mathrm{H_2SO_3}} = \frac{1.0\times10^{-14}}{1.3\times10^{-2}} = 7.7\times10^{-13}$$

$$K_b = 7.7\times10^{-13} = \frac{\left[\mathrm{H_2SO_3}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{HSO_3^-}\right]} = \frac{y(0.00028+y)}{0.00028-y} \approx \frac{0.00028\,y}{0.00028} = y$$

The assumption is valid ($y << 0.00028$) and $y = \left[\mathrm{H_2SO_3}\right] = 7.7\times10^{-13}$ M. Clearly, the second hydrolysis makes a negligible contribution to the acidity of the solution. For the entire solution, then

$\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right] = -\log(0.00028) = 3.55$ $\qquad$ $\mathrm{pH} = 14.00 - 3.55 = 10.45$

INTEGRATIVE EXAMPLE

A. **(D)**

From the given information, the following can be calculated:

pH of the solution = 2.716 therefore, $[\mathrm{H^+}] = 1.92\times10^{-3}$

pH at the halfway point = $\mathrm{p}K_a$
pH = 4.602 = $\mathrm{p}K_a$
$\mathrm{p}K_a = -\log K_a$ therefore $K_a = 2.50\times10^{-5}$

$\mathrm{FP} = 0^\circ\mathrm{C} + \Delta T_f$

$\Delta T_f = -i \times K_f \times m$

$\Delta T_f = -1 \times 1.86^\circ\mathrm{C}/m \times \text{molality}$

$$\text{molality} = \frac{\#\text{ moles solute}}{\text{kg solvent}} = \frac{\#\text{ moles solute}}{0.500\text{ kg} - 0.00750\text{ kg}}$$

To determine the number of moles of solute, convert 7.50 g of unknown acid to moles by using its molar mass. The molar mass can be calculated as follows:

$\text{pH} = 2.716 \qquad [\text{H}^+] = 1.92\times10^{-3}$

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial	$\frac{7.50\text{ g}}{\text{MM}} \Big/ 0.500\text{ L}$		0		0
Change	$-x$		x		x
Equilibrium	$\left(\frac{7.50\text{ g}}{\text{MM}} \Big/ 0.500\text{ L}\right) - 1.92\times10^{-3}$		1.92×10^{-3}		1.92×10^{-3}

$$2.50\times10^{-5} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$2.50\times10^{-5} = \frac{(1.92\times10^{-3})^2}{\left(\frac{7.50/\text{MM}}{0.500} - 1.92\times10^{-3}\right)}$$

$$\text{MM} = 100.4\text{ g/mol}$$

$$\#\text{moles of solute} = 7.50\text{ g} \times \frac{1\text{ mol}}{100.4\text{ g}} = 0.0747\text{ mol}$$

$$\text{Molality} = \frac{\#\text{ moles solute}}{\text{Kg solvent}} = \frac{0.0747\text{ mol}}{0.500\text{ Kg} - 0.00750\text{ Kg}} = 0.152\ m$$

$$\Delta T_f = -i \times K_f \times m$$

$$\Delta T_f = -1 \times 1.86\ ^\circ\text{C}/m \times 0.152\ m$$

$$\Delta T_f = -0.283\ ^\circ\text{C}$$

$$\text{FP} = 0^\circ\text{C} + \Delta T_f = 0^\circ\text{C} - 0.283\ ^\circ\text{C} = -0.283\ ^\circ\text{C}$$

B. **(M)** By looking at the titration curve provided, one can deduce that the titrant was a strong acid. The pH before titrant was added was basic, which means that the substance that was titrated was a base. The pH at the end of the titration after excess titrant was added was acidic, which means that the titrant was an acid.

Based on the titration curve provided, the equivalence point is at approximately 50 mL of titrant added. At the halfway point, of approximately 25 mL, the pH = pK_a. A pH ~8 is obtained by extrapolation a the halfway point.

$pH = 8 = pK_a$
$K_a = 10^{-8} = 1 \times 10^{-8}$
$K_b = K_w/K_a = 1 \times 10^{-6}$

~50 mL of 0.2 M strong acid (1×10^{-2} mol) was needed to reach the equivalence point. This means that the unknown contained 1×10^{-2} mol of weak base. The molar mass of the unknown can be determined as follows:

$$\frac{0.800\text{ g}}{1\times10^{-2}\text{ mol}} = 80\text{ g/mol}$$

EXERCISES

The Common-Ion Effect

1. **(M)**

(a) Note that HI is a strong acid and thus the initial $\left[H_3O^+\right] = \left[HI\right] = 0.0892M$

$$\begin{array}{lllll}
\text{Equation:} & HC_3H_5O_2 & + \; H_2O \rightleftharpoons & C_3H_5O_2^- & + \quad H_3O^+ \\
\text{Initial:} & 0.275\text{ M} & - & 0\text{M} & 0.0892\text{M} \\
\text{Changes:} & -x\text{ M} & - & +x\text{ M} & +x\text{ M} \\
\text{Equil:} & (0.275-x)\text{ M} & - & x\text{ M} & (0.0892+x)\text{ M}
\end{array}$$

$$K_a = \frac{\left[C_3H_5O_2^-\right]\left[H_3O^+\right]}{\left[HC_3H_5O_2\right]} = 1.3\times10^{-5} = \frac{x(0.0892+x)}{0.275-x} \approx \frac{0.0892x}{0.275} \qquad x = 4.0\times10^{-5}\text{ M}$$

The assumption that $x \ll 0.0892$ M is correct. $\left[H_3O^+\right] = 0.0892M$

(b) $\left[OH^-\right] = \dfrac{K_w}{\left[H_3O^+\right]} = \dfrac{1.0\times10^{-14}}{0.0892} = 1.1\times10^{-13}\text{ M}$

(c) $\left[C_3H_5O_2^-\right] = x = 4.0\times10^{-5}\text{ M}$

(d) $\left[\mathrm{I}^-\right] = \left[\mathrm{HI}\right]_{\mathrm{int}} = 0.0892\ \mathrm{M}$

2. **(M)**

(a) The NH_4Cl dissociates completely, and thus, $\left[\mathrm{NH}_4^+\right]_{\mathrm{int}} = \left[\mathrm{Cl}^-\right]_{\mathrm{int}} = 0.102\ \mathrm{M}$

Equation:	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
Initial:	0.164 M		–		0.102 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.164 - x)$M		–		$(0.102 + x)$M		x M

$$K_b = \frac{\left[\mathrm{NH}_4^+\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{NH}_3\right]} = \frac{(0.102 + x)x}{0.164 - x} = 1.8\times10^{-5} \approx \frac{0.102x}{0.164};\ \ x = 2.9\times10^{-5}\,\mathrm{M}$$

Assumed $x \ll 0.102\ \mathrm{M}$, a clearly valid assumption. $\left[\mathrm{OH}^-\right] = x = 2.9\times10^{-5}\ \mathrm{M}$

(b) $\left[\mathrm{NH}_4^+\right] = 0.102 + x = 0.102\,\mathrm{M}$

(c) $\left[\mathrm{Cl}^-\right] = 0.102\,\mathrm{M}$

(d) $\left[\mathrm{H}_3\mathrm{O}^+\right] = \dfrac{1.0\times10^{-14}}{2.9\times10^{-5}} = 3.4\times10^{-10}\ \mathrm{M}$

3. **(M)**

(a) We first determine the pH of 0.100 M HNO_2.

Equation	$HNO_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NO_2^-(aq)$	+	$H_3O^+(aq)$
Initial :	0.100 M		–		0 M		≈ 0 M
Changes :	$-x$ M		–		$+x$ M		$+x$ M
Equil :	$(0.100 - x)$ M		–		x M		x M

$$K_a = \frac{\left[\mathrm{NO}_2^-\right]\left[\mathrm{H}_3\mathrm{O}^+\right]}{\left[\mathrm{HNO}_2\right]} = 7.2\times10^{-4} = \frac{x^2}{0.100 - x}$$

Via the quadratic equation roots formula or via successive approximations, $x = 8.1\times10^{-3}\,\mathrm{M} = \left[\mathrm{H}_3\mathrm{O}^+\right]$.

Thus $\mathrm{pH} = -\log\left(8.1\times10^{-3}\right) = 2.09$

When 0.100 mol $NaNO_2$ is added to 1.00 L of a 0.100 M HNO_2, a solution with $\left[\mathrm{NO}_2^-\right] = 0.100\mathrm{M} = \left[\mathrm{HNO}_2\right]$ is produced. The answer obtained with the Henderson-Hasselbalch equation, is $\mathrm{pH} = \mathrm{p}K_a = -\log\left(7.2\times10^{-4}\right) = 3.14$. Thus, the addition has caused a pH change of 1.05 units.

(b) $NaNO_3$ contributes nitrate ion, NO_3^-, to the solution. Since, however, there is no molecular $HNO_3(aq)$ in equilibrium with hydrogen and nitrate ions, there is no equilibrium to be shifted by the addition of nitrate ions. The $[H_3O^+]$ and the pH are thus unaffected by the addition of $NaNO_3$ to a solution of nitric acid. The pH changes are not the same because there is an equilibrium system to be shifted in the first solution, whereas there is no equilibrium, just a change in total ionic strength, for the second solution.

4. **(M)** The explanation for the different result is that each of these solutions has acetate ion present, $C_2H_3O_2^-$, which is produced in the ionization of acetic acid. The presence of this ion suppresses the ionization of acetic acid, thus minimizing the increase in $\left[H_3O^+\right]$. All three solutions are buffer solutions and their pH can be found with the aid of the Henderson-Hasselbalch equation.

(a)

$$\text{pH} = \text{p}K_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 4.74 + \log\frac{0.10}{1.0} = 3.74 \qquad \left[H_3O^+\right] = 10^{-3.74} = 1.8\times10^{-4}\text{ M}$$

$$\%\text{ ionization} = \frac{\left[H_3O^+\right]}{\left[HC_2H_3O_2\right]}\times100\% = \frac{1.8\times10^{-4}\text{ M}}{1.0\text{M}}\times100\% = 0.018\%$$

(b)

$$\text{pH} = \text{p}K_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 4.74 + \log\frac{0.10}{0.10} = 4.74$$

$$\left[H_3O^+\right] = 10^{-4.74} = 1.8\times10^{-5}\text{M}$$

$$\%\text{ ionization} = \frac{\left[H_3O^+\right]}{\left[HC_2H_3O_2\right]}\times100\% = \frac{1.8\times10^{-5}\text{M}}{0.10\text{M}}\times100\% = 0.018\%$$

(c)

$$\text{pH} = \text{p}K_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 4.74 + \log\frac{0.10}{0.010} = 5.74$$

$$\left[H_3O^+\right] = 10^{-5.74} = 1.8\times10^{-6}\text{M}$$

$$\%\text{ ionization} = \frac{\left[H_3O^+\right]}{\left[HC_2H_3O_2\right]}\times100\% = \frac{1.8\times10^{-6}\text{M}}{0.010\text{M}}\times100\% = 0.018\%$$

5. **(M)**

(a) The strong acid HCl suppresses the ionization of the weak acid HOCl to such an extent that a negligible concentration of H_3O^+ is contributed to the solution by HOCl. Thus, $\left[H_3O^+\right] = [HCl] = 0.035\text{M}$

(b) This is a buffer solution. Consequently, we can use the Henderson-Hasselbalch equation to determine its pH. $\mathrm{p}K_\mathrm{a} = -\log\left(7.2\times10^{-4}\right) = 3.14$;

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{\left[\mathrm{NO_2}^-\right]}{\left[\mathrm{HNO_2}\right]} = 3.14 + \log\frac{0.100\,\mathrm{M}}{0.0550\,\mathrm{M}} = 3.40$$

$$\left[\mathrm{H_3O^+}\right] = 10^{-3.40} = 4.0\times10^{-4}\ \mathrm{M}$$

(c) This also is a buffer solution, as we see by an analysis of the reaction between the components.

Equation:	$\mathrm{H_3O^+}\left(\mathrm{aq,\ _{from\ HCl}}\right)$	$+\ \mathrm{C_2H_3O_2}^-\left(\mathrm{aq,\ _{from\ NaC_2H_3O_2}}\right)$	$\rightarrow \mathrm{HC_2H_3O_2}\left(\mathrm{aq}\right)$	$+\ \mathrm{H_2O(l)}$
In soln:	0.0525 M	0.0768 M	0 M	–
Produce HAc:	–0.0525 M	–0.0525 M	+0.0525 M	–
Initial:	≈ 0M	0.0243 M	0.0525 M	–

Now the Henderson-Hasselbalch equation can be used to find the pH.

$$\mathrm{p}K_\mathrm{a} = -\log\left(1.8\times10^{-5}\right) = 4.74$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{\left[\mathrm{C_2H_3O_2}^-\right]}{\left[\mathrm{HC_2H_3O_2}\right]} = 4.74 + \log\frac{0.0243\,\mathrm{M}}{0.0525\,\mathrm{M}} = 4.41$$

$$\left[\mathrm{H_3O^+}\right] = 10^{-4.41} = 3.9\times10^{-5}\ \mathrm{M}$$

6. **(M)**

(a) Neither $\mathrm{Ba^{2+}(aq)}$ nor $\mathrm{Cl^-(aq)}$ hydrolyzes to a measurable extent and hence they have no effect on the solution pH. Consequently, $\left[\mathrm{OH^-}\right]$ is determined entirely by the $\mathrm{Ba(OH)_2}$ solute.

$$\left[\mathrm{OH^-}\right] = \frac{0.0062\ \mathrm{mol\ Ba(OH)_2}}{1\ \mathrm{L\ soln}}\times\frac{2\,\mathrm{mol\ OH^-}}{1\mathrm{mol\ Ba(OH)_2}} = 0.012\ \mathrm{M}$$

(b) We use the Henderson-Hasselbalch equation to find the pH for this buffer solution.

$$\left[\mathrm{NH_4}^+\right] = 0.315\ \mathrm{M\,(NH_4)_2SO_4}\times\frac{2\ \mathrm{mol\ NH_4}^+}{1\ \mathrm{mol\ (NH_4)_2SO_4}} = 0.630\ \mathrm{M} \qquad \mathrm{p}K_\mathrm{a} = 9.26\ \text{for}\ \mathrm{NH_4}^+.$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{\left[\mathrm{NH_3}\right]}{\left[\mathrm{NH_4}^+\right]} = 9.26 + \log\frac{0.486\ \mathrm{M}}{0.630\ \mathrm{M}} = 9.15 \qquad \mathrm{pOH} = 14.00 - 9.15 = 4.85$$

$$\left[\mathrm{OH^-}\right] = 10^{-4.85} = 1.4\times10^{-5}\ \mathrm{M}$$

(c) This solution also is a buffer, as analysis of the reaction between its components shows.

$$\begin{array}{llllll}
\text{Equation:} & NH_4^+\,(\text{aq, from } NH_4Cl) & + \; OH^-\,(\text{aq, from NaOH}) & \rightarrow NH_3\,(aq) & + \; H_2O(l) \\
\text{In soln:} & 0.264\text{ M} & 0.196\text{ M} & 0\text{ M} & - \\
\text{Form } NH_3\text{:} & -0.196\text{ M} & -0.196\text{ M} & +0.196\text{ M} & - \\
\text{Initial:} & 0.068\text{ M} & \approx 0\text{M} & 0.196\text{ M} & -
\end{array}$$

$$\text{pH} = \text{p}K_a + \log\frac{[NH_3]}{[NH_4^+]} = 9.26 + \log\frac{0.196\,\text{M}}{0.068\,\text{M}} = 9.72 \qquad \text{pOH} = 14.00 - 9.72 = 4.28$$

Buffer Solutions

7. **(M)** $[H_3O^+] = 10^{-4.06} = 8.7\times10^{-5}\,\text{M}$. We let $S = [CHO_2^-]_{\text{int}}$

$$\begin{array}{llllll}
\text{Equation:} & HCHO_2\,(aq) & + \; H_2O(l) \rightleftharpoons & CHO_2^-\,(aq) & + & H_3O^+\,(aq) \\
\text{Initial:} & 0.366\,\text{M} & - & S\,\text{M} & & \approx 0\,\text{M} \\
\text{Changes:} & -8.7\times10^{-5}\,\text{M} & - & +8.7\times10^{-5}\,\text{M} & & +8.7\times10^{-5}\,\text{M} \\
\text{Equil:} & 0.366\,\text{M} & - & (S + 8.7\times10^{-5})\,\text{M} & & 8.7\times10^{-5}\,\text{M}
\end{array}$$

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = 1.8\times10^{-4} = \frac{(S + 8.7\times10^{-5})8.7\times10^{-5}}{0.366} \approx \frac{8.7\times10^{-5}S}{0.366};\; S = 0.76\text{ M}$$

To determine S, we assumed $S \gg 8.7\times10^{-5}\,\text{M}$, which is clearly a valid assumption. Or, we could have used the Henderson-Hasselbalch equation (see below). $\text{p}K_a = -\log(1.8\times10^{-4}) = 3.74$

$$4.06 = 3.74 + \log\frac{[CHO_2^-]}{[HCHO_2]}; \qquad \frac{[CHO_2^-]}{[HCHO_2]} = 2.1; \qquad [CHO_2^-] = 2.1\times0.366 = 0.77\,\text{M}$$

The difference in the two answers is due simply to rounding.

8. **(E)** We use the Henderson-Hasselbalch equation to find the required $[NH_3]$.

$$\text{p}K_b = -\log(1.8\times10^{-5}) = 4.74$$

$$\text{p}K_a = 14.00 - \text{p}K_b = 14.00 - 4.74 = 9.26 \qquad \text{pH} = 9.12 = 9.26 + \log\frac{[NH_3]}{[NH_4^+]}$$

$$\frac{[NH_3]}{[NH_4^+]} = 10^{-0.14} = 0.72 \qquad [NH_3] = 0.72\times[NH_4^+] = 0.72\times0.732\,\text{M} = 0.53\,\text{M}$$

9. **(M)**

(a)

Equation:	$HC_7H_5O_2(aq)$	$+ H_2O(l) \rightleftharpoons$	$C_7H_5O_2^-(aq)$	$+ H_3O^+(aq)$
Initial:	0.012 M	–	0.033 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.012-x)$M	–	$(0.033+x)$M	x M

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = 6.3\times10^{-5} = \frac{x(0.033+x)}{0.012-x} \approx \frac{0.033x}{0.012} \qquad x = 2.3\times10^{-5}\text{M}$$

To determine the value of x, we assumed $x \ll 0.012$ M, which is an assumption that clearly is correct.

$$[H_3O^+] = 2.3\times10^{-5}\text{M} \qquad \text{pH} = -\log(2.3\times10^{-5}) = 4.64$$

(b)

Equation:	$NH_3(aq)$	$+ H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$	$+ OH^-(aq)$
Initial :	0.408 M	–	0.153 M	≈ 0 M
Changes :	$-x$ M	–	$+x$ M	$+x$ M
Equil :	$(0.408-x)$ M	–	$(0.153+x)$ M	x M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5} = \frac{x(0.153+x)}{0.408-x} \approx \frac{0.153x}{0.408} \qquad x = 4.8\times10^{-5}\text{M}$$

To determine the value of x, we assumed $x \ll 0.153$, which clearly is a valid assumption.

$$[OH^-] = 4.8\times10^{-5}\text{M}; \ \text{pOH} = -\log(4.8\times10^{-5}) = 4.32; \quad \text{pH} = 14.00 - 4.32 = 9.68$$

10. **(M)** Since the mixture is a buffer, we can use the Henderson-Hasselbalch equation to determine K_a of lactic acid.

$$[C_3H_5O_3^-] = \frac{1.00\text{ g }NaC_3H_5O_3}{100.0\text{ mL soln}} \times \frac{1000\text{ mL}}{1\text{ L soln}} \times \frac{1\text{ mol }NaC_3H_5O_3}{112.1\text{ g }NaC_3H_5O_3} \times \frac{1\text{ mol }C_3H_5O_3^-}{1\text{ mol }NaC_3H_5O_3} = 0.0892\text{ M}$$

$$\text{pH} = 4.11 = \text{p}K_a + \log\frac{[C_3H_5O_3^-]}{[HC_3H_5O_3]} = \text{p}K_a + \log\frac{0.0892\text{ M}}{0.0500\text{ M}} = \text{p}K_a + 0.251$$

$$\text{p}K_a = 4.11 - 0.251 = 3.86; \quad K_a = 10^{-3.86} = 1.4\times10^{-4}$$

11. **(M)**

(a) 0.100 M NaCl is not a buffer solution. Neither ion reacts with water to a detectable extent.

(b) 0.100 M NaCl—0.100 M NH_4Cl is not a buffer solution. Although a weak acid, NH_4^+, is present, its conjugate base, NH_3, is not.

(c) 0.100 M CH_3NH_2 and 0.150 M $CH_3NH_3^+Cl^-$ is a buffer solution. Both the weak base, CH_3NH_2, and its conjugate acid, $CH_3NH_3^+$, are present in approximately equal concentrations.

(d) 0.100 M HCl—0.050 M $NaNO_2$ is not a buffer solution. All the NO_2^- has converted to HNO_2 and thus the solution is a mixture of a strong acid and a weak acid.

(e) 0.100 M HCl—0.200 M $NaC_2H_3O_2$ is a buffer solution. All of the HCl reacts with half of the $C_2H_3O_2^-$ to form a solution with 0.100 M $HC_2H_3O_2$, a weak acid, and 0.100 M $C_2H_3O_2^-$, its conjugate base.

(f) 0.100 M $HC_2H_3O_2$ and 0.125 M $NaC_3H_5O_2$ is not a buffer in the strict sense because it does not contain a weak acid and its conjugate base, but rather the conjugate base of another weak acid. These two weak acids (acetic, $K_a = 1.8 \times 10^{-5}$, and propionic, $K_a = 1.35 \times 10^{-5}$) have approximately the same strength, however, this solution would resist changes in its pH on the addition of strong acid or strong base, consequently, it could be argued that this system should also be called a buffer.

12. **(M)**

(a) Reaction with added acid: $HPO_4^{2-} + H_3O^+ \rightarrow H_2PO_4^- + H_2O$

Reaction with added base: $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$

(b) We assume initially that the buffer has equal concentrations of the two ions, $\left[H_2PO_4^-\right] = \left[HPO_4^{2-}\right]$

$$\text{pH} = \text{p}K_{a_2} + \log\frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 7.20 + 0.00 = 7.20 \text{ (pH at which the buffer is most effective).}$$

(c) $$\text{pH} = 7.20 + \log\frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 7.20 + \log\frac{0.150\text{ M}}{0.050\text{ M}} = 7.20 + 0.48 = 7.68$$

<u>13.</u> **(M)** $$\text{moles of solute} = 1.15\text{ mg} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol } C_6H_5NH_3^+Cl^-}{129.6\text{ g}} \times \frac{1\text{ mol } C_6H_5NH_3^+}{1\text{mol } C_6H_5NH_3^+Cl^-}$$

$$= 8.87 \times 10^{-6}\text{ mol } C_6H_5NH_3^+$$

$$\left[C_6H_5NH_3^+\right] = \frac{8.87 \times 10^{-6}\text{mol } C_6H_5NH_3^+}{3.18\text{ L soln}} = 2.79 \times 10^{-6}\text{ M}$$

Equation:	$C_6H_5NH_2(aq)$	+ $H_2O(l)$ $\rightleftharpoons$	$C_6H_5NH_3^+(aq)$	+ $OH^-(aq)$
Initial:	0.105 M	–	2.79×10^{-6} M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.105 - x)$M	–	$(2.79 \times 10^{-6} + x)$M	x M

$$K_b = \frac{\left[C_6H_5NH_3^+\right]\left[OH^-\right]}{\left[C_6H_5NH_2\right]} = 7.4\times10^{-10} = \frac{\left(2.79\times10^{-6}+x\right)x}{0.105-x}$$

$$7.4\times10^{-10}\left(0.105-x\right) = \left(2.79\times10^{-6}+x\right)x; \quad 7.8\times10^{-11} - 7.4\times10^{-10}x = 2.79\times10^{-6}x + x^2$$

$$x^2 + \left(2.79\times10^{-6} + 7.4\times10^{-10}\right)x - 7.8\times10^{-11} = 0; \quad x^2 + 2.79\times10^{-6}x - 7.8\times10^{-11} = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-2.79\times10^{-6}\pm\sqrt{7.78\times10^{-12}+3.1\times10^{-10}}}{2} = 7.5\times10^{-6}\ \text{M} = \left[OH^-\right]$$

$$\text{pOH} = -\log\left(7.5\times10^{-6}\right) = 5.12 \qquad \text{pH} = 14.00 - 5.12 = 8.88$$

14. **(M)** We determine the concentration of the cation of the weak base.

$$[C_6H_5NH_3^+] = \frac{8.50\ \text{g}\times\dfrac{1\ \text{mmol}\ C_6H_5NH_3^+Cl^-}{129.6\ \text{g}}\times\dfrac{1\ \text{mmol}\ C_6H_5NH_3^+}{1\ \text{mmol}\ C_6H_5NH_3^+Cl^-}}{750\ \text{mL}\times\dfrac{1\ \text{L}}{1000\ \text{mL}}} = 0.0874\ \text{M}$$

In order to be an effective buffer, each concentration must exceed the ionization constant $\left(K_b = 7.4\times10^{-10}\right)$ by a factor of at least 100, which clearly is true. Also, the ratio of the two concentrations must fall between 0.1 and 10:

$$\frac{\left[C_6H_5NH_3^+\right]}{\left[C_6H_5NH_2\right]} = \frac{0.0874\text{M}}{0.215\text{M}} = 0.407\,.$$

Since both criteria are met, this solution will be an effective buffer.

15. **(M)**

(a) First use the Henderson-Hasselbalch equation. $\text{p}K_b = -\log\left(1.8\times10^{-5}\right) = 4.74$, $\text{p}K_a = 14.00 - 4.74 = 9.26$ to determine $\left[NH_4^+\right]$ in the buffer solution.

$$\text{pH} = 9.45 = \text{p}K_a + \log\frac{[NH_3]}{\left[NH_4^+\right]} = 9.26 + \log\frac{[NH_3]}{\left[NH_4^+\right]}; \quad \log\frac{[NH_3]}{\left[NH_4^+\right]} = 9.45 - 9.26 = +0.19$$

$$\frac{[NH_3]}{\left[NH_4^+\right]} = 10^{0.19} = 1.5\underline{5} \qquad \left[NH_4^+\right] = \frac{[NH_3]}{1.5\underline{5}} = \frac{0.258\text{M}}{1.5\underline{5}} = 0.17\text{M}$$

We now assume that the volume of the solution does not change significantly when the solid is added.

$$\text{mass}\left(NH_4\right)_2SO_4 = 425\ \text{mL}\times\frac{1\ \text{L soln}}{1000\,\text{mL}}\times\frac{0.17\ \text{mol}\,NH_4^+}{1\ \text{L soln}}\times\frac{1\ \text{mol}\left(NH_4\right)_2SO_4}{2\ \text{mol}\,NH_4^+}$$

$$\times\frac{132.1\ \text{g}\left(NH_4\right)_2SO_4}{1\ \text{mol}\left(NH_4\right)_2SO_4} = 4.8\ \text{g}\ \left(NH_4\right)_2SO_4$$

(b) We can use the Henderson-Hasselbalch equation to determine the ratio of concentrations of cation and weak base in the altered solution.

$$\text{pH} = 9.30 = \text{p}K_a + \log\frac{[\text{NH}_3]}{[\text{NH}_4{}^+]} = 9.26 + \log\frac{[\text{NH}_3]}{[\text{NH}_4{}^+]} \qquad \log\frac{[\text{NH}_3]}{[\text{NH}_4{}^+]} = 9.30 - 9.26 = +0.04$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4{}^+]} = 10^{0.04} = 1.1 = \frac{0.258}{0.17\text{ M} + x\text{ M}} \qquad 0.19 + 1.1x = 0.258 \quad x = 0.062\,M$$

The reason we decided to add x to the denominator follows. (Notice we cannot remove a component.) A pH of 9.30 is more acidic than a pH of 9.45 and therefore the conjugate acid's $(\text{NH}_4{}^+)$ concentration must increase. Additionally, mathematics tells us that for the concentration ratio to decrease from 1.5$\underline{5}$ to 1.1, its denominator must increase. We solve this expression for x to find a value of 0.062 M. We need to add $\text{NH}_4{}^+$ to increase its concentration by 0.062 M in 100 mL of solution.

$$(\text{NH}_4)_2\text{SO}_4 \text{ mass} = 0.100\,\text{L} \times \frac{0.062\,\text{mol NH}_4^+}{1\,\text{L}} \times \frac{1\,\text{mol}(\text{NH}_4)_2\text{SO}_4}{2\,\text{mol NH}_4^+} \times \frac{132.1\text{g } (\text{NH}_4)_2\text{SO}_4}{1\text{mol } (\text{NH}_4)_2\text{SO}_4}$$

$$= 0.41\text{g } (\text{NH}_4)_2\text{SO}_4 \qquad \text{Hence, we need to add} \simeq 0.4\text{ g}$$

16. (M)

(a) $$n_{\text{HC}_7\text{H}_5\text{O}_2} = 2.00\text{ g HC}_7\text{H}_5\text{O}_2 \times \frac{1\text{mol HC}_7\text{H}_5\text{O}_2}{122.1\text{g HC}_7\text{H}_5\text{O}_2} = 0.0164\,\text{mol HC}_7\text{H}_5\text{O}_2$$

$$n_{\text{C}_7\text{H}_5\text{O}_2{}^-} = 2.00\text{ g NaC}_7\text{H}_5\text{O}_2 \times \frac{1\text{mol NaC}_7\text{H}_5\text{O}_2}{144.1\text{g NaC}_7\text{H}_5\text{O}_2} \times \frac{1\text{mol C}_7\text{H}_5\text{O}_2{}^-}{1\text{mol NaC}_7\text{H}_5\text{O}_2}$$

$$= 0.0139\,\text{mol C}_7\text{H}_5\text{O}_2{}^-$$

$$\text{pH} = \text{p}K_a + \log\frac{[\text{C}_7\text{H}_5\text{O}_2{}^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = -\log(6.3\times10^{-5}) + \log\frac{0.0139\,\text{mol C}_7\text{H}_5\text{O}_2{}^-/0.7500\,\text{L}}{0.0164\,\text{mol HC}_7\text{H}_5\text{O}_2/0.7500\,\text{L}}$$

$$= 4.20 - 0.0718 = 4.13$$

(b) To lower the pH of this buffer solution, that is, to make it more acidic, benzoic acid must be added. The quantity is determined as follows. We use moles rather than concentrations because all components are present in the same volume of solution.

$$4.00 = 4.20 + \log\frac{0.0139\,\text{mol C}_7\text{H}_5\text{O}_2{}^-}{x\,\text{mol HC}_7\text{H}_5\text{O}_2} \qquad \log\frac{0.0139\,\text{mol C}_7\text{H}_5\text{O}_2{}^-}{x\,\text{mol HC}_7\text{H}_5\text{O}_2} = -0.20$$

$$\frac{0.0139\,\text{mol C}_7\text{H}_5\text{O}_2^-}{x\,\text{mol HC}_7\text{H}_5\text{O}_2} = 10^{-0.20} = 0.63 \qquad x = \frac{0.0139}{0.63} = 0.022\,\text{mol HC}_7\text{H}_5\text{O}_2 \text{ (required)}$$

$$\text{HC}_7\text{H}_5\text{O}_2 \text{ that must be added} = \text{amount required} - \text{amount already in solution}$$

$$\text{HC}_7\text{H}_5\text{O}_2 \text{ that must be added} = 0.022\,\text{mol HC}_7\text{H}_5\text{O}_2 - 0.0164\,\text{mol HC}_7\text{H}_5\text{O}_2$$

$$\text{HC}_7\text{H}_5\text{O}_2 \text{ that must be added} = 0.006\,\text{mol HC}_7\text{H}_5\text{O}_2$$

$$\text{added mass HC}_7\text{H}_5\text{O}_2 = 0.006\,\text{mol HC}_7\text{H}_5\text{O}_2 \times \frac{122.1\,\text{g HC}_7\text{H}_5\text{O}_2}{1\,\text{mol HC}_7\text{H}_5\text{O}_2} = 0.7\,\text{g HC}_7\text{H}_5\text{O}_2$$

17. **(M)** The added HCl will react with the ammonia, and the pH of the buffer solution will decrease. The original buffer solution has $[\text{NH}_3] = 0.258\text{ M}$ and $[\text{NH}_4^+] = 0.17\text{ M}$. We first calculate the [HCl] in solution, reduced from 12 M because of dilution. [HCl] added $= 12\,\text{M} \times \dfrac{0.55\,\text{mL}}{100.6\,\text{mL}} = 0.066\,\text{M}$ We then determine $\text{p}K_a$ for ammonium ion:

$$\text{p}K_b = -\log(1.8 \times 10^{-5}) = 4.74 \quad \text{p}K_a = 14.00 - 4.74 = 9.26$$

Equation:	$\text{NH}_3(\text{aq})$ +	$\text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons$	$\text{NH}_4^+(\text{aq})$	$+ \text{H}_2\text{O}(\text{l})$
Buffer:	0.258 M	≈ 0 M	0.17 M	–
Added:		+0.066 M		
Changes:	–0.066 M	–0.066 M	+0.066 M	–
Final:	0.192 M	0 M	0.24 M	–

$$\text{pH} = \text{p}K_a + \log\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.26 + \log\frac{0.192}{0.24} = 9.16$$

18. **(M)** The added NH_3 will react with the benzoic acid, and the pH of the buffer solution will increase. Original buffer solution has $[\text{C}_7\text{H}_5\text{O}_2^-] = 0.0139\text{ mol C}_7\text{H}_5\text{O}_2^-/0.750\text{ L} = 0.0185\text{ M}$ and $[\text{HC}_7\text{H}_5\text{O}_2] = 0.0164\,\text{mol HC}_7\text{H}_5\text{O}_2/0.7500\,\text{L} = 0.0219\,\text{M}$. We first calculate the $[\text{NH}_3]$ in solution, reduced from 15 M because of dilution.

$$[\text{NH}_3]\text{ added} = 15\text{ M} \times \frac{0.35\text{ mL}}{750.35\text{ mL}} = 0.0070\text{ M}$$

For benzoic acid, $\text{p}K_a = -\log(6.3 \times 10^{-5}) = 4.20$

Equation:	$\text{NH}_3(\text{aq})$ +	$\text{HC}_7\text{H}_5\text{O}_2(\text{aq}) \rightleftharpoons$	$\text{NH}_4^+(\text{aq})$ +	$\text{C}_7\text{H}_5\text{O}_2^-(\text{aq})$
Buffer:	0 M	0.0219 M	0 M	0.0185 M
Added:	0.0070 M			
Changes:	–0.0070M	– 0.0070 M	+ 0.0070 M	+ 0.0070 M
Final:	0.000 M	0.0149 M	0.0070 M	0.0255 M

$$\text{pH} = \text{p}K_a + \log\frac{[\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = 4.20 + \log\frac{0.0255}{0.0149} = 4.43$$

19. **(M)** The $\mathrm{p}K_\mathrm{a}$'s of the acids help us choose the one to be used in the buffer. It is the acid with a $\mathrm{p}K_\mathrm{a}$ within 1.00 pH unit of 3.50 that will do the trick. $\mathrm{p}K_\mathrm{a} = 3.74$ for $HCHO_2$, $\mathrm{p}K_\mathrm{a} = 4.74$ for $HC_2H_3O_2$, and $\mathrm{p}K_{a1} = 2.15$ for H_3PO_4. Thus, we choose $HCHO_2$ and $NaCHO_2$ to prepare a buffer with $\mathrm{pH} = 3.50$. The Henderson-Hasselbalch equation is used to determine the relative amount of each component present in the buffer solution.

$$\mathrm{pH} = 3.50 = 3.74 + \log\frac{[CHO_2^-]}{[HCHO_2]} \qquad \log\frac{[CHO_2^-]}{[HCHO_2]} = 3.50 - 3.74 = -0.24$$

$$\frac{[CHO_2^-]}{[HCHO_2]} = 10^{-0.24} = 0.58$$

This ratio of concentrations is also the ratio of the number of moles of each component in the buffer solution, since both concentrations are a number of moles in a certain volume, and the volumes are the same (the two solutes are in the same solution). This ratio also is the ratio of the volumes of the two solutions, since both solutions being mixed contain the same concentration of solute. If we assume 100. mL of acid solution, $V_\mathrm{acid} = 100.\ \mathrm{mL}$. Then the volume of salt solution is

$V_\mathrm{salt} = 0.58 \times 100.\ \mathrm{mL} = 58\ \mathrm{mL}\ 0.100\ \mathrm{M}\ NaCHO_2$

20. **(D)** We can lower the pH of the 0.250 M $HC_2H_3O_2$ — 0.560 M $C_2H_3O_2^-$ buffer solution by increasing $[HC_2H_3O_2]$ or lowering $[C_2H_3O_2^-]$. Small volumes of NaCl solutions will have no effect, and the addition of NaOH(aq) or $NaC_2H_3O_2(aq)$ will raise the pH. The addition of 0.150 M HCl will raise $[HC_2H_3O_2]$ and lower $[C_2H_3O_2^-]$ through the reaction $H_3O^+(aq) + C_2H_3O_2^-(aq) \rightleftharpoons HC_2H_3O_2(aq) + H_2O(l)$ and bring about the desired lowering of the pH. We first use the Henderson-Hasselbalch equation to determine the ratio of the concentrations of acetate ion and acetic acid.

$$\mathrm{pH} = 5.00 = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$\log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 5.00 - 4.74 = 0.26; \qquad \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{0.26} = 1.8$$

Now we compute the amount of each component in the original buffer solution.

$$\text{amount of } C_2H_3O_2^- = 300.\ \mathrm{mL} \times \frac{0.560\ \mathrm{mmol}\ C_2H_3O_2^-}{1\ \mathrm{mL\ soln}} = 168\,\mathrm{mmol}\ C_2H_3O_2^-$$

$$\text{amount of } HC_2H_3O_2 = 300.\ \mathrm{mL} \times \frac{0.250\,\mathrm{mmol}\ HC_2H_3O_2}{1\mathrm{mL\ soln}} = 75.0\,\mathrm{mmol}\ HC_2H_3O_2$$

Now let x represent the amount of H_3O^+ added in mmol.

$$1.8 = \frac{168 - x}{75.0 + x}; \quad 168 - x = 1.8(75 + x) = 135 + 1.8x \qquad 168 - 135 = 2.8x$$

$$x = \frac{168 - 135}{2.7} = 12\,\text{mmol } H_3O^+$$

$$\text{Volume of } 0.150\text{ M HCl} = 12\,\text{mmol } H_3O^+ \times \frac{1\,\text{mmol HCl}}{1\,\text{mmol } H_3O^+} \times \frac{1\,\text{mL soln}}{0.150\,\text{mmol HCl}}$$

$$= 80\,\text{mL } 0.150\,\text{M HCl solution}$$

<u>21.</u> **(M)**

(a) The pH of the buffer is determined via the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log\frac{[C_3H_5O_2^-]}{[HC_3H_5O_2]} = 4.89 + \log\frac{0.100\text{M}}{0.100\text{M}} = 4.89$$

The effective pH range is the same for every propionate buffer: from $\text{pH} = 3.89$ to $\text{pH} = 5.89$, one pH unit on either side of $\text{p}K_a$ for propionic acid, which is 4.89.

(b) To each liter of 0.100 M $HC_3H_5O_2$ — 0.100M $NaC_3H_5O_2$ we can add 0.100 mol OH^- before all of the $HC_3H_5O_2$ is consumed, and we can add 0.100 mol H_3O^+ before all of the $C_3H_5O_2^-$ is consumed. The buffer capacity thus is 100. millimoles (0.100 mol) of acid or base per liter of buffer solution.

22. **(M)**

(a) The solution will be an effective buffer one pH uniton either side of the $\text{p}K_a$ of methylammonium ion, $CH_3NH_3^+$, $K_b = 4.2\times10^{-4}$ for methylamine, $\text{p}K_b = -\log(4.2\times10^{-4}) = 3.38$. For methylammonium cation, $\text{p}K_a = 14.00 - 3.38 = 10.62$. Thus, this buffer will be effective from a pH of 9.62 to a pH of 11.62.

(b) The capacity of the buffer is reached when all of the weak base or all of the conjugate acid has been neutralized by the added strong acid or strong base. Because their concentrations are the same, the number of moles of base is equal to the number of moles of conjugate acid in the same volume of solution.

$$\text{amount of weak base} = 125\text{ mL} \times \frac{0.0500\text{ mmol}}{1\text{ mL}} = 6.25\text{ mmol } CH_3NH_2 \text{ or } CH_3NH_3^+$$

Thus, the buffer capacity is 6.25 millimoles of acid or base per 125 mL buffer solution.

23. **(M)**

(a) The pH of this buffer solution is determined with the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = -\log(1.8\times10^{-4}) + \log\frac{8.5\,\text{mmol}/75.0\,\text{mL}}{15.5\,\text{mmol}/75.0\,\text{mL}}$$

$$= 3.74 - 0.26 = 3.48$$

[Note: the solution is not a good buffer, as $[\text{CHO}_2^-] = 1.1\times10^{-1}$, which is only ~ 600 times K_a]

(b) Amount of added $\text{OH}^- = 0.25\,\text{mmol Ba(OH)}_2 \times \frac{2\,\text{mmol OH}^-}{1\,\text{mmol Ba(OH)}_2} = 0.50\,\text{mmol OH}^-$

The OH^- added reacts with the formic acid and produces formate ion.

Equation:	$HCHO_2$(aq)	+	OH^-(aq)	$\rightleftharpoons$	CHO_2^-(aq)	+	H_2O(l)
Buffer:	15.5 mmol		≈ 0 M		8.5 mmol		–
Add base:			+0.50 mmol				
React:	–0.50 mmol		–0.50 mmol		+0.50 mmol		–
Final:	15.0 mmol		0 mmol		9.0 mmol		–

$$\text{pH} = \text{p}K_a + \log\frac{[\text{CHO}_2^-]}{[\text{HCHO}_2]} = -\log(1.8\times10^{-4}) + \log\frac{9.0\,\text{mmol}/75.0\,\text{mL}}{15.0\,\text{mmol}/75.0\,\text{mL}}$$

$$= 3.74 - 0.22 = 3.52$$

(c) Amount of added $\text{H}_3\text{O}^+ = 1.05\text{ mL acid} \times \frac{12\text{ mmol HCl}}{1\text{ mL acid}} \times \frac{1\text{ mmol H}_3\text{O}^+}{1\text{ mmol HCl}} = 13\text{ mmol H}_3\text{O}^+$

The H_3O^+ added reacts with the formate ion and produces formic acid.

Equation:	CHO_2^-(aq)	+	H_3O^+(aq)	$\rightleftharpoons$	$HCHO_2$(aq)	+	H_2O(l)
Buffer :	8.5 mmol		≈ 0 mmol		15.5 mmol		–
Add acid :			+13 mmol				
React :	– 8.5 mmol		– 8.5 mmol		+8.5 mmol		–
Final :	0 mmol		4.5 mmol		24.0 mmol		–

The buffer's capacity has been exceeded. The pH of the solution is determined by the excess strong acid present.

$$[\text{H}_3\text{O}^+] = \frac{4.5\,\text{mmol}}{75.0\,\text{mL} + 1.05\,\text{mL}} = 0.059\,\text{M}; \qquad \text{pH} = -\log(0.059) = 1.23$$

24. **(D)** For $NH_3, pK_b = -\log\left(1.8\times10^{-5}\right)$ For $NH_4{}^+, pK_a = 14.00 - pK_b = 14.00 - 4.74 = 9.26$

(a) $$\left[NH_3\right] = \frac{1.68\,\text{g NH}_3}{0.500\text{ L}}\times\frac{1\text{ mol NH}_3}{17.03\text{ g NH}_3} = 0.197\text{ M}$$

$$\left[NH_4{}^+\right] = \frac{4.05\text{ g }\left(NH_4\right)_2SO_4}{0.500\,\text{L}}\times\frac{1\text{ mol}\left(NH_4\right)_2SO_4}{132.1\text{ g }\left(NH_4\right)_2SO_4}\times\frac{2\,\text{mol NH}_4{}^+}{1\text{mol }\left(NH_4\right)_2SO_4} = 0.123\text{ M}$$

$$\text{pH} = pK_a + \log\frac{\left[NH_3\right]}{\left[NH_4{}^+\right]} = 9.26 + \log\frac{0.197\text{ M}}{0.123\text{ M}} = 9.46$$

(b) The $OH^-(aq)$ reacts with the $NH_4{}^+(aq)$ to produce an equivalent amount of $NH_3(aq)$.

$$\left[OH^-\right]_i = \frac{0.88\text{ g NaOH}}{0.500\,\text{L}}\times\frac{1\text{mol NaOH}}{40.00\text{ g NaOH}}\times\frac{1\text{mol OH}^-}{1\text{mol NaOH}} = 0.044\,\text{M}$$

$$\begin{array}{llllll}
\text{Equation:} & NH_4{}^+(aq)\; + & OH^-(aq) & \rightleftharpoons & NH_3(aq) & +\quad H_2O(l)\\
\text{Initial:} & 0.123\,\text{M} & \approx 0\,\text{M} & & 0.197\,\text{M} & -\\
\text{Add NaOH:} & & +0.044\,\text{M} & & & \\
\text{React:} & -0.044\,\text{M} & -0.044\,\text{M} & & +0.044\,\text{M} & -\\
\text{Final:} & 0.079\,\text{M} & 0.0000\,\text{M} & & 0.241\,\text{M} & -
\end{array}$$

$$\text{pH} = pK_a + \log\frac{\left[NH_3\right]}{\left[NH_4{}^+\right]} = 9.26 + \log\frac{0.241\,\text{M}}{0.079\,\text{M}} = 9.74$$

(c)
$$\begin{array}{llllll}
\text{Equation:} & NH_3(aq)\; + & H_3O^+(aq) & \rightleftharpoons & NH_4{}^+(aq) & +\quad H_2O(l)\\
\text{Initial:} & 0.197\,\text{M} & \approx 0\,\text{M} & & 0.123\,\text{M} & -\\
\text{Add HCl:} & & +x\,\text{M} & & & \\
\text{React:} & -x\,\text{M} & -x\,\text{M} & & +x\,\text{M} & -\\
\text{Final:} & (0.197-x)\,\text{M} & 1\times10^{-9}\text{ M}\approx 0 & & (0.123+x)\,\text{M} & -
\end{array}$$

$$\text{pH} = 9.00 = pK_a + \log\frac{\left[NH_3\right]}{\left[NH_4{}^+\right]} = 9.26 + \log\frac{(0.197-x)\,\text{M}}{(0.123+x)\,\text{M}}$$

$$\log\frac{(0.197-x)\,\text{M}}{(0.123+x)\,\text{M}} = 9.00 - 9.26 = -0.26 \qquad \frac{(0.197-x)\,\text{M}}{(0.123+x)\,\text{M}} = 10^{-0.26} = 0.55$$

$$0.197 - x = 0.55(0.123 + x) = 0.068 + 0.55x \quad 1.55x = 0.197 - 0.068 = 0.129$$

$$x = \frac{0.129}{1.55} = 0.0832\,\text{M}$$

$$\text{volume HCl} = 0.500\,\text{L}\times\frac{0.0832\text{ mol H}_3\text{O}^+}{1\text{L soln}}\times\frac{1\text{mol HCl}}{1\text{mol H}_3\text{O}^+}\times\frac{1000\,\text{mL HCl}}{12\text{ mol HCl}} = 3.5\,\text{mL}$$

25. (D)

(a) We use the Henderson-Hasselbalch equation to determine the pH of the solution. The total solution volume is

$$36.00\,\text{mL} + 64.00\,\text{mL} = 100.00\,\text{mL}.\ \text{p}K_\text{a} = 14.00 - \text{p}K_\text{b} = 14.00 + \log\left(1.8\times10^{-5}\right) = 9.26$$

$$\left[\text{NH}_3\right] = \frac{36.00\,\text{mL}\times0.200\,\text{M NH}_3}{100.00\,\text{mL}} = \frac{7.20\,\text{mmol NH}_3}{100.0\ \text{mL}} = 0.0720\ \text{M}$$

$$\left[\text{NH}_4^{\ +}\right] = \frac{64.00\,\text{mL}\times0.200\,\text{M NH}_4^{\ +}}{100.00\,\text{mL}} = \frac{12.8\,\text{mmol NH}_4^{\ +}}{100.0\,\text{mL}} = 0.128\,\text{M}$$

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{NH}_3]}{[\text{NH}_4^{\ +}]} = 9.26 + \log\frac{0.0720\ \text{M}}{0.128\,\text{M}} = 9.01\ \approx\ 9.00$$

(b) The solution has $\left[\text{OH}^-\right] = 10^{-4.99} = 1.0\times10^{-5}\ \text{M}$

The Henderson-Hasselbalch equation depends on the assumption that:

$$\left[\text{NH}_3\right] \gg 1.8\times10^{-5}\ \text{M} \ll \left[\text{NH}_4^{\ +}\right]$$

If the solution is diluted to 1.00 L, $\left[\text{NH}_3\right] = 7.20\times10^{-3}\ \text{M}$, and

$\left[\text{NH}_4^{\ +}\right] = 1.28\times10^{-2}\ \text{M}$. These concentrations are consistent with the assumption.

However, if the solution is diluted to 1000. L, $\left[\text{NH}_3\right] = 7.2\times10^{-6}\ \text{M}$, and $\left[\text{NH}_3\right] = 1.28\times10^{-5}\ \text{M}$, and these two concentrations are not consistent with the assumption. Thus, in 1000. L of solution, the given quantities of NH_3 and $\text{NH}_4^{\ +}$ will not produce a solution with $\text{pH} = 9.00$. With sufficient dilution, the solution will become indistinguishable from pure water (i.e.; its pH will equal 7.00).

(c) The 0.20 mL of added 1.00 M HCl does not significantly affect the volume of the solution, but it does add $0.20\,\text{mL}\times1.00\,\text{M HCl} = 0.20\,\text{mmol H}_3\text{O}^+$. This added H_3O^+ reacts with NH_3, decreasing its amount from 7.20 mmol NH_3 to 7.00 mmol NH_3, and increasing the amount of $\text{NH}_4^{\ +}$ from 12.8 mmol $\text{NH}_4^{\ +}$ to 13.0 mmol $\text{NH}_4^{\ +}$, as the reaction: $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^{\ +} + \text{H}_2\text{O}$

$$\text{pH} = 9.26 + \log\frac{7.00\,\text{mmol NH}_3\,/\,100.20\,\text{mL}}{13.0\ \text{mmol NH}_4^{\ +}\,/\,100.20\,\text{mL}} = 8.99$$

(d) We see in the calculation of part (c) that the total volume of the solution does not affect the pOH of the solution, at least as long as the Henderson-Hasselbalch equation is obeyed. We let x represent the number of millimoles of H_3O^+ added, through 1.00 M HCl. This increases the amount of NH_4^+ and decreases the amount of NH_3, through the reaction $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$

$$\text{pH} = 8.90 = 9.26 + \log\frac{7.20 - x}{12.8 + x}; \quad \log\frac{7.20 - x}{12.8 + x} = 8.90 - 9.26 = -0.36$$

Inverting, we have:

$$\frac{12.8 + x}{7.20 - x} = 10^{0.36} = 2.29; \quad 12.8 + x = 2.29(7.20 - x) = 16.5 - 2.29x$$

$$x = \frac{16.5 - 12.8}{1.00 + 2.29} = 1.1 \text{ mmol } H_3O^+$$

$$\text{vol } 1.00\,\text{M HCl} = 1.1\,\text{mmol } H_3O^+ \times \frac{1\,\text{mmol HCl}}{1\,\text{mmol } H_3O^+} \times \frac{1\,\text{mL soln}}{1.00\,\text{mmol HCl}} = 1.1\,\text{mL } 1.00\,\text{M HCl}$$

26. **(D)**

(a)

$$\left[C_2H_3O_2^-\right] = \frac{12.0\,\text{g } NaC_2H_3O_2}{0.300\,\text{L soln}} \times \frac{1\,\text{mol } NaC_2H_3O_2}{82.03\,\text{g } NaC_2H_3O_2} \times \frac{1\,\text{mol } C_2H_3O_2^-}{1\,\text{mol } NaC_2H_3O_2} = 0.488\,\text{M } C_2H_3O_2^-$$

Equation :	$HC_2H_3O_2$	$+ H_2O \rightleftharpoons$	$C_2H_3O_2^-$	$+ \quad H_3O^+$
Initial :	0 M	–	0 M	0.200 M
Add $C_2H_3O_2^-$	0 M	–	+0.488 M	0 M
Consume H_3O^+	+ 0.200 M	–	–0.200 M	–0.200 M
Buffer :	0.200 M	–	0.288 M	≈ 0 M

Then use the Henderson-Hasselbalch equation to find the pH.

$$\text{pH} = \text{p}K_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 4.74 + \log\frac{0.288\,\text{M}}{0.200\,\text{M}} = 4.74 + 0.16 = 4.90$$

(b) We first calculate the initial $\left[OH^-\right]$ due to the added $Ba(OH)_2$.

$$\left[OH^-\right] = \frac{1.00\,\text{g } Ba(OH)_2}{0.300\,\text{L}} \times \frac{1\,\text{mol } Ba(OH)_2}{171.3\,\text{g } Ba(OH)_2} \times \frac{2\,\text{mol } OH^-}{1\,\text{mol } Ba(OH)_2} = 0.0389\,\text{M}$$

Then $HC_2H_3O_2$ is consumed in the neutralization reaction shown directly below.

Equation:	$HC_2H_3O_2$	$+ \quad OH^-$	$\rightleftharpoons \quad C_2H_3O_2^-$	$+ \quad H_2O$
Initial:	0.200 M	0.0389 M	0.288 M	—
Consume OH^-:	-0.0389 M	-0.0389 M	+0.0389 M	—
Buffer:	0.161 M	~ 0M	0.327 M	—

Then use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log\frac{0.327\,\text{M}}{0.161\,\text{M}} = 4.74 + 0.31 = 5.05$$

(c) Ba(OH)_2 can be added up until all of the $\text{HC}_2\text{H}_3\text{O}_2$ is consumed.

$$\text{Ba(OH)}_2 + 2\text{HC}_2\text{H}_3\text{O}_2 \longrightarrow \text{Ba(C}_2\text{H}_3\text{O}_2)_2 + 2\text{H}_2\text{O}$$

$$\text{moles of Ba(OH)}_2 = 0.300\,\text{L} \times \frac{0.200\,\text{mol HC}_2\text{H}_3\text{O}_2}{1\,\text{L soln}} \times \frac{1\,\text{mol Ba(OH)}_2}{2\,\text{mol HC}_2\text{H}_3\text{O}_2} = 0.0300\,\text{mol Ba(OH)}_2$$

$$\text{mass of Ba(OH)}_2 = 0.0300\,\text{mol Ba(OH)}_2 \times \frac{171.3\,\text{g Ba(OH)}_2}{1\,\text{mol Ba(OH)}_2} = 5.14\,\text{g Ba(OH)}_2$$

(d) 0.36 g Ba(OH)_2 is too much for the buffer to handle and it is the excess of OH^- originating from the Ba(OH)_2 that determines the pOH of the solution.

$$[\text{OH}^-] = \frac{0.36\,\text{g Ba(OH)}_2}{0.300\,\text{L soln}} \times \frac{1\,\text{mol Ba(OH)}_2}{171.3\,\text{g Ba(OH)}_2} \times \frac{2\,\text{mol OH}^-}{1\,\text{mol Ba(OH)}_2} = 1.4 \times 10^{-2}\,\text{M OH}^-$$

$$\text{pOH} = -\log(1.4 \times 10^{-2}) = 1.85 \qquad \text{pH} = 14.00 - 1.85 = 12.15$$

Acid–Base Indicators

27. **(E)**

(a) The pH color change range is 1.00 pH unit on either side of $\text{p}K_\text{HIn}$. If the pH color change range is below $\text{pH} = 7.00$, the indicator changes color in acidic solution. If it is above $\text{pH} = 7.00$, the indicator changes color in alkaline solution. If $\text{pH} = 7.00$ falls within the pH color change range, the indicator changes color near the neutral point.

Indicator	K_HIn	$\text{p}K_\text{HIn}$	pH Color Change Range	Changes Color in?
Bromphenol blue	1.4×10^{-4}	3.85	2.9 (yellow) to 4.9 (blue)	acidic solution
Bromcresol green	2.1×10^{-5}	4.68	3.7 (yellow) to 5.7 (blue)	acidic solution
Bromthymol blue	7.9×10^{-8}	7.10	6.1 (yellow) to 8.1 (blue)	neutral solution
2,4-Dinitrophenol	1.3×10^{-4}	3.89	2.9 (colorless) to 4.9 (yellow)	acidic solution
Chlorophenol red	1.0×10^{-6}	6.00	5.0 (yellow) to 7.0 (red)	acidic solution
Thymolphthalein	1.0×10^{-10}	10.00	9.0 (colorless) to 11.0 (blue)	basic solution

(b) If bromcresol green is green, the pH is between 3.7 and 5.7, probably about $\text{pH} = 4.7$. If chlorophenol red is orange, the pH is between 5.0 and 7.0, probably about $\text{pH} = 6.0$.

28. **(M)** We first determine the pH of each solution, and then use the answer in Exercise 27 (a) to predict the color of the indicator. (The weakly acidic or basic character of the indicator does not affect the pH of the solution, since very little indicator is added.)

(a) $\left[H_3O^+\right] = 0.100 \text{ M HCl} \times \frac{1 \text{ mol } H_3O^+}{1 \text{ mol HCl}} = 0.100 \text{ M}; \quad pH = -\log(0.100 \text{ M}) = 1.000$
2,4-dinitrophenol is colorless.

(b) Solutions of NaCl(aq) are pH neutral, with $pH = 7.000$. Chlorphenol red assumes its neutral color in such a solution; the solution is red/orange.

(c)

Equation:	$NH_3(aq)$	+ $H_2O(l)$	$\rightleftharpoons$ $NH_4^+(aq)$	+ $OH^-(aq)$
Initial:	1.00 M	—	0 M	≈ 0 M
Changes:	$-x$ M	—	$+x$ M	$+x$ M
Equil:	$(1.00 - x)$ M	—	x M	x M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00} \qquad x = 4.2 \times 10^{-3} \text{M} = [OH^-]$$

(x << 1.00 M, thus the approximation was valid).

$pOH = -\log(4.2 \times 10^{-3}) = 2.38 \qquad pH = 14.00 - 2.38 = 11.62$

Thus, thymolphthalein assumes its blue color in solutions with $pH > 11.62$.

(d) From Figure 17-8, seawater has $pH = 7.00$ to 8.50. Bromcresol green solution is blue.

29. **(M)**

(a) In an Acid–Base titration, the pH of the solution changes sharply at a definite pH that is known prior to titration. (This pH change occurs during the addition of a very small volume of titrant.) Determining the pH of a solution, on the other hand, is more difficult because the pH of the solution is not known precisely in advance. Since each indicator only serves to fix the pH over a quite small region, often less than 2.0 pH units, several indicators—carefully chosen to span the entire range of 14 pH units—must be employed to narrow the pH to ± 1 pH unit or possibly lower.

(b) An indicator is, after all, a weak acid. Its addition to a solution will affect the acidity of that solution. Thus, one adds only enough indicator to show a color change and not enough to affect solution acidity.

30. **(E)**

(a) We use an equation similar to the Henderson-Hasselbalch equation to determine the relative concentrations of HIn, and its anion, In^-, in this solution.

$$\text{pH} = \text{p}K_{\text{HIn}} + \log\frac{[\text{In}^-]}{[\text{HIn}]};\quad 4.55 = 4.95 + \log\frac{[\text{In}^-]}{[\text{HIn}]};\quad \log\frac{[\text{In}^-]}{[\text{HIn}]} = 4.55 - 4.95 = -0.40$$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = 10^{-0.40} = 0.40 = \frac{x}{100-x}\qquad x = 40 - 0.40x\qquad x = \frac{40}{1.40} = 29\%\ \text{In}^-\ \text{and}\ 71\%\ \text{HIn}$$

(b) When the indicator is in a solution whose pH equals its $\text{p}K_a$ (4.95), the ratio $[\text{In}^-]/[\text{HIn}] = 1.00$. And yet, at the midpoint of its color change range (about $\text{pH} = 5.3$), the ratio $[\text{In}^-]$/[HIn] is greater than 1.00. Even though $[\text{HIn}] < [\text{In}^-]$ at this midpoint, the contribution of HIn to establishing the color of the solution is about the same as the contribution of In^-. This must mean that HIn (red) is more strongly colored than In^- (yellow).

31. **(E)**

(a) 0.10 M KOH is an alkaline solution and phenol red will display its basic color in such a solution; the solution will be red.

(b) 0.10 M $HC_2H_3O_2$ is an acidic solution, although that of a weak acid, and phenol red will display its acidic color in such a solution; the solution will be yellow.

(c) 0.10 M NH_4NO_3 is an acidic solution due to the hydrolysis of the ammonium ion. Phenol red will display its acidic color, that is, yellow, in this solution.

(d) 0.10 M HBr is an acidic solution, the aqueous solution of a strong acid. Phenol red will display its acidic color in this solution; the solution will be yellow.

(e) 0.10 M NaCN is an alkaline solution because of the hydrolysis of the cyanide ion. Phenol red will display its basic color, red, in this solution.

(f) An equimolar acetic acid–potassium acetate buffer has $\text{pH} = \text{p}K_a = 4.74$ for acetic acid. In this solution phenol red will display its acid color, namely, yellow.

32. **(M)**

(a) $\text{pH} = -\log(0.205) = 0.688$ The indicator is red in this solution.

(b) The total volume of the solution is 600.0 mL. We compute the amount of each solute.

$$\text{amount } H_3O^+ = 350.0\ \text{mL} \times 0.205\ \text{M} = 71.8\,\text{mmol } H_3O^+$$

$$\text{amount } NO_2^- = 250.0\,\text{mL} \times 0.500\,\text{M} = 125\,\text{mmol } NO_2^-$$

$$[H_3O^+] = \frac{71.8\,\text{mmol}}{600.0\,\text{mL}} = 0.120\,\text{M}\qquad [NO_2^-] = \frac{125\,\text{mmol}}{600.0\,\text{mL}} = 0.208\,\text{M}$$

The H_3O^+ and NO_2^- react to produce a buffer solution in which $[HNO_2] = 0.120\,\text{M}$ and $[NO_2^-] = 0.208 - 0.120 = 0.088\,\text{M}$. We use the

Henderson-Hasselbalch equation to determine the pH of this solution.

$pK_a = -\log\left(7.2\times10^{-4}\right) = 3.14$

$\text{pH} = pK_a + \log\frac{\left[NO_2^-\right]}{\left[HNO_2\right]} = 3.14 + \log\frac{0.088\,M}{0.120\,M} = 3.01$ The indicator is yellow in this solution.

(c) The total volume of the solution is 750. mL. We compute the amount and then the concentration of each solute. Amount $OH^- = 150\,mL \times 0.100\,M = 15.0\,mmol\ OH^-$

This OH^- reacts with HNO_2 in the buffer solution to neutralize some of it and leave 56.8 mmol ($= 71.8 - 15.0$) unneutralized.

$\left[HNO_2\right] = \frac{56.8\,mmol}{750.\ mL} = 0.0757\,M \qquad \left[NO_2^-\right] = \frac{(125+15)\,mmol}{750.\ mL} = 0.187\,M$

We use the Henderson-Hasselbalch equation to determine the pH of this solution.

$\text{pH} = pK_a + \log\frac{\left[NO_2^-\right]}{\left[HNO_2\right]} = 3.14 + \log\frac{0.187\,M}{0.0757\,M} = 3.53$

The indicator is yellow in this solution.

(d) We determine the $\left[OH^-\right]$ due to the added $Ba(OH)_2$.

$\left[OH^-\right] = \frac{5.00\,g\ Ba(OH)_2}{0.750\,L} \times \frac{1\,mol\ Ba(OH)_2}{171.34\,g\ Ba(OH)_2} \times \frac{2\,mol\ OH^-}{1\,mol\ Ba(OH)_2} = 0.0778\,M$

This is sufficient $\left[OH^-\right]$ to react with the existing $\left[HNO_2\right]$ and leave an excess

$\left[OH^-\right] = 0.0778\,M - 0.0757\,M = 0.0021\,M.$ $\text{pOH} = -\log\left(0.0021\right) = 2.68.$

$\text{pH} = 14.00 - 2.68 = 11.32$ The indicator is blue in this solution.

<u>**33.**</u> **(M)** Moles of HCl = $C \times V$ = 0.04050 M × 0.01000 L = 4.050×10^{-4} moles
Moles of $Ba(OH)_2$ at endpoint = $C \times V$ = 0.01120 M × 0.01790 L = 2.005×10^{-4} moles.
Moles of HCl that react with $Ba(OH)_2$ = 2 × moles $Ba(OH)_2$
Moles of HCl in excess 4.050×10^{-4} moles – 4.010×10^{-4} moles = $4.0\underline{5} \times 10^{-6}$ moles
Total volume at the equivalence point = (10.00 mL + 17.90 mL) = 27.90 mL

$[HCl]_{excess} = \frac{4.05\times10^{-6}\ \text{mole HCl}}{0.02790\ \text{L}} = 1.45 \times 10^{-4}\ M;\quad \text{pH} = -\log(1.45 \times 10^{-4}) = 3.84$

(a) The approximate pK_{HIn} = 3.84 (generally $\pm$ 1 pH unit)

(b) This is a relatively good indicator (with ≈ 1 % of the equivalence point volume), however, pK_{Hin} is not very close to the theoretical pH at the equivalence point (pH = 7.000) For very accurate work, a better indicator is needed (i.e., bromthymol blue (pK_{Hin} = 7.1). Note: 2,4-dinitrophenol works relatively well here because the pH near the equivalence point of a strong acid/strong base titration rises very sharply (≈ 6 pH units for an addition of only 2 drops (0.10 mL)).

34. Solution (a): 100.0 mL of 0.100 M HCl, $[H_3O^+] = 0.100$ M and pH = 1.000 (yellow)
Solution (b): 150 mL of 0.100 M $NaC_2H_3O_2$
K_a of $HC_2H_3O_3 = 1.8 \times 10^{-5}$ K_b of $C_2H_3O_2^- = 5.6 \times 10^{-10}$

$$C_2H_3O_2^-(aq) + H_2O(l) \xrightleftharpoons{K_b = 5.6 \times 10^{-10}} HC_2H_3O_2(aq) + OH^-(aq)$$

Initial	0.100 M	—	0 M	~ 0 M
Change	$-x$	—	$+x$	$+x$
Equil.	$0.100 - x$	—	x	x

Assume x is small: $5.6 \times 10^{-11} = x^2$; $x = 7.4\underline{8} \times 10^{-6}$ M (assumption valid by inspection)
$[OH^-] = x = 7.4\underline{8} \times 10^{-6}$ M, pOH = 5.13 and pH = 8.87 (green-blue)
Mixture of solution (a) and (b). Total volume = 250.0 mL
$n_{HCl} = C \times V = 0.1000 \text{ L} \times 0.100 \text{ M} = 0.0100$ mol HCl
$n_{C_2H_3O_2^-} = C \times V = 0.1500 \text{ L} \times 0.100 \text{ M} = 0.0150$ mol $C_2H_3O_2^-$
HCl is the limiting reagent. Assume 100% reaction.
Therefore, 0.0050 mole $C_2H_3O_2^-$ is left unreacted, and 0.0100 moles of $HC_2H_3O_2$ form.

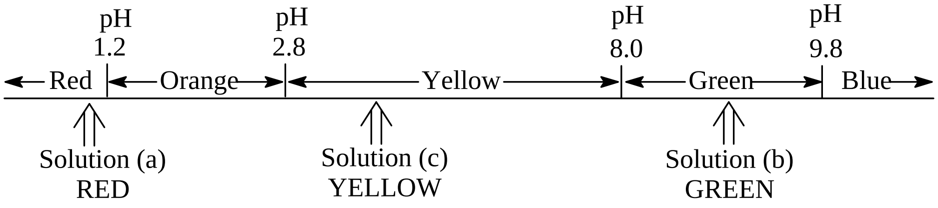
$$[C_2H_3O_2^-] = \frac{n}{V} = \frac{0.0050 \text{ mol}}{0.250 \text{ L}} = 0.020 \text{ M} \qquad [HC_2H_3O_2] = \frac{n}{V} = \frac{0.0100 \text{ mol}}{0.250 \text{ L}} = 0.0400 \text{ M}$$

$$HC_2H_3O_2(aq) + H_2O(l) \xrightleftharpoons{K_a = 1.8 \times 10^{-5}} C_2H_3O_2^-(aq) + H_3O^+(aq)$$

Initial	0.0400 M	—	0.020 M	~ 0 M
Change	$-x$	—	$+x$	$+x$
Equil.	$0.0400 - x$	—	$0.020 + x$	x

$$1.8 \times 10^{-5} = \frac{x(0.020 + x)}{0.0400 - x} \approx \frac{x(0.020)}{0.0400} \qquad x = 3.6 \times 10^{-5}$$

(proof 0.18 % < 5%, the assumption was valid)
$[H_3O^+] = 3.6 \times 10^{-5}$ pH = 4.44 Color of thymol blue at various pHs:



Neutralization Reactions

35. **(E)** The reaction (to second equiv. pt.) is: $H_3PO_4(aq) + 2\,KOH(aq) \longrightarrow K_2HPO_4(aq) + 2H_2O(l)$. The molarity of the H_3PO_4 solution is determined in the following manner.

$$H_3PO_4 \text{ molarity} = \frac{31.15\,\text{mL KOH soln} \times \dfrac{0.2420\,\text{mmol KOH}}{1\,\text{mL KOH soln}} \times \dfrac{1\,\text{mmol } H_3PO_4}{2\,\text{mmol KOH}}}{25.00\,\text{mL } H_3PO_4 \text{ soln}} = 0.1508\,\text{M}$$

36. **(E)** The reaction (first to second equiv. pt.) is:

$NaH_2PO_4(aq) + NaOH(aq) \longrightarrow Na_2HPO_4(aq) + H_2O(l)$. The molarity of the H_3PO_4 solution is determined in the following manner.

$$H_3PO_4 \text{ molarity} = \frac{18.67\,\text{mL NaOH soln} \times \dfrac{0.1885\,\text{mmol NaOH}}{1\,\text{mL NaOH soln}} \times \dfrac{1\,\text{mmol } H_3PO_4}{1\,\text{mmol NaOH}}}{20.00\,\text{mL } H_3PO_4 \text{ soln}} = 0.1760\,\text{M}$$

37. **(M)** Here we must determine the amount of H_3O^+ or OH^- in each solution, and the amount of excess reagent.

$$\text{amount } H_3O^+ = 50.00\,\text{mL} \times \frac{0.0150\,\text{mmol } H_2SO_4}{1\,\text{mL soln}} \times \frac{2\,\text{mmol } H_3O^+}{1\,\text{mmol } H_2SO_4} = 1.50\,\text{mmol } H_3O^+$$

(assuming complete ionization of H_2SO_4 and HSO_4^- in the presence of OH^-)

$$\text{amount } OH^- = 50.00\,\text{mL} \times \frac{0.0385\,\text{mmol NaOH}}{1\,\text{mL soln}} \times \frac{1\,\text{mmol } OH^-}{1\,\text{mmol NaOH}} = 1.93\,\text{mmol } OH^-$$

$$\begin{array}{lllcl} \text{Result: Titration reaction:} & OH^-(aq) & + \; H_3O^+(aq) & \rightleftharpoons & 2H_2O(l) \\ \text{Initial amounts:} & 1.93\,\text{mmol} & \;\; 1.50\,\text{mmol} & & \\ \text{After reaction:} & 0.43\,\text{mmol} & \;\; \approx 0\,\text{mmol} & & \end{array}$$

$$\left[OH^-\right] = \frac{0.43\,\text{mmol } OH^-}{100.0\,\text{mL soln}} = 4.3 \times 10^{-3}\,\text{M}$$

$$\text{pOH} = -\log\left(4.3 \times 10^{-3}\right) = 2.37 \qquad \text{pH} = 14.00 - 2.37 = 11.63$$

38. **(M)** Here we must determine the amount of solute in each solution, followed by the amount of excess reagent.

$$\left[H_3O^+\right] = 10^{-2.50} = 0.0032\,M$$

$$\text{mmol HCl} = 100.0\,\text{mL} \times \frac{0.0032\,\text{mmol } H_3O^+}{1\,\text{mL soln}} \times \frac{1\,\text{mmol HCl}}{1\,\text{mmol } H_3O^+} = 0.32\,\text{mmol HCl}$$

$$\text{pOH} = 14.00 - 11.00 = 3.00 \qquad \left[OH^-\right] = 10^{-3.00} = 1.0\times10^{-3}\,M$$

$$\text{mmol NaOH} = 100.0\,\text{mL} \times \frac{0.0010\,\text{mmol } OH^-}{1\,\text{mL soln}} \times \frac{1\,\text{mmol NaOH}}{1\,\text{mmol } OH^-} = 0.10\,\text{mmol NaOH}$$

Result:

Titration reaction:	$NaOH(aq)$	+	$HCl(aq)$	$\longrightarrow$	$NaCl(aq)$	+	$H_2O(l)$
Initial amounts:	0.10 mmol		0.32 mmol		0 mmol		–
After reaction:	0.00 mmol		0.22 mmol		0.10 mmol		–

$$\left[H_3O^+\right] = \frac{0.22\,\text{mmol HCl}}{200.0\,\text{mL soln}} \times \frac{1\,\text{mmol } H_3O^+}{1\,\text{mmol HCl}} = 1.1\times10^{-3}\,M \qquad \text{pH} = -\log\left(1.1\times10^{-3}\right) = 2.96$$

Titration Curves

39. **(M)** First we calculate the amount of HCl. The relevant titration reaction is

$$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$$

$$\text{amount HCl} = 25.00\text{ mL} \times \frac{0.160\text{ mmol HCl}}{1\text{ mL soln}} = 4.00\text{ mmol HCl} = 4.00\text{ mmol } H_3O^+ \text{present}$$

Then, in each case, we calculate the amount of OH^- that has been added, determine which ion, $OH^-(aq)$ or $H_3O^+(aq)$, is in excess, compute the concentration of that ion, and determine the pH.

(a) $\text{amount } OH^- = 10.00\text{ mL} \times \frac{0.242\text{ mmol } OH^-}{1\text{ mL soln}} = 2.42\text{ mmol } OH^-$; H_3O^+ is in excess.

$$[H_3O^+] = \frac{4.00\text{ mmol } H_3O^+ - \left(2.42\text{ mmol } OH^- \times \frac{1\text{ mmol } H_3O^+}{1\text{ mmol } OH^-}\right)}{25.00\text{ mL originally} + 10.00\text{ mL titrant}} = 0.0451\text{ M}$$

$$\text{pH} = -\log(0.0451) = 1.346$$

(b) amount $\text{OH}^- = 15.00\ \text{mL} \times \dfrac{0.242\ \text{mmol OH}^-}{1\ \text{mL soln}} = 3.63\ \text{mmol OH}^-$; H_3O^+ is in excess.

$$[\text{H}_3\text{O}^+] = \frac{4.00\ \text{mmol H}_3\text{O}^+ - \left(3.63\ \text{mmol OH}^- \times \dfrac{1\ \text{mmol H}_3\text{O}^+}{1\ \text{mmol OH}^-}\right)}{25.00\ \text{mL originally} + 15.00\ \text{mL titrant}} = 0.00925\ \text{M}$$

$$\text{pH} = -\log(0.00925) = 2.034$$

40. **(M)** The relevant titration reaction is $\text{KOH(aq)} + \text{HCl(aq)} \rightarrow \text{KCl(aq)} + \text{H}_2\text{O(l)}$

$$\text{mmol of KOH} = 20.00\ \text{mL} \times \frac{0.275\ \text{mmol KOH}}{1\ \text{mL soln}} = 5.50\ \text{mmol KOH}$$

(a) The total volume of the solution is $V = 20.00\ \text{mL} + 15.00\ \text{mL} = 35.00\ \text{mL}$

$$\text{mmol HCl} = 15.00\ \text{mL} \times \frac{0.350\ \text{mmol HCl}}{1\ \text{mL soln}} = 5.25\ \text{mmol HCl}$$

$$\text{mmol excess OH}^- = (5.50\ \text{mmol KOH-}5.25\ \text{mmol HCl}) \times \frac{1\ \text{mmol OH}^-}{1\ \text{mmol KOH}} = 0.25\ \text{mmol OH}^-$$

$$\left[\text{OH}^-\right] = \frac{0.25\ \text{mmol OH}^-}{35.00\ \text{mL soln}} = 0.0071\text{M} \qquad \text{pOH} = -\log(0.0071) = 2.15$$

$$\text{pH} = 14.00 - 2.15 = 11.85$$

(b) The total volume of solution is $V = 20.00\ \text{mL} + 20.00\ \text{mL} = 40.00\ \text{mL}$

$$\text{mmol HCl} = 20.00\ \text{mL} \times \frac{0.350\ \text{mmol HCl}}{1\ \text{mL soln}} = 7.00\ \text{mmol HCl}$$

$$\text{mmol excess H}_3\text{O}^+ = (7.00\ \text{mmol HCl} - 5.50\ \text{mmol KOH}) \times \frac{1\ \text{mmol H}_3\text{O}^+}{1\ \text{mmol HCl}}$$

$$= 1.50\ \text{mmol H}_3\text{O}^+$$

$$\left[\text{H}_3\text{O}^+\right] = \frac{1.50\ \text{mmol H}_3\text{O}^+}{40.00\ \text{mL}} = 0.0375\ \text{M} \qquad \text{pH} = -\log(0.0375) = 1.426$$

41. **(M)** The relevant titration reaction is $\text{HNO}_2\text{(aq)} + \text{NaOH(aq)} \rightarrow \text{NaNO}_2\text{(aq)} + \text{H}_2\text{O(l)}$

$$\text{amount HNO}_2 = 25.00\ \text{mL} \times \frac{0.132\ \text{mmol HNO}_2}{1\ \text{mL soln}} = 3.30\ \text{mmol HNO}_2$$

(a) The volume of the solution is $25.00\text{ mL} + 10.00\text{ mL} = 35.00\text{ mL}$

$$\text{amount NaOH} = 10.00\text{ mL} \times \frac{0.116\text{ mmol NaOH}}{1\text{ mL soln}} = 1.16\text{ mmol NaOH}$$

1.16 mmol $NaNO_2$ are formed in this reaction and there is an excess of (3.30 mmol HNO_2 $-$1.16 mmol NaOH) = 2.14 mmol HNO_2. We can use the Henderson-Hasselbalch equation to determine the pH of the solution.

$$\text{p}K_a = -\log\left(7.2 \times 10^{-4}\right) = 3.14$$

$$\text{pH} = \text{p}K_a + \log\frac{\left[NO_2^-\right]}{\left[HNO_2\right]} = 3.14 + \log\frac{1.16\text{ mmol }NO_2^- / 35.00\text{ mL}}{2.14\text{ mmol }HNO_2 / 35.00\text{ mL}} = 2.87$$

(b) The volume of the solution is $25.00\text{ mL} + 20.00\text{ mL} = 45.00\text{ mL}$

$$\text{amount NaOH} = 20.00\text{ mL} \times \frac{0.116\text{ mmol NaOH}}{1\text{ mL soln}} = 2.32\text{ mmol NaOH}$$

2.32 mmol $NaNO_2$ are formed in this reaction and there is an excess of (3.30 mmol HNO_2 – 2.32 mmol NaOH =) 0.98 mmol HNO_2.

$$\text{pH} = \text{p}K_a + \log\frac{\left[NO_2^-\right]}{\left[HNO_2\right]} = 3.14 + \log\frac{2.32\text{ mmol }NO_2^- / 45.00\text{ mL}}{0.98\text{ mmol }HNO_2 / 45.00\text{ mL}} = 3.51$$

42. **(M)** In this case the titration reaction is $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

$$\text{amount }NH_3 = 20.00\text{ mL} \times \frac{0.318\text{ mmol }NH_3}{1\text{ mL soln}} = 6.36\text{ mmol }NH_3$$

(a) The volume of the solution is $20.00\text{ mL} + 10.00\text{ mL} = 30.00\text{ mL}$

$$\text{amount HCl} = 10.00\text{ mL} \times \frac{0.475\text{ mmol NaOH}}{1\text{ mL soln}} = 4.75\text{ mmol HCl}$$

4.75 mmol NH_4Cl is formed in this reaction and there is an excess of (6.36 mmol NH_3 – 4.75 mmol HCl =) 1.61 mmol NH_3. We can use the Henderson-Hasselbalch equation to determine the pH of the solution.

$$\text{p}K_b = -\log\left(1.8 \times 10^{-5}\right) = 4.74; \quad \text{p}K_a = 14.00 - \text{p}K_b = 14.00 - 4.74 = 9.26$$

$$\text{pH} = \text{p}K_a + \log\frac{\left[NH_3\right]}{\left[NH_4^+\right]} = 9.26 + \log\frac{1.61\text{ mmol }NH_3 / 30.00\text{ mL}}{4.75\text{ mmol }NH_4^+ / 30.00\text{ mL}} = 8.79$$

(b) The volume of the solution is $20.00\text{ mL} + 15.00\text{ mL} = 35.00\text{ mL}$

$$\text{amount HCl} = 15.00\text{ mL} \times \frac{0.475\text{ mmol NaOH}}{1\text{ mL soln}} = 7.13\text{ mmol HCl}$$

6.36 mmol NH_4Cl is formed in this reaction and there is an excess of (7.13 mmol HCl – 6.36 mmol NH_3 =) 0.77 mmol HCl; this excess HCl determines the pH of the solution.

$$\left[H_3O^+\right] = \frac{0.77\,\text{mmol HCl}}{35.00\,\text{mL soln}} \times \frac{1\,\text{mmol } H_3O^+}{1\,\text{mmol HCl}} = 0.022\,\text{M} \quad \text{pH} = -\log(0.022) = 1.66$$

43. **(E)** In each case, the volume of acid and its molarity are the same. Thus, the amount of acid is the same in each case. The volume of titrant needed to reach the equivalence point will also be the same in both cases, since the titrant has the same concentration in each case, and it is the same amount of base that reacts with a given amount (in moles) of acid. Realize that, as the titration of a weak acid proceeds, the weak acid will ionize, replenishing the H_3O^+ in solution. This will occur until all of the weak acid has ionized and all of the released H^+ has subsequently reacted with the strong base. At the equivalence point in the titration of a strong acid with a strong base, the solution contains ions that do not hydrolyze. But the equivalence point solution of the titration of a weak acid with a strong base contains the anion of a weak acid, which will hydrolyze to produce a basic (alkaline) solution. (Don't forget, however, that the inert cation of a strong base is also present.)

44. **(E)**

(a) This equivalence point solution is the result of the titration of a weak acid with a strong base. The CO_3^{2-} in this solution, through its hydrolysis, will form an alkaline, or basic solution. The other ionic species in solution, Na^+, will not hydrolyze. Thus, pH > 7.0.

(b) This is the titration of a strong acid with a weak base. The NH_4^+ present in the equivalence point solution hydrolyzes to form an acidic solution. Cl^- does not hydrolyze. Thus, pH < 7.0.

(c) This is the titration of a strong acid with a strong base. Two ions are present in the solution at the equivalence point, namely, K^+ and Cl^-, neither of which hydrolyzes. Thus the solution will have a pH of 7.00.

45. **(D)**

(a) Initial $\left[OH^-\right] = 0.100\,\text{M OH}^-$ $\quad$ $\text{pOH} = -\log(0.100) = 1.000 \quad \text{pH} = 13.00$

Since this is the titration of a strong base with a strong acid, KI is the solute present at the equivalence point, and since KI is a neutral salt, the $\text{pH} = 7.00$. The titration reaction is:

$$\text{KOH(aq)} + \text{HI(aq)} \longrightarrow \text{KI(aq)} + H_2O(l)$$

$$V_{HI} = 25.0\,\text{mL KOH soln} \times \frac{0.100\,\text{mmol KOH soln}}{1\,\text{mL soln}} \times \frac{1\,\text{mmol HI}}{1\,\text{mmol KOH}} \times \frac{1\,\text{mL HI soln}}{0.200\,\text{mmol HI}}$$

$$= 12.5\,\text{mL HI soln}$$

Initial amount of KOH present = 25.0 mL KOH soln × 0.100 M = 2.50 mmol KOH
At the 40% titration point: 5.00 mL HI soln × 0.200 M HI = 1.00 mmol HI
excess KOH = 2.50 mmol KOH – 1.00 mmol HI = 1.50 mmol KOH

$$\left[\mathrm{OH^-}\right] = \frac{1.50\,\text{mmol KOH}}{30.0\,\text{mL total}} \times \frac{1\,\text{mmol OH}^-}{1\,\text{mmol KOH}} = 0.0500\,\text{M} \quad \text{pOH} = -\log(0.0500) = 1.30$$

$$\text{pH} = 14.00 - 1.30 = 12.70$$

At the 80% titration point: 10.00 mL HI soln × 0.200 M HI = 2.00 mmol HI
excess KOH = 2.50 mmol KOH – 2.00 mmol HI = 0.50 mmol KOH

$$\left[\mathrm{OH^-}\right] = \frac{0.50\,\text{mmol KOH}}{35.0\,\text{mL total}} \times \frac{1\,\text{mmol OH}^-}{1\,\text{mmol KOH}} = 0.0143\,\text{M} \quad \text{pOH} = -\log(0.0143) = 1.84$$

$$\text{pH} = 14.00 - 1.84 = 12.16$$

At the 110% titration point: 13.75 mL HI soln × 0.200 M HI = 2.75 mmol HI
excess HI = 2.75 mmol HI – 2.50 mmol HI = 0.25 mmol HI

$$[\mathrm{H_3O^+}] = \frac{0.25\,\text{mmol HI}}{38.8\,\text{mL total}} \times \frac{1\,\text{mmol H}_3\text{O}^+}{1\,\text{mmol HI}} = 0.0064\,\text{M};\quad \text{pH} = -\log(0.0064) = 2.19$$

Since the pH changes very rapidly at the equivalence point, from about $\text{pH} = 10$ to about $\text{pH} = 4$, most of the indicators in Figure 17-8 can be used. The main exceptions are alizarin yellow R, bromphenol blue, thymol blue (in its acid range), and methyl violet.

(b) *Initial pH*:
Since this is the titration of a weak base with a strong acid, NH_4Cl is the solute present at the equivalence point, and since NH_4^+ is a slightly acidic cation, the pH should be slightly lower than 7. The titration reaction is:

Equation:	$\mathrm{NH_3(aq)}$	$+\ \mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{NH_4^+(aq)}$	$+\ \mathrm{OH^-(aq)}$
Initial:	1.00 M	–		0 M	≈ 0 M
Changes:	$-x$ M	–		$+x$ M	$+x$ M
Equil:	$(1.00-x)$ M	–		x M	x M

$$K_b = \frac{\left[\mathrm{NH_4^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{NH_3}\right]} = 1.8\times10^{-5} = \frac{x^2}{1.00-x} \approx \frac{x^2}{1.00}$$

(x << 1.0, thus the approximation is valid)

$$x = 4.2\times10^{-3}\ \text{M} = \left[\mathrm{OH^-}\right],\ \text{pOH} = -\log\left(4.2\times10^{-3}\right) = 2.38,$$

$$\text{pH} = 14.00 - 2.38 = 11.62 = \text{initial pH}$$

Volume of titrant: $\mathrm{NH_3 + HCl \longrightarrow NH_4Cl + H_2O}$

$$V_{\text{HCl}} = 10.0\,\text{mL} \times \frac{1.00\,\text{mmol NH}_3}{1\,\text{mL soln}} \times \frac{1\,\text{mmol HCl}}{1\,\text{mmol NH}_3} \times \frac{1\,\text{mL HCl soln}}{0.250\,\text{mmol HCl}} = 40.0\,\text{mL HCl soln}$$

pH at equivalence point: The total solution volume at the equivalence point is $(10.0 + 40.0)$ mL = 50.0 mL

Also at the equivalence point, all of the NH_3 has reacted to form NH_4^+. It is this NH_4^+ that hydrolyzes to determine the pH of the solution.

$$[\text{NH}_4^+] = \frac{10.0\,\text{mL} \times \dfrac{1.00\,\text{mmol NH}_3}{1\,\text{mL soln}} \times \dfrac{1\,\text{mmol NH}_4^+}{1\,\text{mmol NH}_3}}{50.0\,\text{mL total solution}} = 0.200\,\text{M}$$

$$\begin{array}{llllll}
\text{Equation:} & \text{NH}_4^+(\text{aq}) + & \text{H}_2\text{O(l)} & \rightleftharpoons \text{NH}_3(\text{aq}) & + \text{H}_3\text{O}^+(\text{aq}) \\
\text{Initial:} & 0.200\,\text{M} & - & 0\,\text{M} & \approx 0\,\text{M} \\
\text{Changes:} & -x\,\text{M} & - & +x\,\text{M} & +x\,\text{M} \\
\text{Equil:} & (0.200 - x)\,\text{M} & - & x\,\text{M} & x\,\text{M}
\end{array}$$

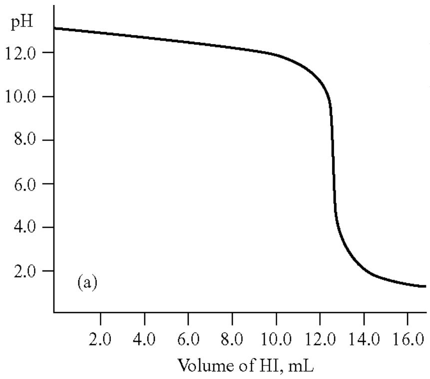
$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_3]} = \frac{x^2}{0.200 - x} \approx \frac{x^2}{0.200}$$

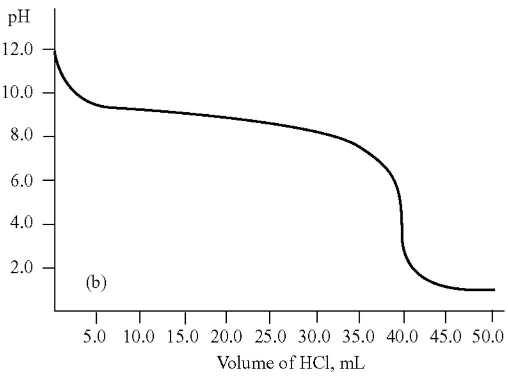
(x << 0.200, thus the approximation is valid)

$$x = 1.1 \times 10^{-5}\,\text{M}; \quad [\text{H}_3\text{O}^+] = 1.1 \times 10^{-5}\,\text{M}; \quad \text{pH} = -\log(1.1 \times 10^{-5}) = 4.96$$

Of the indicators in Figure 17-8, one that has the pH of the equivalence point within its pH color change range is methyl red (yellow at $\text{pH} = 6.2$ and red at $\text{pH} = 4.5$); Bromcresol green would be another choice. At the 50% titration point, $[\text{NH}_3] = [\text{NH}_4^+]$ and $\text{pOH} = \text{pK}_b = 4.74 \qquad \text{pH} = 14.00 - 4.74 = 9.26$

The titration curves for parts **(a)** and **(b)** follow.





46. (M)

(a) This part simply involves calculating the pH of a 0.275 M NH_3 solution.

Equation:	$NH_3(aq)$	$+\ H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$	$+\ OH^-(aq)$
Initial:	$0.275\,M$	–	$0\,M$	$\approx 0\,M$
Changes:	$-x\,M$	–	$+x\,M$	$+x\,M$
Equil:	$(0.275-x)\,M$	–	$x\,M$	$x\,M$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5} = \frac{x^2}{0.275-x} \approx \frac{x^2}{0.275} \qquad x = 2.2\times10^{-3}\,M = [OH^-]$$

(x << 0.275, thus the approximation is valid)

$$pOH = -\log(2.2\times10^{-3}) = 2.66 \qquad pH = 11.34$$

(b) This is the volume of titrant needed to reach the equivalence point.
The relevant titration reaction is $NH_3(aq) + HI(aq) \longrightarrow NH_4I(aq)$

$$V_{HI} = 20.00\ mL\ NH_3(aq) \times \frac{0.275\,mmol\ NH_3}{1\,mL\ NH_3\,soln} \times \frac{1\,mmol\ HI}{1\,mmol\ NH_3} \times \frac{1\,mL\ HI\ soln}{0.325\,mmol\ HI}$$

$$V_{HI} = 16.9\,mL\ HI\ soln$$

(c) The pOH at the half-equivalence point of the titration of a weak base with a strong acid is equal to the pK_b of the weak base.

$$pOH = pK_b = 4.74;\ \ pH = 14.00 - 4.74 = 9.26$$

(d) NH_4^+ is formed during the titration, and its hydrolysis determines the pH of the solution. Total volume of solution = $20.00\,mL + 16.9\,mL = 36.9\,mL$

$$mmol\ NH_4^+ = 20.00\,mL\ NH_3(aq) \times \frac{0.275\,mmol\ NH_3}{1\,mL\ NH_3\,soln} \times \frac{1\,mmol\ NH_4^+}{1\,mmol\ NH_3} = 5.50\,mmol\ NH_4^+$$

$$[NH_4^+] = \frac{5.50\,mmol\ NH_4^+}{36.9\,mL\ soln} = 0.149\,M$$

Equation:	$NH_4^+(aq)$	$+\ H_2O(l) \rightleftharpoons$	$NH_3(aq)$	$+\ H_3O^+(aq)$
Initial:	$0.149\,M$	–	$0\,M$	$\approx 0\,M$
Changes:	$-x\,M$	–	$+x\,M$	$+x\,M$
Equil:	$(0.149-x)\,M$	–	$x\,M$	$x\,M$

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.149-x} \approx \frac{x^2}{0.149}$$

($x \ll 0.149$, thus the approximation is valid)

$x = 9.1\times10^{-6}$ M $= [H_3O^+]$ pH $= -\log(9.1\times10^{-6}) = 5.04$

47. **(M)** A pH greater than 7.00 in the titration of a strong base with a strong acid means that the base is not completely titrated. A pH less than 7.00 means that excess acid has been added.

(a) We can determine $[OH^-]$ of the solution from the pH. $[OH^-]$ is also the quotient of the amount of hydroxide ion in excess divided by the volume of the solution: 20.00 mL base $+x$ mL added acid.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 12.55 = 1.45 \qquad [OH^-] = 10^{-\text{pOH}} = 10^{-1.45} = 0.035\,\text{M}$$

$$[OH^-] = \frac{\left(20.00\,\text{mL base}\times\frac{0.175\,\text{mmol OH}^-}{1\,\text{mL base}}\right)-\left(x\,\text{mL acid}\times\frac{0.200\,\text{mmol H}_3\text{O}^+}{1\,\text{mL acid}}\right)}{20.00\,\text{mL}+x\,\text{mL}} = 0.035\,\text{M}$$

$3.50 - 0.200x = 0.70 + 0.035x$; $3.50 - 0.70 = 0.035x + 0.200x$; $2.80 = 0.235x$

$$x = \frac{2.80}{0.235} = 11.9\,\text{mL acid added.}$$

(b) The set-up here is the same as for part (a).

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.80 = 3.20 \qquad [OH^-] = 10^{-\text{pOH}} = 10^{-3.20} = 0.00063\,\text{M}$$

$$[OH^-] = \frac{\left(20.00\,\text{mL base}\times\frac{0.175\,\text{mmol OH}^-}{1\,\text{mL base}}\right)-\left(x\,\text{mL acid}\times\frac{0.200\,\text{mmol H}_3\text{O}^+}{1\,\text{mL acid}}\right)}{20.00\,\text{mL}+x\,\text{mL}}$$

$$[OH^-] = 0.00063\frac{\text{mmol}}{\text{mL}} = 0.00063\,\text{M}$$

$3.50 - 0.200x = 0.0126 + 0.00063x$; $3.50 - 0.0126 = 0.00063x + 0.200x$; $3.49 = 0.201x$

$$x = \frac{3.49}{0.201} = 17.4\,\text{mL acid added. This is close to the equivalence point at } 17.5\,\text{mL.}$$

(c) Here the acid is in excess, so we reverse the set-up of part (a). We are just slightly beyond the equivalence point. This is close to the "mirror image" of part (b).

$$\left[H_3O^+\right] = 10^{-pH} = 10^{-4.25} = 0.000056\ \text{M}$$

$$[H_3O^+] = \frac{\left(x\ \text{mL acid} \times \frac{0.200\ \text{mmol } H_3O^+}{1\ \text{mL acid}}\right) - \left(20.00\ \text{mL base} \times \frac{0.175\ \text{mmol } OH^-}{1\ \text{mL base}}\right)}{20.00\ \text{mL} + x\ \text{mL}}$$

$$= 5.6 \times 10^{-5}\ \text{M}$$

$$0.200x - 3.50 = 0.0011 + 5.6\times10^{-5}x;\quad 3.50 + 0.0011 = -5.6\times10^{-5}x + 0.200x;$$

$$3.50 = 0.200x$$

$x = \dfrac{3.50}{0.200} = 17.5\,\text{mL}$ acid added, which is the equivalence point for this titration.

48. **(D)** In the titration of a weak acid with a strong base, the middle range of the titration, with the pH within one unit of $\text{p}K_a$ $(= 4.74$ for acetic acid), is known as the buffer region. The Henderson-Hasselbalch equation can be used to determine the ratio of weak acid and anion concentrations. The amount of weak acid then is used in these calculations to determine the amount of base to be added.

(a)

$$\text{pH} = \text{p}K_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 3.85 = 4.74 + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]}$$

$$\log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 3.85 - 4.74 \qquad \frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 10^{-0.89} = 0.13;$$

$$n_{HC_2H_3O_2} = 25.00\,\text{mL} \times \frac{0.100\,\text{mmol } HC_2H_3O_2}{1\,\text{mL acid}} = 2.50\,\text{mmol}$$

Since acetate ion and acetic acid are in the same solution, we can use their amounts in millimoles in place of their concentrations. The amount of acetate ion is the amount created by the addition of strong base, one millimole of acetate ion for each millimole of strong based added. The amount of acetic acid is reduced by the same number of millimoles. $HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$

$$0.13 = \frac{x\,\text{mL base} \times \frac{0.200\,\text{mmol } OH^-}{\text{mL base}} \times \frac{1\ \text{mmol } C_2H_3O_2^-}{1\ \text{mmol } OH^-}}{2.50\,\text{mmol } HC_2H_3O_2 - \left(x\,\text{mL base} \times \frac{0.200\ \text{mmol } OH^-}{\text{mL base}}\right)} = \frac{0.200x}{2.50 - 0.200x}$$

$$0.200x = 0.13(2.50 - 0.200x) = 0.33 - 0.026x \qquad 0.33 = 0.200x + 0.026x = 0.226x$$

$x = \dfrac{0.33}{0.226} = 1.5$ mL of base

(b) This is the same set-up as part (a), except for a different ratio of concentrations.

$$\mathrm{pH} = 5.25 = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 5.25 - 4.74 = 0.51$$

$$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{0.51} = 3.2 \qquad 3.2 = \frac{0.200x}{2.50 - 0.200x}$$

$$0.200\,x = 3.2(2.50 - 0.200\,x) = 8.0 - 0.64\,x \qquad 8.0 = 0.200\,x + 0.64\,x = 0.84\,x$$

$x = \dfrac{8.0}{0.84} = 9.5\,\text{mL}$ base. This is close to the equivalence point, which is reached by adding 12.5 mL of base.

(c) This is after the equivalence point, where the pH is determined by the excess added base.

$$\mathrm{pOH} = 14.00 - \mathrm{pH} = 14.00 - 11.10 = 2.90 \qquad [OH^-] = 10^{-\mathrm{pOH}} = 10^{-2.90} = 0.0013\,\mathrm{M}$$

$$[OH^-] = 0.0013\ \mathrm{M} = \frac{x\,\mathrm{mL} \times \dfrac{0.200\,\mathrm{mmol\,OH^-}}{1\,\mathrm{mL\,base}}}{x\,\mathrm{mL} + (12.50\,\mathrm{mL} + 25.00\,\mathrm{mL})} = \frac{0.200\,x}{37.50 + x}$$

$$0.200\,x = 0.0013(37.50 + x) = 0.049 + 0.0013\,x \qquad x = \frac{0.049}{0.200 - 0.0013} = 0.25\,\mathrm{mL\ excess}$$

Total base added = 12.5 mL to equivalence point + 0.25 mL excess = 12.8 mL

49. **(D)** For each of the titrations, the pH at the half-equivalence point equals the pK_a of the acid.

The initial pH is that of 0.1000 M weak acid: $K_a = \dfrac{x^2}{0.1000 - x} \qquad x = [H_3O^+]$

x must be found using the quadratic formula roots equation unless the approximation is valid.

One method of determining if the approximation will be valid is to consider the ratio C_a/K_a. If the value of C_a/K_a is greater than 1000, the assumption should be valid, however, if the value of C_a/K_a is less than 1000, the quadratic should be solved exactly (i.e., the 5% rule will not be satisfied).

The pH at the equivalence point is that of 0.05000 M anion of the weak acid, for which the $[OH^-]$ is determined as follows.

$$K_b = \frac{K_w}{K_a} \approx \frac{x^2}{0.05000} \qquad x = \sqrt{\frac{K_w}{K_a}0.05000} = [OH^-]$$

We can determine the pH at the quarter and three quarter of the equivalence point by using the Henderson-Hasselbalch equation (effectively ± 0.48 pH unit added to the pK_a).

And finally, when 0.100 mL of base has been added beyond the equivalence point, the pH is determined by the excess added base, as follows (for all three titrations).

$$\left[\mathrm{OH^-}\right]=\frac{0.100\,\mathrm{mL}\times\dfrac{0.1000\,\mathrm{mmol\,NaOH}}{1\,\mathrm{mL\,NaOH\ soln}}\times\dfrac{1\,\mathrm{mmol\,OH^-}}{1\,\mathrm{mmol\,NaOH}}}{20.1\ \mathrm{mL\ soln\ total}}=4.98\times10^{-4}\ \mathrm{M}$$

$$\mathrm{pOH}=-\log\left(4.98\times10^{-4}\right)=3.303\qquad \mathrm{pH}=14.000-3.303=10.697$$

(a) C_a/K_a = 14.3; thus, the approximation is <u>not</u> valid and the full quadratic equation must be solved.

Initial: From the roots equation $x=[\mathrm{H_3O^+}]=0.023\,\mathrm{M}$ pH=1.63

Half equivalence point: pH = pK_a = 2.15

pH at quarter equivalence point = 2.15 - 0.48 = 1.67

pH at three quarter equivalence point = 2.15 + 0.48 = 2.63

Equiv: $x=\left[\mathrm{OH^-}\right]=\sqrt{\dfrac{1.0\times10^{-14}}{7.0\times10^{-3}}\times0.05000}=2.7\times10^{-7}$ pOH = 6.57

pH = 14.00 – 6.57 = 7.43

Indicator: bromthymol blue, yellow at pH = 6.2 and blue at pH = 7.8

(b) C_a/K_a = 333; thus, the approximation is <u>not</u> valid and the full quadratic equation must be solved.

Initial: From the roots equation $x=[\mathrm{H_3O^+}]=0.0053\,\mathrm{M}$ pH=2.28

Half equivalence point: pH = pK_a = 3.52

pH at quarter equivalence point = 3.52 - 0.48 = 3.04

pH at three quarter equivalence point = 3.52 + 0.48 = 4.00

Equiv: $x=\left[\mathrm{OH^-}\right]=\sqrt{\dfrac{1.0\times10^{-14}}{3.0\times10^{-4}}\times0.05000}=1.3\times10^{-6}$

$\mathrm{pOH}=5.89$

$\mathrm{pH}=14.00-5.89=8.11$

Indicator: thymol blue, yellow at pH = 8.0 and blue at pH = 9.6

(c) $C_a/K_a=5\times10^6$; thus, the approximation <u>is</u> valid..

Initial: $[\mathrm{H_3O^+}]=\sqrt{0.1000\times2.0\times10^{-8}}=0.000045\ \mathrm{M}$ pH = 4.35

pH at quarter equivalence point = 4.35 - 0.48 = 3.87

pH at three quarter equivalence point = 4.35 + 0.48 = 4.83

Half equivalence point: pH = pK_a = 7.70

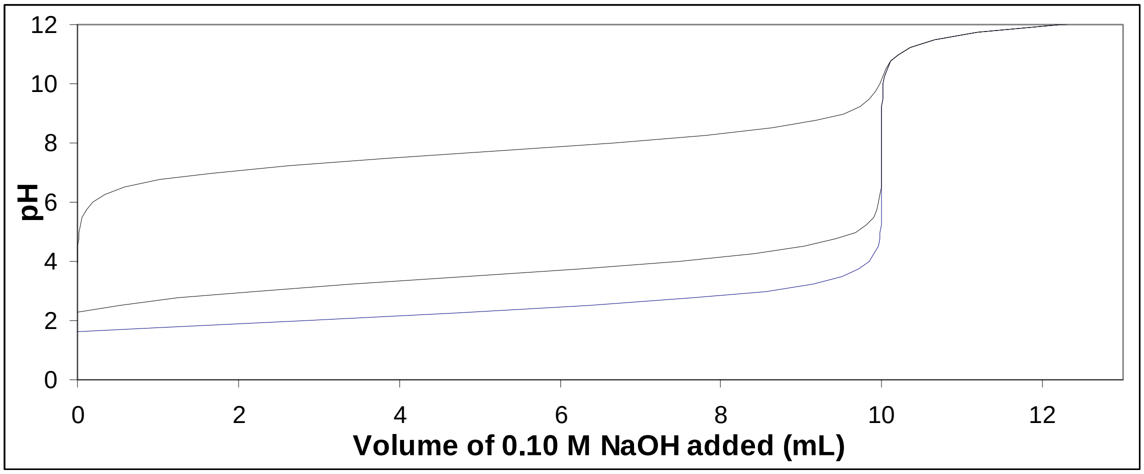
Equiv: $x=\left[\mathrm{OH^-}\right]=\sqrt{\dfrac{1.0\times10^{-14}}{2.0\times10^{-8}}\times0.0500}=1.6\times10^{-4}$

$\mathrm{pOH}=3.80$

$\mathrm{pH}=14.00-3.80=10.20$

Indicator: alizarin yellow R, yellow at $\text{pH} = 10.0$ and violet at $\text{pH} = 12.0$

The three titration curves are drawn with respect to the same axes in the diagram below.



50. **(D)** For each of the titrations, the pOH at the half-equivalence point equals the $\text{p}K_b$ of the base. The initial pOH is that of 0.1000 M weak base, determined as follows.

$K_b = \dfrac{x^2}{0.1000 - x}$; $x \approx \sqrt{0.1000 \times K_a} = [\text{OH}^-]$ if $C_b/K_b > 1000$. For those cases where this is not the case, the approximation is invalid and the complete quadratic equation must be solved. The pH at the equivalence point is that of 0.05000 M cation of the weak base, for which the $\left[\text{H}_3\text{O}^+\right]$ is determined as follows.

$$K_a = \frac{K_w}{K_b} = \frac{x^2}{0.05000} \qquad x = \sqrt{\frac{K_w}{K_b}0.05000} = [\text{H}_3\text{O}^+]$$

And finally, when 0.100 mL of acid has been added beyond the equivalence point, the pH for all three titrations is determined by the excess added acid, as follows.

$$\left[\text{H}_3\text{O}^+\right] = \frac{0.100 \text{ mL HCl} \times \dfrac{0.1000 \text{ mmol HCl}}{1 \text{ mL HCl soln}} \times \dfrac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HCl}}}{20.1 \text{ mL soln total}} = 4.98 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log\left(4.98 \times 10^{-4}\right) = 3.303$$

(a) $C_b/K_b = 100$; thus, the approximation is not valid and the full quadratic equation must be solved.

Initial: From the roots equation $x = 0.0095$. Therefore,
$[\text{OH}^-] = 0.0095$ M pOH=2.02 pH=11.98

Half-equiv: $\text{pOH} = -\log\left(1 \times 10^{-3}\right) = 3.0$ $\text{pH} = 11.0$

Equiv: $x = [\text{H}_3\text{O}^+] = \sqrt{\dfrac{1.0 \times 10^{-14}}{1 \times 10^{-3}} \times 0.05000} = 7 \times 10^{-7}$ pH = 6.2

Indicator: methyl red, yellow at $\mathrm{pH} = 6.3$ and red at $\mathrm{pH} = 4.5$

(b) C_b/K_b = 33,000; thus, the approximation <u>is</u> valid.

Initial: $[\mathrm{OH}^-] = \sqrt{0.1000\times 3\times 10^{-6}} = 5.5\times 10^{-4}$ M pOH=3.3 pH=10.7

Half-equiv: $\mathrm{pOH} = -\log\left(3\times 10^{-6}\right) = 5.5$ pH = 14 – pOH pH = 8.5

Equiv: $x = [\mathrm{H_3O^+}] = \sqrt{\dfrac{1.0\times 10^{-14}}{3\times 10^{-6}}\times 0.05000} = 1\times 10^{-5}$ pH -log(1×10^{-5}) = 5.0

Indicator: methyl red, yellow at $\mathrm{pH} = 6.3$ and red at $\mathrm{pH} = 4.5$

(c) $C_b/K_b = 1.4\times 10^6$; thus, the approximation <u>is</u> valid.

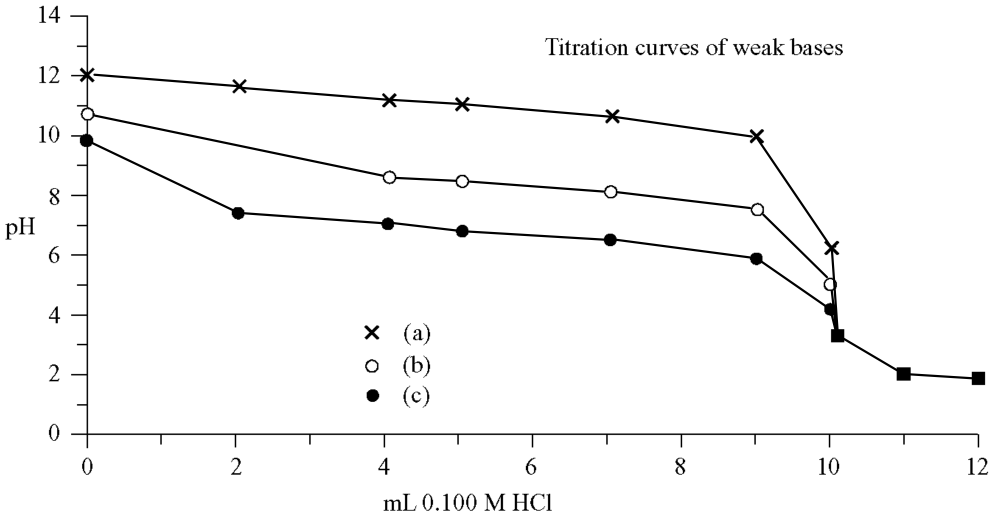
Initial: $[\mathrm{OH}^-] = \sqrt{0.1000\times 7\times 10^{-8}} = 8\times 10^{-5}$ M pOH = 4.1 pH = 9.9

Half-equiv: $\mathrm{pOH} = -\log\left(7\times 10^{-8}\right) = 7.2$ pH = 14 – pOH pH = 6.8

Equiv: $x = [\mathrm{H_3O^+}] = \sqrt{\dfrac{1.0\times 10^{-14}}{7\times 10^{-8}}\times 0.05000} = 8.5\times 10^{-5}$ pH=4.1

Indicator: bromcresol green, blue at $\mathrm{pH} = 5.5$ and yellow at $\mathrm{pH} = 4.0$

The titration curves are drawn with respect to the same axes in the diagram below.



<u>51.</u> **(D)** 25.00 mL of 0.100 M NaOH is titrated with 0.100 M HCl

(i) Initial pOH for 0.100 M NaOH: $[\mathrm{OH^-}] = 0.100$ M, pOH = 1.000 or pH = 13.000

(ii) After addition of 24 mL: $[\mathrm{NaOH}] = 0.100\ \mathrm{M}\times\dfrac{25.00\ \mathrm{mL}}{49.00\ \mathrm{mL}} = 0.0510\ \mathrm{M}$

$$[\mathrm{HCl}] = 0.100\ \mathrm{M}\times\dfrac{24.00\ \mathrm{mL}}{49.00\ \mathrm{mL}} = 0.0490\ \mathrm{M}$$

NaOH is in excess by 0.0020 M = $[OH^-]$ pOH = 2.70

(iii) At the equivalence point (25.00 mL), the pOH should be 7.000 and pH = 7.000

(iv) After addition of 26 mL: $[NaOH] = 0.100M \times \dfrac{25.00}{51.00} = 0.0490$ M

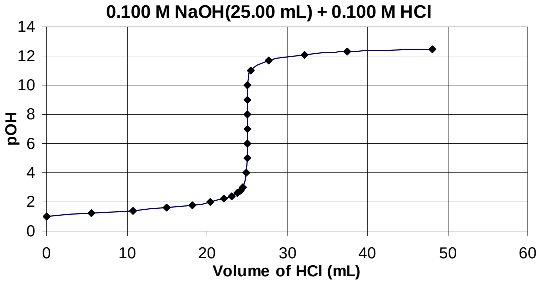
$$[HCl] = 0.100\text{ M} \times \frac{26.00\text{ mL}}{51.00\text{ mL}} = 0.0510\text{ M}$$

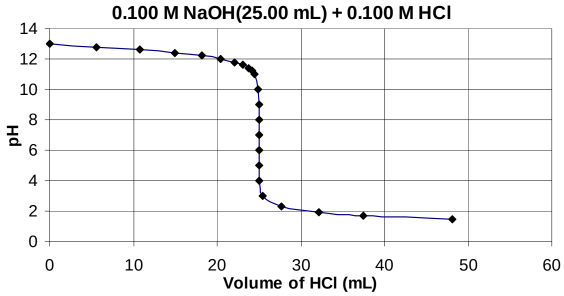
HCl is in excess by 0.0020 M = $[H_3O^+]$ pH = 2.70 or pOH = 11.30

(v) After addition of 33.00 mL HCl(xs) $[NaOH] = 0.100\text{ M} \times \dfrac{25.00\text{ mL}}{58.00\text{ mL}} = 0.0431$ M

$[HCl] = 0.100\text{ M} \times \dfrac{33.00\text{ mL}}{58.00\text{ mL}} = 0.0569$ M $[HCl]_{excess} = 0.0138$ M pH = 1.860, pOH = 12.140

The graphs look to be mirror images of one another. In reality, one must reflect about a horizontal line centered at pH or pOH = 7 to obtain the other curve.





52. **(D)** 25.00 mL of 0.100 M NH_3 is titrated with 0.100 M HCl $K_a = \dfrac{K_w}{K_b} = \dfrac{1\times10^{-14}}{1.8\times10^{-5}} = 5.6 \times 10^{-10}$

(i) For initial pOH, use I.C.E.(initial, change, equilibrium) table.

$$NH_3(aq) + H_2O(l) \xrightleftharpoons{K_b = 1.8 \times 10^{-5}} NH_4^+(aq) + OH^-(aq)$$

	$NH_3(aq)$	$NH_4^+(aq)$	$OH^-(aq)$
Initial	0.100 M	0 M	≈ 0 M
Change	$-x$	$+x$	$+x$
Equil.	$0.100 - x$	x	x

$$1.8 \times 10^{-5} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \text{ (Assume } x \sim 0) \quad x = 1.3 \times 10^{-3}$$

(x < 5% of 0.100, thus, the assumption is valid).

Hence, $x = [OH^-] = 1.3 \times 10^{-3}$ pOH = 2.89, pH = 11.11

(ii) After 2 mL of HCl is added: $[HCl] = 0.100\text{ M} \times \dfrac{2.00\text{ mL}}{27.00\text{ mL}} = 0.00741$ M (after dilution)

$[NH_3] = 0.100\text{ M} \times \dfrac{25.00\text{ mL}}{27.00\text{ mL}} = 0.0926$ M (after dilution)

The equilibrium constant for the neutralization reaction is large ($K_{neut} = K_b/K_w = 1.9\times10^5$) and thus the reaction goes to nearly 100% completion. Assume that the limiting reagent is used up (100% reaction in the reverse direction) and re-establish the equilibrium by a shift in the forward direction. Here H_3O^+ (HCl) is the limiting reagent.

$$NH_4^+(aq) + H_2O(l) \xrightleftharpoons{K_a = 5.6\times10^{-10}} NH_3(aq) + H_3O^+(aq)$$

Initial	0 M	–		0.0926 M	0.00741 M
Change	$+x$	–	$\boldsymbol{x = 0.00741}$	$-x$	$-x$
100% rxn	0.00741	–		0.0852	0
Change	$-y$	–	**re-establish equilibrium**	$+y$	$+y$
Equil	$0.00741-y$	–		$0.0852 + y$	y

$$5.6\times10^{-10} = \frac{y(0.0852+y)}{(0.00741-y)} = \frac{y(0.0852)}{(0.00741)} \text{ (set } y \sim 0\text{)} \quad y = 4.8\times10^{-11}$$

(the approximation is clearly valid)

$y = [H_3O^+] = 4.8\times10^{-11}$; pH = 10.32 and pOH = 3.68

(iii) pH at 1/2 equivalence point = $\text{p}K_a = -\log 5.6\times10^{-10} = 9.25$ and pOH = 4.75

(iv) After addition of 24 mL of HCl:

$$[HCl] = 0.100\text{ M}\times\frac{24.00\text{ mL}}{49.00\text{ mL}} = 0.0490\text{ M};\ [NH_3] = 0.100\text{ M}\times\frac{25.00\text{ mL}}{49.00\text{ mL}} = 0.0510\text{ M}$$

The equilibrium constant for the neutralization reaction is large (see above), and thus the reaction goes to nearly 100% completion. Assume that the limiting reagent is used up (100% reaction in the reverse direction) and re-establish the equilibrium in the reverse direction. Here H_3O^+ (HCl) is the limiting reagent.

$$NH_4^+(aq) + H_2O(l) \xrightleftharpoons{K_a = 5.6\times10^{-10}} NH_3(aq) + H_3O^+(aq)$$

Initial	0 M	–		0.0541 M	0.0490 M
Change	$+x$	–	$\boldsymbol{x = 0.0490}$	$-x$	$-x$
100% rxn	0.0490	–		0.0020	0
Change	$-y$	–	**re-establish equilibrium**	$+y$	$+y$
Equil	$0.0490-y$	–		$0.0020 + y$	y

$$5.6\times10^{-10} = \frac{y(0.0020+y)}{(0.0490-y)} = \frac{y(0.0020)}{(0.0490)} \text{ (Assume } y \sim 0\text{)} \quad y = 1.3\times10^{-8} \text{ (valid)}$$

$y = [H_3O^+] = 1.3\times10^{-8}$; pH = 7.89 and pOH = 6.11

(v) Equiv. point: 100% reaction of $NH_3 \rightarrow NH_4^+$: $[NH_4^+] = 0.100\times\dfrac{25.00\text{ mL}}{50.00\text{ mL}} = 0.0500\text{ M}$

$$NH_4^+(aq) + H_2O(l) \xrightleftharpoons{K_a = 5.6\times10^{-10}} NH_3(aq) + H_3O^+(aq)$$

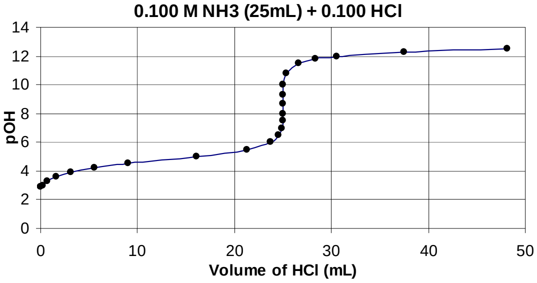
Initial	0.0500 M	–		0 M	~ 0 M
Change	$-x$	–		$+x$	$+x$
Equil	$0.0500-x$	–		x	x

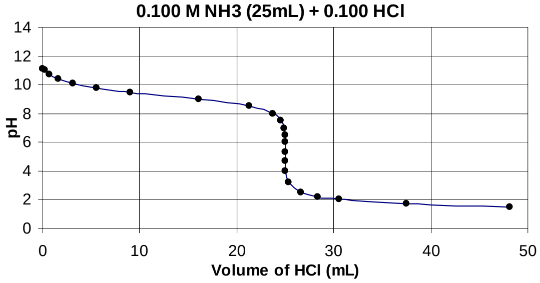
$$5.6\times 10^{-10} = \frac{x^2}{(0.0500 - x)} = \frac{x^2}{0.0500} \quad (\text{Assume } x \sim 0) \quad x = 5.3\times 10^{-6}$$

(the approximation is clearly valid)
$x = [H_3O^+] = 5.3 \times 10^{-6}$; pH = 5.28 and pOH = 8.72

(vi) After addition of 26 mL of HCl, HCl is in excess. The pH and pOH should be the same as those in Exercise 51. pH = 2.70 and pOH = 11.30

(vii) After addition of 33 mL of HCl, HCl is in excess. The pH and pOH should be the same as those in Exercise 51. pH = 1.860 and pOH = 12.140. This time the curves are not mirror images of one another, but rather they are related through a reflection in a horizontal line centered at pH or pOH = 7.





Salts of Polyprotic Acids

53. **(E)** We expect a solution of Na_2S to be alkaline, or basic. This alkalinity is created by the hydrolysis of the sulfide ion, the anion of a very weak acid ($K_2 = 1\times 10^{-19}$ for H_2S).

$$S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$$

54. **(E)** We expect the pH of a solution of sodium dihydrogen citrate, NaH_2Cit, to be acidic because the pK_a values of first and second ionization constants of polyprotic acids are reasonably large. The pH of a solution of the salt is the average of pK_1 and pK_2. For citric acid, in fact, this average is $(3.13 + 4.77) \div 2 = 3.95$. Thus, NaH_2Cit affords acidic solutions.

55. **(M)**

(a) $H_3PO_4(aq) + CO_3^{2-}(aq) \rightleftharpoons H_2PO_4^-(aq) + HCO_3^-(aq)$

$H_2PO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + HCO_3^-(aq)$

$HPO_4^{2-}(aq) + OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + H_2O(l)$

(b) The pH values of 1.00 M solutions of the three ions are;

$1.0\text{ M OH}^- \rightarrow \text{pH} = 14.00 \quad 1.0\text{ M CO}_3^{2-} \rightarrow \text{pH} = 12.16 \quad 1.0\text{ M PO}_4^{3-} \rightarrow \text{pH} = 13.15$

Thus, we see that CO_3^{2-} is not a strong enough base to remove the third proton from H_3PO_4. As an alternative method of solving this problem, we can compute the equilibrium constants of the reactions of carbonate ion with H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-}.

$$H_3PO_4 + CO_3^{2-} \rightleftharpoons H_2PO_4^- + HCO_3^- \quad K = \frac{K_{a1}\{H_3PO_4\}}{K_{a2}\{H_2CO_3\}} = \frac{7.1\times10^{-3}}{4.7\times10^{-11}} = 1.5\times10^{8}$$

$$H_2PO_4^- + CO_3^{2-} \rightleftharpoons HPO_4^{2-} + HCO_3^- \quad K = \frac{K_{a2}\{H_3PO_4\}}{K_{a2}\{H_2CO_3\}} = \frac{6.3\times10^{-8}}{4.7\times10^{-11}} = 1.3\times10^{3}$$

$$HPO_4^{2-} + CO_3^{2-} \rightleftharpoons PO_4^{3-} + HCO_3^- \quad K = \frac{K_{a3}\{H_3PO_4\}}{K_{a2}\{H_2CO_3\}} = \frac{4.2\times10^{-13}}{4.7\times10^{-11}} = 8.9\times10^{-3}$$

Since the equilibrium constant for the third reaction is much smaller than 1.00, we conclude that it proceeds to the right to only a negligible extent and thus is not a practical method of producing PO_4^{3-}. The other two reactions have large equilibrium constants, and products are expected to strongly predominate. They have the advantage of involving an inexpensive base and, even if they do not go to completion, they will be drawn to completion by reaction with OH^- in the last step of the process.

56. **(M)** We expect CO_3^{2-} to hydrolyze and the hydrolysis products to determine the pH of the solution.

Equation:	$HCO_3^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$"H_2CO_3"(aq)$	+	$OH^-(aq)$
Initial	1.00 M		–		0 M		≈ 0 M
Changes:	–x M		–		+x M		+x M
Equil:	(1.00 – x) M		–		x M		x M

$$K_b = \frac{K_w}{K_1} = \frac{1.00\times10^{-14}}{4.4\times10^{-7}} = 2.3\times10^{-8} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = \frac{(x)(x)}{1.00-x} \approx \frac{x^2}{1.00}$$

(C_b/K_b = a very large number; thus, the approximation <u>is</u> valid).

$x = \sqrt{1.00\times2.3\times10^{-8}} = 1.5\times10^{-4}\text{ M} = [OH^-]$; $\text{pOH} = -\log(1.5\times10^{-4}) = 3.82 \quad \text{pH} = 10.18$

For 1.00 M NaOH, $[OH^-] = 1.00 \quad \text{pOH} = -\log(1.00) = 0.00 \qquad \text{pH} = 14.00$

Both 1.00 M $NaHCO_3$ and 1.00 M NaOH have an equal capacity to neutralize acids since one mole of each neutralizes one mole of strong acid.

$$NaOH(aq) + H_3O^+(aq) \rightarrow Na^+(aq) + 2H_2O(l)$$

$$NaHCO_3(aq) + H_3O^+(aq) \rightarrow Na^+(aq) + CO_2(g) + 2H_2O(l).$$

But on a per gram basis, the one with the smaller molar mass is the more effective. Because the molar mass of NaOH is 40.0 g/mol, while that of $NaHCO_3$ is 84.0 g/mol, NaOH(s) is more than twice as effective as $NaHCO_3$(s) on a per gram basis. $NaHCO_3$ is preferred in laboratories for safety and expense reasons. NaOH is not a good choice because it can cause severe burns. $NaHCO_3$, baking soda, by comparison, is relatively non-hazardous. It also is much cheaper than NaOH.

57. **(M)** Malonic acid has the formula $H_2C_3H_2O_4$ MM = 104.06 g/mol

Moles of $H_2C_3H_2O_4$ = 19.5 g × $\frac{1\text{ mol}}{104.06\text{ g}}$ = 0.187 mol

Concentration of $H_2C_3H_2O_4$ = $\frac{\text{moles}}{V} = \frac{0.187\text{ moles}}{0.250\text{ L}}$ = 0.748 M

The second proton that can dissociate has a negligible effect on pH (K_{a_2} is very small). Thus the pH is determined almost entirely by the first proton loss.

	$H_2A(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HA^-(aq)$	+	$H_3O^+(aq)$
Initial	0.748 M		–		0 M		≈ 0 M
Change	$-x$		–		$+x$		$+x$
Equil	$0.748-x$		–		x		x

So, $x = \frac{x^2}{0.748-x} = K_a$; pH = 1.47, therefore, $[H_3O^+]$ = 0.034 M = x,

$$K_{a_1} = \frac{(0.034)^2}{0.748-0.034} = 1.6\times10^{-3}$$

(1.5×10^{-3} in tables, difference owing to ionization of the second proton)

	$HA^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$A^{2-}(aq)$	+	$H_3O^+(aq)$
Initial	0.300 M		–		0 M		≈ 0 M
Change	$-x$		–		$+x$		$+x$
Equil	$0.300-x$		–		x		x

pH = 4.26, therefore, $[H_3O^+] = 5.5\times10^{-5}$ M = x, $K_{a_2} = \frac{(5.5\times10^{-5})^2}{0.300-5.5\times10^{-5}} = 1.0\times10^{-8}$

58. **(M)** *Ortho*-phthalic acid. $K_{a_1} = 1.1\times10^{-3}$, $K_{a_2} = 3.9\times10^{-6}$

(a) We have a solution of HA.

	$HA^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$A^{2-}(aq)$	+	$H_3O^+(aq)$
Initial	0.350 M		–		0 M		~ 0 M
Change	$-x$		–		$+x$		$+x$
Equil	$0.350-x$		–		x		x

$3.9 \times 10^{-6} = \dfrac{x^2}{0.350 - x} \simeq \dfrac{x^2}{0.350}$, $x = 1.2 \times 10^{-3}$

($x \ll 0.350$, thus, the approximation is valid)

$x = [H_3O^+] = 1.2 \times 10^{-3}$, pH = 2.92

(b) 36.35 g of potassium *ortho*-phthalate (MM = 242.314 g mol^{-1})

moles of potassium *ortho*-phthalate = $36.35\text{ g} \times \dfrac{1\text{ mol}}{242.314\text{ g}}$ = 0.150 mol in 1 L

	$A^{2-}(aq)$	+ $H_2O(l)$	$\rightleftharpoons$	$HA^-(aq)$	+ $OH^-(aq)$
Initial	0.150 M	–		0 M	≈ 0 M
Change	$-x$	–		$+x$	$+x$
Equil	$0.150 - x$	–		x	x

$$K_{b,A^{2-}} = \frac{K_w}{K_{a_2}} = \frac{1.0\times10^{-14}}{3.9\times10^{-6}} = 2.6\times10^{-9} = \frac{x^2}{0.150 - x} \approx \frac{x^2}{0.150}$$

$x = 2.0\times10^{-5}$ ($x << 0.150$, so the approximation is valid) = $[OH^-]$

pOH = $-\log 2.0\times10^{-5}$ = 4.70; pH = 9.30

General Acid–Base Equilibria

59. **(E)**

(a) $Ba(OH)_2$ is a strong base.

$pOH = 14.00 - 11.88 = 2.12 \quad [OH^-] = 10^{-2.12} = 0.0076\text{ M}$

$$[Ba(OH)_2] = \frac{0.0076\text{ mol }OH^-}{1\text{ L}} \times \frac{1\text{ mol }Ba(OH)_2}{2\text{ mol }OH^-} = 0.0038\text{ M}$$

(b) $pH = 4.52 = pK_a + \log\dfrac{[C_2H_3O_2{}^-]}{[HC_2H_3O_2]} = 4.74 + \log\dfrac{0.294\text{ M}}{[HC_2H_3O_2]}$

$\log\dfrac{0.294\text{ M}}{[HC_2H_3O_2]} = 4.52 - 4.74 \qquad \dfrac{0.294\text{ M}}{[HC_2H_3O_2]} = 10^{-0.22} = 0.60$

$$[HC_2H_3O_2] = \frac{0.294\text{ M}}{0.60} = 0.49\text{ M}$$

60. **(M)**

(a) $\mathrm{pOH} = 14.00 - 8.95 = 5.05$ $\qquad$ $\left[\mathrm{OH^-}\right] = 10^{-5.05} = 8.9\times10^{-6}\ \mathrm{M}$

Equation:	$C_6H_5NH_2(aq)$	$+\ H_2O(l)$	$\rightleftharpoons\ C_6H_5NH_3^+(aq)$	$+\ OH^-(aq)$
Initial	x M	–	0 M	≈ 0 M
Changes:	-8.9×10^{-6} M	–	$+8.9\times10^{-6}$ M	$+8.9\times10^{-6}$ M
Equil:	$(x-8.9\times10^{-6})$ M	–	8.9×10^{-6} M	8.9×10^{-6} M

$$K_b = \frac{\left[C_6H_5NH_3^+\right]\left[OH^-\right]}{\left[C_6H_5NH_2\right]} = 7.4\times10^{-10} = \frac{\left(8.9\times10^{-6}\right)^2}{x-8.9\times10^{-6}}$$

$$x-8.9\times10^{-6} = \frac{\left(8.9\times10^{-6}\right)^2}{7.4\times10^{-10}} = 0.11\ \mathrm{M} \qquad x = 0.11\ \mathrm{M} = \text{molarity of aniline}$$

(b) $\left[H_3O^+\right] = 10^{-5.12} = 7.6\times10^{-6}\ \mathrm{M}$

Equation:	$NH_4^+(aq)$	$+\ H_2O(l)$	$\rightleftharpoons\ NH_3(aq)$	$+\ H_3O^+(aq)$
Initial	x M	–	0 M	≈ 0 M
Changes:	-7.6×10^{-6} M	–	$+7.6\times10^{-6}$ M	$+7.6\times10^{-6}$ M
Equil:	$(x-7.6\times10^{-6})$ M	–	7.6×10^{-6} M	7.6×10^{-6} M

$$K_a = \frac{\left[NH_3\right]\left[H_3O^+\right]}{\left[NH_4^+\right]} = \frac{K_w}{K_b\ \text{for}\ NH_3} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10} = \frac{\left(7.6\times10^{-6}\right)^2}{x-7.6\times10^{-6}}$$

$$x-7.6\times10^{-6} = \frac{\left(7.6\times10^{-6}\right)^2}{5.6\times10^{-10}} = 0.10\ \mathrm{M} \qquad x = \left[NH_4^+\right] = \left[NH_4Cl\right] = 0.10\ \mathrm{M}$$

61. **(M)**

(a) A solution can be prepared with equal concentrations of weak acid and conjugate base (it would be a buffer, with a buffer ratio of 1.00, where the pH = pK_a = 9.26). Clearly, this solution can be prepared, however, it would not have a pH of 6.07.

(b) These solutes can be added to the same solution, but the final solution will have an appreciable $\left[HC_2H_3O_2\right]$ because of the reaction of $H_3O^+(aq)$ with $C_2H_3O_2^-(aq)$

Equation:	$H_3O^+(aq)$	$+\ C_2H_3O_2^-(aq)$	$\rightleftharpoons\ HC_2H_3O_2(aq)$	$+\ H_2O(l)$
Initial	0.058 M	0.10 M	0 M	–
Changes:	–0.058 M	–0.058 M	+0.058 M	–
Equil:	≈0.000 M	0.04 M	0.058 M	–

Of course, some H_3O^+ will exist in the final solution, but not equivalent to 0.058 M HI.

(c) Both 0.10 M KNO_2 and 0.25 M KNO_3 can exist together. Some hydrolysis of the $NO_2^-(aq)$ ion will occur, forming $HNO_2(aq)$ and $OH^-(aq)$.

(d) $Ba(OH)_2$ is a strong base and will react as much as possible with the weak conjugate acid NH_4^+, to form $NH_3(aq)$. We will end up with a solution of $BaCl_2(aq)$, $NH_3(aq)$, and unreacted $NH_4Cl(aq)$.

(e) This will be a benzoic acid–benzoate ion buffer solution. Since the two components have the same concentration, the buffer solution will have $pH = pK_a = -\log(6.3\times10^{-5}) = 4.20$. This solution can indeed exist.

(f) The first three components contain no ions that will hydrolyze. But $C_2H_3O_2^-$ is the anion of a weak acid and will hydrolyze to form a slightly basic solution. Since $pH = 6.4$ is an acidic solution, the solution described cannot exist.

62. **(M)**

(a) When $[H_3O^+]$ and $[HC_2H_3O_2]$ are high and $[C_2H_3O_2^-]$ is very low, a common ion H_3O^+ has been added to a solution of acetic acid, suppressing its ionization.

(b) When $[C_2H_3O_2^-]$ is high and $[H_3O^+]$ and $[HC_2H_3O_2]$ are very low, we are dealing with a solution of acetate ion, which hydrolyzes to produce a small concentration of $HC_2H_3O_2$.

(c) When $[HC_2H_3O_2]$ is high and both $[H_3O^+]$ and $[C_2H_3O_2^-]$ are low, the solution is an acetic acid solution, in which the solute is partially ionized.

(d) When both $[HC_2H_3O_2]$ and $[C_2H_3O_2^-]$ are high while $[H_3O^+]$ is low, the solution is a buffer solution, in which the presence of acetate ion suppresses the ionization of acetic acid.

INTEGRATIVE AND EXERCISES

63. **(M)**

(a) $NaHSO_4(aq) + NaOH(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$

$HSO_4^-(aq) + OH^-(aq) \longrightarrow SO_4^{2-}(aq) + H_2O(l)$

(b) We first determine the mass of $NaHSO_4$.

$$\text{mass NaHSO}_4 = 36.56\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{0.225\ \text{mol NaOH}}{1\ \text{L}} \times \frac{1\ \text{mol NaHSO}_4}{1\ \text{mol NaOH}}$$

$$\times \frac{120.06\ \text{g NaHSO}_4}{1\ \text{mol NaHSO}_4} = 0.988\ \text{g NaHSO}_4$$

$$\% \quad \text{NaCl} = \frac{1.016 \text{ g sample} - 0.988 \text{ g NaHSO}_4}{1.016 \text{ g sample}} \times 100\% = 2.8\% \text{ NaCl}$$

(c) At the endpoint of this titration the solution is one of predominantly SO_4^{2-}, from which the pH is determined by hydrolysis. Since K_a for HSO_4^- is relatively large (1.1×10^{-2}), base hydrolysis of SO_4^{2-} should not occur to a very great extent. The pH of a neutralized solution should be very nearly 7, and most of the indicators represented in Figure 17-8 would be suitable. A more exact solution follows.

$$[\text{SO}_4^{2-}] = \frac{0.988 \text{ g NaHSO}_4}{0.03656 \text{ L}} \times \frac{1 \text{ mol NaHSO}_4}{120.06 \text{ g NaHSO}_4} \times \frac{1 \text{ mol SO}_4^{2-}}{1 \text{ mol NaHSO}_4} = 0.225 \quad \text{M}$$

Equation:	$SO_4^{2-}(aq)$	+ $H_2O(l)$ $\rightleftharpoons$	$HSO_4^-(aq)$	+ $OH^-(aq)$
Initial:	0.225 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.225 - x)$M	–	x M	x M

$$K_b = \frac{[\text{HSO}_4^-][\text{OH}^-]}{[\text{SO}_4^{2-}]} = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.1 \times 10^{-13} = \frac{x \cdot x}{0.225 - x} \approx \frac{x^2}{0.225}$$

$$[\text{OH}^-] = \sqrt{9.1 \times 10^{-13} \times 0.225} = 4.5 \times 10^{-7} \text{ M}$$

(the approximation was valid since $x << 0.225$ M)

$\text{pOH} = -\log(4.5 \times 10^{-7}) = 6.35$ $\quad\quad$ $\text{pH} = 14.00 - 6.35 = 7.65$

Thus, either bromthymol blue (pH color change range from pH = 6.1 to pH = 7.9) or phenol red (pH color change range from pH = 6.4 to pH = 8.0) would be a suitable indicator, since either changes color at pH = 7.65.

64. **(D)** The original solution contains $250.0 \text{ mL} \times \frac{0.100 \text{ mmol HC}_3\text{H}_5\text{O}_2}{1 \text{ mL soln}} = 25.0 \text{ mmol HC}_3\text{H}_5\text{O}_2$

$\text{p}K_a = -\log(1.35 \times 10^{-5}) = 4.87$ $\quad$ We let V be the volume added to the solution, in mL.

(a) Since we add V mL of HCl solution (and each mL adds 1.00 mmol H_3O^+ to the solution), we have added V mmol H_3O^+ to the solution. Now the final $[H_3O^+] = 10^{-1.00} = 0.100$ M.

$$[\text{H}_3\text{O}^+] = \frac{V \text{ mmol H}_3\text{O}^+}{(250.0 + V) \text{ mL}} = 0.100 \text{ M}$$

$$V = 25.0 + 0.100\,V, \text{ therefore, } V = \frac{25.0}{0.900} = 27.8 \text{ mL added}$$

Now, we check our assumptions. The total solution volume is 250.0 mL+ 27.8 mL = 277.8 mL There are 25.0 mmol $HC_2H_3O_2$ present before equilibrium is established, and 27.8 mmol H_3O^+ also.

$$[HC_2H_3O_2]=\frac{25.0\ \text{mmol}}{277.8\ \text{mL}}=0.0900\ \text{M} \qquad [H_3O^+]=\frac{27.8\ \text{mmol}}{277.8\ \text{mL}}=0.100\ \text{M}$$

Equation:	$HC_3H_5O_2(aq) +$	$H_2O(l) \rightleftharpoons$	$C_3H_5O_2^{\ -}(aq) +$	$H_3O^+(aq)$
Initial:	$0.0900\ \text{M}$	–	$0\ \text{M}$	$0.100\ \text{M}$
Changes:	$-x\ \text{M}$	–	$+x\ \text{M}$	$+x\ \text{M}$
Equil:	$(0.08999-x)\text{M}$	–	$x\ \text{M}$	$(0.100+x)\text{M}$

$$K_a=\frac{[H_3O^+][C_3H_5O_2^{\ -}]}{[HC_3H_5O_2]}=1.35\times10^{-5}=\frac{x\ (0.100+x)}{0.0900-x}\approx\frac{0.100\ x}{0.0900} \qquad x=1.22\times10^{-5}\,\text{M}$$

The assumption used in solving this equilibrium situation, that $x << 0.0900$ clearly is correct. In addition, the tacit assumption that virtually all of the H_3O^+ comes from the HCl also is correct.

(b) The pH desired is within 1.00 pH unit of the pK_a. We use the Henderson-Hasselbalch equation to find the required buffer ratio.

$$\text{pH}=\text{p}K_a+\frac{[A^-]}{[HA]}=\text{p}K_a+\log\frac{n_{A^-}/V}{n_{HA}/V}=\text{P}K_a+\log\frac{n_{A^-}}{n_{HA}}=4.00=4.87+\log\frac{n_{A^-}}{n_{HA}}$$

$$\log\frac{n_{A^-}}{n_{HA}}=-0.87 \qquad \frac{n_{A^-}}{n_{HA}}=10^{-0.87}=0.13=\frac{n_{A^-}}{25.00} \qquad n_{A^-}=3.3$$

$$V_{soln}=3.3\ \text{mmol}\ C_3H_5O_2^{\ -}\times\frac{1\ \text{mmol}\ NaC_3H_5O_2}{1\ \text{mmol}\ C_3H_5O_2^{\ -}}\times\frac{1\ \text{mL soln}}{1.00\ \text{mmol}\ NaC_3H_5O_2}=3.3\ \text{mL added}$$

We have assumed that all of the $C_3H_5O_2^-$ is obtained from the $NaC_3H_5O_2$ solution, since the addition of that ion in the solution should suppress the ionization of $HC_3H_5O_2$.

(c) We let V be the final volume of the solution.

Equation:	$HC_3H_5O_2(aq) +$	$H_2O(l) \rightleftharpoons$	$C_3H_5O_2^{\ -}(aq) +$	$H_3O^+(aq)$
Initial:	$25.0/V$	–	$0\ \text{M}$	$\approx\ 0\ \text{M}$
Changes:	$-x/V\ \text{M}$	–	$+x/V\ \text{M}$	$+x/V\ \text{M}$
Equil:	$(25.0/V-x/V)\ \text{M}$	–	$x/V\ \text{M}$	$x/V\ \text{M}$

$$K_a=\frac{[H_3O^+]\,[C_3H_5O_2^{\ -}]}{[HC_3H_5O_2]}=1.35\times10^{-5}=\frac{(x/V)^2}{25.0/V-x/V}\approx\frac{x^2/V}{25.0}$$

When $V = 250.0$ mL, $x = 0.29$ mmol H_3O^+ $\qquad [H_3O^+]=\dfrac{0.29\ \text{mmol}}{250.0\ \text{mL}}=1.2\times10^{-3}\ \text{M}$

$\text{pH} = -\log(1.2 \times 10^{-3}) = 2.92$
An increase of 0.15 pH unit gives pH = 2.92 + 0.15 = 3.07

$[H_3O^+] = 10^{-3.07} = 8.5 \times 10^{-4}$ M This is the value of x/V. Now solve for V.

$$1.3\times10^{-5} = \frac{(8.5\times10^{-4})^2}{25.0/V - 8.5\times10^{-4}} \qquad 25.0/V - 8.5\times10^{-4} = \frac{(8.5\times10^{-4})^2}{1.3\times10^{-5}} = 0.056$$

$$25.0/V = 0.056 + 0.00085 = 0.057 \qquad V = \frac{25.0}{0.057} = 4.4\times10^{2}\ \text{mL}$$

On the other hand, if we had used $[H_3O^+] = 1.16 \times 10^{-3}$ M (rather than 1.2×10^{-3} M), we would obtain $V = 4.8 \times 10^2$ mL. The answer to the problem thus is sensitive to the last significant figure that is retained. We obtain $V = 4.6 \times 10^2$ mL, requiring the addition of 2.1×10^2 mL of H_2O.

Another possibility is to recognize that $[H_3O^+] = \sqrt{K_a C_a}$ for a weak acid with ionization constant K_a and initial concentration C_a if the approximation is valid.

If C_a is changed to $C_a/2$, $[H_3O^+] = \sqrt{K_a/C_a} \times \sqrt{2}/2$. Since, pH = –log $[H_3O^+]$, the change in pH given by:

$\Delta pH = -\log \sqrt{2} = -\log\ 2^{1/2} = -0.5 \log\ 2 = -0.5 \times 0.30103 = -0.15$.

This corresponds to doubling the solution volume, that is, to adding 250 mL water. Diluted by half with water, $[H_3O^+]$ goes down and pH rises, then $(pH_1 - pH_2) < 0$.

65. **(E)** Carbonic acid is unstable in aqueous solution, decomposing to $CO_2(aq)$ and H_2O. The $CO_2(aq)$, in turn, escapes from the solution, to a degree determined in large part by the partial pressure of $CO_2(g)$ in the atmosphere.

$H_2CO_3(aq) \ll H_2O(l) + CO_2(aq) \ll CO_2(g) + H_2O(l)$

Thus, a solution of carbonic acid in the laboratory soon will reach a low $[H_2CO_3]$, since the partial pressure of $CO_2(g)$ in the atmosphere is quite low. Thus, such a solution would be unreliable as a buffer. In the body, however, the $[H_2CO_3]$ is regulated in part by the process of respiration. Respiration rates increase when it is necessary to decrease $[H_2CO_3]$ and respiration rates decrease when it is necessary to increase $[H_2CO_3]$.

66. **(E)**

(a) At a pH = 2.00, in Figure 17-9 the pH is changing gradually with added NaOH. There would be no sudden change in color with the addition of a small volume of NaOH.

(b) At pH = 2.0 in Figure 17-9, approximately 20.5 mL have been added. Since, equivalence required the addition of 25.0 mL, there are 4.5 mL left to add.

Therefore,

$$\%\ \text{HCl unneutralized} = \frac{4.5}{25.0} \times 100\% = 18\%$$

67. **(D)** Let us begin the derivation with the definition of $[H_3O^+]$.

$$[H_3O^+]=\frac{\text{amount of excess } H_3O^+}{\text{volume of titrant}+\text{volume of solution being titrated}}$$

Let V_a = volume of acid (solution being titrated) V_b = volume of base (titrant)

M_a = molarity of acid M_b = molarity of base

$$[H_3O^+]=\frac{V_a\times M_a-V_b\times M_b}{V_a+V_b}$$

Now we solve this equation for V_b

$$V_a\times M_a-V_b\times M_b=[H_3O^+](V_a+V_b) \qquad V_b([H_3O^+]+M_b)=V_a(M_a-[H_3O^+])$$

$$V_b=\frac{V_a(M_a-[H_3O^+])}{[H_3O^+]+M_b} \qquad V_b=\frac{V_a(M_a-10^{-\text{pH}})}{10^{-\text{pH}}+M_b}$$

(a) $10^{-\text{pH}}=10^{-2.00}=1.0\times10^{-2}\text{ M}$ $\quad V_b=\frac{20.00\text{ mL }(0.1500-0.010)}{0.010+0.1000}=25.4\underline{5}\text{ mL}$

(b) $10^{-\text{pH}}=10^{-3.50}=3.2\times10^{-4}\text{ M}$ $\quad V_b=\frac{20.00\text{ mL }(0.1500-0.0003)}{0.0003+0.1000}=29.85\text{ mL}$

(c) $10^{-\text{pH}}=10^{-5.00}=1.0\times10^{-5}\text{ M}$ $\quad V_b=\frac{20.00\text{ mL }(0.1500-0.00001)}{0.00001+0.1000}=30.00\text{ mL}$

Beyond the equivalence point, the situation is different.

$$[OH^-]=\frac{\text{amount of excess OH}^-}{\text{total solution volume}}=\frac{V_b\times M_b-V_a\times M_a}{V_a+V_b}$$

Solve this equation for V_b. $\quad [OH^-](V_a+V_b)=V_b\times M_b-V_a\times M_a$

$$V_a([OH^-]+M_a)=V_b(M_b-[OH^-]) \qquad V_b=\frac{V_a([OH^-]+M_a)}{M_b-[OH^-]}$$

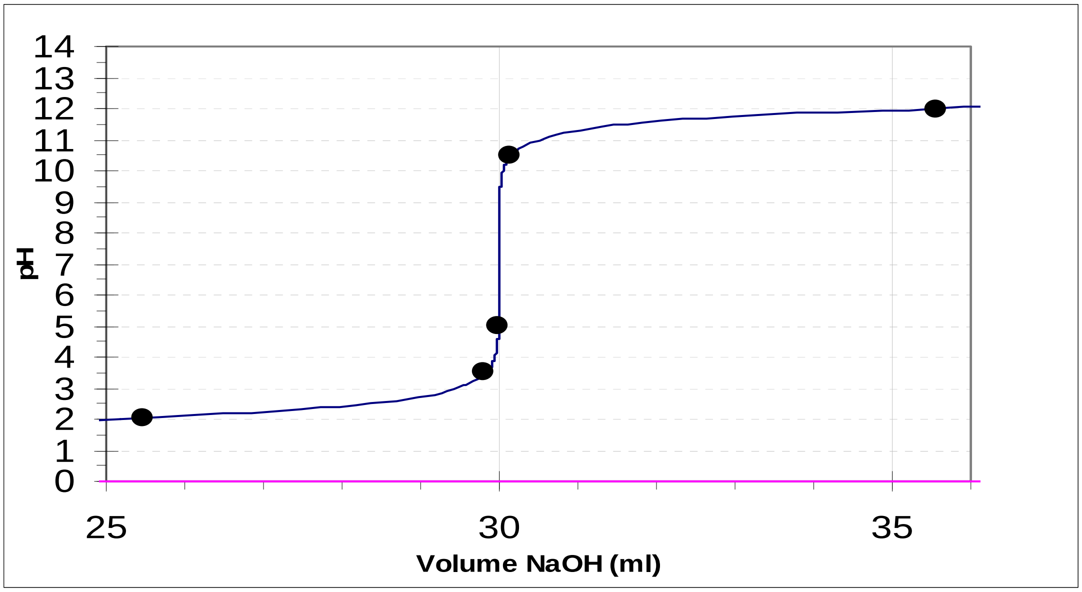
(d) $[OH^-]=10^{-\text{pOH}}=10^{-14.00+\text{pH}}=10^{-3.50}=0.00032\text{ M};$

$$V_b=20.00\text{ mL}\left(\frac{0.00032+0.1500}{0.1000-0.00032}\right)=30.16\text{ mL}$$

(e) $[OH^-]=10^{-\text{pOH}}=10^{-14.00+\text{pH}}=10^{-2.00}=0.010\text{ M};$

$$V_b=20.00\text{ mL}\left(\frac{0.010+0.1500}{0.1000-0.010}\right)=35.5\underline{6}\text{ mL}$$

The initial pH = –log(0.150) = 0.824. The titration curve is sketched below.



68. (D)

(a) The expressions that we obtained in Exercise 67 were for an acid being titrated by a base. For this titration, we need to switch the *a* and *b* subscripts and exchange $[OH^-]$ and $[H_3O^+]$.

Before the equivalence point: $$V_a = V_b \frac{M_b - [OH^-]}{[OH^-] + M_a}$$

After the equivalence point: $$V_a = V_b \frac{[H_3O^+] + M_b}{M_a - [H_3O^+]}$$

$\text{pH} = 13.00 \quad \text{pOH} = 14.00 - 13.00 = 1.00 \quad [OH^-] = 10^{-1.00} = 1.0\times10^{-1} = 0.10\text{ M}$

$$V_a = 25.00\text{ mL}\frac{0.250 - 0.10}{0.10 + 0.300} = 9.38\text{ mL}$$

$\text{pH} = 12.00 \quad \text{pOH} = 14.00 - 12.00 = 2.00 \quad [OH^-] = 10^{-2.00} = 1.0\times10^{-2} = 0.010\text{ M}$

$$V_a = 25.00\text{ mL}\frac{0.250 - 0.010}{0.010 + 0.300} = 19.4\text{ mL}$$

$\text{pH} = 10.00 \quad \text{pOH} = 14.00 - 10.00 = 4.00 \quad [OH^-] = 10^{-4.00} = 1.0\times10^{-4} = 0.00010\text{ M}$

$$V_a = 25.00\text{ mL}\frac{0.250 - 0.00010}{0.00010 + 0.300} = 20.8\text{ mL}$$

$\text{pH} = 4.00 \quad [H_3O^+] = 10^{-4.00} = 1.0\times10^{-4} = 0.00010\text{ M}$

$$V_a = 25.00\ \frac{0.00010 + 0.250}{0.300 - 0.00010} = 20.8\text{ mL}$$

$\text{pH} = 3.00 \quad [H_3O^+] = 10^{-3.00} = 1.0\times10^{-3} = 0.0010\text{ M}$

$$V_a = 25.00\frac{0.0010 + 0.250}{0.300 - 0.0010} = 21.0\text{ mL}$$

(b) Our expression does not include the equilibrium constant, K_a. But K_a is not needed after the equivalence point. pOH = 14.00 – 11.50 = 2.50 $[\mathrm{OH}^-] = 10^{-2.50} = 3.2 \times 10^{-3}$ = 0.0032 M

$$V_b = \frac{V_a(M_a + [\mathrm{O}H^-])}{M_b - [\mathrm{O}H^-]} = \frac{50.00\,\mathrm{mL}\,(0.0100 + 0.0032)}{0.0500 - 0.0032} = 14.1\,\mathrm{mL}$$

Let us use the Henderson-Hasselbalch equation as a basis to derive an expression that incorporates K_a. Note that because the numerator and denominator of that expression are concentrations of substances present in the same volume of solution, those concentrations can be replaced by numbers of moles.
Amount of anion = V_bM_b since the added OH^- reacts 1:1 with the weak acid.
Amount of acid = $V_aM_a - V_bM_b$ the acid left unreacted

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{p}K_\mathrm{a} + \log\frac{V_bM_b}{V_aM_a - V_bM_b}$$

Rearrange and solve for V_b $\quad 10^{\mathrm{pH-pK}} = \dfrac{V_bM_b}{V_aM_a - V_bM_b}$

$$(V_aM_a - V_bM_b)10^{\mathrm{pH-pK}} = V_bM_b \qquad V_b = \frac{V_aM_a\,10^{\mathrm{pH-pK}}}{M_b(1+10^{\mathrm{pH-pK}})}$$

$$\mathrm{pH} = 4.50,\ 10^{\mathrm{pH-pK}} = 10^{4.50-4.20} = 2.0 \quad V_b = \frac{50.00\ \mathrm{mL} \times 0.0100\ \mathrm{M} \times 2.0}{0.0500(1+2.0)} = 6.7\ \mathrm{mL}$$

$$\mathrm{pH} = 5.50,\ 10^{\mathrm{pH-pK}} = 10^{5.50-4.20} = 20. \qquad V_b = \frac{50.00\ \mathrm{mL} \times 0.0100\ \mathrm{M}\ 20}{0.0500(1+20.)} = 9.5\ \mathrm{mL}$$

69. (M)

(a) We concentrate on the ratio of concentrations of which the logarithm is taken.

$$\frac{[\text{conjugate base}]_{\text{eq}}}{[\text{weak acid}]_{\text{eq}}} = \frac{\text{equil. amount conj. base}}{\text{equil. amount weak acid}} = \frac{f \times \text{initial amt. weak acid}}{(1-f)\times\text{initial amt. weak acid}} = \frac{f}{1-f}$$

The first transformation is the result of realizing that the volume in which the weak acid and its conjugate base are dissolved is the same volume, and therefore the ratio of equilibrium amounts is the same as the ratio of concentrations. The second transformation is the result of realizing, for instance, that if 0.40 of the weak acid has been titrated, 0.40 of the original amount of weak acid now is in the form of its conjugate base, and 0.60 of that amount remains as weak acid. Equation 17.2 then is: $\mathrm{pH} = \mathrm{pK_a} + \log(f/(1-f))$

(b) We use the equation just derived. $\mathrm{pH} = 10.00 + \log\dfrac{0.27}{(1\ -\ 0.23)} = 9.56$

70. **(M)**

(a) $\mathrm{pH} = \mathrm{p}K_{a2} + \log\frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H_2PO_4^-}]} = 7.20 + \log\frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H_2PO_4^-}]} = 7.40 \qquad \frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H_2PO_4^-}]} = 10^{+0.20} = 1.6$

(b) In order for the solution to be isotonic, it must have the same concentration of ions as does the isotonic NaCl solution.

$$[\text{ions}] = \frac{9.2\text{ g NaCl}}{1\text{ L soln}} \times \frac{1\text{ mol NaCl}}{58.44\text{ g NaCl}} \times \frac{2\text{ mol ions}}{1\text{ mol NaCl}} = 0.31\text{ M}$$

Thus, 1.00 L of the buffer must contain 0.31 moles of ions. The two solutes that are used to formulate the buffer both ionize: KH_2PO_4 produces 2 mol of ions (K^+ and $H_2PO_4^-$) per mole of solute, while $Na_2HPO_4 \cdot 12\,H_2O$ produces 3 mol of ions (2 Na^+ and HPO_4^{2-}) per mole of solute. We let x = amount of KH_2PO_4 and y = amount of $Na_2HPO_4 \cdot 12\,H_2O$.

$$\frac{y}{x} = 1.6 \quad \text{or} \quad y = 1.6x \qquad 2x + 3y = 0.31 = 2x + 3(1.6x) = 6.8x$$

$$x = \frac{0.31}{6.8} = 0.046\text{ mol } KH_2PO_4 \qquad y = 1.6 \times 0.046 = 0.074\text{ mol } Na_2HPO_4 \cdot 12\,H_2O$$

$$\text{mass } KH_2PO_4 = 0.046\text{ mol } KH_2PO_4 \times \frac{136.08\text{ g } KH_2PO_4}{1\text{ mol } KH_2PO_4} = 6.3\text{ g } KH_2PO_4$$

$$\text{mass of } Na_2HPO_4 \cdot 12H_2O = 0.074\text{ mol } Na_2HPO_4 \cdot 12H_2O \times \frac{358.1\text{ g } Na_2HPO_4 \cdot 12H_2O}{1\text{ mol } Na_2HPO_4 \cdot 12H_2O}$$

$$= 26\text{ g } Na_2HPO_4 \cdot 12H_2O$$

71. **(M)** A solution of NH_4Cl should be acidic, hence, we should add an alkaline solution to make it pH neutral. We base our calculation on the ionization equation for NH_3(aq), and assume that little NH_4^+(aq) is transformed to NH_3(aq) because of the inhibition of that reaction by the added NH_3(aq), and because the added volume of NH_3(aq) does not significantly alter the V_{total}.

Equation:	$NH_3(aq) + H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
Initial:	xM	0.500 M	1.0×10^{-7}M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.500\text{ M})(1.0 \times 10^{-7}\text{ M})}{x\text{ M}} = 1.8 \times 10^{-5}$$

$$x\text{ M} = \frac{(0.500\text{ M})(1.0 \times 10^{-7}\text{ M})}{1.8 \times 10^{-5}\text{ M}} = 2.8 \times 10^{-3}\text{ M} = [NH_3]$$

$$V = 500\text{ mL} \times \frac{2.8 \times 10^{-3}\text{mol } NH_3}{1\text{ L final soln}} \times \frac{1\text{ L conc. soln}}{10.0\text{ mol } NH_3} \times \frac{1\text{ drop}}{0.05\text{ mL}} = 2.8\text{ drops} \cong 3\text{ drops}$$

72. (D)

(a) In order to sketch the titration curve, we need the pH at the following points.

i) Initial point. That is the pH of 0.0100 M *p*-nitrophenol, which we represent by the general formula for an indicator that also is a weak acid, HIn.

Equation:	$HIn(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$In^-(aq)$
Initial:	0.0100 M		–		≈ 0 M		0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.0100–x)$ M		–		x M		x M

$$K_{HIn} = 10^{-7.15} = 7.1\times10^{-8} = \frac{[H_3O^+]\ [In^-]}{[HIn]} = \frac{x\cdot x}{0.0100-x} \approx \frac{x^2}{0.0100}$$

$C_a / K_a = 1\times10^5$; thus, the approximation is valid

$$[H_3O^+] = \sqrt{0.0100\times7.1\times10^{-8}} = 2.7\times10^{-5}\ \text{M} \qquad \text{pH} = -\log(2.7\times10^{-5}) = 4.57$$

ii) At the half-equivalence point, the pH = pK_{HIn} = 7.15

iii) At the equiv point, pH is that of In^-. n_{In-} = 25.00 mL × 0.0100 M = 0.250 mmol In^-

$$V_{titrant} = 0.25\ \text{mmol HIn}\times\frac{1\ \text{mmol NaOH}}{1\ \text{mmol HIn}}\times\frac{1\ \text{mL titrant}}{0.0200\ \text{mmol NaOH}} = 12.5\ \text{mL titrant}$$

$$[In^-] = \frac{0.25\ \text{mmol}\ In^-}{25.00\ \text{mL} + 12.5\ \text{mL}} = 6.67\times10^{-3}\ \text{M} = 0.00667\ \text{M}$$

Equation:	$In^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HIn(aq)$	+	$OH^-(aq)$
Initial:	0.00667 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.00667 - x)$ M		–		x M		x M

$$K_b = \frac{[HIn][OH^-]}{[In^-]} = \frac{K_w}{K_a} = \frac{1.0\times10^{-4}}{7.1\times10^{-8}} = 1.4\times10^{-7} \approx \frac{x\cdot x}{0.00667-x} = \frac{x\cdot x}{0.00667}$$

($C_a/K_a = 1.4\times10^5$; thus, the approximation is valid)

$$[OH^-] = \sqrt{0.00667\times1.4\times10^{-7}} = 3.1\times10^{-5}$$

$$\text{pOH} = -\log(3.1\times10^{-5}) = 4.51;\ \text{therefore, pH} = 14.00 - \text{pOH} = 9.49$$

iv) Beyond the equivalence point, the pH is determined by the amount of excess OH– in solution. After 13.0 mL of 0.0200 M NaOH is added, 0.50 mL is in excess, and the total volume is 38.0 mL.

$$[OH^-] = \frac{0.50\ \text{mL}\times0.0200\ \text{M}}{38.0\ \text{mL}} = 2.63\times10^{-4}\ \text{M} \qquad \text{pOH} = 3.58 \qquad \text{pH} = 10.42$$

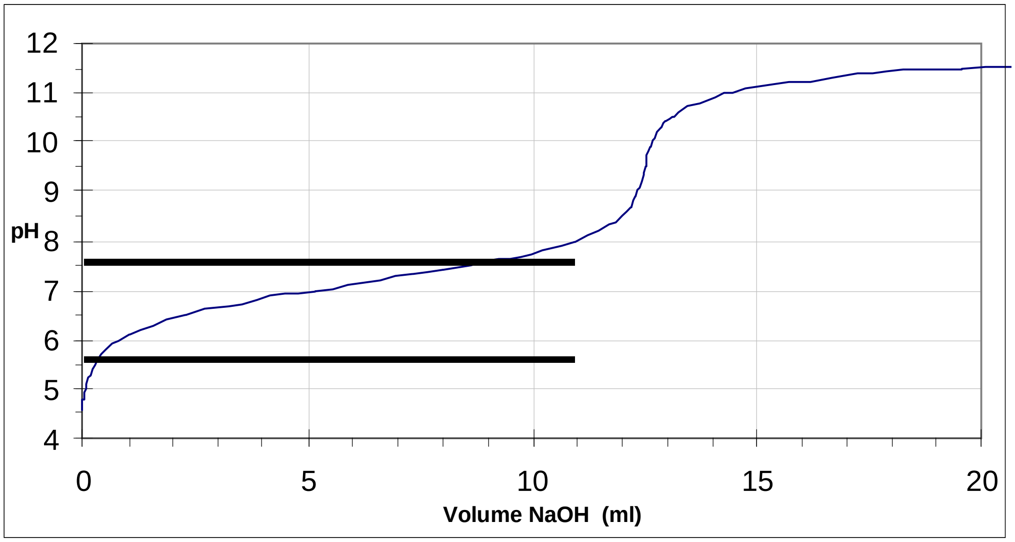
After 14.0 mL of 0.0200 M NaOH is added, 1.50 mL is in excess, and Vtotal = 39.0 mL.

$$[OH^-] = \frac{1.50\ \text{mL}\times0.0200\ \text{M}}{39.0\ \text{mL}} = 7.69\times10^{-4}\ \text{M} \qquad \text{pOH} = 3.11 \qquad \text{pH} = 10.89$$

v) In the buffer region, the pH is determined with the use of the Henderson-Hasselbalch equation.

$$\text{At } f = 0.10,\ \text{pH} = 7.15 + \log\frac{0.10}{0.90} = 6.20 \qquad \text{At } f = 0.90,\ \text{pH} = 7.15 + \log\frac{0.90}{0.10} = 8.10$$

f = 0.10 occurs with 0.10 × 12.5 mL = 1.25 mL added titrant; *f* = 0.90 with 11.25 mL added. The titration curve plotted from these points follows.



(b) The pH color change range of the indicator is shown on the titration curve.

(c) The equivalence point of the titration occurs at a pH of 9.49, far above the pH at which *p*-nitrophenol has turned yellow. In fact, the color of the indicator changes gradually during the course of the titration, making it unsuitable as an indicator for this titration.

Possible indicators are as follows.

Phenolphthalein: pH color change range from colorless at pH = 8.0 to red at pH = 10.0
Thymol blue: pH color change range from yellow at pH = 8.0 to blue at pH = 9.8
Thymolphthalein: pH color change range from colorless at $\text{pH} \approx 9$ to blue at $\text{pH} \approx 11$

The red tint of phenolphthalein will appear orange in the titrated *p*-nitrophenol solution. The blue of thymol blue or thymolphthalein will appear green in the titrated *p*-nitrophenol solution, producing a somewhat better yellow end point than the orange phenolphthalein endpoint.

73. (M)

(a) Equation (1) is the reverse of the equation for the autoionization of water. Thus, its equilibrium constant is simply the inverse of Kw.

$$K = \frac{1}{K_w} = \frac{1}{1.0\times10^{-14}} = 1.00\times10^{14}$$

Equation (2) is the reverse of the hydrolysis reaction for NH4+. Thus, its equilibrium constant is simply the inverse of the acid ionization constant for NH4+, Ka = 5.6 × 10-10

$$K' = \frac{1}{K_a} = \frac{1}{5.6\times10^{-10}} = 1.8\times10^{9}$$

(b) The extremely large size of each equilibrium constant indicates that each reaction goes essentially to completion. In fact, a general rule of thumb suggests that a reaction is considered essentially complete if Keq > 1000 for the reaction.

74. **(D)** The initial pH is that of 0.100 M $HC_2H_3O_2$.

Equation:	$HC_2H_3O_2(aq)$ +	$H_2O(l) \rightleftharpoons$	$C_2H_3O_2^-(aq)$	+	$H_3O^+(aq)$
Initial:	0.100 M	–	0 M		≈ 0 M
Changes:	$-x$ M	–	$+x$ M		$+x$ M
Equil:	$(0.100-x)$ M	–	x M		x M

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8\times10^{-5} = \frac{x\cdot x}{0.100-x} \approx \frac{x^2}{0.100}$$

($C_a/K_a = 5.5\times10^3$; thus, the approximation is valid)

$$[H_3O^+] = \sqrt{0.100\times1.8\times10^{-5}} = 1.3\times10^{-3}\text{ M} \qquad \text{pH} = -\log(1.3\times10^{-3}) = 2.89$$

At the equivalence point, we have a solution of $NH_4C_2H_3O_2$ which has a pH = 7.00, because both NH_4^+ and $C_2H_3O_2^-$ hydrolyze to an equivalent extent, since $K_a(HC_2H_3O_2) \approx K_b(NH_3)$ and their hydrolysis constants also are virtually equal. Total volume of titrant = 10.00 mL, since both acid and base have the same concentrations.

At the half equivalence point, which occurs when 5.00 mL of titrant have been added, pH = pK_a = 4.74. *When the solution has been 90% titrated,* 9.00 mL of 0.100 M NH_3 has been added. We use the Henderson-Hasselbalch equation to find the pH after 90% of the acid has been titrated

$$\text{pH} = \text{p}K_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.74 + \log\frac{9}{1} = 5.69$$

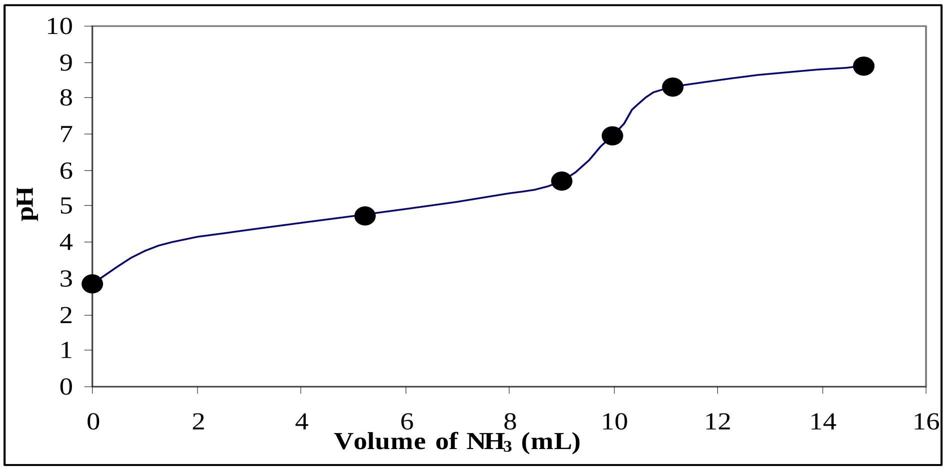
When the solution is 110% titrated, 11.00 mL of 0.100 M NH_3 have been added.
amount NH_3 added = 11.00 mL × 0.100 M = 1.10 mmol NH_3
amount NH_4^+ produced = amount $HC_2H_3O_2$ consumed = 1.00 mmol NH_4^+
amount NH_3 unreacted = 1.10 mmol NH_3 – 1.00 mmol NH_4^+ = 0.10 mmol NH_3
We use the Henderson-Hasselbalch equation to determine the pH of the solution.

$$\text{pOH} = \text{p}K_b + \log\frac{[NH_4^+]}{[NH_3]} = 4.74 + \log\frac{1.00\text{ mmol }NH_4^+}{0.10\text{ mmol }NH_3} = 5.74 \qquad \text{pH} = 8.26$$

When the solution is 150% titrated, 15.00 mL of 0.100 M NH_3 have been added.
amount NH_3 added = 15.00 mL × 0.100 M = 1.50 mmol NH_3
amount NH_4^+ produced = amount $HC_2H_3O_2$ consumed = 1.00 mmol NH_4^+
amount NH_3 unreacted = 1.50 mmol NH_3 – 1.00 mmol NH_4^+ = 0.50 mmol NH_3

$$\text{pOH} = \text{p}K_b + \log\frac{[NH_4^+]}{[NH_3]} = 4.74 + \log\frac{1.00\text{ mmol }NH_4^+}{0.50\text{ mmol }NH_3} = 5.04 \qquad \text{pH} = 8.96$$

The titration curve based on these points is sketched next. We note that the equivalence point is not particularly sharp and thus, satisfactory results are not obtained from acetic acid–ammonia titrations.



75. **(D)** $C_6H_5NH_3^+$ is a weak acid, whose acid ionization constant is determined from $K_b(C_6H_5NH_2) = 7.4 \times 10^{-10}$.

$K_a = \dfrac{1.0\times10^{-14}}{7.4\times10^{-10}} = 1.4\times10^{-5}$ and $pK_a = 4.85$. We first determine the *initial pH.*

Equation:	$C_6H_5NH_3^+(aq)$	+ $H_2O(l)$	$\rightleftharpoons$ $C_6H_5NH_2(aq)$ +	$H_3O^+(aq)$
Initial:	0.0500 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.0500 - x)$ M	–	x M	x M

$$K_a = 1.4\times10^{-5} = \frac{[C_6H_5NH_2]\ [H_3O^+]}{[C_6H_5NH_3^+]} = \frac{x\cdot x}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

(Since $C_a/K_a = 3.6\times10^3$; thus, the approximation is valid)

$[H_3O^+] = \sqrt{0.0500\times1.4\times10^{-5}} = 8.4\times10^{-4}$ M $\quad$ pH $= -\log\ (8.4\times10^{-4}) = 3.08$

At the equivalence point, we have a solution of $C_6H_5NH_2(aq)$. Now find the volume of titrant.

$$V = 10.00\text{ mL}\times\frac{0.0500\text{ mmol } C_6H_5NH_3^+}{1\text{ mL}}\times\frac{1\text{ mmol NaOH}}{1\text{ mmol } C_6H_5NH_3^+}\times\frac{1\text{ mL titrant}}{0.100\text{ mmol NaOH}} = 5.00\text{ mL}$$

amount $C_6H_5NH_2 = 10.00\text{ mL}\times0.0500\text{ M} = 0.500\text{ mmol } C_6H_5NH_2$

$$[C_6H_5NH_2] = \frac{0.500\text{ mmol } C_6H_5NH_2}{10.00\text{ mL} + 5.00\text{ mL}} = 0.0333\text{ M}$$

Equation:	$C_6H_5NH_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$C_6H_5NH_3^+(aq)$	+	$OH^-(aq)$
Initial:	0.0333 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(0.0333-x)$ M		–		x M		x M

$$K_b = 7.4\times10^{-10} = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{x\cdot x}{0.0333-x} \approx \frac{x^2}{0.0333}$$

(C_b/K_b = very large number; thus, the approximation is valid)

$$[OH^-] = \sqrt{0.0333\times7.4\times10^{-10}} = 5.0\times10^{-6} \qquad pOH = 5.30 \qquad pH = 8.70$$

At the half equivalence point, when 5.00 mL of 0.1000 M NaOH has been added, pH = pKa = 4.85. At points in the buffer region, we use the expression derived in Exercise 69.

After 4.50 mL of titrant has been added, $f = 0.90$, pH = 4.85 + $\log\dfrac{0.90}{0.10} = 5.80$

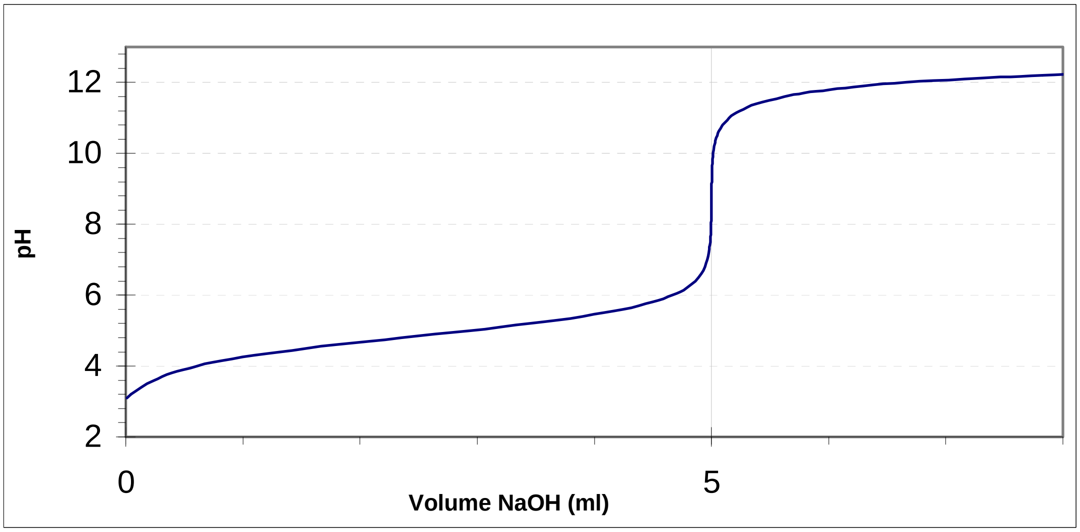
After 4.75 mL of titrant has been added, $f = 0.95$, pH = 4.85 + $\log\dfrac{0.95}{0.05} = 6.13$

After the equivalence point has been reached, with 5.00 mL of titrant added, the pH of the solution is determined by the amount of excess OH^- that has been added.

At 105% titrated, $[OH^-] = \dfrac{0.25\text{ mL}\times0.100\text{ M}}{15.25\text{ mL}} = 0.0016\text{ M} \qquad pOH = 2.80 \qquad pH = 11.20$

At 120% titrated, $[OH^-] = \dfrac{1.00\text{ mL}\times0.100\text{ M}}{16.00\text{ mL}} = 0.00625\text{ M} \qquad pOH = 2.20 \qquad pH = 11.80$

Of course, one could sketch a suitable titration curve by calculating fewer points. Below is the titration curve.



76. In order for a diprotic acid to be titrated to two distinct equivalence points, the acid must initially start out with two undissociated protons and the K_a values for the first and second protons must differ by >1000. This certainly is not the case for H_2SO_4, which is a strong acid (first proton is 100% dissociated). Effectively, this situation is very similar to the titration of a monoprotic acid that has added strong acid (i.e., HCl or HNO_3). With the leveling effect of water, $K_{a1} = 1$ and $K_{a2} = 0.011$, there is a difference of only 100 between K_{a1} and K_{a2} for H_2SO_4.

<u>77</u>. **(D)** For both titration curves, we assume 10.00 mL of solution is being titrated and the concentration of the solute is 1.00 M, the same as the concentration of the titrant. Thus, 10.00 mL of titrant is required in each case. (You may be able to sketch titration curves based on fewer calculated points. Your titration curve will look slightly different if you make different initial assumptions.)

(a) The *initial pH* is that of a solution of HCO_3^-(aq). This is an anion that can ionize to CO_3^{2} (aq) or be hydrolyzed to H_2CO_3(aq). Thus,

$$\text{pH} = \tfrac{1}{2}\,(\text{p}K_{a_1} + \text{p}K_{a_2}) = \tfrac{1}{2}\,(6.35 + 10.33) = 8.34$$

The *final pH* is that of 0.500 M H_2CO_3(aq). All of the NaOH(aq) has been neutralized, as well as all of the HCO_3^-(aq), by the added HCl(aq).

Equation:	$H_2CO_3(aq)$	$+\ H_2O(l)$	$\rightleftharpoons$	$HCO_3^-(aq)$	$+\ H_3O^+(aq)$
Initial:	0.500 M	–		0 M	≈ 0 M
Changes:	$-x$ M	–		$+x$ M	$+x$ M
Equil:	$(0.500 - x)$ M	–		x M	x M

$$K_b = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 4.43\times10^{-7} = \frac{x\cdot x}{0.500 - x} \approx \frac{x^2}{0.500}$$

(C_a/K_a = 1.1×10^6; thus, the approximation is valid)

$$[OH^-] = \sqrt{0.500\times4.4\times10^{-7}} = 4.7\times10^{-4}\,\text{M} \qquad \text{pH} = 3.33$$

During the course of the titration, the pH is determined by the Henderson-Hasselbalch equation, with the numerator being the percent of bicarbonate ion remaining, and as the denominator being the percent of bicarbonate ion that has been transformed to H_2CO_3.

90% titrated: $\text{pH} = 6.35 + \log\dfrac{10\%}{90\%} = 5.40$ 10% titrated: $\text{pH} = 6.35 + \log\dfrac{90\%}{10\%} = 7.30$

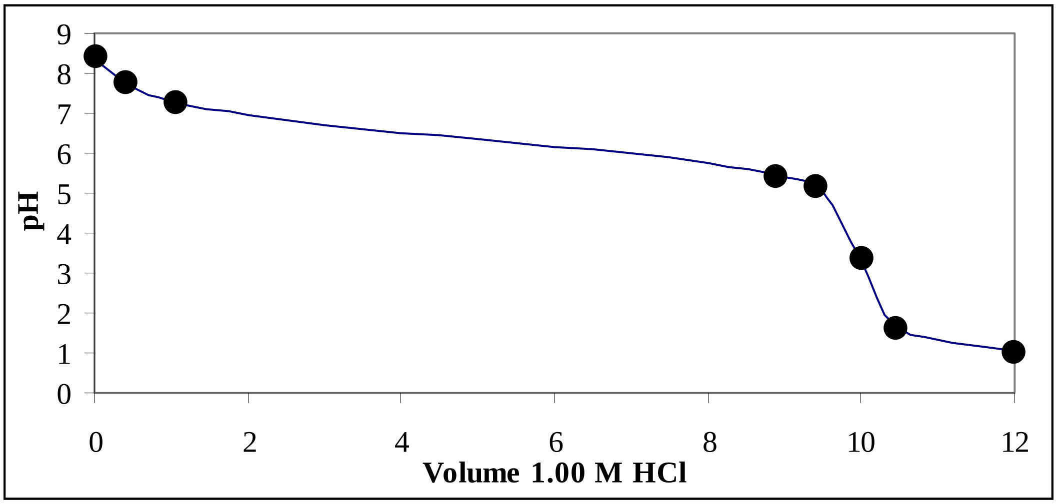
95% titrated: $\text{pH} = 6.35 + \log\dfrac{5\%}{95\%} = 5.07$ 5% titrated: $\text{pH} = 6.35 + \log\dfrac{95\%}{5\%} = 7.63$

After the equivalence point, the pH is determined by the excess H_3O^+.

$$\text{At 105\% titrated, } [H_3O^+] = \frac{0.50\,\text{mL}\times1.00\,\text{M}}{20.5\,\text{mL}} = 0.024 \qquad \text{pH} = 1.61$$

$$\text{At 120\% titrated, } [H_3O^+] = \frac{2.00\text{ mL} \times 1.00\text{ M}}{22.0\text{ mL}} = 0.091\text{ M} \qquad \text{pH} = 1.04$$

The titration curve derived from these data is sketched below.



(b) The *final pH of the first step of the titration* is that of a solution of HCO_3^-(aq). This is an anion that can be ionized to CO_3^{2-}(aq) or hydrolyzed to H_2CO_3(aq). Thus, $\text{pH} = \frac{1}{2}\,(\text{pK}_{a_1} + \text{pK}_{a_2}) = \frac{1}{2}\,(6.35 + 10.33) = 8.34$. The *initial pH* is that of 1.000 M CO_3^{2-}(aq), which pH is the result of the hydrolysis of the anion.

Equation:	CO_3^{2-}(aq)	+	H_2O(l)	$\rightleftharpoons$	HCO_3^-(aq)	+	OH^-(aq)
Initial:	1.000 M		–		0 M		≈ 0 M
Changes:	$-x$ M		–		$+x$ M		$+x$ M
Equil:	$(1.000 - x)$ M		–		x M		x M

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4} = \frac{x \cdot x}{1.000 - x} \approx \frac{x^2}{1.000}$$

$$[OH^-] = \sqrt{1.000 \times 2.1 \times 10^{-4}} = 1.4 \times 10^{-2}\text{ M} \qquad \text{pOH} = 1.85 \qquad \text{pH} = 12.15$$

During the course of the first step of the titration, the pH is determined by the Henderson-Hasselbalch equation, modified as in Exercise 69, but using as the numerator the percent of carbonate ion remaining, and as the denominator the percent of carbonate ion that has been transformed to HCO_3^-.

$$\text{90\% titrated: pH} = 10.33 + \log\frac{10\%}{90\%} = 9.38 \qquad \text{10\% titrated: pH} = 10.33 + \log\frac{90\%}{10\%} = 11.28$$

$$\text{95\% titrated: pH} = 10.33 + \log\frac{5\%}{95\%} = 9.05 \qquad \text{5\% titrated: pH} = 10.33 + \log\frac{95\%}{5\%} = 11.61$$

During the course of the second step of the titration, the values of pH are precisely as they are for the titration of $NaHCO_3$, except the titrant volume is 10.00 mL more (the volume needed to reach the first equivalence point). The solution *at the second* *equivalence* point is 0.333 M H_2CO_3, for which the set-up is similar to that for 0.500 M H_2CO_3.

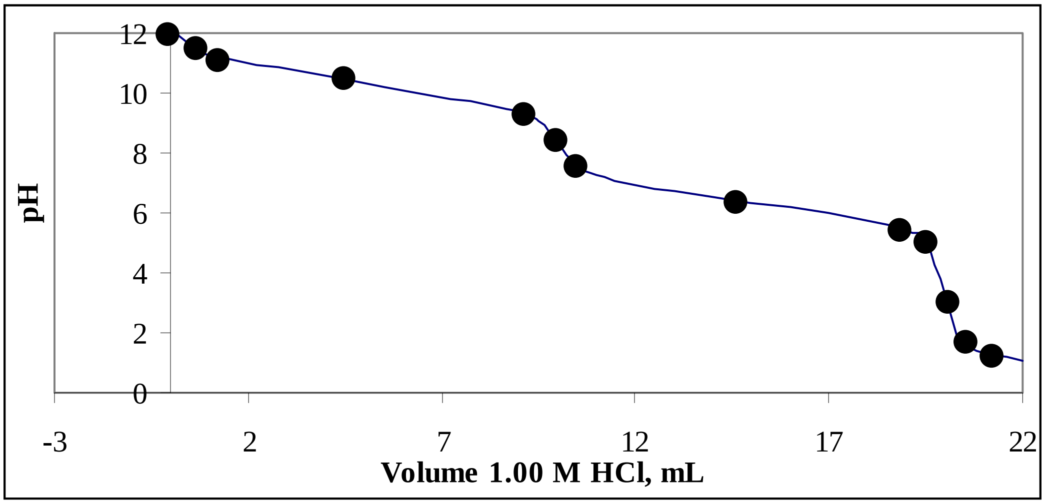
$[H_3O^+] = \sqrt{0.333 \times 4.4 \times 10^{-7}} = 3.8 \times 10^{-4}$ M $\quad$ pH = 3.42

After the equivalence point, the pH is determined by the excess H_3O^+.

At 105% titrated, $\quad [H_3O^+] = \dfrac{0.50 \text{ mL} \times 1.00 \text{ M}}{30.5 \text{ mL}} = 0.0164 \text{ M} \quad \text{pH} = 1.8$

At 120% titrated, $\quad [H_3O^+] = \dfrac{2.00 \text{ mL} \times 1.00 \text{ M}}{32.0 \text{ mL}} = 0.0625 \text{ M} \quad \text{pH} = 1.20$

The titration curve from these data is sketched below.



(c) $V_{HCl} = 1.00 \text{ g NaHCO}_3 \times \dfrac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \dfrac{1 \text{ mol HCl}}{1 \text{ mol NaHCO}_3} \times \dfrac{1000 \text{ mL}}{0.100 \text{ mol HCl}}$

$= 119 \text{ mL } 0.100 \text{ M HCl}$

(d) $V_{HCl} = 1.00 \text{ g Na}_2\text{CO}_3 \times \dfrac{1 \text{ mol Na}_2\text{CO}_3}{105.99 \text{ g Na}_2\text{CO}_3} \times \dfrac{2 \text{ mol HCl}}{1 \text{ mol Na}_2\text{CO}_3} \times \dfrac{1000 \text{ mL}}{0.100 \text{ mol HCl}}$

$= 189 \text{ mL } 0.100 \text{ M HCl}$

(e) The phenolphthalein endpoint occurs at pH = 8.00 and signifies that the NaOH has been neutralized, and that Na_2CO_3 has been half neutralized. The methyl orange endpoint occurs at about pH = 3.3 and is the result of the second equivalence point of Na_2CO_3. The mass of Na_2CO_3 can be determined as follows:

$$\text{mass } Na_2CO_3 = 0.78\text{ mL}\times\frac{1\text{ L}}{1000\text{ mL}}\times\frac{0.1000\text{ mol HCl}}{1\text{ L soln}}\times\frac{1\text{ mol }HCO_3^-}{1\text{ mol HCl}}\frac{1\text{ mol }Na_2CO_3}{1\text{ mol }HCO_3^-}$$

$$\times\frac{105.99\text{ g }Na_2CO_3}{1\text{ mol }Na_2CO_3} = 0.0083\text{ g }Na_2CO_3$$

$$\%\ Na_2CO_3 = \frac{0.0083\text{g}}{0.1000\text{g}}\times 100 = 8.3\%\ Na_2CO_3\text{ by mass}$$

78. **(M)** We shall represent piperazine as Pip in what follows. The cation resulting from the first ionization is $HPiP^+$, and that resulting from the second ionization is H_2Pip^{2+}.

(a) $$[\text{Pip}] = \frac{1.00\,\text{g }C_4H_{10}N_2{\cdot}6H_2O}{0.100\,\text{L}}\times\frac{1\text{mol }C_4H_{10}N_2{\cdot}6H_2O}{194.22\,\text{g }C_4H_{10}N_2{\cdot}6H_2O} = 0.0515M$$

$$\begin{array}{llcccc}
\text{Equation:} & Pip(\text{aq}) & + & H_2O(\text{l}) \rightleftharpoons & HPip^+(\text{aq}) & + \quad OH^-(\text{aq}) \\
\text{Initial:} & 0.0515\text{ M} & & - & 0\text{ M} & \approx 0\text{ M} \\
\text{Changes:} & -x\text{ M} & & - & +x\text{ M} & +x\text{ M} \\
\text{Equil:} & (0.0515-x)\text{ M} & & - & x\text{ M} & x\text{ M}
\end{array}$$

C_a/K_a = 858; thus, the approximation is not valid. The full quadratic equation must be solved.

$$K_{b_1} = 10^{-4.22} = 6.0\times10^{-5} = \frac{[HPip^+][OH^-]}{[Pip]} = \frac{x\cdot x}{0.0515-x}$$

From the roots of the equation, $x = [OH^-] = 1.7\times10^{-3}$ M pOH = 2.77 pH = 11.23

(b) At the half-equivalence point of the first step in the titration, pOH = pK_{b1} = 4.22
pH = 14.00 – pOH = 14.00 – 4.22 = 9.78

(c) $$\text{Volume of HCl} = 100.\text{ mL}\times\frac{0.0515\,\text{mmol Pip}}{1\text{mL}}\times\frac{1\text{mmol HCl}}{1\text{mmol Pip}}\times\frac{1\text{mL titrant}}{0.500\text{ mmol HCl}} = 10.3\,\text{mL}$$

(d) At the first equivalence point we have a solution of $HPip^+$. This ion can react as a base with H_2O to form H_2Pip^{2+} or it can react as an acid with water, forming Pip (i.e. $HPip^+$ is amphoteric). The solution's pH is determined as follows (base hydrolysis predominates):
pOH = ½ (pK_{b1} + pK_{b2}) = ½ (4.22 + 8.67) = 6.45, hence pH = 14.00 – 6.45 = 7.55

(e) The pOH at the half-equivalence point in the second step of the titration equals pK_{b2}.
pOH = pK_{b2} = 8.67 pH = 14.00 – 8.67 = 5.33

(f) The volume needed to reach the second equivalence point is twice the volume needed to reach the first equivalence point, that is 2 × 10.3 mL = 20.6 mL.

(g) The pH at the second equivalence point is determined by the hydrolysis of the H_2Pip^{2+} cation, of which there is 5.15 mmol in solution, resulting from the reaction of $HPip^+$ with HCl. The total solution volume is 100. mL + 20.6 mL = 120.$\underline{6}$ mL

$$[H_2Pip^{2+}] = \frac{5.15\,mmol}{120.\underline{6}\,mL} = 0.0427\,M \qquad K_{b_2} = 10^{-8.67} = 2.1\times10^{-9}$$

Equation:	$H_2Pip^{2+}(aq)$	$+\ H_2O(l) \rightleftharpoons$	$HPip^+(aq)$	$+\ H_3O^+(aq)$
Initial:	0.0427 M	–	0 M	≈ 0 M
Changes:	$-x$ M	–	$+x$ M	$+x$ M
Equil:	$(0.0427 - x)$ M	–	x M	x M

$$K_a = \frac{K_w}{K_{b_2}} = \frac{1.00\times10^{-14}}{2.1\times10^{-9}} = \frac{[HPip^+][H_3O^+]}{[H_2Pip^{2+}]} = 4.8\times10^{-6} = \frac{x\cdot x}{0.0427-x} \approx \frac{x^2}{0.0427}$$

$$x = [H_3O^+] = \sqrt{0.0427\times4.8\times10^{-6}} = 4.5\times10^{-4}\,M \qquad pH = 3.34\underline{7}$$

(x << 0.0427; thus, the approximation is valid).

79. **(M)** Consider the two equilibria shown below.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq) \qquad K_b = K_w/K_{a1} = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]}$$

All of the phosphorus containing species must add up to the initial molarity M.

Hence, mass balance: $[HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] = M$

charge balance: $[H_3O^+] + [Na^+] = [H_2PO_4^-] + 2\times[HPO_4^{2-}]$

Note: $[Na^+]$ for a solution of $NaH_2PO_4 = M$

Thus, $[H_3O^+] + [Na^+] = [H_2PO_4^-] + 2\times[HPO_4^{2-}] = [H_3O^+] + M$ (substitute mass balance equation)

$[H_3O^+] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] = [H_2PO_4^-] + 2\times[HPO_4^{2-}]$ (cancel terms)

$[H_3O^+] = [HPO_4^{2-}] - [H_3PO_4]$

(Note: $[HPO_4^{2-}]$ = initial $[H_3O^+]$ and $[H_3PO_4]$ = initial $[OH^-]$)

Thus: $[H_3O^+]_{equil} = [H_3O^+]_{initial} - [OH^-]_{initial}$ (excess H_3O^+ reacts with OH^- to form H_2O)

Rearrange the expression for K_{a2} to solve for $[HPO_4^{2-}]$, and the expression for K_b to solve for $[H_3PO_4]$.

$$[H_3O^+] = [HPO_4^{2-}] - [H_3PO_4] = \frac{K_{a2}[H_2PO_4^-]}{[H_3O^+]} - \frac{K_b[H_2PO_4^-]}{[OH^-]}$$

$$[H_3O^+] = \frac{K_{a2}[H_2PO_4^-]}{[H_3O^+]} - \frac{\frac{K_w}{K_{a1}}[H_2PO_4^-]}{\frac{K_w}{[H_3O^+]}} = \frac{K_{a2}[H_2PO_4^-]}{[H_3O^+]} - \frac{[H_3O^+][H_2PO_4^-]}{K_{a1}}$$

Multiply through by $[H_3O^+]\,K_{a1}$ and solve for $[H_3O^+]$.

$$K_{a1}[H_3O^+][H_3O^+] = K_{a1}K_{a2}[H_2PO_4^-] - [H_3O^+][H_3O^+][H_2PO_4^-]$$
$$K_{a1}[H_3O^+]^2 = K_{a1}K_{a2}[H_2PO_4^-] - [H_3O^+]^2[H_2PO_4^-]$$
$$K_{a1}[H_3O^+]^2 + [H_3O^+]^2[H_2PO_4^-] = K_{a1}K_{a2}[H_2PO_4^-] = [H_3O^+]^2(K_{a1} + [H_2PO_4^-])$$
$$K_{a1}[H_3O^+]^2 + [H_3O^+]^2[H_2PO_4^-] = K_{a1}K_{a2}[H_2PO_4^-] = [H_3O^+]^2(K_{a1} + [H_2PO_4^-])$$

$[H_3O^+]^2 = \dfrac{K_{a1}K_{a2}[H_2PO_4^-]}{(K_{a1} + [H_2PO_4^-])}$ For moderate concentrations of $[H_2PO_4^-]$, $K_{a1} << [H_2PO_4^-]$

This simplifies our expression to: $[H_3O^+]^2 = \dfrac{K_{a1}K_{a2}[H_2PO_4^-]}{[H_2PO_4^-]} = K_{a1}K_{a2}$

Take the square root of both sides: $[H_3O^+]^2 = K_{a1}K_{a2} \longrightarrow [H_3O^+] = \sqrt{K_{a1}K_{a2}} = (K_{a1}K_{a2})^{1/2}$

Take the -log of both sides and simplify:

$-\log[H_3O^+] = -\log(K_{a1}K_{a2})^{1/2} = -1/2\left(\log(K_{a1}K_{a2})\right) = -1/2(\log K_{a1} + \log K_{a2})$

$-\log[H_3O^+] = 1/2(-\log K_{a1} - \log K_{a2})$ Use $-\log[H_3O^+] = pH$ and $-\log K_{a1} = pK_{a1}$ $-\log K_{a2} = pK_{a2}$

Hence, $-\log[H_3O^+] = +1/2(-\log K_{a1} - \log K_{a2})$ becomes $pH = 1/2(pK_{a1} + pK_{a2})$ (Equation 17.5)

Equation 17.6 can be similarly answered.

80. **(D)** $H_2PO_4^-$ can react with H_2O by both ionization and hydrolysis.

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$
$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$$

The solution cannot have a large concentration of both H_3O^+ and OH^- (cannot be simultaneously an acidic and a basic solution). Since the solution **is** acidic, some of the H_3O^+ produced in the first reaction reacts with virtually all of the OH^- produced in the second. In the first reaction $[H_3O^+] = [HPO_4^{2-}]$ and in the second reaction $[OH^-] = [H_3PO_4]$. Thus, following the neutralization of OH^- by H_3O^+, we have the following.

$$[H_3O^+] = [HPO_4^{2-}] - [H_2PO_4^-] = \frac{K_{a_2}[H_2PO_4^-]}{[H_3O^+]} - \frac{K_b[H_2PO_4^-]}{[OH^-]} = \frac{K_{a_2}[H_2PO_4^-]}{[H_3O^+]} - \frac{\frac{K_w}{K_{a_1}}[H_2PO_4^-]}{\frac{K_w}{[H_3O^+]}}$$

$$= \frac{K_{a_2}[H_2PO_4^-]}{[H_3O^+]} - \frac{[H_3O^+][H_2PO_4^-]}{K_{a_1}}$$

Then multiply through by $[H_3O^+]K_{a_1}$ and solve for $[H_3O^+]$.

$$[H_3O^+]^2 K_{a_1} = K_{a_1}K_{a_2}[H_2PO_4^-] - [H_3O^+]^2[H_2PO_4^-] \qquad [H_3O^+] = \sqrt{\frac{K_{a_1}K_{a_2}[H_2PO_4^-]}{[K_{a_1} + [H_2PO_4^-]]}}$$

But, for a moderate $[H_2PO_4^-]$, from Table 16-6, $K_{a_1} = 7.1 \times 10^{-3} < [H_2PO_4^-]$ and thus $K_{a_1} + [H_2PO_4^-] \approx [H_2PO_4^-]$. Then we have the following expressions for $[H_3O^+]$ and pH.

$$[H_3O^+] = \sqrt{K_{a_1} \times K_{a_2}}$$

$$pH = -\log[H_3O^+] = -\log(K_{a_1} \times K_{a_2})^{1/2} = \tfrac{1}{2}[-\log(K_{a_1} \times K_{a_2})] = \tfrac{1}{2}(-\log K_{a_1} - \log K_{a_2})$$

$$pH = \tfrac{1}{2}\ (pK_{a_1} + pK_{a_2})$$

Notice that we assumed $K_a < [H_2PO_4^-]$. This assumption is not valid in quite dilute solutions because $K_a = 0.0071$.

81. **(D)**

(a) A buffer solution is able to react with small amounts of added acid or base. When strong acid is added, it reacts with formate ion.

$$CHO_2^-(aq) + H_3O^+(aq) \longrightarrow HCHO_2(aq) + H_2O$$

Added strong base reacts with acetic acid.

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow H_2O(l) + C_2H_3O_2^-(aq)$$

Therefore neither added strong acid nor added strong base alters the pH of the solution very much. Mixtures of this type are referred to as buffer solutions.

(b) We begin with the two ionization reactions.

$$HCHO_2(aq) + H_2O(l) \rightleftharpoons CHO_2^-(aq) + H_3O^+(aq)$$
$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+(aq)$$

$$[Na^+] = 0.250 \qquad [OH^-] \approx 0 \qquad [H_3O^+] = x \qquad [C_2H_3O_2^-] = y \qquad [CHO_2^-] = z$$

$$0.150 = [HC_2H_3O_2] + [C_2H_3O_2^-] \qquad [HC_2H_3O_2] = 0.150 - [C_2H_3O_2^-] = 0.150 - y$$
$$0.250 = [HCHO_2] + [CHO_2^-] \qquad [HCHO_2] = 0.250 - [CHO_2^-] = 0.250 - z$$

$$[Na^+] + [H_3O^+] = [C_2H_3O_2^-] + [CHO_2^-] + [OH^-] \text{ (electroneutrality)}$$
$$0.250 + x = [C_2H_3O_2^-] + [CHO_2^-] = y + z \qquad (1)$$

$$\frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_A = 1.8 \times 10^{-5} = \frac{x \cdot y}{0.150 - y} \qquad (2)$$

$$\frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = K_F = 1.8 \times 10^{-4} = \frac{x \cdot z}{0.250 - z} \qquad (3)$$

There now are three equations—(1), (2), and (3)—in three unknowns—*x*, *y*, and *z*. We solve equations (2) and (3), respectively, for *y* and *z* in terms of *x*.

$$0.150\,K_A - y\,K_A = xy \qquad y = \frac{0.150\,K_A}{K_A + x}$$

$$0.250\,K_F - z\,K_F = xz \qquad z = \frac{0.250\,K_F}{K_F + x}$$

Then we substitute these expressions into equation (1) and solve for *x*.

$$0.250 + x = \frac{0.150\,K_A}{K_A + x} + \frac{0.250\,K_F}{K_F + x} \approx 0.250 \qquad \text{since } x << 0.250$$

$$0.250\,(K_F + x)\,(K_A + x) = 0.150\,K_A\,(K_F + x) + 0.250\,K_F\,(K_A + x)$$

$$K_A K_F + (K_A + K_F)x + x^2 = 1.60\,K_A K_F + x(0.600\,K_A + 1.00\,K_F)$$

$$x^2 + 0.400\,K_A x - 0.600\,K_A K_F = 0 = x^2 + 7.2\times10^{-6}\,x - 1.9\times10^{-9}$$

$$x = \frac{-7.2\times10^{-6} \pm \sqrt{5.2\times10^{-11} + 7.6\times10^{-9}}}{2} = 4.0\times10^{-5}\text{ M} = [H_3O^+]$$

$$\text{pH} = 4.40$$

(c) Adding 1.00 L of 0.100 M HCl to 1.00 L of buffer of course dilutes the concentrations of all components by a factor of 2. Thus, $[Na^+]$ = 0.125 M; total acetate concentration = 0.0750 M; total formate concentration = 0.125 M. Also, a new ion is added to the solution, namely, $[Cl^-]$ = 0.0500 M.

$$[Na^+] = 0.125 \quad [OH^-] \approx 0 \quad [H_3O^+] = x \quad [Cl^-] = 0.0500\text{ M} \quad [C_2H_3O_2^-] = y \quad [CHO_2^-] = z$$

$$0.0750 = [HC_2H_3O_2] + [C_2H_3O_2^-] \qquad [HC_2H_3O_2] = 0.0750 - [C_2H_3O_2^-] = 0.0750 - y$$

$$0.125 = [HCHO_2] + [CHO_2^-] \qquad [HCHO_2] = 0.125 - [CHO_2^-] = 0.125 - z$$

$$[Na^+] + [H_3O^+] = [C_2H_3O_2^-] + [OH^-] + [CHO_2^-] + [Cl^-] \text{ (electroneutrality)}$$

$$0.125 + x = [C_2H_3O_2^-] + [CHO_2^-] + [Cl^-] = y + z + 0 + 0.0500 \quad 0.075 + x = y + z$$

$$\frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = K_A = 1.8\times10^{-5} = \frac{x \cdot y}{0.0750 - y}$$

$$\frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = K_F = 1.8\times10^{-4} = \frac{x \cdot z}{0.125 - z}$$

Again, we solve the last two equations for *y* and *z* in terms of *x*.

$$0.0750\,K_A - y\,K_A = xy \qquad y = \frac{0.0750\,K_A}{K_A + x}$$

$$0.125\,K_F - z\,K_F = xz \qquad z = \frac{0.125\,K_F}{K_F + x}$$

Then we substitute these expressions into equation (1) and solve for *x*.

$$0.0750 + \mathrm{x} = \frac{0.0750\ \mathrm{K_A}}{\mathrm{K_A + x}} + \frac{0.125\ \mathrm{K_F}}{\mathrm{K_F + x}} \approx 0.0750 \qquad \text{since x} \ll 0.0750$$

$$0.0750\ (\mathrm{K_F + x})\ (\mathrm{K_A + x}) = 0.0750\ \mathrm{K_A}\ (\mathrm{K_F + x}) + 0.125\ \mathrm{K_F}\ (\mathrm{K_A + x})$$

$$\mathrm{K_AK_F} + (\mathrm{K_A} + \mathrm{K_F})\mathrm{x} + \mathrm{x}^2 = 2.67\ \mathrm{K_AK_F} + \mathrm{x}(1.67\ \mathrm{K_F} + 1.00\ \mathrm{K_A})$$

$$\mathrm{x}^2 - 0.67\ \mathrm{K_F x} - 1.67\ \mathrm{K_AK_F} = 0 = \mathrm{x}^2 - 1.2\times10^{-4}\,\mathrm{x} - 5.4\times10^{-9}$$

$$\mathrm{x} = \frac{1.2\times10^{-4} \pm \sqrt{1.4\times10^{-8} + 2.2\times10^{-8}}}{2} = 1.55\times10^{-4}\ \mathrm{M} = [\mathrm{H_3O^+}]$$

$$\mathrm{pH} = 3.81 \approx 3.8$$

As expected, the addition of HCl(aq), a strong acid, caused the pH to drop. The decrease in pH was relatively small, nonetheless, because the H_3O^+(aq) was converted to the much weaker acid $HCHO_2$ via the neutralization reaction:

CHO_2^-(aq) + H_3O^+(aq) → $HCHO_2$(aq) + H_2O(l) (buffering action)

<u>82.</u> **(M)** First we find the pH at the equivalence point:

$$\mathrm{CH_3CH(OH)COOH(aq)} + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{CH_3CH(OH)COO^-(aq)} + \mathrm{H_2O(l)}$$

1 mmol 1 mmol 1 mmol

The concentration of the salt is 1×10^{-3}mol/0.1 L = 0.01 M

The lactate anion undergoes hydrolysis thus:

	$\mathrm{CH_3CH(OH)COO^-}(aq)$	$+\,\mathrm{H_2O(l)}$	$\rightleftharpoons \mathrm{CH_3CH(OH)COOH(aq)}$	$+\ \mathrm{OH^-}(aq)$
Initial	0.01 M	–	0 M	≈ 0 M
Change	$-x$	–	$+x$	$+x$
Equilibrium	$(0.01-x)$ M	–	x	x

Where *x* is the [hydrolyzed lactate ion], as well as that of the [OH^-] produced by hydrolysis

$$\text{K for the above reaction} = \frac{[\mathrm{CH_3CH(OH)COOH}][\mathrm{OH^-}]}{[\mathrm{CH_3CH(OH)COO^-}]} = \frac{\mathrm{K_w}}{\mathrm{K_a}} = \frac{1.0\times10^{-14}}{10^{-3.86}} = 7.2\times10^{-11}$$

$$\text{so} \quad \frac{x^2}{0.01-x} \approx \frac{x^2}{0.01} = 7.2\times10^{-11} \text{and } x = [\mathrm{OH^-}] = 8.49\times10^{-7}\,\mathrm{M}$$

$x \ll 0.01$, thus, the assumption is valid

$$pOH = -\log\ (8.49\times10^{-7}M) = 6.07 \quad pH = 14 - pOH = 14.00 - 6.07 = 7.93$$

(a) Bromthymol blue or phenol red would be good indicators for this titration since they change color over this pH range.

(b) The $H_2PO_4^-/HPO_4^{2-}$ system would be suitable because the pK_a for the acid (namely, $H_2PO_4^-$) is close to the equivalence point pH of 7.93. An acetate buffer would be too acidic, an ammonia buffer too basic.

(c) $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \quad K_{a2} = 6.3\times10^{-8}$

Solving for $\dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \dfrac{K_{a2}}{[H_3O^+]} = \dfrac{6.3\times10^{-8}}{10^{-7.93}} = 5.4$ (buffer ratio required)

<u>83.</u> (M)

$$H_2O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HO_2^-(aq) \quad K_a = \frac{[H_3O^+][HO_2^-]}{[H_2O_2]}$$

Data taken from experiments 1 and 2:

$[H_2O_2]+[HO_2^-] = 0.259\text{ M} \qquad (6.78)\times(0.00357\text{ M})+[HO_2^-] = 0.259\text{ M}$

$[HO_2^-] = 0.235\text{ M} \qquad [H_2O_2] = (6.78)(0.00357\text{ M}) = 0.0242\text{ M}$

$[H_3O^+] = 10^{-(pKw-pOH)}$

$-\log\left(0.250 - 0.235)\text{ M NaOH}\right) = -\log(0.015\text{ M NaOH}) = 1.82\underline{4}$

$[H_3O^+] = 10^{-(14.94-1.82\underline{4})} = 7.7\times10^{-14}$

$$K_a = \frac{[H_3O^+][HO_2^-]}{[H_2O_2]} = \frac{(7.7\times10^{-14}\text{ M})(0.235\text{ M})}{(0.0242\text{ M})} = 7.4\times10^{-13}$$

$pK_a = 12.14$

From data taken from experiments 1 and 3:

$[H_2O_2]+[HO_2^-] = 0.123\text{ M} \qquad (6.78)(0.00198\text{ M})+[HO_2^-] = 0.123\text{ M}$

$[HO_2^-] = 0.109\underline{6}\text{ M}$

$[H_2O_2] = (6.78)(0.00198\text{ M}) = 0.0134\text{ M}$

$[H_3O^+] = 10^{-(pKw-pOH)}$, pOH = $-\log[(0.125 - 0.109\underline{6})\text{ M NaOH}] = 1.81$

$[H_3O^+] = 10^{-(14.94-1.81)} = 7.41\times10^{-14}$

$$K_a = \frac{[H_3O^+][HO_2^-]}{[H_2O_2]} = \frac{(7.41\times10^{-14}\text{ M})(0.1096\text{ M})}{(0.0134\text{ M})} = 6.06\times10^{-13}$$

$pK_a = -\log(6.06\times10^{-13}) = 12.22$

Average value for $pK_a = 12.17$

84. **(D)** Let's consider some of the important processes occurring in the solution.

$$\text{(1) } HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq) \qquad K_{(1)} = K_{a2} = 4.2\times10^{-13}$$

$$\text{(2) } HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{(2)} = K_b = \frac{1.0\times10^{-14}}{6.3\times10^{-8}} = 1.6\times10^{-7}$$

$$\text{(3) } NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_{(3)} = K_a = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

$$\text{(4) } NH_4^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + NH_3(aq) \qquad K_{(4)} = \frac{1}{1.8\times10^{-5}} = 5.6\times10^4$$

May have interaction between NH_4^+ and OH^- formed from the hydrolysis of HPO_4^{2-}.

	$NH_4^+(aq)$	$+$	$HPO_4^{2-}(aq)$	$\rightleftharpoons$	$H_2PO_4^-(aq)$	$+$	$NH_3(aq)$
Initial	0.10M		0.10M		0 M		0 M
Change	$-x$		$-x$		$+x$		$+x$
Equil.	$0.100-x$		$0.100-x$		x		x

(where x is the molar concentration of NH_4^+ that hydrolyzes)

$$K = K_{(2)}\times K_{(4)} = (1.6\times10^{-7})\times(5.6\times10^4) = 9.0\times10^{-3}$$

$$K = \frac{[H_2PO_4^-]\,[NH_3]}{[NH_4^+]\,[HPO_4^{2-}]} = \frac{[x]^2}{[0.10\text{-}x]^2} = 9.0\times10^{-3} \text{ and } x = 8.7\times10^{-3}\text{M}$$

Finding the pH of this buffer system:

$$pH = pK_a + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = -\log(6.3\times10^{-8}) + \log\left(\frac{0.100\text{-}8.7\times10^{-3}\text{M}}{8.7\times10^{-3}\text{M}}\right) = 8.2$$

As expected, we get the same result using the NH_3/NH_4^+ buffer system.

85. Consider the two weak acids and the equilibrium for water (autodissociation)

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad K_{HA} = \frac{[H_3O^+][A^-]}{[HA]} \qquad [HA] = \frac{[H_3O^+][A^-]}{K_{HA}}$$

$$HB(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B^-(aq) \quad K_{HB} = \frac{[H_3O^+][B^-]}{[HB]} \qquad [HB] = \frac{[H_3O^+][B^-]}{K_{HB}}$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad K_w = [H_3O^+][OH^-] \qquad [OH^-] = \frac{K_w}{[H_3O^+]}$$

Mass Balance: $[HA]_{initial}=[HA]+[A^-] \; = \dfrac{[H_3O^+][A^-]}{K_{HA}}+[A^-] = [A^-]\left(\dfrac{[H_3O^+]}{K_{HA}}+1\right)$

From which: $[A^-] = \dfrac{[HA]_{initial}}{\left(\dfrac{[H_3O^+]}{K_{HA}}+1\right)}$

$[HB]_{initial} = [HB] + [B^-] = \dfrac{[H_3O^+][B^-]}{K_{HB}} + [B^-] = [B^-]\left(\dfrac{[H_3O^+]}{K_{HB}}+1\right)$

From which: $[B^-] = \dfrac{[HB]_{initial}}{\left(\dfrac{[H_3O^+]}{K_{HB}}+1\right)}$

Charge Balance: $[H_3O^+] = [A^-] + [B^-] + [OH^-]$ (substitute above expressions)

$$[H_3O^+] = \frac{[HA]_{initial}}{\left(\frac{[H_3O^+]}{K_{HA}}+1\right)} + \frac{[HB]_{initial}}{\left(\frac{[H_3O^+]}{K_{HB}}+1\right)} + \frac{K_w}{[H_3O^+]}$$

86. **(D)** We are told that the solution is 0.050 M in acetic acid (Ka = 1.8 ×10-5) and 0.010 M in phenyl acetic acid (Ka = 4.9 ×10-5). Because the Ka values are close, both equilibria must be satisfied simultaneously. Note: [H3O+] is common to both equilibria (assume z is the concentration of [H3O+]).

Reaction:	HC2H3O2(aq)	+	H2O(l)	$\rightleftharpoons$	C2H3O2-(aq)	+	H3O+(aq)
Initial:	0.050 M		—		0 M		≈ 0 M
Change:	-x M		—		+ x M		+ z M
Equilibrium	(0.050 – x)M		—		x M		z M

For acetic acid: $K_a \; = \dfrac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \dfrac{xz}{(0.050-x)} = 1.8\times10^{-5}$ or $x = \dfrac{1.8\times10^{-5}(0.050-x)}{z}$

Reaction:	HC8H7O2(aq)	+	H2O(l)	$\rightleftharpoons$	C8H7O2-(aq)	+	H3O+(aq)
Initial:	0.010 M		—		0 M		≈ 0 M
Change:	-y M		—		+ y M		+ z M
Equilibrium	(0.010 – y)M		—		y M		z M

For phenylacetic acid: $K_a \; = \dfrac{[H_3O^+][C_8H_7O_2^-]}{[HC_8H_7O_2]} = \dfrac{yz}{(0.010-y)} = 4.9\times10^{-5}$

or $y = \dfrac{4.9\times10^{-5}(0.010-y)}{z}$

There are now three variables: x = [C2H3O2-], y = [C8H7O2-], and z = [H3O+]
These are the only charged species, hence, x + y = z.
(This equation neglects contribution from the [H3O+] from water.)
Next we substitute in the values of x and y from the rearranged Ka expressions above.

$$x + y = z = \frac{1.8\times10^{-5}(0.050-x)}{z} + \frac{4.9\times10^{-5}(0.010-y)}{z}$$

Since these are weak acids, we can simplify this expression by assuming that x << 0.050 and y << 0.010.

$$z = \frac{1.8\times10^{-5}(0.050)}{z} + \frac{4.9\times10^{-5}(0.010)}{z}$$ Simplify even further by multiplying through by z.

z2 = 9.0×10-7 + 4.9×10-7 = 1.4 ×10-6

z = 1.18×10-3 = [H3O+] From which we find that x = 7.6 × 10-4 and y = 4.2×10-4
(as a quick check, we do see that x + y = z).

We finish up by checking to see if the approximation is valid (5% rule)..

$$\text{For } x: \frac{7.6\times10^{-4}}{0.050}\times100\% = 1.5\% \qquad \text{For } y: \frac{4.2\times10^{-4}}{0.010}\times100\% = 4.2\%$$

Since both are less than 5%, we can be assured that the assumption is valid.
The pH of the solution = -log(1.18×10-3) = 2.93.
(If we simply plug the appropriate values into the equation developed in the previous question we get the exact answer 2.933715 (via the method of successive approximations), but the final answers can only be reported to 2 significant figures. Hence the best we can do is say that the pH is expected to be 2.93 (which is the same level of precision as that for the result obtained following the 5% rule).

87. (D)

(a) By using dilution, there are an infinite number of ways of preparing the pH = 7.79 buffer. We will consider a method that does not use dilution.

Let TRIS = weak base and $TRISH^+$ be the conjugate acid.

pKb = 5.91, pKa = 14 – pKb = 8.09 Use the Henderson Hasselbalch equation.

$pH = pKa + \log(TRIS/TRISH^+) = 7.79 = 8.09 + \log(TRIS/TRISH^+)$

$\log(TRIS/TRISH^+) = 7.79 - 8.09 = -0.30$ Take antilog of both sides

$(TRIS/TRISH^+)$ = 10-0.30 = 0.50; Therefore, $nTRIS = 0.50(nTRISH^+)$

Since there is no guidance given on the capacity of the buffer, we will choose an arbitrary starting point. We start with 1.00 L of 0.200 M TRIS (0.200 moles). We need to convert 2/3 of this to the corresponding acid (TRISH$^+$) using 10.0 M HCl, in order for the TRIS/TRISH$^+$ ratio to be 0.5. In all, we need (2/3)×0.200 mol of HCl, or a total of 0.133 moles of HCl.

Volume of HCl required = 0.133 mol ÷ 10.0 mol/L = 0.0133 L or 13.3 mL.

This would give a total volume of 1013.3 mL, which is almost a liter (within 1.3%).
If we wish to make up exactly one liter, we should only use 987 mL of 0.200 M TRIS.
This would require 13.2 mL of HCl, resulting in a final volume of 1.0002 L.

Let's do a quick double check of our calculations.
*n*HCl = 0.0132 L×10.0 M = 0.132 mol = nTRISH$^+$
*n*TRIS = ninitial – nreacted = 0.200 M×0.987 L – 0.132 mol = 0.0654 mol
pH = pKa + log (TRIS/TRISH$^+$) = 8.09+ log (0.0654 mol/0.132 mol) = 7.785

We have prepared the desired buffer (realize that this is just one way of preparing the buffer).

(b) To 500 mL of the buffer prepared above, is added 0.030 mol H_3O^+.
In the 500 mL of solution we have 0.132 mol ÷ 2 mol TRISH$^+$ = 0.0660 mol TRISH$^+$ and 0.0654 mol ÷ 2 mol TRIS = 0.032$\underline{7}$ mol TRIS (we will assume no change in volume).

HCl will completely react (≈ 100%) with TRIS, converting it to TRISH$^+$.
After complete reaction, there will be no excess HCl, 0.0327 mol – 0.0300 mol = 0.0027 mol TRIS and 0.0660 mol + 0.0300 mol = 0.0960 mol TRISH$^+$.

By employing the Henderson Hasselbalch equation, we can estimate the pH of the resulting solution:

pH = pK_a + log (TRIS/TRISH$^+$) = 8.09 + log (0.0027 mol/0.0960 mol) = 6.54

This represents a pH change of 1.25 units. The buffer is nearly exhausted owing to the fact that almost all of the TRIS has been converted to TRISH$^+$. Generally, a pH change of 1 unit suggests that the capacity of the buffer has been pretty much completely expended. This is the case here.

(Alternatively, you may solve this question using an I.C.E. table).

(c) Addition of 20.0 mL of 10.0 M HCl will complete exhaust the buffer (in part (b) we saw that addition of 3 mL of HCl used up most of the TRIS in solution). The buffer may be regenerated by adding 20.0 mL of 10.0 M NaOH. The buffer will be only slightly diluted after the addition of HCl and NaOH (500 mL → 540 mL). Through the slow and careful addition of NaOH, one can regenerate the pH = 7.79 buffer in this way (if a pH meter is used to monitor the addition).

88. **(M)**

(a) The formula given needs to be rearranged to isolate α, as shown below.

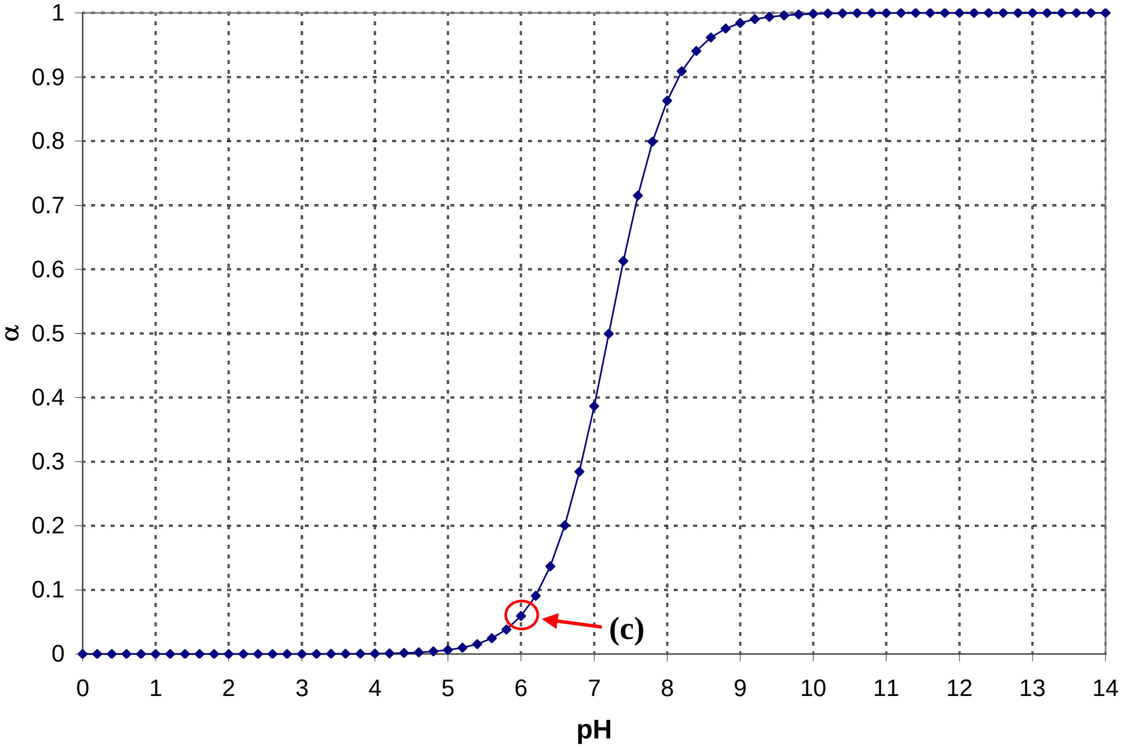
$$\mathrm{pH} = \mathrm{pK_a} - \log\left(\frac{1}{\alpha} - 1\right)$$

$$\mathrm{pH} - \mathrm{pKa} = -\log\left(\frac{\left[\mathrm{H_3O^+}\right]}{\mathrm{K_a}}\right) = -\log\left(\frac{1}{\alpha} - 1\right)$$

$$\frac{\left[\mathrm{H_3O^+}\right]}{\mathrm{K_a}} = \frac{1}{\alpha} - 1$$

$$\alpha = \frac{\mathrm{K_a}}{\left[\mathrm{H_3O^+}\right] + \mathrm{K_a}} = \frac{\mathrm{K_a}}{10^{-\mathrm{pH}} + \mathrm{K_a}}$$

Now, use the given K_a (6.3×10^{-8}) and calculate α for a range of pH values.



(b) When pH = pK_a, α = 0.5 or 50%.

(c) At a pH of 6.0, $\alpha = \frac{\mathrm{K_a}}{10^{-\mathrm{pH}} + \mathrm{K_a}} = \frac{6.3\times10^{-8}}{10^{-6.0} + 6.3\times10^{-8}} = 0.059$ or 5.9%.

89. **(D)**
(a) We start by writing the equilibrium expression for all reactions:

$$K_1 = \frac{\left[CO_2(aq)\right]}{\left[CO_2(g)\right]} \qquad K_2 = \left[Ca^{2+}\right]\left[CO_3^{2-}\right]$$

$$K_3 = \frac{\left[HCO_3^-\right]}{\left[H_3O^+\right]\left[CO_3^{2-}\right]} \qquad K_4 = \frac{\left[CO_2(aq)\right]}{\left[HCO_3^-\right]\left[H_3O^+\right]}$$

First, we have to express [H_3O^+] using the available expressions:

$$\left[H_3O^+\right] = \frac{\left[HCO_3^-\right]}{K_3\left[CO_3^{2-}\right]}$$

$$\left[H_3O^+\right] = \frac{\left[CO_2(aq)\right]}{K_4\left[HCO_3^-\right]}$$

$$\left[H_3O^+\right]^2 = \frac{\left[HCO_3^-\right]}{K_3\left[CO_3^{2-}\right]} \times \frac{\left[CO_2(aq)\right]}{K_4\left[HCO_3^-\right]} = \frac{\left[CO_2(aq)\right]}{K_3 \cdot K_4\left[CO_3^{2-}\right]}$$

From the expression for K_1, we know that [CO_2(aq)] = K_1[CO_2(g)]. Therefore,

$$\left[H_3O^+\right]^2 = \frac{K_1\left[CO_2(g)\right]}{K_3 \cdot K_4\left[CO_3^{2-}\right]}$$

Now, the expression for K_2 can be plugged into the above expression as follows:

$$\left[H_3O^+\right]^2 = \frac{K_1\left[CO_2(g)\right]}{K_3 \cdot K_4\left[CO_3^{2-}\right]} = \frac{K_1\left[CO_2(g)\right]\left[Ca^{2+}\right]}{K_2 \cdot K_3 \cdot K_4}$$

$$\left[H_3O^+\right] = \sqrt{\frac{K_1\left[CO_2(g)\right]\left[Ca^{2+}\right]}{K_2 \cdot K_3 \cdot K_4}}$$

(b) The K values for the reactions are as follows:
$K_1 = 0.8317$ (given in the problem)
$K_2 = K_{sp}$ ($CaCO_3$) = 2.8×10^{-9}
K_3 = 1/Ka of HCO_3^- = $1/(4.7\times10^{-11}) = 2.13\times10^{10}$
K_4 = 1/Ka of H_2CO_3 = $1/(4.4\times10^{-7}) = 2.27\times10^{6}$

$$\left[CO_2(g)\right] = \frac{280\times10^{-6}\text{ L }CO_2}{\text{L air}} \times \frac{1\text{ mol }CO_2}{24.45\text{ L }CO_2} = 1.145\times10^{-5}\ \frac{\text{mol }CO_2}{\text{L air}}$$

$$\left[H_3O^+\right]=\sqrt{\frac{K_1\left[CO_2(g)\right]\left[Ca^{2+}\right]}{K_2\cdot K_3\cdot K_4}}=\sqrt{\frac{(0.8317)(1.145\times10^{-5})(10.24\times10^{-3})}{(2.8\times10^{-9})(2.13\times10^{10})(2.27\times10^{6})}}$$

$$=2.684\times10^{-8}\text{ M}$$

$$\text{pH}=-\log\left(2.684\times10^{-8}\right)=7.57$$

90. **(M)** To determine pH, we must first determine what is the final charge balance of the solution *without* adding any H_3O^+ or OH^- ions. As such, we have to calculate the number of moles of each ion (assume 1 L):

Moles of Na^+: 23.0 g Na^+ × (1 mol/23.0 g) = 1.00 mol Na^+
Moles of Ca^{2+}: 10.0 g Ca^{2+} × (1 mol/40.0 g) = 0.250 mol Ca^{2+}
Moles of CO_3^{2-}: 40.02 g CO_3^{2-} × (1 mol/60.01 g) = 0.670 mol CO_3^{2-}
Moles of SO_4^{2-}: 9.6 g SO_4^{2-} × (1 mol/96.056 g) = 0.100 mol

Looking at the list of ions and consulting the solubility guide, we note that Ca^{2+} will precipitate with both SO_4^{2-} and CO_3^{2-}. Since both of these anions have a 2– charge, it doesn't matter with which anion the precipitation occurs (in reality, it does a little, but the effects are small compared to the effects of adding H_3O^+ or OH^- ions).

Moles of anions left = (0.670 + 0.100) – 0.250 = 0.520 moles

Since we have 0.520 moles of 2– ions, we must have 1.04 moles of 1+ ions to balance. However, we only have 1 mole of Na^+. The difference in charge is:
1.04(-) – 1.0(+) = 0.04(-) moles of ions

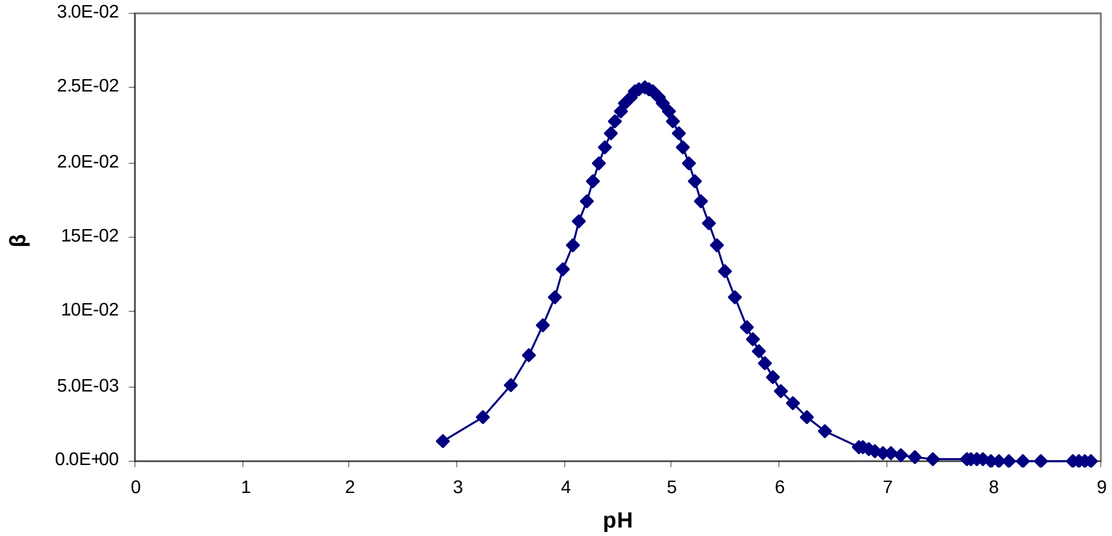
To balance, we need 0.04 moles of H_3O^+. The pH = –log (0.04) = 1.40.

<u>91.</u> **(M)**
(a) We note that the pH is 5.0. Therefore, $\left[H_3O^+\right]=10^{-5.0}=1.0\times10^{-5}\text{ M}$

$$\beta=\frac{C\cdot K_a\cdot\left[H_3O^+\right]}{\left(K_a+\left[H_3O^+\right]\right)^2}=\frac{(2.0\times10^{-2})(1.8\times10^{-5})(1.0\times10^{-5})}{(1.8\times10^{-5}+1.0\times10^{-5})^2}=4.6\times10^{-3}$$

(b)
$$\beta\approx-dC_A/d(\text{pH})\Rightarrow d(\text{pH})\approx-dC_A/\beta$$
$$d(\text{pH})=-(1.0\times10^{-3})/4.6\times10^{-3}=-0.22$$
$$\text{pH}=5-0.22=4.78$$

(c) At an acetic acid concentration of 0.1 M, C is also 0.1, because C is the total concentration of the acetic acid and acetate. The maximum buffer index β (2.50×10^{-2}) happens at a pH of 4.75, where [HAc] = [Ac$^-$]. The minima are located at pH values of 8.87 (which correspond to pH of a solution of 0.1 M acetic acid and 0.1 M acetate, respectively).



FEATURE PROBLEMS

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92. **(D)**

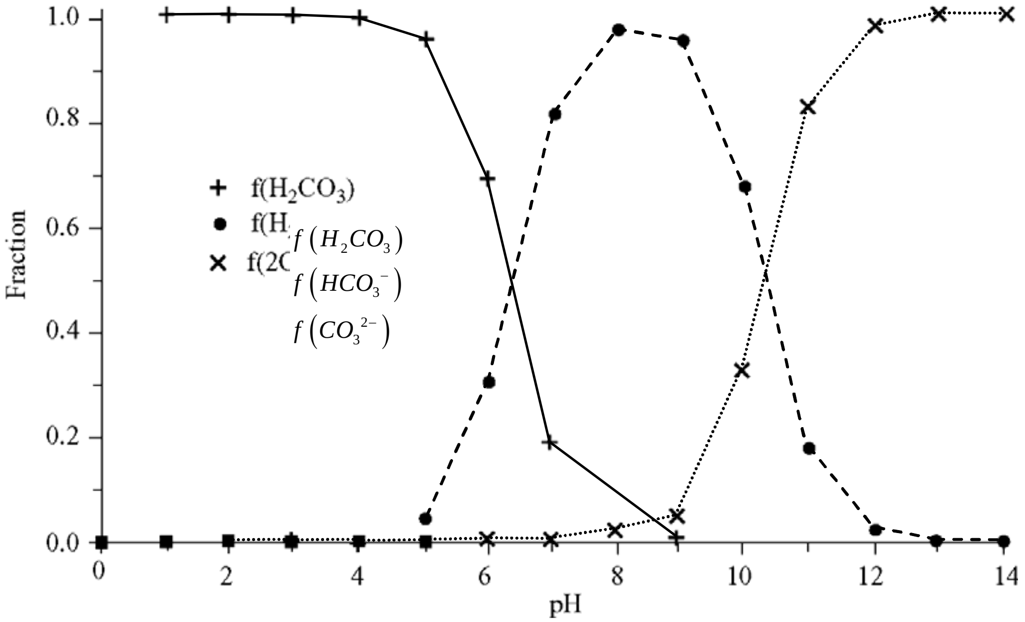
(a) The two curves cross the point at which half of the total acetate is present as acetic acid and half is present as acetate ion. This is the half equivalence point in a titration, where $\text{pH} = \text{p}K_\text{a} = 4.74$.

(b) For carbonic acid, there are three carbonate containing species: "H_2CO_3" which predominates at low pH, HCO_3^-, and CO_3^{2-}, which predominates in alkaline solution. The points of intersection should occur at the half-equivalence points in each step-wise titration: at $\text{pH} = \text{p}K_{\text{a}_1} = -\log\left(4.4 \times 10^{-7}\right) = 6.36$ and at $\text{pH} = \text{p}K_{\text{a}_2} = -\log\left(4.7 \times 10^{-11}\right) = 10.33$. The following graph was computer-calculated (and then drawn) from these equations. f in each instance represents the fraction of the species whose formula is in parentheses.

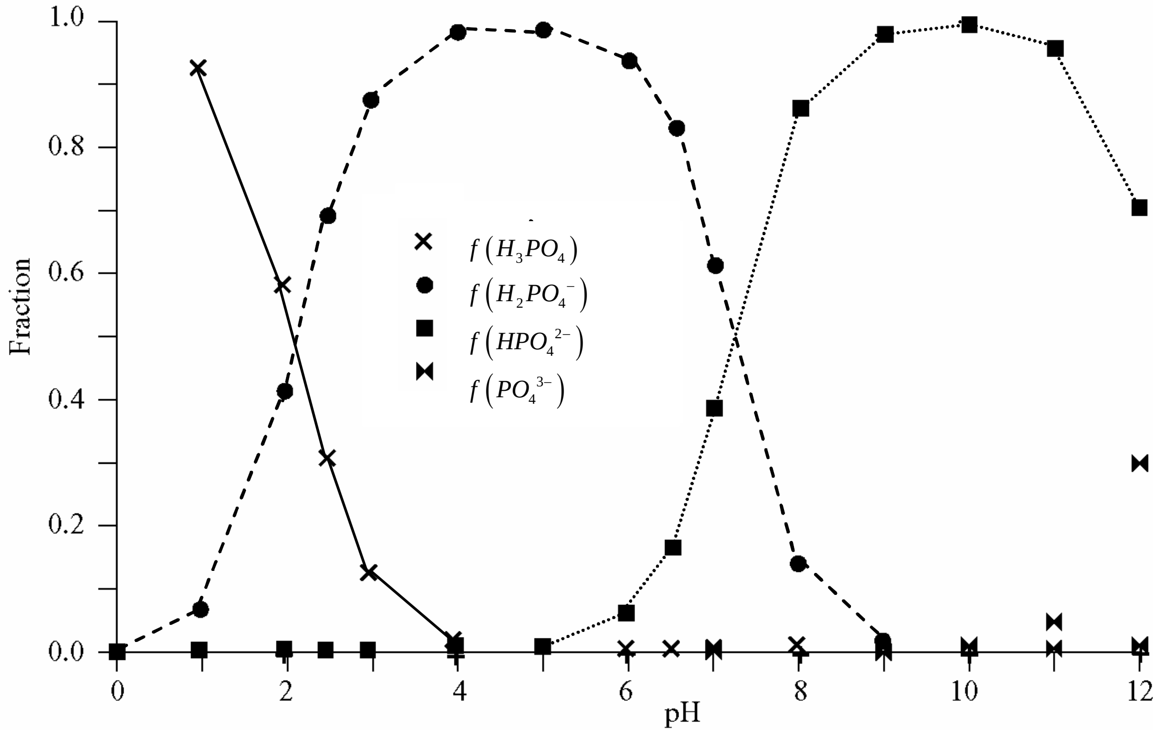
$$\frac{1}{f\left(\text{H}_2\text{A}\right)} = 1 + \frac{K_1}{\left[\text{H}^+\right]} + \frac{K_1 K_2}{\left[\text{H}^+\right]^2}$$

$$\frac{1}{f\left(\text{HA}^-\right)} = \frac{\left[\text{H}^+\right]}{K_1} + 1 + \frac{K_2}{\left[\text{H}^+\right]}$$

$$\frac{1}{f\left(\text{A}^{2-}\right)} = \frac{\left[\text{H}^+\right]^2}{K_1\ K_2} + \frac{\left[\text{H}^+\right]}{K_2} + 1$$

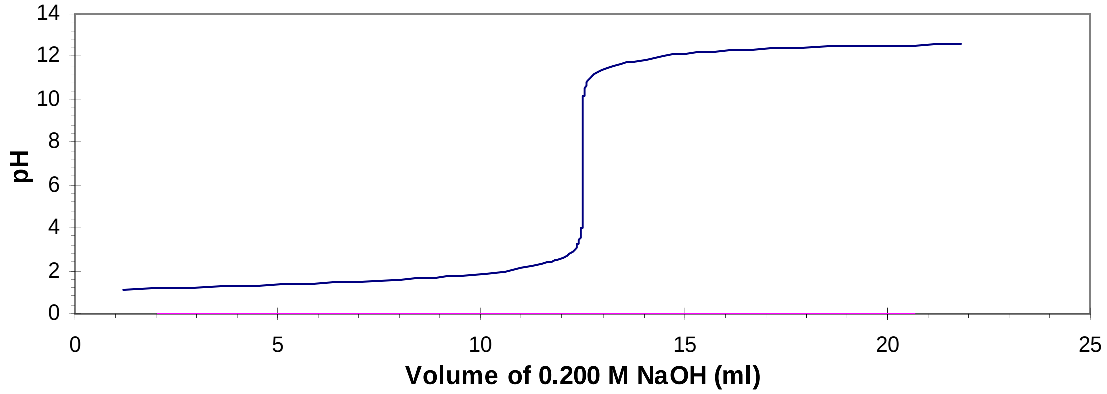


(c) For phosphoric acid, there are four phosphate containing species: H_3PO_4 under acidic conditions, $H_2PO_4^{-}$, HPO_4^{2-}, and PO_4^{3-}, which predominates in alkaline solution. The points of intersection should occur at $pH = pK_{a_1} = -\log(7.1\times10^{-3}) = 2.15$, $pH = pK_{a_2} = -\log(6.3\times10^{-8}) = 7.20$, and $pH = pK_{a_3} = -\log(4.2\times10^{-13}) = 12.38$, a quite alkaline solution. The graph that follows was computer-calculated and drawn.



93. (D)

(a) This is exactly the same titration curve we would obtain for the titration of 25.00 mL of 0.200 M HCl with 0.200 M NaOH, because the acid species being titrated is H_3O^+. Both acids are strong acids and have ionized completely before titration begins. The initial pH is that of 0.200 M H_3O^+ = [HCl] + [HNO_3]; $pH = -\log(0.200) = 0.70$. At the equivalence point, $pH = 7.000$. We treat this problem as we would for the titration of a single strong acid with a strong base.



(b) In Figure 17-9, we note that the equivalence point of the titration of a strong acid occurs at $pH = 7.00$, but that the strong acid is essentially completely neutralized at pH = 4. In Figure 17-13, we see that the first equivalence point of H_3PO_4 occurs at about pH = 4.6. Thus, the first equivalence point represents the complete neutralization of HCl and the neutralization of H_3PO_4 to $H_2PO_4^-$. Then, the second equivalence point represents the neutralization of $H_2PO_4^-$ to HPO_4^{2-}. To reach the first equivalence point requires about 20.0 mL of 0.216 M NaOH, while to reach the second one requires a total of 30.0 mL of 0.216 M NaOH, or an additional 10.0 mL of base beyond the first equivalence point. The equations for the two titration reactions are as follows.

To the first equivalence point: $NaOH + H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

To the second equivalence point: $NaOH + NaH_2PO_4 \longrightarrow Na_2HPO_4 + H_2O$

There is a third equivalence point, not shown in the figure, which would require an additional 10.0 mL of base to reach. Its titration reaction is represented by the following equation.

To the third equivalence point: $NaOH + Na_2HPO_4 \longrightarrow Na_3PO_4 + H_2O$

We determine the molar concentration of H_3PO_4 and then of HCl. Notice that only 10.0 mL of the NaOH needed to reach the first equivalence point reacts with the HCl(aq); the rest reacts with H_3PO_4.

$$\frac{(30.0-20.0)\ \text{mL NaOH(aq)}\times\frac{0.216\ \text{mmol NaOH}}{1\ \text{mL NaOH soln}}\times\frac{1\ \text{mmol}\ H_3PO_4}{1\ \text{mmol NaOH}}}{10.00\ \text{mL acid soln}}=0.216\ \text{M}\ H_3PO_4$$

$$\frac{(20.0-10.0)\ \text{mL NaOH(aq)}\times\frac{0.216\ \text{mmol NaOH}}{1\ \text{mL NaOH soln}}\times\frac{1\ \text{mmol HCl}}{1\ \text{mmol NaOH}}}{10.00\ \text{mL acid soln}}=0.216\ \text{M HCl}$$

(c) We start with a phosphoric acid-dihydrogen phosphate buffer solution and titrate until all of the H_3PO_4 is consumed. We begin with

$$10.00\ \text{mL}\times\frac{0.0400\ \text{mmol}\ H_3PO_4}{1\ \text{mL}}=0.400\ \text{mmol}\ H_3PO_4$$

and the diprotic anion,

$$10.00\ \text{mL}\times\frac{0.0150\ \text{mmol}\ H_2PO_4^{-}}{1\ \text{mL}}=0.150\ \text{mmol}\ H_2PO_4^{2-}$$

. The volume of 0.0200 M

NaOH needed is: $0.400\ \text{mmol}\ H_3PO_4\times\frac{1\ \text{mmol NaOH}}{1\ \text{mmol}\ H_3PO_4}\times\frac{1\ \text{mL NaOH}}{0.0200\ \text{mmol NaOH}}=20.00\ \text{mL}$

To reach the first equivalence point. The pH value of points during this titration are computed with the Henderson-Hasselbalch equation.

$$\text{Initially: pH}=\text{p}K_1+\log\frac{[H_2PO_4^{-}]}{[H_3PO_4]}=-\log\left(7.1\times10^{-3}\right)+\log\frac{0.0150}{0.0400}=2.15-0.43=1.72$$

$$\text{At 5.00 mL: pH}=2.15+\log\frac{0.150+0.100}{0.400-0.100}=2.15-0.08=2.07$$

$$\text{At 10.0 mL, pH}=2.15+\log\frac{0.150+0.200}{0.400-0.200}=2.15+0.24=2.39$$

$$\text{At 15.0 mL, pH}=2.15+\log\frac{0.150+0.300}{0.400-0.300}=2.15+0.65=2.80$$

This is the first equivalence point, a solution of 30.00 mL (= 10.00 mL originally + 20.00 mL titrant), containing 0.400 mmol $H_2PO_4^{-}$ from the titration and the 0.150 mmol $H_2PO_4^{2-}$ originally present.
This is a solution with

$$\left[H_2PO_4^-\right] = \frac{(0.400+0.150)\ \text{mmol}\ H_2PO_4^-}{30.00\ \text{mL}} = 0.0183\ \text{M}$$, which has

$$\text{pH} = \frac{1}{2}\left(\text{p}K_1 + \text{p}K_2\right) = 0.50\left(2.15 - \log\left(6.3\times10^{-8}\right)\right) = 0.50\left(2.15+7.20\right) = 4.68$$

To reach the second equivalence point means titrating 0.550 mmol $H_2PO_4^-$, which requires an additional volume of titrant given by

$$0.550\ \text{mmol}\ H_2PO_4^- \times \frac{1\ \text{mmol NaOH}}{1\ \text{mmol}\ H_2PO_4^-} \times \frac{1\ \text{mL NaOH}}{0.0200\ \text{mmol NaOH}} = 27.5\ \text{mL}.$$

To determine pH during this titration, we divide the region into five equal portions of 5.5 mL and use the Henderson-Hasselbalch equation.

At $(20.0+5.5)$ mL,

$$\text{pH} = \text{p}K_2 + \log\frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 7.20 + \log\frac{(0.20\times0.550)\ \text{mmol}\ HPO_4^{2-}\ \text{formed}}{(0.80\times0.550)\ \text{mmol}\ H_2PO_4^-\ \text{remaining}}$$

$$\text{pH} = 7.20 - 0.60 = 6.60$$

At $(20.0+11.0)\ \text{mL} = 31.0\ \text{mL}$, $\text{pH} = 7.20 + \log\frac{0.40\times0.550}{0.60\times0.550} = 7.02$

At 36.5 mL, pH = 7.38 At 42.0 mL, pH = 7.80

The pH at the second equivalence point is given by

$$\text{pH} = \frac{1}{2}\left(\text{p}K_2 + \text{p}K_3\right) = 0.50\left(7.20 - \log\left(4.2\times10^{-13}\right)\right) = 0.50\ \left(7.20+12.38\right) = 9.79.$$

Another 27.50 mL of 0.020 M NaOH would be required to reach the third equivalence point. pH values at each of four equally spaced volumes of 5.50 mL additional 0.0200 M NaOH are computed as before, assuming the Henderson-Hasselbalch equation is valid.

At $(47.50+5.50)\ \text{mL} = 53.00\ \text{mL}$, $\text{pH} = \text{p}K_3 + \log\frac{\left[PO_4^{3-}\right]}{\left[HPO_4^{2-}\right]} = 12.38 + \log\frac{0.20\times0.550}{0.80\times0.550}$

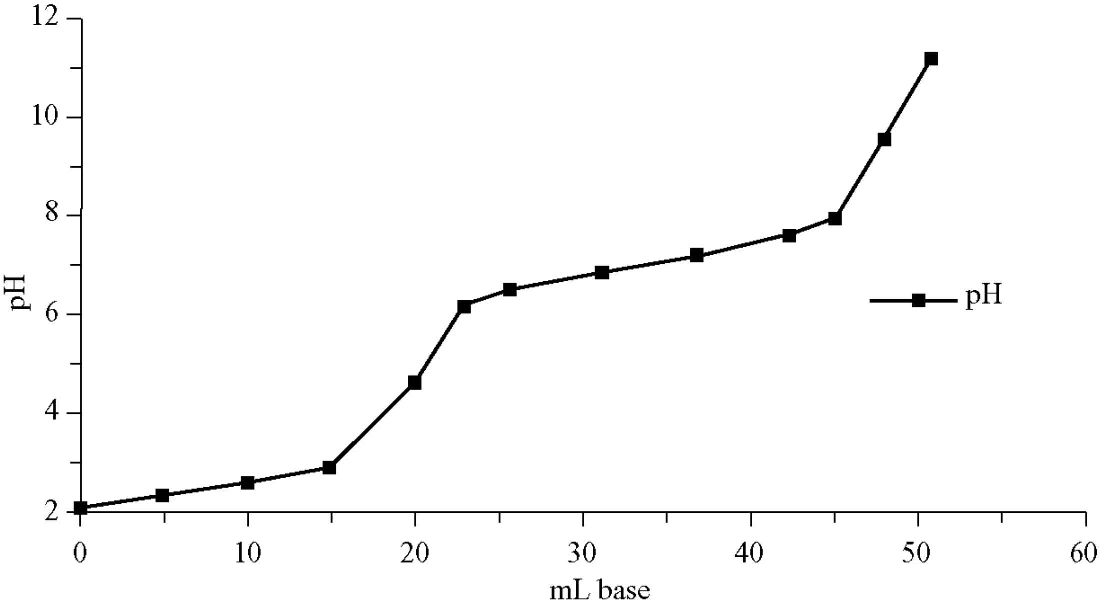
$$= 12.38 - 0.60 = 11.78$$

At $58.50\ \text{mL, pH} = 12.20$ At $64.50\ \text{mL, pH} = 12.56$ At $70.00\ \text{mL, pH} = 12.98$
But at infinite dilution with 0.0200 M NaOH, the pH = 12.30, so this point can't be reached.

At the last equivalence point, the solution will contain 0.550 mmol PO_4^{3-} in a total of $10.00 + 20.00 + 27.50 + 27.50\ \text{mL} = 85.00\ \text{mL}$ of solution, with

$\left[PO_4^{3-}\right] = \dfrac{0.550\ \text{mmol}}{85.00\ \text{mL}} = 0.00647\ \text{M}$. But we can never reach this point, because the

pH of the 0.0200 M NaOH titrant is 12.30. Moreover, the titrant is diluted by its addition to the solution. Thus, our titration will cease sometime shortly after the second equivalence point. We never will see the third equivalence point, largely because the titrant is too dilute. Our results are plotted below.



94. **(D)** $\mathrm{p}K_{a_1} = 2.34$; $K_{a_1} = 4.6 \times 10^{-3}$ and $\mathrm{p}K_{a_2} = 9.69$; $K_{a_2} = 2.0 \times 10^{-10}$

(a) Since the K_a values are so different, we can treat alanine (H_2A^+) as a monoprotic acid with $K_{a_1} = 4.6 \times 10^{-3}$. Hence:

	$H_2A^+(aq)$	+ $H_2O(l)$	$\rightleftharpoons$ $HA(aq)$	+ $H_3O^+(aq)$
Initial	0.500 M	—	0 M	≈ 0 M
Change	$-x$ M	—	$+x$ M	$+x$ M
Equilibrium	$(0.500 - x)$ M	—	x M	x M

$$K_{a_1} = \frac{[HA][H_3O^+]}{[H_2A^+]} = \frac{(x)(x)}{(0.500-x)} = 4.6 \times 10^{-3} \approx \frac{x^2}{0.500}$$

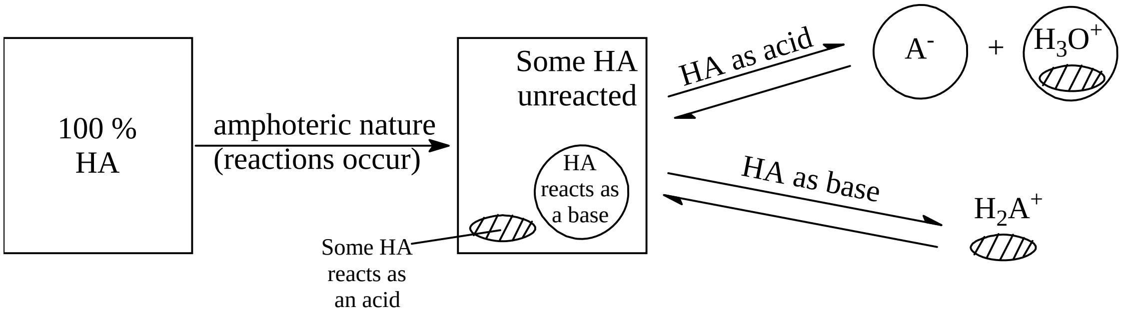
$x = 0.048$ M $= [H_3O^+]$ ($x = 0.0457$, solving the quadratic equation)

$\mathrm{pH} = -\log[H_3O^+] = -\log(0.046) = 1.34$

(b) At the first half-neutralization point a buffer made up of H_2A^+/HA is formed, where $[H_2A^+] = [HA]$. The Henderson-Hasselbalch equation gives $\mathrm{pH} = \mathrm{p}K_a = 2.34$.

(c) At the first equivalence point, all of the $H_2A^+(aq)$ is converted to HA(aq). HA(aq) is involved in both K_{a_1} and K_{a_2}, so both ionizations must be considered.

If we assume that the solution is converted to 100% HA, we must consider two reactions. HA may act as a weak acid ($HA \rightarrow A^- + H^+$) or HA may act as a base ($HA + H^+ \rightarrow H_2A^+$). See the following diagram.



Using the diagram above, we see that the following relations must hold true.
$[A^-] = [H_3O^+] + [H_2A^+]$

$$K_{a_2} = \frac{[A^-][H_3O^+]}{[HA]} \text{ or } [A^-] = \frac{K_{a_2}[HA]}{[H_3O^+]} \;\&\; K_{a_1} = \frac{[HA][H_3O^+]}{[H_2A^+]} \text{ or } [H_2A^+] = \frac{[H_3O^+][HA]}{K_{a_1}}$$

Substitute for $[A^-]$ and $[H_2A^+]$ in $[A^-] = [H_3O^+] + [H_2A^+]$

$$\frac{K_{a_2}[\mathrm{HA}]}{[\mathrm{H_3O^+}]} = [\mathrm{H_3O^+}] + \frac{[\mathrm{H_3O^+}][\mathrm{HA}]}{K_{a_1}} \text{ (multiply both sides by } K_{a_1}[\mathrm{H_3O^+}])$$

$$K_{a_1}K_{a_2}[\mathrm{HA}] = K_{a_1}[\mathrm{H_3O^+}][\mathrm{H_3O^+}] + [\mathrm{H_3O^+}][\mathrm{H_3O^+}][\mathrm{HA}]$$

$$K_{a_1}K_{a_2}[\mathrm{HA}] = [\mathrm{H_3O^+}]^2(K_{a_1} + [\mathrm{HA}])$$

$$[\mathrm{H_3O^+}]^2 = \frac{K_{a_1}K_{a_2}[\mathrm{HA}]}{(K_{a_1} + [\mathrm{HA}])} \quad \text{Usually, } [\mathrm{HA}] \gg K_{a_1} \text{ (Here, } 0.500 \gg 4.6 \times 10^{-3})$$

Make the assumption that $K_{a_1} + [\mathrm{HA}] \approx [\mathrm{HA}]$

$$[\mathrm{H_3O^+}]^2 = \frac{K_{a_1}K_{a_2}[\mathrm{HA}]}{[\mathrm{HA}]} = K_{a_1}K_{a_2} \qquad \text{Take } -\log \text{ of both sides}$$

$$-\log[\mathrm{H_3O^+}]^2 = -2\log[\mathrm{H_3O^+}] = 2(\mathrm{pH}) = -\log K_{a_1}K_{a_2} = -\log K_{a_1} - \log K_{a_2} = \mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}$$

$$2(\mathrm{pH}) = \mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}$$

$$\mathrm{pH} = \frac{\mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}}{2} = \frac{2.34 + 9.69}{2} = 6.02$$

(d) Half-way between the first and second equivalence points, half of the HA(aq) is converted to A^-(aq). We have a HA/A^- buffer solution where $[HA] = [A^-]$. The Henderson-Hasselbalch equation yields $\mathrm{pH} = \mathrm{p}K_{a_2} = 9.69$.

(e) At the second equivalence point, all of the H_2A^+(aq) is converted to A^-(aq). We can treat this simply as a weak base in water having:

$$K_b = \frac{K_w}{K_{a_2}} = \frac{1\times10^{-14}}{2.0\times10^{-10}} = 5.0 \times 10^{-5}$$

Note: There has been a 1:3 dilution, hence the $[A^-] = 0.500\text{ M} \times \frac{1\text{ V}}{3\text{ V}} = 0.167\text{ M}$

	A^-(aq)	+	H_2O(l)	$\rightleftharpoons$	HA(aq)	+	OH^-(aq)
Initial	0.167 M		—		0 M		≈ 0 M
Change	$-x$ M		—		$+x$ M		$+x$ M
Equilibrium	$(0.167 - x)$ M		—		x M		x M

$$K_b = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = \frac{(x)(x)}{(0.167 - x)} = 5.0 \times 10^{-5} \approx \frac{x^2}{0.167}$$

$x = 0.0029\text{ M} = [OH^-]$; $\mathrm{pOH} = -\log[OH^-] = 2.54$;

$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 2.54 = 11.46$

(f) All of the points required in (f) can be obtained using the Henderson-Hasselbalch equation (the chart below shows that the buffer ratio for each point is within the acceptable range (0.25 to 4.0))

mL NaOH →	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	100.0	110.0
$\%H_2A^+$ →	100	80	60	40	20	0	0	0	0	0	0	0
%HA →	0	20	40	60	80	100	80	60	40	20	0	0
$\%A^-$ →	0	0	0	0	0	0	20	40	60	80	100	100
buffer ratio $= \frac{\text{base}}{\text{acid}}$ →	0	0.25	0.67	1.5	4.0	∞	0.25	0.67	1.5	4.0	∞	∞

May use Henderson-Hasselbalch equation

May use Henderson-Hasselbalch equation

(i) After 10.0 mL

Here we will show how to obtain the answer using both the Henderson-Hasselbalch equation and setting up the I. C. E. (Initial, Change, Equilibrium) table. The results will differ within accepted experimental limitation of the experiment ($\underline{+}$ 0.01 pH units)

$n_{H_2A^+}$ = (C×V) = (0.500 M)(0.0500 L) = 0.0250 moles H_2A^-

n_{OH^-} = (C×V) = (0.500 M)(0.0100 L) = 0.00500 moles OH^-

V_{total} = (50.0 + 10.0) mL = 60.0 mL or 0.0600 L

$$[H_2A^+] = \frac{n_{H_2A^+}}{V_{total}} = \frac{0.0250\,\text{mol}}{0.0600\,\text{L}} = 0.417\,\text{M} \qquad [OH^-] = \frac{n_{OH^-}}{V_{total}} = \frac{0.00500\,\text{mol}}{0.0600\,\text{L}} = 0.0833\,\text{M}$$

$$K_{eq}\text{ for titration reaction} = \frac{1}{K_{b(HA)}} = \frac{1}{\left(\frac{K_w}{K_{a_1}}\right)} = \frac{K_{a_1}}{K_w} = \frac{4.6\times10^{-3}}{1.00\times10^{-14}} = 4.6\times10^{11}$$

	$H_2A^+(aq)$	+	$OH^-(aq)$	$\rightleftharpoons$	HA(aq)	+	$H_2O(l)$
Initial:	0.417 M		0.0833 M		0 M		—
100% rxn:	-0.0833		-0.0833 M		+0.0833 M		—
New initial:	0.334 M		0 M		0.0833 M		—
Change:	+*x* M		+*x* M		−*x* M		—
Equilibrium:	≈0.334 M		*x* M		≈0.0833 M		—

$$4.6\times10^{11} = \frac{(0.0833)}{(0.334)(x)}\ ;\ x = \frac{(0.0833)}{(0.334)(4.6\times10^{11})} = 5.4\times10^{-13}\text{ (valid assumption)}$$

x = 5.4 × 10–13 = [OH–]; pOH = –log(5.4 × 10–13) = 12.27;
pH = 14.00 – pOH = 14.00 – 12.27 = 1.73
Alternative method using the Henderson-Hasselbalch equation:

(i) After 10.0 mL, 20% of H2A+ reacts, forming the conjugate base HA.
Hence the buffer solution is 80% H2A+ (acid) and 20% HA (base).

$$\text{pH} = \text{p}K_{a_1} + \log\frac{\text{base}}{\text{acid}} = 2.34 + \log\frac{20.0}{80.0} = 2.34 + (-0.602) = 1.74 \text{ (within + 0.01)}$$

For the remainder of the calculations we will employ the Henderson-Hasselbalch equation with the understanding that using the method that employs the I.C.E. table gives the same result within the limitation of the data.

(ii) After 20.0 mL, 40% of H_2A^+ reacts, forming the conjugate base HA.
Hence the buffer solution is 60% H_2A^+ (acid) and 40% HA (base).

$$\text{pH} = \text{p}K_{a_1} + \log\frac{\text{base}}{\text{acid}} = 2.34 + \log\frac{40.0}{60.0} = 2.34 + (-0.176) = 2.16$$

(iii) After 30.0 mL, 60% of H_2A^+ reacts, forming the conjugate base HA.
Hence the buffer solution is 40% H_2A^+ (acid) and 60% HA (base).

$$\text{pH} = \text{p}K_{a_1} + \log\frac{\text{base}}{\text{acid}} = 2.34 + \log\frac{60.0}{40.0} = 2.34 + (+0.176) = 2.52$$

(iv) After 40.0 mL, 80% of H_2A^+ reacts, forming the conjugate base HA.
Hence the buffer solution is 20% H_2A^+ (acid) and 80% HA (base).

$$\text{pH} = \text{p}K_{a_1} + \log\frac{\text{base}}{\text{acid}} = 2.34 + \log\frac{80.0}{20.0} = 2.34 + (0.602) = 2.94$$

(v) After 50 mL, all of the $H_2A^+(aq)$ has reacted, and we begin with essentially 100% HA(aq), which is a weak acid. Addition of base results in the formation of the conjugate base (buffer system) $A^-(aq)$. We employ a similar solution, however, now we must use $\text{p}K_{a_2} = 9.69$.

(vi) After 60.0 mL, 20% of HA reacts, forming the conjugate base A^-.
Hence the buffer solution is 80% HA (acid) and 20% A^- (base)

$$\text{pH} = \text{p}K_{a_2} + \log\frac{\text{base}}{\text{acid}} = 9.69 + \log\frac{20.0}{80.0} = 9.69 + (-0.602) = 9.09$$

(vii) After 70.0 mL, 40% of HA reacts, forming the conjugate base A^-.
Hence the buffer solution is 60% HA (acid) and 40% A^- (base).

$$\text{pH} = \text{p}K_{a_2} + \log\frac{\text{base}}{\text{acid}} = 9.69 + \log\frac{40.0}{60.0} = 9.69 + (-0.176) = 9.51$$

(viii) After 80.0 mL, 60% of HA reacts, forming the conjugate base A^-.
Hence the buffer solution is 40% HA (acid) and 60% A^- (base).

$$pH = pK_{a_2} + \log\frac{\text{base}}{\text{acid}} = 9.69 + \log\frac{60.0}{40.0} = 9.69 + (+0.176) = 9.87$$

(ix) After 90.0 mL, 80% of HA reacts, forming the conjugate base A^-.
Hence the buffer solution is 20% HA (acid) and 80% A^- (base).

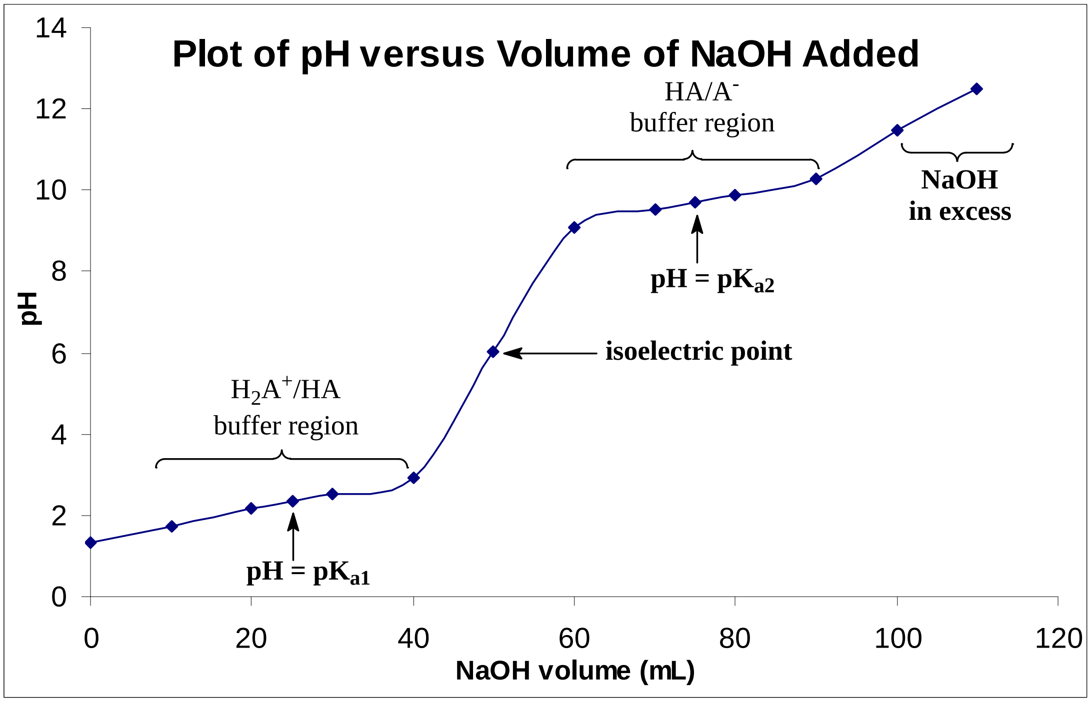
$$pH = pK_{a_2} + \log\frac{\text{base}}{\text{acid}} = 9.69 + \log\frac{80.0}{20.0} = 9.69 + (0.602) = 10.29$$

(x) After the addition of 110.0 mL, NaOH is in excess. (10.0 mL of 0.500 M NaOH is in excess, or, 0.00500 moles of NaOH remains unreacted). The pH of a solution that has NaOH in excess is determined by the $[OH^-]$ that is in excess.
(For a diprotic acid, this occurs after the second equivalence point.)

$$[OH^-]_{\text{excess}} = \frac{n_{OH^-}}{V_{\text{total}}} = \frac{0.00500\,\text{mol}}{0.1600\,\text{L}} = 0.0312\underline{5}\,\text{M}\,;\ \ pOH = -\log(0.0312\underline{5}) = 1.51$$

$$pH = 14.00 - pOH = 14.00 - 1.51 = 12.49$$

(g) A sketch of the titration curve for the 0.500 M solution of alanine hydrochloride, with some significant points labeled on the plot, is shown below.



SELF-ASSESSMENT EXERCISES

95. **(E)**

(a) mmol: millimoles, or 1×10^{-3} mol

(b) HIn: An indicator, which is a weak acid

(c) Equivalence point of a titration: When the moles of titrant equals the moles of the substance being titrated

(d) Titration curve: A curve of pH of the solution being titrated versus the pH of the titrating solution

96. **(E)**

(a) The common-ion effect: A process by which ionization of a compound is suppressed by having present one of the product ions (from another source) in the solution

(b) use of buffer to maintain constant pH: A buffer is a solution of a weak acid and its conjugate base, and it resists large changes in pH when small amounts of an acid or base are added.

(c) determination of pK_a from titration curve: At the half-way point (when half of the species being titrated is consumed, the concentration of that species and its conjugate is the same, and the equilibrium expression simplifies to $pK_a = pH$

(d) measurement of pH with an indicator: An approximate method of measuring the pH, where the color of an ionizable organic dye changes based on the pH

97. **(E)**

(a) Buffer capacity and buffer range: Buffer capacity is a measure of how much acid or base can be added to the buffer without an appreciable change in the pH, and is determined by the concentration of the weak acid and conjugate base in the buffer solution. The buffer range, however, refers to the range over which a buffer effectively neutralizes added acids and bases and maintains a fairly constant pH.

(b) Hydrolysis and neutralization: Hydrolysis is reaction of an acid or base with water molecules, which causes water to split into hydronium and hydroxide ions. Neutralization is the reaction of H_3O^+ and OH^- together to make water.

(c) First and second equivalence points in the titration of a weak diprotic acid: First equivalence point is when the first proton of a weak diprotic acid is completely abstracted and the resulting acid salt and base have been consumed and neither is in excess. Second equivalence point is the equivalence point at which all protons are abstracted from the acid and what remains is the (2-) anion.

(d) Equivalence point of a titration and end point of an indicator: Equivalence point of a titration is when the moles of titrant added are the same as the moles of acid or base in the solution being titrated. The endpoint of an indicator is when the indicator changes color because of abstraction or gain of a proton, and is ideally as close as possible to the pH of the equivalence point.

98. **(E)**

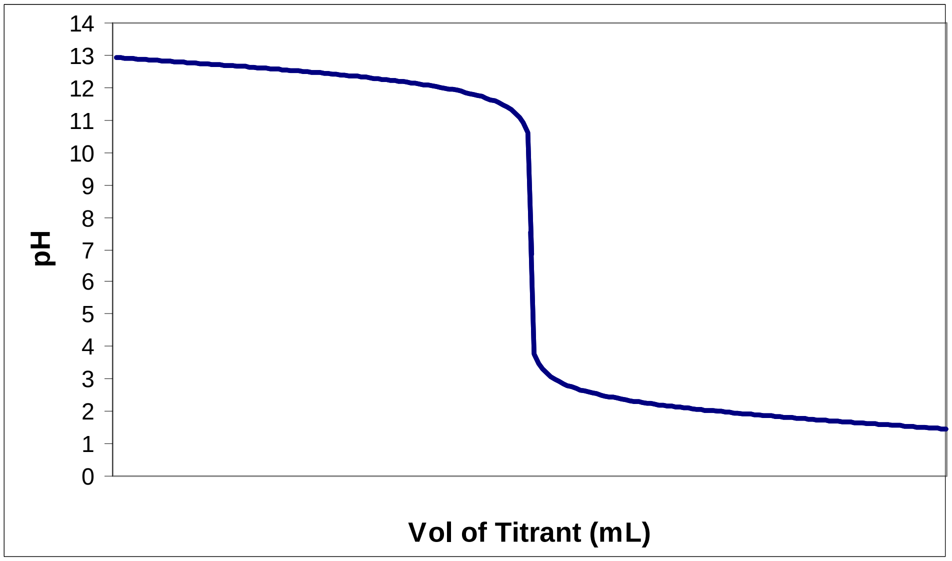
(a) $HCHO_2 + OH^- \rightarrow CHO_2^- + H_2O$
$CHO_2^- + H_3O^+ \rightarrow HCHO_2 + H_2O$

(b) $C_6H_5NH_3^+ + OH^- \rightarrow C_6H_5NH_2 + H_2O$
$C_6H_5NH_2 + H_3O^+ \rightarrow C_6H_5NH_3^+ + H_2O$

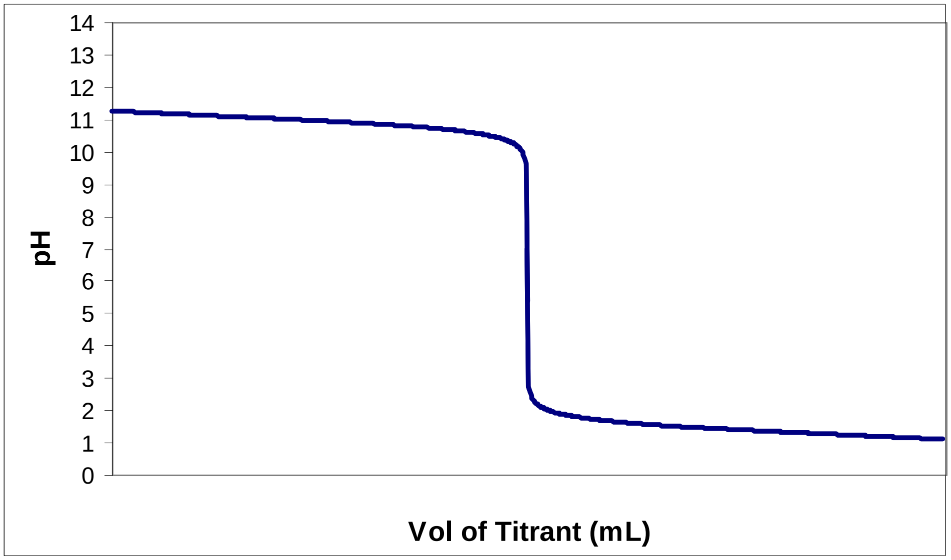
(c) $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$
$HPO_4^{2-} + H_3O^+ \rightarrow H_2PO_4^- + H_2O$

99. **(M)**

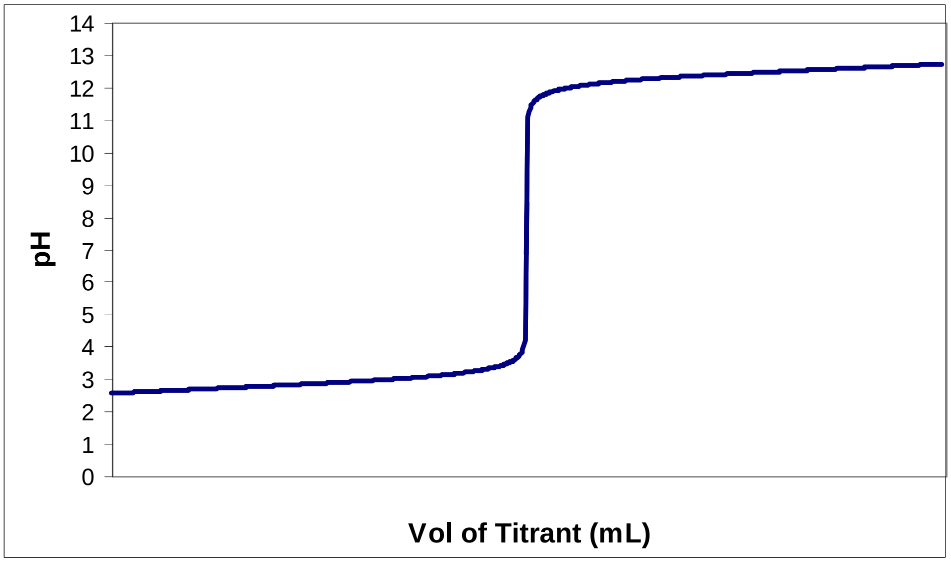
(a) The pH at theequivalence point is 7. Use bromthymol blue.



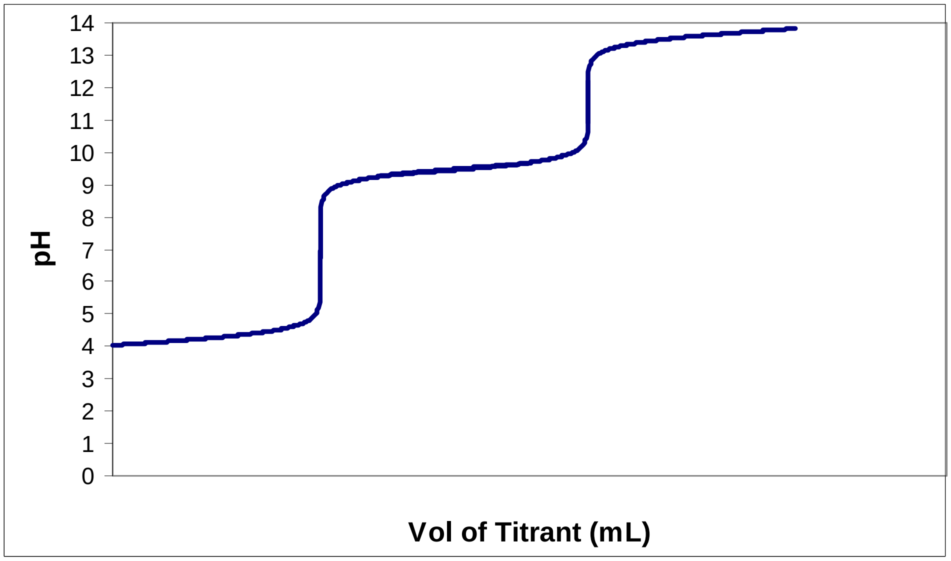
(b) The pH at the equivalence point is ~5.3 for a 0.1 M solution. Use methyl red.



(c) The pH at the equivalence point is ~8.7 for a 0.1 M solution. Use phenolphthalein, because it just begins to get from clear to pink around the equivalence point.



(d) The pH for the first equivalence point ($NaH_2PO_4^-$ to $Na_2HPO_4^{2-}$) for a 0.1 M solution is right around ~7, so use bromthymol blue.



100. **(D)**

(a) This is the initial equilibrium before any base has reacted with the acid. The reaction that dominates, along with changes in concentration, is shown below:

$HC_7H_5O_2$	+	H_2O	$\rightleftharpoons$	$C_7H_5O_2^-$	+	H_3O^+
0.0100				0		0
$-x$				$+x$		$+x$
$0.0100-x$				x		x

$$K_a=\frac{\left[H_3O^+\right]\left[C_7H_5O_2^-\right]}{\left[HC_7H_5O_2\right]}$$

$$6.3\times10^{-5}=\frac{(x)(x)}{0.0100-x}$$

Solving for x using the quadratic formula, $x = 7.63\times10^{-4}$ M.

$$\text{pH} = -\log\left[H_3O^+\right]=-\log\left(7.63\times10^{-4}\right)=3.12$$

(b) In this case, we titrate the base with 0.00625 L of $Ba(OH)_2$. Therefore, we have to calculate the final moles of the base and the total volume to determine the concentration.

$$\text{mol } HC_7H_5O_2 = 0.02500\text{ L}\times0.0100\text{ M } HC_7H_5O_2 = 2.5\times10^{-4}\text{ mol}$$

$$\text{mol } OH^- = 0.00625\text{ L}\times0.0100\text{ M } Ba\left(OH\right)_2\times\frac{2\text{ mol } OH^-}{1\text{ mol } Ba\left(OH\right)_2} = 1.25\times10^{-4}\text{ mol}$$

Since the amount of OH^- is half of the initial amount of $HC_7H_5O_2$, the moles of $HC_7H_5O_2$ and $C_7H_5O_2^-$ are equal. Therefore, $K_a = [H_3O^+]$, and pH = $-\log(6.3\times10^{-5}) = 4.20$.

(c) At the equivalence point, there is initially no $HC_7H_5O_2$. The equilibrium is dominated by $C_7H_5O_2^-$ hydrolyzing water. The concentration of $C_7H_5O_2^-$ is:
Total moles of $HC_7H_5O_2 = 2.5\times10^{-4}$ mol as shown previously. At the equivalence point, the moles of acid equal moles of OH^-.

$$\text{mol } Ba\left(OH\right)_2 = 2.5\times10^{-4}\text{ mol } OH^-\times\frac{1\text{ mol } Ba\left(OH\right)_2}{2\text{ mol } OH^-} = 1.25\times10^{-4}\text{ mol}$$

Vol of $Ba(OH)_2 = 1.25\times10^{-4}$ mol / 0.0100 M = 0.0125 L

Total volume of the solution at the equivalence point is the sum of the initial volume plus the volume of $Ba(OH)_2$ added. That is,

V_{TOT} = 0.02500 L + 0.0125 L = 0.0375 L

Therefore, the concentration of $C_7H_5O_2^- = 2.5\times10^{-4}/0.0375$ L = 0.00667 M.

$C_7H_5O_2^-$	+	H_2O	$\rightleftharpoons$	$HC_7H_5O_2$	+	OH^-
0.00667				0		0
$-x$				$+x$		$+x$
$0.00667 - x$				x		x

Since this is a base reaction, $K_b = K_w / K_a = \left(1.00\times10^{-4}\right)\big/ 6.3\times10^{-5} = 1.587\times10^{-10}$.

$$K_b = \frac{\left[OH^-\right]\left[HC_7H_5O_2\right]}{\left[C_7H_5O_2^-\right]}$$

$$1.59\times10^{-10} = \frac{(x)(x)}{0.00667 - \cancel{x}}$$

solving for x (by simplifying the formula above) yields $x = 1.03\times10^{-6}$ M.

$$\text{pH} = 14 - \text{pOH} = 14 - \left[-\log\left(1.03\times10^{-6}\right)\right] = 14 - 6.00 = 8.00$$

(d) In this part, we have an excess of a strong base. As such, we have to determine how much excess base there is and what is the final volume of the solution.

$$\text{mol}\left(OH^-\right) = 0.01500\text{ L} \times 0.0100\ \frac{\text{mol Ba}\left(OH\right)_2}{\text{L}} \times \frac{2\text{ mol }OH^-}{1\text{ mol Ba}\left(OH\right)_2}$$

$$= 3.000\times10^{-4}\text{ mol }OH^-$$

$$\text{Excess mol }OH^- = \text{mol }HC_7H_5O_2 - \text{mol }OH^- = 3.000\times10^{-4} - 2.500\times10^{-4}$$

$$= 5.000\times10^{-5}\text{ mol}$$

$$\left[OH^-\right] = \frac{5.0\times10^{-5}\text{mol}}{\left(0.02500\text{ L}+0.01500\text{ L}\right)} = 0.00125\text{ M}$$

$$\text{pH} = 14 - \text{pOH} = 14 - \left[-\log\left(0.00125\right)\right] = 14 - 2.903 = 11.1$$

101. **(E)** The answer is (c); because of the common ion-effect, the presence of HCO_2^- will repress ionization of formic acid.

102. **(E)** The answer is (d), because $NaHCO_3$ is a weak base and will react with protons in water, shifting the formic acid ionization equilibrium to the right.

103. **(E)** The answer is (b), raise the pH. NH_4^+ is an acid, and to be converted to its conjugate base, it must react with a base to abstract its proton.

104. **(E)** The answer is (b), because at that point, the number of moles of weak base remaining is the same as its conjugate acid, and the equilibrium expression simplifies to $K_a = [H_3O^+]$.

<u>105.</u> (M) The base, $C_2H_5NH_2$, is reacted with $HClO_4$. The reaction is:

$$C_2H_5NH_2 + HClO_4 \rightarrow C_2H_5NH_3^+ + ClO_4^-$$

Assuming a volume of 1 L for each solution,

$$\left[C_2H_5NH_2\right] = \frac{1.49 \text{ mol} - 1.001 \text{ mol}}{2 \text{ L}} = \frac{0.489 \text{ mol}}{2 \text{ L}} = 0.2445 \text{ M}$$

$$\left[C_2H_5NH_3^+\right] = \frac{1.001 \text{ mol}}{2 \text{ L}} = 0.5005 \text{ M}$$

$$4.3\times10^{-4} = \frac{\left[C_2H_5NH_3^+\right]\left[OH^-\right]}{\left[C_2H_5NH_2\right]} = \frac{(0.5005 + \cancel{x})(x)}{(0.2445 - \cancel{x})}$$

$$x = 2.10\times10^{-4}$$

$$\text{pOH} = -\log\left(2.10\times10^{-4}\right) = 3.68$$

$$\text{pH} = 14 - 3.68 = 10.32$$

<u>106.</u> (D) We assume that all of $Ca(HSe)_2$ dissociates in water. The concentration of HSe^- is therefore:

$$0.5 \text{ M Ca}\left(\text{HSe}\right)_2 \times \frac{2 \text{ mol HSe}^-}{1 \text{ mol Ca}\left(\text{HSe}\right)_2} = 1.0 \text{ M HSe}^-$$

We note that HSe^- is amphoteric; that is, it can act either as an acid or a base. The acid reaction of HSe^- and the concentration of $[H_3O^+]$ generated, are as follows:

$$HSe^- + H_2O \rightleftharpoons Se^{2-} + H_3O^+$$

$$1.00\times10^{-11} = \frac{\left[Se^{2-}\right]\left[H_3O^+\right]}{\left[HSe^-\right]} = \frac{(x)(x)}{(1.00 - \cancel{x})}$$

$$x = \sqrt{1.00\times10^{-11}} = 3.16\times10^{-6}$$

The basic reaction of HSe^- and the concentration of $[OH^-]$ generated, are as follows:

$$HSe^- + H_2O \rightleftharpoons H_2Se + OH^-$$

$K_b = 1.00\times10^{-14}/1.3\times10^{-4} = 7.69\times10^{-11}$

$$7.69\times10^{-11} = \frac{\left[H_2Se\right]\left[OH^-\right]}{\left[HSe^-\right]} = \frac{(x)(x)}{(1.00 - \cancel{x})}$$

$$x = \sqrt{7.69\times10^{-11}} = 8.77\times10^{-6}$$

Therefore, we have $[H_3O^+] = 3.16\times10^{-6}$ and $[OH^-] = 8.77\times10^{-6}$. Since these two react to give H_2O, the result is $8.77\times10^{-6} - 3.16\times10^{-6} = 5.61\times10^{-6}$ M $[OH^-]$. The pH of the solution is:

pH = 14 – pOH = 14 – 5.25 = 8.75

107. **(E)** The answer is (a). The solution system described is a buffer, and will resist large changes in pH. Adding KOH should raise the pH slightly.

108. **(E)** The answer is (b), because HSO_3^- is a much stronger acid ($K_a = 1.3\times10^{-2}$) than $H_2PO_4^-$ ($K_a = 6.3\times10^{-8}$).

109. **(E)** The answer is (b). The pK_a of the acid is 9, which puts it squarely in the middle of the 8–10 pH range for the equivalence point.

110. **(E)**

(a) $NaHCO_3$ titrated with NaOH: pH > 7, because HCO_3^- is itself slightly basic, and is being titrated with NaOH to yield CO_3^{2-} at the equivalence point, which is even more basic.

(b) HCl titrated with NH_3: pH < 7, because the resulting NH_4^+ at the equivalence point is acidic.

(c) KOH titrated with HI: pH = 7, because a strong base is being titrated by a strong acid, and the resulting anions and cations are all non-basic and non-acidic.

111. **(M)** The concepts that define Sections 17-2, 17-3, and 17-4 are buffers, indicators, and titrations. For buffers, after definition, there are a number of concepts, such as composition, application, the equilibrium expression (the Henderson-Hasselbalch equation is a subtopic of the equilibrium expression). Under composition, there are other subtopics such as buffer range and capacity. For indicators, after defining it, there are subtopics such as equilibrium expression and usage. With titration, topics such as form (weak acid titrated by strong base, and weak base titrated by strong acid), the titration curve, and the equivalence point. Look at these sections to find inter-related terminology and other concepts.

CHAPTER 18

SOLUBILITY AND COMPLEX-ION EQUILIBRIA

PRACTICE EXAMPLES

1A **(E)** In each case, we first write the balanced equation for the solubility equilibrium and then the equilibrium constant expression for that equilibrium, the K_{sp} expression:

(a) $\mathrm{MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)}$ $\qquad K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{CO_3^{2-}}]$

(b) $\mathrm{Ag_3PO_4(s) \rightleftharpoons 3Ag^{+}(aq) + PO_4^{3-}(aq)}$ $\qquad K_{sp} = [\mathrm{Ag^{+}}]^3[\mathrm{PO_4^{3-}}]$

1B **(E)**

(a) Provided the $[\mathrm{OH^-}]$ is not too high, the hydrogen phosphate ion is not expected to ionize in aqueous solution to a significant extent because of the quite small values for the second and third ionization constants of phosphoric acid.

$\mathrm{CaHPO_4(s) \rightleftharpoons Ca^{2+}(aq) + HPO_4^{2-}(aq)}$

(b) The solubility product constant is written in the manner of a K_c expression:

$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{HPO_4^{2-}}] = 1. \times 10^{-7}$

2A **(M)** We calculate the solubility of silver cyanate, s, as a molarity. We then use the solubility equation to (1) relate the concentrations of the ions and (2) write the K_{sp} expression.

$$s = \frac{7\text{ mg AgOCN}}{100\text{ mL}} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol AgOCN}}{149.9\text{ g AgOCN}} = 5\times10^{-4}\text{ moles/L}$$

Equation: $\mathrm{AgOCN(s) \rightleftharpoons Ag^{+}(aq) + OCN^{-}(aq)}$

Solubility Product: $\qquad s \qquad s$

$$K_{sp} = \left[\mathrm{Ag^+}\right]\left[\mathrm{OCN^-}\right] = (s)\times(s) = s^2 = \left(5\times10^{-4}\right)^2 = 3\times10^{-7}$$

2B **(E)** We calculate the solubility of lithium phosphate, s, as a molarity. We then use the solubility equation to (1) relate the concentrations of the ions and (2) write the K_{sp} expression.

$$s = \frac{0.034\text{ g }\mathrm{Li_3PO_4}}{100\text{ mL soln}} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1\text{ mol }\mathrm{Li_3PO_4}}{115.79\text{ g }\mathrm{Li_3PO_4}} = 0.0029\text{ moles/L}$$

Equation: $\mathrm{Li_3PO_4(s) \rightleftharpoons 3Li^{+}(aq) + PO_4^{3-}(aq)}$

Solubility Product: $\qquad (3\,s)^3 \qquad s$

$$K_{sp} = \left[\mathrm{Li^+}\right]^3\left[\mathrm{PO_4^{3-}}\right] = (3s)^3\cdot(s) = 27s^4 = 27(0.0029)^4 = 1.9\times10^{-9}$$

3A **(E)** We use the solubility equilibrium to write the K_{sp} expression, which we then solve to obtain the molar solubility, s, of $Cu_3(AsO_4)_2$.

$$Cu_3(AsO_4)_2.(s) \rightleftharpoons 3\ Cu^{2+}(aq) + 2\ AsO_4^{-}(aq)$$

$$K_{sp} = \left[Cu^{2+}\right]^3 \left[AsO_4^{-}\right]^2 = (3s)^3 (2s)^2 = 108s^5 = 7.6\times10^{-36}$$

Solubility : $$s = \sqrt[5]{\frac{7.6\times10^{-36}}{108}} = 3.7\times10^{-8}\,M$$

3B **(E)** First we determine the solubility of $BaSO_4$, and then find the mass dissolved.

$$BaSO_4(aq) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right] = s^2$$

The last relationship is true because $\left[Ba^{2+}\right] = \left[SO_4^{2-}\right]$ in a solution produced by dissolving $BaSO_4$ in pure water. Thus, $s = \sqrt{K_{sp}} = \sqrt{1.1\times10^{-10}} = 1.05\times10^{-5}\,M.$

$$\text{mass } BaSO_4 = 225\ mL \times \frac{1.05\times10^{-5}\,\text{mmol } BaSO_4}{1\ \text{mL sat'd soln}} \times \frac{233.39\,\text{mg } BaSO_4}{1\,\text{mmol } BaSO_4} = 0.55\,\text{mg } BaSO_4$$

4A **(M)** For $PbI_2, K_{sp} = \left[Pb^{2+}\right]\left[I^{-}\right]^2 = 7.1\times10^{-9}$. The solubility equilibrium is the basis of the calculation.

Equation:	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2I^{-}(aq)$
Initial:	—		0.10 M		0 M
Changes:	—		+s M		+2s M
Equil:	—		(0.10 + s) M		2s M

$$K_{sp} = \left[Pb^{2+}\right]\left[I^{-}\right]^2 = 7.1\times10^{-9} = (0.10+s)(2s)^2 \approx 0.40\,s^2 \qquad s = \sqrt{\frac{7.1\times10^{-9}}{0.40}} = 1.3\times10^{-4}\,M$$

(assumption $0.10 \gg s$ is valid)
This value of s is the solubility of PbI_2 in 0.10 M $Pb(NO_3)_2(aq)$.

4B **(E)** We find pOH from the given pH:
pOH = 14.00 – 8.20 = 5.80; $[OH^{-}] = 10^{-pOH} = 10^{-5.80} = 1.6\times10^{-6}$ M.
We assume that pOH remains constant, and use the K_{sp} expression for $Fe(OH_3)$.

$$K_{sp} = \left[Fe^{3+}\right]\left[OH^{-}\right]^3 = 4\times10^{-38} = \left[Fe^{3+}\right]\left(1.6\times10^{-6}\right)^3 \qquad \left[Fe^{3+}\right] = \frac{4\times10^{-38}}{\left(1.6\times10^{-6}\right)^3} = 9.8\times10^{-21}\,M$$

Therefore, the molar solubility of $Fe(OH)_3$ is 9.8×10^{-21} M.

The dissolved $Fe(OH)_3$ does not significantly affect $\left[OH^{-}\right]$.

5A **(M)** First determine $\left[\mathrm{I}^-\right]$ as altered by dilution. We then compute Q_{sp} and compare it with K_{sp}.

$$\left[\mathrm{I}^-\right]=\frac{3\,\text{drops}\times\dfrac{0.05\,\text{mL}}{1\,\text{drop}}\times\dfrac{0.20\,\text{mmol KI}}{1\,\text{mL}}\times\dfrac{1\,\text{mmol I}^-}{1\,\text{mmol KI}}}{100.0\,\text{mL soln}}=3\times10^{-4}\,\text{M}$$

$$Q_{\mathrm{sp}}=\left[\mathrm{Ag}^+\right]\left[\mathrm{I}^-\right]=(0.010\ )\left(3\times10^{-4}\right)=3\times10^{-6}$$

$Q_{\mathrm{sp}}>8.5\times10^{-17}=K_{\mathrm{sp}}$ Thus, precipitation should occur.

5B **(M)** We first use the solubility product constant expression for $\mathrm{PbI_2}$ to determine the $\left[\mathrm{I}^-\right]$ needed in solution to just form a precipitate when $\left[\mathrm{Pb}^{2+}\right]=0.010$ M. We assume that the volume of solution added is small and that $\left[\mathrm{Pb}^{2+}\right]$ remains at 0.010 M throughout.

$$K_{\mathrm{sp}}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{I}^-\right]^2=7.1\times10^{-9}=(0.010)\left[\mathrm{I}^-\right]^2 \qquad \left[\mathrm{I}^-\right]=\sqrt{\frac{7.1\times10^{-9}}{0.010}}=8.4\times10^{-4}\,\text{M}$$

We determine the volume of 0.20 M KI needed.

$$\text{volume of KI(aq)}=100.0\,\text{mL}\times\frac{8.4\times10^{-4}\,\text{mmol I}^-}{1\text{ mL}}\times\frac{1\text{ mmol KI}}{1\text{ mmol I}^-}\times\frac{1\text{ mL KI(aq)}}{0.20\text{ mmol KI}}\times\frac{1\text{ drop}}{0.050\text{ mL}}$$

$$=8.4\,\text{drops}=9\,\text{drops}$$

Since one additional drop is needed, 10 drops will be required. This is an insignificant volume compared to the original solution, so $\left[\mathrm{Pb}^{2+}\right]$ remains constant.

6A **(E)** Here we must find the maximum $\left[\mathrm{Ca}^{2+}\right]$ that can coexist with $\left[\mathrm{OH}^-\right]=0.040\,\text{M}$.

$$K_{\mathrm{sp}}=5.5\times10^{-6}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{OH}^-\right]^2=\left[\mathrm{Ca}^{2+}\right](0.040)^2;\quad \left[\mathrm{Ca}^{2+}\right]=\frac{5.5\times10^{-6}}{(0.040)^2}=3.4\times10^{-3}\,\text{M}$$

For precipitation to be considered complete, $\left[\mathrm{Ca}^{2+}\right]$ should be less than 0.1% of its original value. $3.4\times10^{-3}\,\text{M}$ is 34% of 0.010 M and therefore precipitation of $\mathrm{Ca(OH)_2}$ is not complete under these conditions.

6B **(E)** We begin by finding $\left[\mathrm{Mg}^{2+}\right]$ that corresponds to $1\,\mu\text{g Mg}^{2+}/\text{L}$.

$$\left[\mathrm{Mg}^{2+}\right]=\frac{1\,\mu\text{g Mg}^{2+}}{1\text{ L soln}}\times\frac{1\text{ g}}{10^6\,\mu\text{g}}\times\frac{1\text{ mol Mg}^{2+}}{24.3\text{ g Mg}^{2+}}=4\times10^{-8}\,\text{M}$$

Now we use the K_{sp} expression for $\mathrm{Mg(OH)_2}$ to determine $\left[\mathrm{OH}^-\right]$.

$$K_{\mathrm{sp}}=1.8\times10^{-11}=\left[\mathrm{Mg}^{2+}\right]\left[\mathrm{OH}^-\right]^2=\left(4\times10^{-8}\right)\left[\mathrm{OH}^-\right]^2 \qquad \left[\mathrm{OH}^-\right]=\sqrt{\frac{1.8\times10^{-11}}{4\times10^{-8}}}=0.02\,\text{M}$$

7A **(M)** Let us first determine $\left[\mathrm{Ag}^{+}\right]$ when AgCl(s) just begins to precipitate. At this point, Q_{sp} and K_{sp} are equal.

$$K_{\mathrm{sp}} = 1.8\times10^{-10} = \left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right] = Q_{\mathrm{sp}} = \left[\mathrm{Ag}^{+}\right]\times 0.115\mathrm{M} \qquad \left[\mathrm{Ag}^{+}\right] = \frac{1.8\times10^{-10}}{0.115} = 1.6\times10^{-9}\,\mathrm{M}$$

Now let us determine the maximum $\left[\mathrm{Br}^{-}\right]$ that can coexist with this $\left[\mathrm{Ag}^{+}\right]$.

$$K_{\mathrm{sp}} = 5.0\times10^{-13} = \left[\mathrm{Ag}^{+}\right]\left[\mathrm{Br}^{-}\right] = 1.6\times10^{-9}\,\mathrm{M}\times\left[\mathrm{Br}^{-}\right]; \;\; \left[\mathrm{Br}^{-}\right] = \frac{5.0\times10^{-13}}{1.6\times10^{-9}} = 3.1\times10^{-4}\,\mathrm{M}$$

The remaining bromide ion has precipitated as AgBr(s) with the addition of $\mathrm{AgNO_3(aq)}$.

$$\text{Percent of } \mathrm{Br}^{-} \text{ remaining} = \frac{[\mathrm{Br}^{-}]_{\mathrm{final}}}{[\mathrm{Br}^{-}]_{\mathrm{initial}}}\times100\% = \frac{3.1\times10^{-4}\,\mathrm{M}}{0.264\,\mathrm{M}}\times100\% = 0.12\%$$

7B **(M)** Since the ions have the same charge and the same concentrations, we look for two K_{sp} values for the salt with the same anion that are as far apart as possible. The K_{sp} values for the carbonates are very close, while those for the sulfates and fluorides are quite different. However, the difference in the K_{sp} values is greatest for the chromates; K_{sp} for $\mathrm{BaCrO_4}\left(1.2\times10^{-10}\right)$ is so much smaller than K_{sp} for $\mathrm{SrCrO_4}\left(2.2\times10^{-5}\right)$, $\mathrm{BaCrO_4}$ will precipitate first and $\mathrm{SrCrO_4}$ will begin to precipitate when $\left[\mathrm{CrO_4}^{2-}\right]$ has the value:

$$\left[\mathrm{CrO_4}^{2-}\right] = \frac{K_{\mathrm{sp}}}{\left[\mathrm{Sr}^{2+}\right]} = \frac{2.2\times10^{-5}}{0.10} = 2.2\times10^{-4}\ \mathrm{M}.$$

At this point $\left[\mathrm{Ba}^{2+}\right]$ is found as follows.

$$\left[\mathrm{Ba}^{2+}\right] = \frac{K_{\mathrm{sp}}}{\left[\mathrm{CrO_4}^{2-}\right]} = \frac{1.2\times10^{-10}}{2.2\times10^{-4}} = 5.5\times10^{-7}\ \mathrm{M};$$

$[\mathrm{Ba}^{2+}]$ has dropped to 0.00055% of its initial value and therefore is considered to be completely precipitated, before $\mathrm{SrCrO_4}$ begins to precipitate. The two ions are thus effectively separated as chromates. The best precipitating agent is a group 1 chromate salt.

8A **(M)** First determine $\left[\mathrm{OH}^{-}\right]$ resulting from the hydrolysis of acetate ion.

Equation:	$\mathrm{C_2H_3O_2^-(aq)}$	+	$\mathrm{H_2O(l)}$	$\rightleftharpoons$	$\mathrm{HC_2H_3O_2(aq)}$	+	$\mathrm{OH^-(aq)}$
Initial:	0.10 M		—		0 M		$\approx 0\,\mathrm{M}$
Changes:	$-x\,\mathrm{M}$		—		$+x\,\mathrm{M}$		$+x\,\mathrm{M}$
Equil:	$(0.10-x)\,\mathrm{M}$		—		$x\,\mathrm{M}$		$x\,\mathrm{M}$

$$K_b = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{x\cdot x}{0.10-x} \approx \frac{x^2}{0.10}$$

$x = [OH^-] = \sqrt{0.10\times5.6\times10^{-10}} = 7.5\times10^{-6}\,M$ (the assumption $x \ll 0.10$ was valid)
Now compute the value of the ion product in this solution and compare it with the value of K_{sp} for $Mg(OH)_2$.

$$Q_{sp} = [Mg^{2+}][OH^-]^2 = (0.010M)(7.5\times10^{-6}M)^2 = 5.6\times10^{-13} < 1.8\times10^{-11} = K_{sp}[Mg(OH)_2]$$

Because Q_{sp} is smaller than K_{sp}, this solution is unsaturated and precipitation of $Mg(OH)_2(s)$ will not occur.

8B **(M)** Here we can use the Henderson–Hasselbalch equation to determine the pH of the buffer.

$$pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = -\log(1.8\times10^{-5}) + \log\frac{0.250\,M}{0.150\,M} = 4.74 + 0.22 = 4.96$$

$$pOH = 14.00 - pH = 14.00 - 4.96 = 9.04 \qquad [OH^-] = 10^{-pOH} = 10^{-9.04} = 9.1\times10^{-10}\,M$$

Now we determine Q_{sp} to see if precipitation will occur.

$$Q_{sp} = [Fe^{3+}][OH^-]^3 = (0.013\,M)(9.1\times10^{-10})^3 = 9.8\times10^{-30}$$

$Q_{sp} > 4\times10^{-38} = K_{sp}$; Thus, $Fe(OH)_3$ precipitation should occur.

9A **(M)** Determine $[OH^-]$, and then the pH necessary to prevent the precipitation of $Mn(OH)_2$.

$$K_{sp} = 1.9\times10^{-13} = [Mn^{2+}][OH^-]^2 = (0.0050M)[OH^-]^2 \quad [OH^-] = \sqrt{\frac{1.9\times10^{-13}}{0.0050}} = 6.2\times10^{-6}\,M$$

$$pOH = -\log(6.2\times10^{-6}) = 5.21 \qquad pH = 14.00 - 5.21 = 8.79$$

We will use this pH in the Henderson–Hasselbalch equation to determine $[NH_4^+]$.

$pK_b = 4.74$ for NH_3.

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = 8.79 = (14.00 - 4.74) + \log\frac{0.025\,M}{[NH_4^+]}$$

$$\log\frac{0.025\,M}{[NH_4^+]} = 8.79 - (14.00 - 4.74) = -0.47 \qquad \frac{0.025}{[NH_4^+]} = 10^{-0.47} = 0.34$$

$$[NH_4^+] = \frac{0.025}{0.34} = 0.074M$$

9B **(M)** First we must calculate the $[H_3O^+]$ in the buffer solution that is being employed to dissolve the magnesium hydroxide:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)\ ;\ K_b = 1.8 \times 10^{-5}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[0.100M][OH^-]}{[0.250M]} = 1.8 \times 10^{-5}$$

$$[OH^-] = 4.5 \times 10^{-5}\,M;\ [H_3O^+] = \frac{1.00 \times 10^{-14}\,M^2}{4.5 \times 10^{-5}\,M} = 2.2_2 \times 10^{-10}\,M$$

Now we can employ Equation 18.4 to calculate the molar solubility of $Mg(OH)_2$ in the buffer solution; molar solubility $Mg(OH)_2 = [Mg^{2+}]_{equil}$

$$\begin{array}{lccccccc} & Mg(OH)_2(s) & + & 2\,H_3O^+(aq) & \xrightleftharpoons{K = 1.8 \times 10^{17}} & Mg^{2+}(aq) & + & 4H_2O(l)\ ; \\ \text{Equilibrium} & - & & 2.2 \times 10^{-10} & & x & & - \end{array}$$

$$K = \frac{[Mg^{2+}]}{[H_3O^+]^2} = \frac{x}{[2.2 \times 10^{-10}\,M]^2} = 1.8 \times 10^{17} \qquad x = 8.7 \times 10^{-3}\,M = [Mg^{2+}]_{equil}$$

So, the molar solubility for $Mg(OH)_2 = 8.7 \times 10^{-3}$M.

10A **(M)**

(a) In solution are $Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $Na^+(aq)$, and $OH^-(aq)$.

$$Cu^{2+}(aq) + 2\,OH^-(aq) \rightarrow Cu(OH)_2(s)$$

(b) In the solution above, $Cu(OH)_2(s)$ is $Cu^{2+}(aq)$:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\,OH^-(aq)$$

This $Cu^{2+}(aq)$ reacts with the added $NH_3(aq)$:

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

The overall result is: $Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2\,OH^-(aq)$

(c) $HNO_3(aq)$ (a strong acid), forms $H_3O^+(aq)$, which reacts with $OH^-(aq)$ and $NH_3(aq)$.

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2\,H_2O(l); \qquad NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$

As $NH_3(aq)$ is consumed, the reaction below shifts to the left.

$$Cu(OH)_2(s) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2\,OH^-(aq)$$

But as $OH^-(aq)$ is consumed, the dissociation reactions shift to the side with the dissolved ions: $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\,OH^-(aq)$

The species in solution at the end of all this are

$Cu^{2+}(aq),\ NO_3^-(aq),\ NH_4^+(aq),$ excess $H_3O^+(aq),\ Na^+(aq),$ and $SO_4^{2-}(aq)$ (probably HSO_4^-(aq) as well).

10B **(M)**

(a) In solution are Zn^{2+}(aq), SO_4^{2-}(aq), and NH_3(aq),

$$Zn^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons \left[Zn(NH_3)_4\right]^{2+}(aq)$$

(b) $HNO_3(aq)$, a strong acid, produces $H_3O^+(aq)$, which reacts with $NH_3(aq)$. $NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$ As $NH_3(aq)$ is consumed, the tetrammine complex ion is destroyed.

$$\left[Zn(NH_3)_4\right]^{2+}(aq) + 4H_3O^+(aq) \rightleftharpoons \left[Zn(H_2O)_4\right]^{2+}(aq) + 4NH_4^+(aq)$$

(c) NaOH(aq) is a strong base that produces $OH^-(aq)$, forming a hydroxide precipitate.

$$\left[Zn(H_2O)_4\right]^{2+}(aq) + 2\,OH^-(aq) \rightleftharpoons Zn(OH)_2(s) + 4\,H_2O(l)$$

Another possibility is a reversal of the reaction of part (**b**).

$$\left[Zn(H_2O)_4\right]^{2+}(aq) + 4\,NH_4^+(aq) + 4\,OH^-(aq) \rightleftharpoons \left[Zn(NH_3)_4\right]^{2+}(aq) + 8\,H_2O(l)$$

(d) The precipitate dissolves in excess base.

$$Zn(OH)_2(s) + 2\,OH^-(aq) \rightleftharpoons \left[Zn(OH)_4\right]^{2-}(aq)$$

11A **(M)** We first determine $\left[Ag^+\right]$ in a solution that is 0.100 M Ag^+(aq) (from $AgNO_3$) and 0.225 M $NH_3(aq)$. Because of the large value of $K_f = 1.6\times10^7$, we start by having the reagents form as much complex ion as possible, and approach equilibrium from this point.

Equation:	$Ag^+(aq)$ +	$2\,NH_3(aq)$ $\rightleftharpoons$	$\left[Ag(NH_3)_2\right]^+(aq)$
In soln	0.100 M	0.225 M	0 M
Form complex	–0.100 M	–0.200 M	+0.100 M
Initial	0 M	0.025 M	0.100 M
Changes	+*x* M	+2*x* M	–*x* M
Equil	*x* M	(0.025 + *x*) M	(0.100 – *x*) M

$$K_f = 1.6\times10^7 = \frac{\left[\left[Ag(NH_3)_2\right]^+\right]}{\left[Ag^+\right]\left[NH_3\right]^2} = \frac{0.100 - x}{x(0.025+2x)^2} \approx \frac{0.100}{x(0.025)^2}$$

$$x = \frac{0.100}{(0.025)^2 1.6\times10^7} = 1.0\times10^{-5}\,M = \left[Ag^+\right] = \text{concentration of free silver ion}$$

(x << 0.025 M, so the approximation was valid)

The $\left[Cl^-\right]$ is diluted: $\left[Cl^-\right]_{final} = \left[Cl^-\right]_{initial} \times \dfrac{1.00\,mL_{initial}}{1{,}500\,mL_{final}} = 3.50\,M \div 1500 = 0.00233\,M$

Finally we compare Q_{sp} with K_{sp} to determine if precipitation of AgCl(s) will occur.

$$Q_{sp} = [Ag^+][Cl^-] = (1.0\times10^{-5}\text{ M})(0.00233\text{M}) = 2.3\times10^{-8} > 1.8\times10^{-10} = K_{sp}$$

Because the value of the Q_{sp} is larger than the value of the K_{sp}, precipitation of AgCl(s) should occur.

11B **(M)** We organize the solution around the balanced equation of the formation reaction.

Equation:	$Pb^{2+}(aq)$	+	$EDTA^{4-}(aq)$	$\rightleftharpoons$	$[PbEDTA]^{2-}(aq)$
Initial	0.100 M		0.250 M		0 M
Form Complex:	–0.100 M		(0.250 – 0.100) M		0.100 M
Equil	x M		$(0.150+x)$ M		$(0.100-x)$ M

$$K_f = \frac{[[PbEDTA]^{2-}]}{[Pb^{2+}][EDTA^{4-}]} = 2\times10^{18} = \frac{0.100-x}{x(0.150+x)} \approx \frac{0.100}{0.150\,x}$$

$$x = \frac{0.100}{0.150\times2\times10^{18}} = 3\times10^{-19}\text{ M}$$ (x << 0.100 M, thus the approximation was valid.)

We calculate Q_{sp} and compare it to K_{sp} to determine if precipitation will occur.

$$Q_{sp} = [Pb^{2+}][I^-]^2 = (3\times10^{-19}\text{M})(0.10\text{M})^2 = 3\times10^{-21}\ .$$

$Q_{sp} < 7.1\times10^{-9} = K_{sp}$ Thus precipitation will not occur.

12A **(M)** We first determine the maximum concentration of free Ag^+.

$$K_{sp} = [Ag^+][Cl^-] = 1.8\times10^{-10} \qquad [Ag^+] = \frac{1.8\times10^{-10}}{0.0075} = 2.4\times10^{-8}\text{ M.}$$

This is so small that we assume that all the Ag^+ in solution is present as complex ion:

$[[Ag(NH_3)_2]^+] = 0.13$ M. We use K_f to determine the concentration of free NH_3.

$$K_f = \frac{[[Ag(NH_3)_2]^+]}{[Ag^+][NH_3]^2} = 1.6\times10^7 = \frac{0.13\text{M}}{2.4\times10^{-8}[NH_3]^2}$$

$$[NH_3] = \sqrt{\frac{0.13}{2.4\times10^{-8}\times1.6\times10^7}} = 0.58\text{M.}$$

If we combine this with the ammonia present in the complex ion, the total ammonia concentration is $0.58\text{M} + (2\times0.13\text{M}) = 0.84\text{M}$. Thus, the minimum concentration of ammonia necessary to keep AgCl(s) from forming is 0.84 M.

12B **(M)** We use the solubility product constant expression to determine the maximum $\left[\mathrm{Ag}^{+}\right]$ that can be present in 0.010 M Cl^{-} without precipitation occurring.

$$K_{\mathrm{sp}} = 1.8\times10^{-10} = \left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right] = \left[\mathrm{Ag}^{+}\right](0.010\,\mathrm{M}) \qquad \left[\mathrm{Ag}^{+}\right] = \frac{1.8\times10^{-10}}{0.010} = 1.8\times10^{-8}\,\mathrm{M}$$

This is also the concentration of free silver ion in the K_{f} expression. Because of the large value of K_{f}, practically all of the silver ion in solution is present as the complex ion, $[\mathrm{Ag(S_2O_3)_2}]^{3-}$]. We solve the expression for $[\mathrm{S_2O_3}^{2-}]$ and then add the $[\mathrm{S_2O_3}^{2-}]$ "tied up" in the complex ion.

$$K_{\mathrm{f}} = 1.7\times10^{13} = \frac{\left[\left[\mathrm{Ag(S_2O_3)_2}\right]^{3-}\right]}{\left[\mathrm{Ag}^{+}\right]\left[\mathrm{S_2O_3}^{2-}\right]^{2}} = \frac{0.10\ \mathrm{M}}{1.8\times10^{-8}\ \mathrm{M}\left[\mathrm{S_2O_3}^{2-}\right]^{2}}$$

$$\left[\mathrm{S_2O_3}^{2-}\right] = \sqrt{\frac{0.10}{1.8\times10^{-8}\times1.7\times10^{13}}} = 5.7\times10^{-4}\,\mathrm{M} = \text{concentration of free } \mathrm{S_2O_3}^{2-}$$

$$\text{total } \left[\mathrm{S_2O_3}^{2-}\right] = 5.7\times10^{-4}\ \mathrm{M} + 0.10\,\mathrm{M}\left[\mathrm{Ag(S_2O_3)_2}\right]^{3-} \times \frac{2\,\mathrm{mol\ S_2O_3}^{2-}}{1\,\mathrm{mol}\left[\mathrm{Ag(S_2O_3)_2}\right]^{3-}}$$

$$= 0.20\ \mathrm{M} + 0.00057\,\mathrm{M} = 0.20\,\mathrm{M}$$

13A **(M)** We must combine the two equilibrium expressions, for K_{f} and for K_{sp}, to find K_{overall}.

$$\mathrm{Fe(OH)_3(s)} \rightleftharpoons \mathrm{Fe^{3+}(aq)} + 3\mathrm{OH^{-}(aq)} \qquad K_{\mathrm{sp}} = 4\times10^{-38}$$

$$\mathrm{Fe^{3+}(aq)} + 3\mathrm{C_2O_4}^{2-}\mathrm{(aq)} \rightleftharpoons \left[\mathrm{Fe(C_2O_4)_3}\right]^{3-}\mathrm{(aq)} \qquad K_{\mathrm{f}} = 2\times10^{20}$$

$$\mathrm{Fe(OH)_3(s)} + 3\mathrm{C_2O_4}^{2-}\mathrm{(aq)} \rightleftharpoons \left[\mathrm{Fe(C_2O_4)_3}\right]^{3-}\mathrm{(aq)} + 3\mathrm{OH^{-}(aq)} \qquad K_{\mathrm{overall}} = 8\times10^{-18}$$

Initial	0.100 M	0 M	$\approx 0\,\mathrm{M}$
Changes	$-3x\,\mathrm{M}$	$+x\,\mathrm{M}$	$+3x\,\mathrm{M}$
Equil	$(0.100-3x)\,\mathrm{M}$	x M	$3x\,\mathrm{M}$

$$K_{\mathrm{overall}} = \frac{\left[\left[\mathrm{Fe(C_2O_4)_3}\right]^{3-}\right]\left[\mathrm{OH}^{-}\right]^{3}}{\left[\mathrm{C_2O_4^{2-}}\right]^{3}} = \frac{(x)(3x)^{3}}{(0.100-3x)^{3}} = 8\times10^{-18} \approx \frac{27x^{4}}{(0.100)^{3}}$$

(3x << 0.100 M, thus the approximation was valid.)

$$x = \sqrt[4]{\frac{(0.100)^{3}8\times10^{-18}}{27}} = 4\times10^{-6}\,\mathrm{M} \text{ The assumption is valid.}$$

Thus the solubility of $\mathrm{Fe(OH)_3}$ in 0.100 M $\mathrm{C_2O_4}^{2-}$ is $4\times10^{-6}\,\mathrm{M}$.

13B **(M)** In Example 18-13 we saw that the expression for the solubility, s, of a silver halide in an aqueous ammonia solution, where $[\mathrm{NH_3}]$ is the concentration of aqueous ammonia, is given by:

$$K_{\mathrm{sp}} \times K_{\mathrm{f}} = \left(\frac{s}{[\mathrm{NH_3}] - 2s} \right)^2 \qquad or \qquad \sqrt{K_{\mathrm{sp}} \times K_{\mathrm{f}}} = \frac{s}{[\mathrm{NH_3}] - 2s}$$

For all scenarios, the $[\mathrm{NH_3}]$ stays fixed at $0.1000\ \mathrm{M}$ and K_{f} is always 1.6×10^7.
We see that s will decrease as does K_{sp}. The relevant values are:

$K_{\mathrm{sp}}(\mathrm{AgCl}) = 1.8 \times 10^{-10}$, $K_{\mathrm{sp}}(\mathrm{AgBr}) = 5.0 \times 10^{-13}$, $K_{\mathrm{sp}}(\mathrm{AgI}) = 8.5 \times 10^{-17}$.
Thus, the order of decreasing solubility must be: AgI > AgBr > AgCl.

14A **(M)** For FeS, we know that $K_{\mathrm{spa}} = 6 \times 10^2$; for $\mathrm{Ag_2S}, K_{\mathrm{spa}} = 6 \times 10^{-30}$.

We compute the value of Q_{spa} in each case, with $[\mathrm{H_2S}] = 0.10\,\mathrm{M}$ and $[\mathrm{H_3O^+}] = 0.30\,\mathrm{M}$.

$$\text{For FeS, } Q_{\mathrm{spa}} = \frac{0.020 \times 0.10}{(0.30)^2} = 0.022 < 6 \times 10^2 = K_{\mathrm{spa}}$$

Thus, precipitation of FeS should not occur.

$$\text{For } \mathrm{Ag_2S},\ Q_{\mathrm{spa}} = \frac{(0.010)^2 \times 0.10}{(0.30)^2} = 1.1 \times 10^{-4}$$

$Q_{\mathrm{spa}} > 6 \times 10^{-30} = K_{\mathrm{spa}}$; thus, precipitation of $\mathrm{Ag_2S}$ should occur.

14B **(M)** The $[\mathrm{H_3O^+}]$ needed to just form a precipitate can be obtained by direct substitution of the provided concentrations into the K_{spa} expression. When that expression is satisfied, a precipitate will just form.

$$K_{\mathrm{spa}} = \frac{[\mathrm{Fe^{2+}}][\mathrm{H_2S}]}{[\mathrm{H_3O^+}]^2} = 6 \times 10^2 = \frac{(0.015\,\mathrm{M\,Fe^{2+}})(0.10\,\mathrm{M\,H_2S})}{[\mathrm{H_3O^+}]^2},\ [\mathrm{H_3O^+}] = \sqrt{\frac{0.015 \times 0.10}{6 \times 10^2}} = 0.002\,\mathrm{M}$$

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(0.002) = 2.7$$

INTEGRATIVE EXAMPLES

A. **(D)** To determine the amount of $Ca(NO_3)_2$ needed, one has to calculate the amount of Ca^{2+} that will result in only 1.00×10^{-12} M of PO_4^{3-}

$$Ca_3(PO_4)_2 \rightleftharpoons 3\,Ca^{2+} + 2\,PO_4^{3-}$$

$$K_{sp} = (3s)^3(2s)^2$$

Using the common–ion effect, we will try to determine what concentration of Ca^{2+} ions forces the equilibrium in the lake to have only 1.00×10^{-12} M of phosphate, noting that (2s) is the equilibrium concentration of phosphate.

$$1.30\times10^{-32} = \left[Ca^{2+}\right]^3\left(1.00\times10^{-12}\right)^2$$

Solving for $[Ca^{2+}]$ yields a concentration of 0.00235 M.

The volume of the lake: $V = 300\text{ m} \times 150\text{ m} \times 5\text{ m} = 225000\text{ m}^3$ or 2.25×10^8 L.

Mass of $Ca(NO_3)_2$ is determined as follows:

$$\text{mass }Ca(NO_3)_2 = 2.25\times10^8\text{ L}\times\frac{0.00235\text{ mol }Ca^{2+}}{\text{L}}\times\frac{1\text{ mol }Ca(NO_3)_2}{1\text{ mol }Ca^{2+}}\times\frac{164.1\text{ g }Ca(NO_3)_2}{1\text{ mol }Ca(NO_3)_2}$$

$$= 87\times10^6\text{ g }Ca(NO_3)_2$$

B. **(M)** The reaction of $AgNO_3$ and Na_2SO_4 is as follows:

$$2AgNO_3 + Na_2SO_4 \rightarrow 2NaNO_3 + Ag_2SO_4$$

$$\text{mol }Ag_2SO_4 = (0.350\text{ L} \times 0.200\text{ M})\ AgNO_3 \times \frac{1\text{ mol }Ag_2SO_4}{2\text{ mol }AgNO_3} = 3.5\times10^{-2}\text{ mol}$$

$$\text{mol }NaNO_3 = (0.250\text{ L} \times 0.240\text{ M})\ Na_2SO_4 \times \frac{2\text{ mol }NaNO_3}{1\text{ mol }Na_2SO_4} = 0.12\text{ mol}$$

Ag_2SO_4 is the precipitate. Since it is also the limiting reagent, there are 3.5×10^{-2} moles of Ag_2SO_4 produced.

The reaction of Ag_2SO_4 with $Na_2S_2O_3$ is as follows:

$$Na_2S_2O_3 + Ag_2SO_4 \rightarrow Na_2SO_4 + Ag_2S_2O_3$$

$$\text{mol }Na_2S_2O_3 = (0.400\text{ L} \times 0.500\text{ M})\ Na_2S_2O_3 = 0.200\text{ mol}$$

Ag_2SO_4 is the limiting reagent, so no Ag_2SO_4 precipitate is left.

EXERCISES

K_{sp} and Solubility

1. **(E)**

(a) $Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq)$ $\quad K_{sp} = [Ag^+]^2[SO_4^{2-}]$

(b) $Ra(IO_3)_2(s) \rightleftharpoons Ra^{2+}(aq) + 2\,IO_3^-(aq)$ $\quad K_{sp} = [Ra^{2+}][IO_3^-]^2$

(c) $Ni_3(PO_4)_2(s) \rightleftharpoons 3\,Ni^{2+}(aq) + 2\,PO_4^{3-}(aq)$ $\quad K_{sp} = [Ni^{2+}]^3[PO_4^{3-}]^2$

(d) $PuO_2CO_3(s) \rightleftharpoons PuO_2^{2+}(aq) + CO_3^{2-}(aq)$ $\quad K_{sp} = [PuO_2^{2+}][CO_3^{2-}]$

2. **(E)**

(a) $K_{sp} = [Fe^{3+}][OH^-]^3$ $\quad Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$

(b) $K_{sp} = [BiO^+][OH^-]$ $\quad BiOOH(s) \rightleftharpoons BiO^+(aq) + OH^-(aq)$

(c) $K_{sp} = [Hg_2^{2+}][I^-]^2$ $\quad Hg_2I_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,I^-(aq)$

(d) $K_{sp} = [Pb^{2+}]^3[AsO_4^{3-}]^2$ $\quad Pb_3(AsO_4)_2(s) \rightleftharpoons 3\,Pb^{2+}(aq) + 2\,AsO_4^{3-}(aq)$

3. **(E)**

(a) $CrF_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\,F^-(aq)$ $\quad K_{sp} = [Cr^{3+}][F^-]^3 = 6.6 \times 10^{-11}$

(b) $Au_2(C_2O_4)_3(s) \rightleftharpoons 2\,Au^{3+}(aq) + 3\,C_2O_4^{2-}(aq)$ $\quad K_{sp} = [Au^{3+}]^2[C_2O_4^{2-}]^3 = 1 \times 10^{-10}$

(c) $Cd_3(PO_4)_2(s) \rightleftharpoons 3\,Cd^{2+}(aq) + 2\,PO_4^{3-}(aq)$ $\quad K_{sp} = [Cd^{2+}]^3[PO_4^{3-}]^2 = 2.1 \times 10^{-33}$

(d) $SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2\,F^-(aq)$ $\quad K_{sp} = [Sr^{2+}][F^-]^2 = 2.5 \times 10^{-9}$

4. **(E)** Let $s = \text{solubility}$ of each compound in moles of compound per liter of solution.

(a) $K_{sp} = [Ba^{2+}][CrO_4^{2-}] = (s)(s) = s^2 = 1.2 \times 10^{-10}$ $\quad s = 1.1 \times 10^{-5}\text{ M}$

(b) $K_{sp} = [Pb^{2+}][Br^-]^2 = (s)(2s)^2 = 4s^3 = 4.0 \times 10^{-5}$ $\quad s = 2.2 \times 10^{-2}\text{ M}$

(c) $K_{sp} = [Ce^{3+}][F^-]^3 = (s)(3s)^3 = 27s^4 = 8 \times 10^{-16}$ $\quad s = 7 \times 10^{-5}\text{ M}$

(d) $K_{sp} = [Mg^{2+}]^3[AsO_4^{3-}]^2 = (3s)^3(2s)^2 = 108s^5 = 2.1 \times 10^{-20}$ $\quad s = 4.5 \times 10^{-5}\text{ M}$

5. **(E)** We use the value of K_{sp} for each compound in determining the molar solubility in a saturated solution. In each case, s represents the molar solubility of the compound.

AgCN $\quad K_{sp} = \left[\text{Ag}^+\right]\left[\text{CN}^-\right] = (s)(s) = s^2 = 1.2\times10^{-16} \quad s = 1.1\times10^{-8}\,\text{M}$

$\text{AgIO}_3 \quad K_{sp} = \left[\text{Ag}^+\right]\left[\text{IO}_3^{\ -}\right] = (s)(s) = s^2 = 3.0\times10^{-8} \quad s = 1.7\times10^{-4}\,\text{M}$

AgI $\quad K_{sp} = \left[\text{Ag}^+\right]\left[\text{I}^-\right] = (s)(s) = s^2 = 8.5\times10^{-17} \quad s = 9.2\times10^{-9}\,\text{M}$

$\text{AgNO}_2 \quad K_{sp} = \left[\text{Ag}^+\right]\left[\text{NO}_2^{\ -}\right] = (s)(s) = s^2 = 6.0\times10^{-4} \quad s = 2.4\times10^{-2}\,\text{M}$

$\text{Ag}_2\text{SO}_4 \quad K_{sp} = \left[\text{Ag}^+\right]^2\left[\text{SO}_4^{2-}\right] = (2s)^2(s) = 4s^3 = 1.4\times10^{-5} \quad s = 1.5\times10^{-2}\,\text{M}$

Thus, in order of increasing molar solubility, from smallest to largest:

$\text{AgI} < \text{AgCN} < \text{AgIO}_3 < \text{Ag}_2\text{SO}_4 < \text{AgNO}_2$

6. **(E)** We use the value of K_{sp} for each compound in determining $\left[\text{Mg}^{2+}\right]$ in its saturated solution. In each case, s represents the molar solubility of the compound.

(a) $\text{MgCO}_3 \quad K_{sp} = \left[\text{Mg}^{2+}\right]\left[\text{CO}_3^{\ 2-}\right] = (s)(s) = s^2 = 3.5\times10^{-8}$

$s = 1.9\times10^{-4}\,\text{M} \qquad \left[\text{Mg}^{2+}\right] = 1.9\times10^{-4}\,\text{M}$

(b) $\text{MgF}_2 \quad K_{sp} = \left[\text{Mg}^{2+}\right]\left[\text{F}^-\right]^2 = (s)(2s)^2 = 4s^3 = 3.7\times10^{-8}$

$s = 2.1\times10^{-3}\,\text{M} \qquad \left[\text{Mg}^{2+}\right] = 2.1\times10^{-3}\,\text{M}$

(c) $\text{Mg}_3(\text{PO}_4)_2 \quad K_{sp} = \left[\text{Mg}^{2+}\right]^3\left[\text{PO}_4^{\ 3-}\right]^2 = (3s)^3(2s)^2 = 108s^5 = 2.1\times10^{-25}$

$s = 4.5\times10^{-6}\,\text{M} \qquad \left[\text{Mg}^{2+}\right] = 1.4\times10^{-5}\ \text{M}$

Thus a saturated solution of MgF_2 has the highest $\left[\text{Mg}^{2+}\right]$.

7. **(M)** We determine $\left[\text{F}^-\right]$ in saturated CaF_2, and from that value the concentration of F^- in ppm.

For $\text{CaF}_2 \quad K_{sp} = \left[\text{Ca}^{2+}\right]\left[\text{F}^-\right]^2 = (s)(2s)^2 = 4s^3 = 5.3\times10^{-9} \qquad s = 1.1\times10^{-3}\,\text{M}$

The solubility in ppm is the number of grams of CaF_2 in 10^6 g of solution. We assume a solution density of 1.00 g/mL.

$$\text{mass of F}^- = 10^6\,\text{g soln}\times\frac{1\,\text{mL}}{1.00\,\text{g soln}}\times\frac{1\,\text{L soln}}{1000\,\text{mL}}\times\frac{1.1\times10^{-3}\,\text{mol CaF}_2}{1\,\text{L soln}}$$
$$\times\frac{2\,\text{mol F}^-}{1\,\text{mol CaF}_2}\times\frac{19.0\,\text{g F}^-}{1\,\text{mol F}^-} = 42\,\text{g F}^-$$

This is 42 times more concentrated than the optimum concentration of fluoride ion for fluoridation. CaF_2 is, in fact, more soluble than is necessary. Its uncontrolled use might lead to excessive F^- in solution.

8. **(E)** We determine $\left[OH^-\right]$ in a saturated solution. From this $\left[OH^-\right]$ we determine the pH.

$K_{sp} = \left[BiO^+\right]\left[OH^-\right] = 4\times10^{-10} = s^2$ $\qquad s = 2\times10^{-5}\,M = \left[OH^-\right] = \left[BiO^+\right]$

$pOH = -\log\left(2\times10^{-5}\right) = 4.7$ $\qquad pH = 9.3$

9. **(M)** We first assume that the volume of the solution does not change appreciably when its temperature is lowered. Then we determine the mass of $Mg\left(C_{16}H_{31}O_2\right)_2$ dissolved in each solution, recognizing that the molar solubility of $Mg\left(C_{16}H_{31}O_2\right)_2$ equals the cube root of one fourth of its solubility product constant, since it is the only solute in the solution.

$K_{sp} = 4s^3$ $\qquad s = \sqrt[3]{K_{sp}/4}$

At $50^\circ C$: $s = \sqrt[3]{4.8\times10^{-12}/4} = 1.1\times10^{-4}$ M; At $25^\circ C$: $s = \sqrt[3]{3.3\times10^{-12}/4} = 9.4\times10^{-5}$ M

$$\text{amount of } Mg\left(C_{16}H_{31}O_2\right)_2\,(50^\circ C) = 0.965\,L\times\frac{1.1\times10^{-4}\,mol\ Mg\left(C_{16}H_{31}O_2\right)_2}{1\,L\ soln} = 1.1\times10^{-4}\,mol$$

$$\text{amount of } Mg\left(C_{16}H_{31}O_2\right)_2\,(25^\circ C) = 0.965\,L\times\frac{9.4\times10^{-5}\,mol\ Mg\left(C_{16}H_{31}O_2\right)_2}{1\,L\ soln} = 0.91\times10^{-4}\,mol$$

mass of $Mg\left(C_{16}H_{31}O_2\right)_2$ precipitated:

$$= \left(1.1-0.91\right)\times10^{-4}\,mol\times\frac{535.15\,g\ Mg\left(C_{16}H_{31}O_2\right)_2}{1\,mol\ Mg\left(C_{16}H_{31}O_2\right)_2}\times\frac{1000\,mg}{1\,g} = 11\,mg$$

10. **(M)** We first assume that the volume of the solution does not change appreciably when its temperature is lowered. Then we determine the mass of CaC_2O_4 dissolved in each solution, recognizing that the molar solubility of CaC_2O_4 equals the square root of its solubility product constant, since it is the only solute in the solution.

At $95^\circ C$ $\quad s = \sqrt{1.2\times10^{-8}} = 1.1\times10^{-4}$ M; At $13^\circ C$: $\quad s = \sqrt{2.7\times10^{-9}} = 5.2\times10^{-5}$ M

$$\text{mass of } CaC_2O_4\,(95\ ^\circ C) = 0.725\ L\times\frac{1.1\times10^{-4}\ mol\ CaC_2O_4}{1\ L\ soln}\times\frac{128.1\,g\ CaC_2O_4}{1\ mol\ CaC_2O_4} = 0.010\,g\ CaC_2O_4$$

$$\text{mass of } CaC_2O_4\,(13\ ^\circ C) = 0.725\ L\times\frac{5.2\times10^{-5}\,mol\ \ PbSO_4}{1\ L\ soln}\times\frac{128.1\,g\ CaC_2O_4}{1\,mol\ CaC_2O_4} = 0.0048\,g\ CaC_2O_4$$

$$\text{mass of } CaC_2O_4 \text{ precipitated} = \left(0.010\ g-0.0048\ g\right)\times\frac{1000\ mg}{1\,g} = 5.2\,mg$$

11. **(M)** First we determine $\left[\text{I}^-\right]$ in the saturated solution.

$$K_{\text{sp}} = \left[\text{Pb}^{2+}\right]\left[\text{I}^-\right]^2 = 7.1\times10^{-9} = (s)(2s)^2 = 4s^3 \qquad s = 1.2\times10^{-3}\,\text{M}$$

The AgNO_3 reacts with the I^- in this saturated solution in the titration.

$\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI(s)}$ We determine the amount of Ag^+ needed for this titration, and then $\left[\text{AgNO}_3\right]$ in the titrant.

$$\text{moles Ag}^+ = 0.02500\,\text{L}\times\frac{1.2\times10^{-3}\,\text{mol PbI}_2}{1\,\text{L soln}}\times\frac{2\,\text{mol I}^-}{1\,\text{mol PbI}_2}\times\frac{1\,\text{mol Ag}^+}{1\,\text{mol I}^-} = 6.0\times10^{-5}\,\text{mol Ag}^+$$

$$\text{AgNO}_3\ \text{molarity} = \frac{6.0\times10^{-5}\,\text{mol Ag}^+}{0.0133\,\text{L soln}}\times\frac{1\,\text{mol AgNO}_3}{1\,\text{mol Ag}^+} = 4.5\times10^{-3}\,\text{M}$$

12. **(M)** We first determine $\left[\text{C}_2\text{O}_4{}^{2-}\right] = s,$ the solubility of the saturated solution.

$$\left[\text{C}_2\text{O}_4{}^{2-}\right] = \frac{4.8\,\text{mL}\times\dfrac{0.00134\,\text{mmol KMnO}_4}{1\ \text{mL soln}}\times\dfrac{5\ \text{mmol C}_2\text{O}_4{}^{2-}}{2\ \text{mmol MnO}_4{}^-}}{250.0\,\text{mL}} = 6.4\times10^{-5}\ \text{M} = s = \left[\text{Ca}^{2+}\right]$$

$$K_{\text{sp}} = \left[\text{Ca}^{2+}\right]\left[\text{C}_2\text{O}_4{}^{2-}\right] = (s)(s) = s^2 = \left(6.4\times10^{-5}\right)^2 = 4.1\times10^{-9}$$

13. **(M)** We first use the ideal gas law to determine the moles of H_2S gas used.

$$n = \frac{PV}{RT} = \frac{\left(748\ \text{mmHg}\times\dfrac{1\,\text{atm}}{760\ \text{mmHg}}\right)\times\left(30.4\ \text{mL}\times\dfrac{1\ \text{L}}{1000\ \text{mL}}\right)}{0.08206\ \text{L atm mol}^{-1}\,\text{K}^{-1}\times(23+273)\,\text{K}} = 1.23\times10^{-3}\ \text{moles}$$

If we assume that all the H_2S is consumed in forming Ag_2S, we can compute the $\left[\text{Ag}^+\right]$ in the AgBrO_3 solution. This assumption is valid if the equilibrium constant for the cited reaction is large, which is the case, as shown below:

$$2\text{Ag}^+(\text{aq}) + \text{HS}^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Ag}_2\text{S(s)} + \text{H}_2\text{O(l)} \qquad K_{\text{a}_2}/K_{\text{sp}} = \frac{1.0\times10^{-19}}{2.6\times10^{-51}} = 3.8\times10^{31}$$

$$\text{H}_2\text{S(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HS}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \qquad K_1 = 1.0\times10^{-7}$$

$$2\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \qquad K_{\text{w}} = 1.0\times10^{-14}$$

$$2\text{Ag}^+(\text{aq}) + \text{H}_2\text{S(aq)} + 2\text{H}_2\text{O(l)} \rightleftharpoons \text{Ag}_2\text{S(s)} + 2\text{H}_3\text{O}^+(\text{aq})$$

$$K_{\text{overall}} = (K_{\text{a}_2}/K_{\text{sp}})(K_1)(K_{\text{w}}) = (3.8\times10^{31})(1.0\times10^{-7})(1.0\times10^{-14}) = 3.8\times10^{10}$$

$$\left[\text{Ag}^+\right] = \frac{1.23\times10^{-3}\,\text{mol H}_2\text{S}}{338\ \text{mL soln}}\times\frac{1000\ \text{mL}}{1\ \text{L soln}}\times\frac{2\ \text{mol Ag}^+}{1\ \text{mol H}_2\text{S}} = 7.28\times10^{-3}\,\text{M}$$

Then, for AgBrO_3, $K_{\text{sp}} = \left[\text{Ag}^+\right]\left[\text{BrO}_3{}^-\right] = \left(7.28\times10^{-3}\right)^2 = 5.30\times10^{-5}$

14. **(M)** The titration reaction is $Ca(OH)_2(aq) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$

$$[OH^-] = \frac{10.7\ \text{mL HCl} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{0.1032\ \text{mol HCl}}{1\ \text{L}} \times \frac{1\ \text{mol OH}^-}{1\ \text{mol HCl}}}{50.00\ \text{mL Ca(OH)}_2\ \text{soln} \times \frac{1\ \text{L}}{1000\ \text{mL}}} = 0.0221\ \text{M}$$

In a saturated solution of $Ca(OH)_2$, $[Ca^{2+}] = [OH^-] \div 2$

$K_{sp} = [Ca^{2+}][OH^-]^2 = (0.0221 \div 2)(0.0221)^2 = 5.40 \times 10^{-6}$ (5.5×10^{-6} in Appendix D).

The Common-Ion Effect

15. **(E)** We let s = molar solubility of $Mg(OH)_2$ in moles solute per liter of solution.

(a) $K_{sp} = [Mg^{2+}][OH^-]^2 = (s)(2s)^2 = 4s^3 = 1.8 \times 10^{-11}$ $\qquad s = 1.7 \times 10^{-4}\ \text{M}$

(b)

Equation:	$Mg(OH)_2(s)$	$\rightleftharpoons$ $Mg^{2+}(aq)$	+	$2OH^-(aq)$
Initial:	–	$0.0862\ \text{M}$		$\approx 0\ \text{M}$
Changes:	–	$+s\ \text{M}$		$+2s\ \text{M}$
Equil:	–	$(0.0862 + s)\ \text{M}$		$2s\ \text{M}$

$K_{sp} = (0.0862 + s) \times (2s)^2 = 1.8 \times 10^{-11} \approx (0.0862) \times (2s)^2 = 0.34s^2$ $\quad s = 7.3 \times 10^{-6}\ \text{M}$

(s << 0.0802 M, thus, the approximation was valid.)

(c) $[OH^-] = [KOH] = 0.0355\ \text{M}$

Equation:	$Mg(OH)_2(s)$	$\rightleftharpoons$ $Mg^{2+}(aq)$	+	$2OH^-(aq)$
Initial:	–	$0\ \text{M}$		$0.0355\ \text{M}$
Changes:	–	$+s\ \text{M}$		$+2s\ \text{M}$
Equil:	–	$s\ \text{M}$		$(0.0355 + 2s)\ \text{M}$

$K_{sp} = (s)(0.0355 + 2s)^2 = 1.8 \times 10^{-11} \approx (s)(0.0355)^2 = 0.0013s$ $\qquad s = 1.4 \times 10^{-8}\ \text{M}$

16. **(E)** The solubility equilibrium is $\qquad CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

(a) The addition of $Na_2CO_3(aq)$ produces $CO_3^{2-}(aq)$ in solution. This common ion suppresses the dissolution of $CaCO_3(s)$.

(b) HCl(aq) is a strong acid that reacts with carbonate ion:
$CO_3^{2-}(aq) + 2H_3O^+(aq) \rightarrow CO_2(g) + 3H_2O(l)$.

This decreases $[CO_3^{2-}]$ in the solution, allowing more $CaCO_3(s)$ to dissolve.

(c) $HSO_4^-(aq)$ is a moderately weak acid. It is strong enough to protonate appreciable concentrations of carbonate ion, thereby decreasing $[CO_3^{2-}]$ and enhancing the solubility of $CaCO_3(s)$, as the value of K_c indicates.

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$

$$K_c = \frac{K_a(HSO_4^-)}{K_a(HCO_3^-)} = \frac{0.011}{4.7\times10^{-11}} = 2.3\times10^{8}$$

<u>17.</u> **(E)** The presence of KI in a solution produces a significant $[I^-]$ in the solution. Not as much AgI can dissolve in such a solution as in pure water, since the ion product, $[Ag^+][I^-]$, cannot exceed the value of K_{sp} (i.e., the I^- from the KI that dissolves represses the dissociation of AgI(s). In similar fashion, $AgNO_3$ produces a significant $[Ag^+]$ in solution, again influencing the value of the ion product; not as much AgI can dissolve as in pure water.

18. **(E)** If the solution contains KNO_3, more AgI will end up dissolving than in pure water, because the activity of each ion will be less than its molarity. On an ionic level, the reason is that ion pairs, such as $Ag^+NO_3^-$ (aq) and K^+I^- (aq) form in the solution, preventing Ag^+ and I^- ions from coming together and precipitating.

<u>19.</u> **(E)**

Equation:	$Ag_2SO_4(s)$	$\rightleftharpoons$	$2Ag^+(aq)$	+	$SO_4^{2-}(aq)$
Original:	—		0 M		0.150 M
Add solid:	—		$+2x$ M		$+x$ M
Equil:	—		$2x$ M		$(0.150+x)$ M

$$2x = [Ag^+] = 9.7\times10^{-3}\,M; \quad x = 0.0048\underline{5}\,M$$

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2x)^2(0.150+x) = (9.7\times10^{-3})^2(0.150+0.0048\underline{5}) = 1.5\times10^{-5}$$

20. **(M)**

Equation:	$CaSO_4(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$SO_4^{2-}(aq)$.
Soln:	—		0 M		0.0025 M
Add $CaSO_4(s)$	—		$+x$ M		$+x$ M
Equil:	—		x M		$(0.0025+x)$ M

If we use the approximation that $x << 0.0025$, we find $x = 0.0036$. Clearly, x is larger than 0.0025 and thus the approximation is <u>not</u> valid. The quadratic equation must be solved.

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 9.1\times10^{-6} = x(0.0025+x) = 0.0025x + x^2$$

$$x^2 + 0.0025x - 9.1\times10^{-6} = 0$$

$$x=\frac{-b\pm\sqrt{b^2-4ac}}{2a}=\frac{-0.0025\pm\sqrt{6.3\times10^{-6}+3.6\times10^{-5}}}{2}=2.0\times10^{-3}\,\text{M}=\left[\text{CaSO}_4\right]$$

$$\text{mass CaSO}_4=0.1000\,\text{L}\times\frac{2.0\times10^{-3}\text{ mol CaSO}_4}{1\text{ L soln}}\times\frac{136.1\text{ g CaSO}_4}{1\text{ mol CaSO}_4}=0.027\text{ g CaSO}_4$$

21. **(M)** For $\text{PbI}_2, K_{\text{sp}}=7.1\times10^{-9}=\left[\text{Pb}^{2+}\right]\left[\text{I}^-\right]^2$

In a solution where 1.5×10^{-4} mol PbI_2 is dissolved, $\left[\text{Pb}^{2+}\right]=1.5\times10^{-4}$ M, and $\left[\text{I}^-\right]=2\left[\text{Pb}^{2+}\right]=3.0\times10^{-4}$ M

Equation:	$\text{PbI}_2(\text{s})$ $\rightleftharpoons$	$\text{Pb}^{2+}(\text{aq})$ +	$2\text{I}^-(\text{aq})$
Initial:	—	1.5×10^{-4} M	3.0×10^{-4} M
Add lead(II):	—	$+x$ M	
Equil:	—	$(0.00015+x)$ M	0.00030 M

$K_{\text{sp}}=7.1\times10^{-9}=(0.00015+x)(0.00030)^2;(0.00015+x)=0.079;x=0.079\text{ M}=\left[\text{Pb}^{2+}\right]$

22. **(M)** For $\text{PbI}_2, K_{\text{sp}}=7.1\times10^{-9}=\left[\text{Pb}^{2+}\right]\left[\text{I}^-\right]^2$

In a solution where 1.5×10^{-5} mol PbI_2/L is dissolved, $\left[\text{Pb}^{2+}\right]=1.5\times10^{-5}$ M, and $\left[\text{I}^-\right]=2\left[\text{Pb}^{2+}\right]=3.0\times10^{-5}$ M

Equation:	$\text{PbI}_2(\text{s})$ $\rightleftharpoons$	$\text{Pb}^{2+}(\text{aq})$ +	$2\text{I}^-(\text{aq})$
Initial:	—	1.5×10^{-5} M	3.0×10^{-5} M
Add KI:	—		$+x$ M
Equil:	—	1.5×10^{-5} M	$(3.0\times10^{-5}+x)$ M

$K_{\text{sp}}=7.1\times10^{-9}=(1.5\times10^{-5})\times(3.0\times10^{-5}+x)^2$
$(3.0\times10^{-5}+x)=(7.1\times10^{-9}\div1.5\times10^{-5})^{1/2}$
$x=(2.2\times10^{-2})-(3.0\times10^{-5})=2.1\times10^{-2}\text{ M}=[\text{I}^-]$

23. **(D)** For Ag_2CrO_4, $K_{\text{sp}}=1.1\times10^{-12}=\left[\text{Ag}^+\right]^2\left[\text{CrO}_4^{\;2-}\right]$

In a 5.0×10^{-8} M solution of Ag_2CrO_4, $\left[\text{CrO}_4^{\;2-}\right]=5.0\times10^{-8}$ M and $\left[\text{Ag}^+\right]=1.0\times10^{-7}$ M

Equation:	$\text{Ag}_2\text{CrO}_4(\text{s})$ $\rightleftharpoons$	$2\text{Ag}^+(\text{aq})$ +	$\text{CrO}_4^{\;2-}(\text{aq})$
Initial:	—	1.0×10^{-7} M	5.0×10^{-8} M
Add chromate:	—		$+x$ M
Equil:	—	1.0×10^{-7} M	$(5.0\times10^{-8}+x)$M

$K_{\text{sp}}=1.1\times10^{-12}=(1.0\times10^{-7})^2(5.0\times10^{-8}+x);\quad(5.0\times10^{-8}+x)=1.1\times10^2=\left[\text{CrO}_4^{\;2-}\right].$

This is an impossibly high concentration to reach. Thus, we cannot lower the solubility of Ag_2CrO_4 to 5.0×10^{-8} M with CrO_4^{2-} as the common ion. Let's consider using Ag^+ as the common ion.

Equation:	$Ag_2CrO_4(s)$	$\rightleftharpoons$	$2Ag^+(aq)$	+	$CrO_4^{2-}(aq)$
Initial:	—		1.0×10^{-7} M		5.0×10^{-8} M
Add silver(I) ion:	—		$+x$ M		
Equil:	—		$\left(1.0\times10^{-7}+x\right)$ M		5.0×10^{-8} M

$$K_{sp} = 1.1\times10^{-12} = \left(1.0+x\right)^2\left(5.0\times10^{-8}\right) \qquad \left(1.0\times10^{-7}+x\right) = \sqrt{\frac{1.1\times10^{-12}}{5.0\times10^{-8}}} = 4.7\times10^{-3}$$

$x = 4.7\times10^{-3} - 1.0\times10^{-7} = 4.7\times10^{-3}\,\text{M} = \left[I^-\right]$; this is an easy-to-reach concentration. Thus, the solubility can be lowered to 5.0×10^{-8} M by carefully adding Ag^+(aq).

24. **(M)** Even though $BaCO_3$ is more soluble than $BaSO_4$, it will still precipitate when 0.50 M $Na_2CO_3(aq)$ is added to a saturated solution of $BaSO_4$ because there is a sufficient $\left[Ba^{2+}\right]$ in such a solution for the ion product $\left[Ba^{2+}\right]\left[CO_3^{2-}\right]$ to exceed the value of K_{sp} for the compound. An example will demonstrate this phenomenon. Let us assume that the two solutions being mixed are of equal volume and, to make the situation even more unfavorable, that the saturated $BaSO_4$ solution is not in contact with solid $BaSO_4$, meaning that it does not maintain its saturation when it is diluted. First we determine $\left[Ba^{2+}\right]$ in saturated $BaSO_4(aq)$.

$$K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right] = 1.1\times10^{-10} = s^2 \qquad s = \sqrt{1.1\times10^{-10}} = 1.0\times10^{-5}\ \text{M}$$

Mixing solutions of equal volumes means that the concentrations of solutes not common to the two solutions are halved by dilution.

$$\left[Ba^{2+}\right] = \frac{1}{2}\times\frac{1.0\times10^{-5}\,\text{mol BaSO}_4}{1\ \text{L}}\times\frac{1\ \text{mol Ba}^{2+}}{1\ \text{mol BaSO}_4} = 5.0\times10^{-6}\ \text{M}$$

$$\left[CO_3^{2-}\right] = \frac{1}{2}\times\frac{0.50\ \text{mol Na}_2\text{CO}_3}{1\ \text{L}}\times\frac{1\ \text{mol CO}_3^{2-}}{1\ \text{mol Na}_2\text{CO}_3} = 0.25\ \text{M}$$

$$Q_{sp}\{BaCO_3\} = \left[Ba^{2+}\right]\left[CO_3^{2-}\right] = \left(5.0\times10^{-6}\right)\left(0.25\right) = 1.3\times10^{-6} > 5.0\times10^{-9} = K_{sp}\{BaCO_3\}$$

Thus, precipitation of $BaCO_3$ indeed should occur under the conditions described.

25. **(E)** $\left[Ca^{2+}\right] = \dfrac{115\,\text{g Ca}^{2+}}{10^6\,\text{g soln}}\times\dfrac{1\ \text{mol Ca}^{2+}}{40.08\ \text{g Ca}^{2+}}\times\dfrac{1000\ \text{g soln}}{1\ \text{L soln}} = 2.87\times10^{-3}\ \text{M}$

$$\left[Ca^{2+}\right]\left[F^-\right]^2 = K_{sp} = 5.3\times10^{-9} = \left(2.87\times10^{-3}\right)\left[F^-\right]^2 \qquad \left[F^-\right] = 1.4\times10^{-3}\ \text{M}$$

$$\text{ppm F}^- = \frac{1.4\times10^{-3}\,\text{mol F}^-}{1\ \text{L soln}}\times\frac{19.00\,\text{g F}^-}{1\ \text{mol F}^-}\times\frac{1\ \text{L soln}}{1000\ \text{g}}\times10^6\,\text{g soln} = 27\ \text{ppm}$$

26. **(M)** We first calculate the $\left[\text{Ag}^+\right]$ and the $\left[\text{Cl}^-\right]$ in the saturated solution.

$K_{\text{sp}} = \left[\text{Ag}^+\right]\left[\text{Cl}^-\right] = 1.8\times10^{-10} = (s)(s) = s^2 \qquad s = 1.3\times10^{-5}\,\text{M} = \left[\text{Ag}^+\right] = \left[\text{Cl}^-\right]$

Both of these concentrations are marginally diluted by the addition of 1 mL of NaCl(aq)

$$\left[\text{Ag}^+\right] = \left[\text{Cl}^-\right] = 1.3\times10^{-5}\,\text{M}\times\frac{100.0\text{ mL}}{100.0\text{ mL}+1.0\text{ mL}} = 1.3\times10^{-5}\,\text{M}$$

The $\left[\text{Cl}^-\right]$ in the NaCl(aq) also is diluted. $\left[\text{Cl}^-\right] = 1.0\text{ M}\times\frac{1.0\text{ mL}}{100.0\text{ mL}+1.0\text{ mL}} = 9.9\times10^{-3}\text{ M}$

Let us use this $\left[\text{Cl}^-\right]$ to determine the $\left[\text{Ag}^+\right]$ that can exist in this solution.

$$\left[\text{Ag}^+\right]\left[\text{Cl}^-\right] = 1.8\times10^{-10} = \left[\text{Ag}^+\right]\left(9.9\times10^{-3}\text{ M}\right) \qquad \left[\text{Ag}^+\right] = \frac{1.8\times10^{-10}}{9.9\times10^{-3}} = 1.8\times10^{-8}\text{ M}$$

We compute the amount of AgCl in this final solution, and in the initial solution.

$$\text{mmol AgCl final} = 101.0\text{ mL}\times\frac{1.8\times10^{-8}\text{mol Ag}^+}{1\text{ L soln}}\times\frac{1\text{ mmol AgCl}}{1\text{ mmol Ag}^+} = 1.8\times10^{-6}\text{mmol AgCl}$$

$$\text{mmol AgCl initial} = 100.0\text{ mL}\times\frac{1.3\times10^{-5}\text{mol Ag}^+}{1\text{ L soln}}\times\frac{1\text{ mmol AgCl}}{1\text{ mmol Ag}^+} = 1.3\times10^{-3}\text{mmol AgCl}$$

The difference between these two amounts is the amount of AgCl that precipitates. Next we compute its mass.

$$\text{mass AgCl} = \left(1.3\times10^{-3} - 1.8\times10^{-6}\right)\text{ mmol AgCl}\times\frac{143.3\text{ mg AgCl}}{1\text{ mmol AgCl}} = 0.19\text{ mg}$$

We conclude that the precipitate will not be visible to the unaided eye, since its mass is less than 1 mg.

Criteria for Precipitation from Solution

27. **(E)** We first determine $\left[\text{Mg}^{2+}\right]$, and then the value of Q_{sp} in order to compare it to the value of K_{sp}. We express molarity in millimoles per milliliter, entirely equivalent to moles per liter.

$$[\text{Mg}^{2+}] = \frac{22.5\,\text{mg MgCl}_2}{325\,\text{mL soln}}\times\frac{1\text{mmol MgCl}_2\cdot6\text{H}_2\text{O}}{203.3\,\text{mg MgCl}_2\cdot6\text{H}_2\text{O}}\times\frac{1\text{mmol Mg}^{2+}}{1\text{mmol MgCl}_2} = 3.41\times10^{-4}\text{ M}$$

$$Q_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^-]^2 = (3.41\times10^{-4})(0.035)^2 = 4.2\times10^{-7} > 3.7\times10^{-8} = K_{\text{sp}}$$

Thus, precipitation of $\text{MgF}_2(\text{s})$ should occur from this solution.

28. **(E)** The solutions mutually dilute each other.

$$\left[\text{Cl}^-\right] = 0.016\text{ M}\times\frac{155\text{ mL}}{155\text{ mL}+245\text{ mL}} = 6.2\times10^{-3}\text{ M}$$

$$\left[\text{Pb}^{2+}\right] = 0.175\text{ M}\times\frac{245\text{ mL}}{245\text{ mL}+155\text{ mL}} = 0.107\text{ M}$$

Then we compute the value of the ion product and compare it to the solubility product constant value.

$$Q_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2 = (0.107)\left(6.2\times10^{-3}\right)^2 = 4.1\times10^{-6} < 1.6\times10^{-5} = K_{sp}$$

Thus, precipitation of $PbCl_2(s)$ will not occur from these mixed solutions.

29. **(E)** We determine the $\left[OH^-\right]$ needed to just initiate precipitation of $Cd(OH)_2$.

$$K_{sp} = \left[Cd^{2+}\right]\left[OH^-\right]^2 = 2.5\times10^{-14} = (0.0055\text{M})\left[OH^-\right]^2 \qquad \left[OH^-\right] = \sqrt{\frac{2.5\times10^{-14}}{0.0055}} = 2.1\times10^{-6}\text{M}$$

$$\text{pOH} = -\log\left(2.1\times10^{-6}\right) = 5.68 \qquad \text{pH} = 14.00 - 5.68 = 8.32$$

Thus, $Cd(OH)_2$ will precipitate from a solution with $\text{pH} > 8.32$.

30. **(E)** We determine the $\left[OH^-\right]$ needed to just initiate precipitation of $Cr(OH)_3$.

$$K_{sp} = [Cr^{3+}][OH^-]^3 = 6.3\times10^{-31} = (0.086\text{ M})\,[OH^-]^3;\ [OH^-] = \sqrt[3]{\frac{6.3\times10^{-31}}{0.086}} = 1.9\times10^{-10}\text{ M}$$

$$\text{pOH} = -\log\left(1.9\times10^{-10}\right) = 9.72 \qquad \text{pH} = 14.00 - 9.72 = 4.28$$

Thus, $Cr(OH)_3$ will precipitate from a solution with pH > 4.28.

31. **(D)**

(a) First we determine $\left[Cl^-\right]$ due to the added NaCl.

$$\left[Cl^-\right] = \frac{0.10\text{ mg NaCl}}{1.0\text{ L soln}}\times\frac{1\text{ g}}{1000\text{ mg}}\times\frac{1\text{ mol NaCl}}{58.4\text{ g NaCl}}\times\frac{1\text{ mol Cl}^-}{1\text{ mol NaCl}} = 1.7\times10^{-6}\text{ M}$$

Then we determine the value of the ion product and compare it to the solubility product constant value.

$$Q_{sp} = \left[Ag^+\right]\left[Cl^-\right] = (0.10)\left(1.7\times10^{-6}\right) = 1.7\times10^{-7} > 1.8\times10^{-10} = K_{sp} \text{ for AgCl}$$

Thus, precipitation of AgCl(s) should occur.

(b) The KBr(aq) is diluted on mixing, but the $\left[Ag^+\right]$ and $\left[Cl^-\right]$ are barely affected by dilution.

$$\left[Br^-\right] = 0.10\text{ M}\times\frac{0.05\text{ mL}}{0.05\text{ mL} + 250\text{ mL}} = 2\times10^{-5}\text{M}$$

Now we determine $\left[Ag^+\right]$ in a saturated AgCl solution.

$$K_{sp} = \left[Ag^+\right]\left[Cl^-\right] = (s)(s) = s^2 = 1.8\times10^{-10} \qquad s = 1.3\times10^{-5}\text{M}$$

Then we determine the value of the ion product for AgBr and compare it to the solubility product constant value.

$$Q_{sp} = [Ag^+][Br] = (1.3\times10^{-5})(2\times10^{-5}) = 3\times10^{-10} > 5.0\times10^{-13} = K_{sp} \text{ for AgBr}$$

Thus, precipitation of AgBr(s) should occur.

(c) The hydroxide ion is diluted by mixing the two solutions.

$$[OH^-] = 0.0150 \text{ M}\times\frac{0.05 \text{ mL}}{0.05 \text{ mL}+3000 \text{ mL}} = 2.5\times10^{-7}\text{M}$$

But the $[Mg^{2+}]$ does not change significantly.

$$[Mg^{2+}] = \frac{2.0 \text{ mg } Mg^{2+}}{1.0 \text{ L soln}}\times\frac{1 \text{ g}}{1000 \text{ mg}}\times\frac{1 \text{ mol } Mg^{2+}}{24.3 \text{ g Mg}} = 8.2\times10^{-5} \text{ M}$$

Then we determine the value of the ion product and compare it to the solubility product constant value.

$$Q_{sp} = [Mg^{2+}][OH^-]^2 = (2.5\times10^{-7})^2(8.2\times10^{-5}) = 5.1\times10^{-18}$$

$Q_{sp} < 1.8\times10^{-11} = K_{sp}$ for $Mg(OH)_2$ Thus, no precipitate forms.

32. First we determine the moles of H_2 produced during the electrolysis, then determine [OH^-].

$$\text{moles } H_2 = \frac{PV}{RT} = \frac{752 \text{ mmHg}\times\frac{1 \text{ atm}}{760 \text{ mmHg}}\times0.652 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}\times295 \text{ K}} = 0.0267 \text{ mol } H_2$$

$$[OH^-] = \frac{0.0267 \text{ mol } H_2\times\frac{2 \text{ mol } OH^-}{1 \text{ mol } H_2}}{0.315 \text{ L sample}} = 0.170 \text{ M}$$

$$Q_{sp} = [Mg^{2+}][OH^-]^2 = (0.185)(0.170)^2 = 5.35\times10^{-3} > 1.8\times10^{-11} = K_{sp}$$

Thus, yes, precipitation of $Mg(OH)_2(s)$ should occur during the electrolysis.

33. **(D)** First we must calculate the initial [$H_2C_2O_4$] upon dissolution of the solid acid:

$$[H_2C_2O_4]_{\text{initial}} = 1.50 \text{ g } H_2C_2O_4\times\frac{1 \text{ mol } H_2C_2O_4}{90.036 \text{ g } H_2C_2O_4}\times\frac{1}{0.200 \text{ L}} = 0.0833 \text{ M}$$

(We assume the volume of the solution stays at 0.200 L.)
Next we need to determine the [$C_2O_4^{2-}$] in solution after the hydrolysis reaction between oxalic acid and water reaches equilibrium. To accomplish this we will need to solve two I.C.E. tables:

Table 1:	$H_2C_2O_4(aq)$	$+\ H_2O(l)$	$\xrightleftharpoons{K_{a1}=5.2\times10^{-2}}$	$HC_2O_4^-(aq)$	$+\ H_3O^+(aq)$
Initial:	0.0833 M	—		0 M	0 M
Change:	$-x$	—		$+x$ M	$+x$ M
Equilibrium:	$0.0833 - x$ M	—		x M	x M

Since $C_a/K_a = 1.6$, the approximation cannot be used, and thus the full quadratic equation must be solved: $x^2/(0.0833 - x) = 5.2\times10^{-2}$; $x^2 + 5.2\times10^{-2}x - 4.3\underline{3}\times10^{-3}$

$$x = \frac{-5.2\times10^{-2} \pm \sqrt{2.7\times10^{-3} + 0.0173}}{2} \qquad x = 0.045 \text{ M} = [HC_2O_4^-] \approx [H_3O^+]$$

Now we can solve the I.C.E. table for the second proton loss:

Table 2:	$HC_2O_4^-(aq)$	$+\ H_2O(l)$	$\xrightleftharpoons{K_{a1}=5.4\times10^{-5}}$	$C_2O_4^{2-}(aq)$	$+\ H_3O^+(aq)$
Initial:	0.045 M	—		0 M	≈ 0.045 M
Change:	$-y$	—		$+y$ M	$+y$ M
Equilibrium:	$(0.045 - y)$ M	—		y M	$\approx (0.045 + y)$ M

Since $C_a/K_a = 833$, the approximation may not be valid and we yet again should solve the full quadratic equation:

$$\frac{y\times(0.045+y)}{(0.045-y)} = 5.4\times10^{-5}; \qquad y^2 + 0.045y = 2.4\underline{3}\times10^{-6} - 5.4\times10^{-5}y$$

$$y = \frac{-0.045 \pm \sqrt{2.0\underline{3}\times10^{-3} + 9.7\underline{2}\times10^{-6}}}{2} \qquad y = 8.2\times10^{-5} \text{ M} = [C_2O_4^{2-}]$$

Now we can calculate the Q_{sp} for the calcium oxalate system:

$Q_{sp} = [Ca^{2+}]_{initial}\times[C_2O_4^{2-}]_{initial} = (0.150)(8.2\times10^{-5}) = 1.2\times10^{-5} > 1.3\times10^{-9}$ (K_{sp} for CaC_2O_4)

Thus, CaC_2O_4 should precipitate from this solution.

34. **(D)** The solutions mutually dilute each other. We first determine the solubility of each compound in its saturated solution and then its concentration after dilution.

$$K_{sp} = \left[Ag^+\right]^2\left[SO_4^{2-}\right] = 1.4\times10^{-5} = (2s)^2 s = 4s^3 \qquad s = \sqrt[3]{\frac{1.4\times10^{-5}}{4}} = 1.5\times10^{-2} \text{ M}$$

$$\left[SO_4^{2-}\right] = 0.015 \text{ M} \times \frac{100.0 \text{ mL}}{100.0 \text{ mL} + 250.0 \text{ mL}} = 0.0043 \text{ M} \qquad \left[Ag^+\right] = 0.0086 \text{ M}$$

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 2.8\times10^{-13} = (s)(s) = s^2 \qquad s = \sqrt{2.8\times10^{-13}} = 5.3\times10^{-7} \text{ M}$$

$$\left[Pb^{2+}\right] = \left[CrO_4^{2-}\right] = 5.3\times10^{-7} \times \frac{250.0 \text{ mL}}{250.0 \text{ mL} + 100.0 \text{ mL}} = 3.8\times10^{-7} \text{ M}$$

From the balanced chemical equation, we see that the two possible precipitates are $PbSO_4$ and Ag_2CrO_4. (Neither $PbCrO_4$ nor Ag_2SO_4 can precipitate because they have been diluted below their saturated concentrations.) $PbCrO_4 + Ag_2SO_4 \rightleftharpoons PbSO_4 + Ag_2CrO_4$

Thus, we compute the value of Q_{sp} for each of these compounds and compare those values with the solubility constant product value.

$$Q_{sp} = \left[Pb^{2+}\right]\left[SO_4{}^{2-}\right] = \left(3.8\times10^{-7}\right)\left(0.0043\right) = 1.6\times10^{-9} < 1.6\times10^{-8} = K_{sp} \text{ for } PbSO_4$$

Thus, $PbSO_4(s)$ will not precipitate.

$$Q_{sp} = \left[Ag^+\right]^2\left[CrO_4{}^{2-}\right] = \left(0.0086\right)^2\left(3.8\times10^{-7}\right) = 2.8\times10^{-11} > 1.1\times10^{-12} = K_{sp} \text{ for } Ag_2CrO_4$$

Thus, $Ag_2CrO_4(s)$ should precipitate.

Completeness of Precipitation

35. **(M)** First determine that a precipitate forms. The solutions mutually dilute each other.

$$\left[CrO_4{}^{2-}\right] = 0.350\text{ M}\times\frac{200.0\text{ mL}}{200.0\text{ mL}+200.0\text{ mL}} = 0.175\text{ M}$$

$$\left[Ag^+\right] = 0.0100\text{ M}\times\frac{200.0\text{ mL}}{200.0\text{ mL}+200.0\text{ mL}} = 0.00500\text{ M}$$

We determine the value of the ion product and compare it to the solubility product constant value.

$$Q_{sp} = \left[Ag^+\right]^2\left[CrO_4{}^{2-}\right] = \left(0.00500\right)^2\left(0.175\right) = 4.4\times10^{-6} > 1.1\times10^{-12} = K_{sp} \text{ for } Ag_2CrO_4$$

Ag_2CrO_4 should precipitate.

Now, we assume that as much solid forms as possible, and then we approach equilibrium by dissolving that solid in a solution that contains the ion in excess.

Equation:	$Ag_2CrO_4(s)$	$\xrightleftharpoons{1.1\times10^{-12}}$	$2Ag^+(aq)$	+	$CrO_4{}^{2-}(aq)$
Orig. soln :	–		0.00500 M		0.175 M
Form solid :	–		–0.00500 M		– 0.00250 M
Not at equilibrium	–		0 M		0.173 M
Changes :	–		$+2x$ M		$+x$ M
Equil :	–		$2x$ M		$(0.173+x)$ M

$$K_{sp} = \left[Ag^+\right]^+\left[CrO_4{}^{2-}\right] = 1.1\times10^{-12} = (2x)^2(0.173+x) \approx \left(4x^2\right)(0.173)$$

$$x = \sqrt{1.1\times10^{-12}/(4\times0.173)} = 1.3\times10^{-6}\text{M} \qquad \left[Ag^+\right] = 2x = 2.6\times10^{-6}\text{M}$$

$$\%\ Ag^+ \text{ unprecipitated } = \frac{2.6\times10^{-6}\text{ M final}}{0.00500\text{ M initial}}\times100\% = 0.052\% \text{ unprecipitated}$$

36. **(M)** $[Ag^+]_{diluted} = 0.0208\text{ M}\times\frac{175\text{ mL}}{425\text{ mL}} = 0.00856\underline{5}\text{ M}$

$[CrO_4{}^{2-}]_{diluted} = 0.0380\text{ M}\times\frac{250\text{ mL}}{425\text{ mL}} = 0.0223\underline{5}\text{ M}$

$$Q_{sp} = \left[Ag^+\right]^2\left[CrO_4{}^{2-}\right] = 1.6\times10^{-6} > K_{sp}$$

Because $Q_{sp} > K_{sp}$, then more $Ag_2Cr_2O_4$ precipitates out. Assume that the limiting reagent is used up (100% reaction in the reverse direction) and re-establish the equilibrium in the reverse direction. Here Ag^+ is the limiting reagent.

	$Ag_2CrO_4(s)$	$\xrightleftharpoons{K_{sp(Ag_2CrO_4)} = 1.1 \times 10^{-12}}$	$2\ Ag^+(aq)$	+	$CrO_4^{2-}(aq)$
Initial	–		$0.00856\underline{5}$ M		$0.0223\underline{5}$ M
Change	–	$\boldsymbol{x = 0.00428}$ **M**	$-2x$		$-x$
100% rxn	–		0		0.0181
Change	–	**re-establish equil**	$+2y$		$+y$
Equil	–	**(assume $\boldsymbol{y \sim 0}$)**	$2y$		$0.0181 + y$

$1.1 \times 10^{-12} = (2y)^2(0.0181 + y) \approx (2y)^2(0.0181) \qquad y = 3.9 \times 10^{-6}$ M

$y << 0.0181$, so this assumption is valid.

$2y = [Ag^+] = 7.8 \times 10^{-6}$ M after precipitation is complete.

$\%\ [Ag^+]_{unprecipitated} = \dfrac{7.8 \times 10^{-6}}{0.00856} \times 100\% = 0.091\%$ (precipitation is essentially quantitative)

37. **(M)** We first use the solubility product constant expression to determine $\left[Pb^{2+}\right]$ in a solution with 0.100 M Cl^-.

$$K_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2 = 1.6 \times 10^{-5} = \left[Pb^{2+}\right](0.100)^2 \qquad \left[Pb^{2+}\right] = \frac{1.6 \times 10^{-5}}{(0.100)^2} = 1.6 \times 10^{-3}\ \text{M}$$

Thus, % unprecipitated $= \dfrac{1.6 \times 10^{-3}\ \text{M}}{0.065\ \text{M}} \times 100\% = 2.5\%$

Now, we want to determine what $[Cl^-]$ must be maintained to keep $[Pb^{2+}]_{final} = 1\%$;

$[Pb^{2+}]_{initial} = 0.010 \times 0.065\,\text{M} = 6.5 \times 10^{-4}$ M

$$K_{sp} = \left[Pb^{2+}\right]\left[Cl^-\right]^2 = 1.6 \times 10^{-5} = \left(6.5 \times 10^{-4}\right)\left[Cl^-\right]^2 \qquad \left[Cl^-\right] = \sqrt{\frac{6 \times 10^{-5}}{6.5 \times 10^{-4}}} = 0.16\ \text{M}$$

38. **(M)** Let's start by assuming that the concentration of Pb^{2+} in the untreated wine is no higher than 1.5×10^{-4}M (this assumption is not unreasonable.) As long as the Pb^{2+} concentration is less than 1.5×10^{-4} M, then the final sulfate ion concentration in the $CaSO_4$ treated wine should be virtually the same as the sulfate ion concentration in a saturated solution of $CaSO_4$ formed by dissolving solid $CaSO_4$ in pure water (i.e., with $[Pb^{2+}]$ less than or equal to 1.5×10^{-4} M, the $[SO_4^{2-}]$ will not drop significantly below that for a saturated solution, $\approx 3.0 \times 10^{-3}$ M.) Thus, the addition of $CaSO_4$ to the wine would result in the precipitation of solid $PbSO_4$, which would continue until the concentration of Pb^{2+} was equal to the K_{sp} for $PbSO_4$ divided by the concentration of dissolved sulfate ion, i.e.,

$[Pb^{2+}]_{max} = 1.6 \times 10^{-8}\text{M}^2/3.0 \times 10^{-3}\ \text{M} = 5.3 \times 10^{-6}$ M.

Fractional Precipitation

39. **(M)** First, assemble all of the data. K_{sp} for $Ca(OH)_2 = 5.5\times10^{-6}$, K_{sp} for $Mg(OH)_2 = 1.8\times10^{-11}$

$$[Ca^{2+}] = \frac{440\text{ g }Ca^{2+}}{1000\text{ kg seawater}}\times\frac{1\text{ mol }Ca^{2+}}{40.078\text{ g }Ca^{2+}}\times\frac{1\text{ kg seawater}}{1000\text{ g seawater}}\times\frac{1.03\text{ kg seawater}}{1\text{ L seawater}} = 0.0113\text{ M}$$

$[Mg^{2+}] = 0.059$ M, obtained from Example 18-6. $[OH^-] = 0.0020$ M (maintained)

(a) $Q_{sp} = [Ca^{2+}]\times[OH^-]^2 = (0.0113)(0.0020)^2 = 4.5\times10^{-8}$ $Q_{sp} < K_{sp}$ $\therefore$ no precipitate forms.

(b) For the separation to be complete, >>99.9 % of the Mg^{2+} must be removed before Ca^{2+} begins to precipitate. We have already shown that Ca^{2+} will not precipitate if the $[OH^-] = 0.0020$ M and is maintained at this level. Let us determine how much of the 0.059 M Mg^{2+} will still be in solution when $[OH^-] = 0.0020$ M.

$K_{sp} = [Mg^{2+}]\times[OH^-]^2 = (x)(0.0020)^2 = 1.8\times10^{-11}$ $x = 4.5\times10^{-6}$ M

The percent Mg^{2+} ion left in solution $= \dfrac{4.5\times10^{-6}}{0.059}\times100\% = 0.0076\ \%$

This means that 100% - 0.0076 % Mg = 99.992 % has precipitated.

Clearly, the magnesium ion has been separated from the calcium ion (i.e., >> 99.9% of the Mg^{2+} ions have precipitated and virtually all of the Ca^{2+} ions are still in solution.)

40. **(D)**

(a) 0.10 M NaCl will not work at all, since both $BaCl_2$ and $CaCl_2$ are soluble in water.

(b) $K_{sp} = 1.1\times10^{-10}$ for $BaSO_4$ and $K_{sp} = 9.1\times10^{-6}$ for $CaSO_4$. Since these values differ by more than 1000, 0.05 M Na_2SO_4 would effectively separate Ba^{2+} from Ca^{2+}.

We first compute $[SO_4^{2-}]$ when $BaSO_4$ begins to precipitate.

$$[Ba^{2+}][SO_4^{2-}] = (0.050)[SO_4^{2-}] = 1.1\times10^{-10};\quad [SO_4^{2-}] = \frac{1.1\times10^{-10}}{0.050} = 2.2\times10^{-9}\text{ M}$$

And then we calculate $[SO_4^{2-}]$ when $[Ba^{2+}]$ has decreased to 0.1% of its initial value, that is, to 5.0×10^{-5} M.

$$[Ba^{2+}][SO_4^{2-}] = (5.0\times10^{-5})[SO_4^{2-}] = 1.1\times10^{-10};\ [SO_4^{2-}] = \frac{1.1\times10^{-10}}{5.0\times10^{-5}} = 2.2\times10^{-6}\text{ M}$$

And finally, $[SO_4^{2-}]$ when $CaSO_4$ begins to precipitate.

$$[Ca^{2+}][SO_4^{2-}] = (0.050)[SO_4^{2-}] = 9.1\times10^{-6};\quad [SO_4^{2-}] = \frac{9.1\times10^{-6}}{0.050} = 1.8\times10^{-4}\text{ M}$$

(c) Now, $K_{sp} = 5\times10^{-3}$ for $Ba(OH)_2$ and $K_{sp} = 5.5\times10^{-6}$ for $Ca(OH)_2$. The fact that these two K_{sp} values differ by almost a factor of 1000 does not tell the entire story, because $[OH^-]$ is squared in both K_{sp} expressions. We compute $[OH^-]$ when $Ca(OH)_2$ begins to precipitate.

$$[Ca^{2+}][OH^-]^2 = 5.5\times10^{-6} = (0.050)[OH^-]^2 \quad [OH^-] = \sqrt{\frac{5.5\times10^{-6}}{0.050}} = 1.0\times10^{-2}\text{ M}$$

Precipitation will not proceed, as we only have 0.001 M NaOH, which has $[OH^-] = 1\times10^{-3}$ M.

(d) $K_{sp} = 5.1\times10^{-9}$ for $BaCO_3$ and $K_{sp} = 2.8\times10^{-9}$ for $CaCO_3$. Since these two values differ by less than a factor of 2, 0.50 M Na_2CO_3 would not effectively separate Ba^{2+} from Ca^{2+}.

41. **(M)**

(a) Here we need to determine $[I^-]$ when AgI just begins to precipitate, and $[I^-]$ when PbI_2 just begins to precipitate.

$$K_{sp} = [Ag^+][I^-] = 8.5\times10^{-17} = (0.10)[I^-] \qquad [I^-] = 8.5\times10^{-16}\text{M}$$

$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.1\times10^{-9} = (0.10)[I^-]^2 \qquad [I^-] = \sqrt{\frac{7.1\times10^{-9}}{0.10}} = 2.7\times10^{-4}\text{ M}$$

Since 8.5×10^{-16}M is less than 2.7×10^{-4} M, AgI will precipitate before PbI_2.

(b) $[I^-]$ must be equal to 2.7×10^{-4} M before the second cation, Pb^{2+}, begins to precipitate.

(c) $K_{sp} = [Ag^+][I^-] = 8.5\times10^{-17} = [Ag^+](2.7\times10^{-4}) \qquad [Ag^+] = 3.1\times10^{-13}$M

(d) Since $[Ag^+]$ has decreased to much less than 0.1% of its initial value before any PbI_2 begins to precipitate, we conclude that Ag^+ and Pb^{2+} can be separated by precipitation with iodide ion.

42. **(D)** Normally we would worry about the mutual dilution of the two solutions, but the values of the solubility product constants are so small that only a very small volume of 0.50 M $Pb(NO_3)_2$ solution needs to be added, as we shall see.

(a) Since the two anions are present at the same concentration and they have the same type of formula (one anion per cation), the one forming the compound with the smallest K_{sp} value will precipitate first. Thus, CrO_4^{2-} is the first anion to precipitate.

(b) At the point where SO_4^{2-} begins to precipitate, we have

$$K_{sp} = \left[Pb^{2+}\right]\left[SO_4^{2-}\right] = 1.6\times10^{-8} = \left[Pb^{2+}\right](0.010M);\left[Pb^{2+}\right] = \frac{1.6\times10^{-8}}{0.010} = 1.6\times10^{-6}\text{ M}$$

Now we can test our original assumption, that only a very small volume of 0.50 M $Pb(NO_3)_2$ solution has been added. We assume that we have 1.00 L of the original solution, the one with the two anions dissolved in it, and compute the volume of 0.50 M $Pb(NO_3)_2$ that has to be added to achieve $\left[Pb^{2+}\right] = 1.6\times10^{-6}$ M.

$$V_{added} = 1.00\text{ L}\times\frac{1.6\times10^{-6}\text{ mol Pb}^{2+}}{1\text{ L soln}}\times\frac{1\text{ mol Pb}(NO_3)_2}{1\text{ mol Pb}^{2+}}\times\frac{1\text{ L Pb}^{2+}\text{soln}}{0.50\text{ mol Pb}(NO_3)_2}$$

$$V_{added} = 3.2\times10^{-5}\text{ L Pb}^{2+}\text{soln} = 0.0032\text{mL Pb}^{2+}\text{soln}$$

This is less than one drop (0.05 mL) of the Pb^{2+} solution, clearly a very small volume.

(c) The two anions are effectively separated if $\left[Pb^{2+}\right]$ has not reached 1.6×10^{-6} M when $\left[CrO_4^{2-}\right]$ is reduced to 0.1% of its original value, that is, to

$$0.010\times10^{-3}\text{ M} = 1.0\times10^{-5}\text{ M} = \left[CrO_4^{2-}\right]$$

$$K_{sp} = \left[Pb^{2+}\right]\left[CrO_4^{2-}\right] = 2.8\times10^{-13} = \left[Pb^{2+}\right](1.0\times10^{-5})$$

$$\left[Pb^{2+}\right] = \frac{2.8\times10^{-13}}{1.0\times10^{-5}} = 2.8\times10^{-8}\text{ M}$$

Thus, the two anions can be effectively separated by fractional precipitation.

<u>43.</u> **(M)** First, let's assemble all of the data. K_{sp} for AgCl = 1.8×10^{-10} K_{sp} for AgI = 8.5×10^{-17}
$[Ag^+] = 2.00$ M $[Cl^-] = 0.0100$ M $[I^-] = 0.250$ M

(a) AgI(s) will be the first to precipitate by virtue of the fact that the K_{sp} value for AgI is about 2 million times smaller than that for AgCl.

(b) AgCl(s) will begin to precipitate when the Q_{sp} for AgCl(s) > K_{sp} for AgCl(s). The concentration of Ag^+ required is: $K_{sp} = [Ag^+][Cl^-] = 1.8\times10^{-10} = (0.0100)\times(x)$ $x = 1.8\times10^{-8}$ M
Using this data, we can determine the remaining concentration of I^- using the K_{sp}.
$K_{sp} = [Ag^+][I^-] = 8.5\times10^{-17} = (x)\times(1.8\times10^{-8})$ $x = 4.7\times10^{-9}$ M

(c) In part (b) we saw that the $[I^-]$ drops from 0.250 M → 4.7×10^{-9} M. Only a small percentage of the ion remains in solution. $\frac{4.7\times10^{-9}}{0.250}\times100\% = 0.0000019\ \%$
This means that 99.999998% of the I^- ion has been precipitated before any of the Cl^- ion has precipitated. Clearly, the fractional separation of Cl^- from I^- is feasible.

44. **(M)**

(a) We first determine the $\left[\mathrm{Ag}^+\right]$ needed to initiate precipitation of each compound.

$$\mathrm{AgCl}: K_{\mathrm{sp}} = \left[\mathrm{Ag}^+\right]\left[\mathrm{Cl}^-\right] = 1.8\times10^{-10} = \left[\mathrm{Ag}^+\right](0.250);\quad \left[\mathrm{Ag}^+\right] = \frac{1.8\times10^{-10}}{0.250} = 7.2\times10^{-10}\ \mathrm{M}$$

$$\mathrm{AgBr}: K_{\mathrm{sp}} = \left[\mathrm{Ag}^+\right]\left[\mathrm{Br}^-\right] = 5.0\times10^{-13} = \left[\mathrm{Ag}^+\right](0.0022);\quad \left[\mathrm{Ag}^+\right] = \frac{5.0\times10^{-13}}{0.0022} = 2.3\times10^{-10}\ \mathrm{M}$$

Thus, Br^- precipitates first, as AgBr, because it requires a lower $\left[\mathrm{Ag}^+\right]$.

(b) $\left[\mathrm{Ag}^+\right] = 7.2\times10^{-10}$ M when chloride ion, the second anion, begins to precipitate.

(c) Cl^- and Br^- cannot be separated by this fractional precipitation. $\left[\mathrm{Ag}^+\right]$ will have to rise to 1000 times its initial value, to 2.3×10^{-7} M, before AgBr is completely precipitated. But as soon as $\left[\mathrm{Ag}^+\right]$ reaches 7.2×10^{-10} M, AgCl will begin to precipitate.

Solubility and pH

45. **(E)** In each case we indicate whether the compound is more soluble in water. We write the net ionic equation for the reaction in which the solid dissolves in acid. Substances are more soluble in acid if either (1) an acid-base reaction occurs or (2) a gas is produced, since escape of the gas from the reaction mixture causes the reaction to shift to the right.

Same: KCl (K^+ and Cl^- do not react appreciably with H_2O)

Acid: $\mathrm{MgCO_3(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)}$

Acid: $\mathrm{FeS(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2S(g)}$

Acid: $\mathrm{Ca(OH)_2(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + 2H_2O(l)}$

Water: $\mathrm{C_6H_5COOH}$ is less soluble in acid, because of the $\mathrm{H_3O^+}$ common ion.

46. **(E)** In each case we indicate whether the compound is more soluble in base than in water. We write the net ionic equation for the reaction in which the solid dissolves in base. Substances are soluble in base if either (1) acid-base reaction occurs [as in (b)] or (2) a gas is produced, since escape of the gas from the reaction mixture causes the reaction to shift to the right.

Water: $\mathrm{BaSO_4}$ is less soluble in base, hydrolysis of $\mathrm{SO_4^{2-}}$ will be repressed.

Base: $\mathrm{H_2C_2O_4(s) + 2OH^-(aq) \longrightarrow C_2O_4^{2-}(aq) + 2H_2O(l)}$

Water: $\mathrm{Fe(OH)_3}$ is less soluble in base because of the $\mathrm{OH^-}$ common ion.

Same: $\mathrm{NaNO_3}$ (neither Na^+ nor NO_3^- react with H_2O to a measurable extent).

Water: MnS is less soluble in base because hydrolysis of $\mathrm{S^{2-}}$ will be repressed.

47. **(E)** We determine $\left[\mathrm{Mg^{2+}}\right]$ in the solution.

$$\left[\mathrm{Mg^{2+}}\right]=\frac{0.65\text{ g Mg(OH)}_2}{1\text{ L soln}}\times\frac{1\text{ mol Mg(OH)}_2}{58.3\text{ g Mg(OH)}_2}\times\frac{1\text{ mol Mg}^{2+}}{1\text{ mol Mg(OH)}_2}=0.011\,\mathrm{M}$$

Then we determine $\left[\mathrm{OH^-}\right]$ in the solution, and its pH.

$$K_{\mathrm{sp}}=\left[\mathrm{Mg^{2+}}\right]\left[\mathrm{OH^-}\right]^2=1.8\times10^{-11}=(0.011)\left[\mathrm{OH^-}\right]^2;\ \left[\mathrm{OH^-}\right]=\sqrt{\frac{1.8\times10^{-11}}{0.011}}=4.0\times10^{-5}\ \mathrm{M}$$

$$\mathrm{pOH}=-\log\left(4.0\times10^{-5}\right)=4.40 \qquad \mathrm{pH}=14.00-4.40=9.60$$

48. **(M)** First we determine the $[\mathrm{Mg^{2+}}]$ and $[\mathrm{NH_3}]$ that result from dilution to a total volume of 0.500 L.

$$\left[\mathrm{Mg^{2+}}\right]=0.100\,\mathrm{M}\times\frac{0.150\text{ L}_{\text{initial}}}{0.500\text{ L}_{\text{final}}}=0.0300\,\mathrm{M};\ \left[\mathrm{NH_3}\right]=0.150\ \mathrm{M}\times\frac{0.350\text{ L}_{\text{initial}}}{0.500\text{ L}_{\text{final}}}=0.105\ \mathrm{M}$$

Then determine the $\left[\mathrm{OH^-}\right]$ that will allow $\left[\mathrm{Mg^{2+}}\right]=0.0300\ \mathrm{M}$ in this solution.

$$K_{\mathrm{sp}}=1.8\times10^{-11}=\left[\mathrm{Mg^{2+}}\right]\left[\mathrm{OH^-}\right]^2=(0.0300)\left[\mathrm{OH^-}\right]^2;\ \left[\mathrm{OH^-}\right]=\sqrt{\frac{1.8\times10^{-11}}{0.0300}}=2.4\times10^{-5}\ \mathrm{M}$$

This $\left[\mathrm{OH^-}\right]$ is maintained by the $\mathrm{NH_3/NH_4^+}$ buffer; since it is a buffer, we can use the Henderson–Hasselbalch equation to find the $[\mathrm{NH_4^+}]$.

$$\mathrm{pH}=14.00-\mathrm{pOH}=14.00+\log\left(2.4\times10^{-5}\right)=9.38=\mathrm{p}K_{\mathrm{a}}+\log\frac{\left[\mathrm{NH_3}\right]}{\left[\mathrm{NH_4^+}\right]}=9.26+\log\frac{\left[\mathrm{NH_3}\right]}{\left[\mathrm{NH_4^+}\right]}$$

$$\log\frac{\left[\mathrm{NH_3}\right]}{\left[\mathrm{NH_4^+}\right]}=9.38-9.26=+0.12;\quad \frac{\left[\mathrm{NH_3}\right]}{\left[\mathrm{NH_4^+}\right]}=10^{+0.12}=1.3;\quad \left[\mathrm{NH_4^+}\right]=\frac{0.105\text{ M NH}_3}{1.3}=0.081\ \mathrm{M}$$

$$\text{mass }(\mathrm{NH_4})_2\mathrm{SO_4}=0.500\ \mathrm{L}\times\frac{0.081\text{ mol NH}_4^+}{\text{L soln}}\times\frac{1\text{ mol }(\mathrm{NH_4})_2\mathrm{SO_4}}{2\text{ mol NH}_4^+}\times\frac{132.1\text{ g }(\mathrm{NH_4})_2\mathrm{SO_4}}{1\text{ mol }(\mathrm{NH_4})_2\mathrm{SO_4}}=2.7\ \mathrm{g}$$

49. **(M)**

(a) Here we calculate $\left[\mathrm{OH^-}\right]$ needed for precipitation.

$$K_{\mathrm{sp}}=[\mathrm{Al^{3+}}][\mathrm{OH^-}]^3=1.3\times10^{-33}=(0.075\ \mathrm{M})[\mathrm{OH^-}]^3$$

$$[\mathrm{OH^-}]=\sqrt[3]{\frac{1.3\times10^{-33}}{0.075}}=2.6\times10^{-11}\quad \mathrm{pOH}=-\log\left(2.6\times10^{-11}\right)=10.59$$

$$\mathrm{pH}=14.00-10.59=3.41$$

(b) We can use the Henderson–Hasselbalch equation to determine $\left[\mathrm{C_2H_3O_2}^-\right]$.

$$\mathrm{pH} = 3.41 = \mathrm{p}K_\mathrm{a} + \log\frac{\left[\mathrm{C_2H_3O_2}^-\right]}{\left[\mathrm{HC_2H_3O_2}\right]} = 4.74 + \log\frac{\left[\mathrm{C_2H_3O_2}^-\right]}{1.00\ \mathrm{M}}$$

$$\log\frac{\left[\mathrm{C_2H_3O_2}^-\right]}{1.00\ \mathrm{M}} = 3.41 - 4.74 = -1.33;\quad \frac{\left[\mathrm{C_2H_3O_2}^-\right]}{1.00\ \mathrm{M}} = 10^{-1.33} = 0.047;\quad \left[\mathrm{C_2H_3O_2}^-\right] = 0.047\ \mathrm{M}$$

This situation does not quite obey the guideline that the ratio of concentrations must fall in the range 0.10 to 10.0, but the resulting error is a small one in this circumstance.

$$\text{mass } \mathrm{NaC_2H_3O_2} = 0.2500\ \mathrm{L} \times \frac{0.047\ \mathrm{mol\ C_2H_3O_2}^-}{1\ \mathrm{L\ soln}} \times \frac{1\ \mathrm{mol\ NaC_2H_3O_2}}{1\ \mathrm{mol\ C_2H_3O_2}^-} \times \frac{82.03\ \mathrm{g\ NaC_2H_3O_2}}{1\ \mathrm{mol\ NaC_2H_3O_2}}$$
$$= 0.96\ \mathrm{g\ NaC_2H_3O_2}$$

50. (D)

(a) Since HI is a strong acid, $\left[\mathrm{I}^-\right] = 1.05\times10^{-3}\ \mathrm{M} + 1.05\times10^{-3}\ \mathrm{M} = 2.10\times10^{-3}\ \mathrm{M}$.

We determine the value of the ion product and compare it to the solubility product constant value.

$$Q_\mathrm{sp} = \left[\mathrm{Pb}^{2+}\right]\left[\mathrm{I}^-\right]^2 = \left(1.1\times10^{-3}\right)\left(2.10\times10^{-3}\right)^2 = 4.9\times10^{-9} < 7.1\times10^{-9} = K_\mathrm{sp} \text{ for } \mathrm{PbI_2}$$

Thus a precipitate of $\mathrm{PbI_2}$ will not form under these conditions.

(b) We compute the $\left[\mathrm{OH}^-\right]$ needed for precipitation.

$$K_\mathrm{sp} = \left[\mathrm{Mg}^{2+}\right]\left[\mathrm{OH}^-\right]^2 = 1.8\times10^{-11} = (0.0150)\left[\mathrm{OH}^-\right]^2;\ \left[\mathrm{OH}^-\right] = \sqrt{\frac{1.8\times10^{-11}}{0.0150}} = 3.5\times10^{-5}\ \mathrm{M}$$

Then we compute $\left[\mathrm{OH}^-\right]$ in this solution, resulting from the ionization of $\mathrm{NH_3}$.

$$\left[\mathrm{NH_3}\right] = 6.00\ \mathrm{M} \times \frac{0.05\times10^{-3}\ \mathrm{L}}{2.50\ \mathrm{L}} = 1.\underline{2}\times10^{-4}\ \mathrm{M}$$

Even though $\mathrm{NH_3}$ is a weak base, the $\left[\mathrm{OH}^-\right]$ produced from the $\mathrm{NH_3}$ hydrolysis reaction will approximate 4×10^{-5} M (3.85 if you solve the quadratic) in this very dilute solution. (Recall that degree of ionization is high in dilute solution.) And since $\left[\mathrm{OH}^-\right] = 3.5\times10^{-5}$ M is needed for precipitation to occur, we conclude that $\mathrm{Mg(OH)_2}$ will precipitate from this solution (note: not much of a precipitate is expected).

(c) 0.010 M $\mathrm{HC_2H_3O_2}$ and 0.010 M $\mathrm{NaC_2H_3O_2}$ is a buffer solution with $\mathrm{pH} = \mathrm{p}K_\mathrm{a}$ of acetic acid (the acid and its anion are present in equal concentrations.) From this, we determine the $\left[\mathrm{OH}^-\right]$.

$$\text{pH} = 4.74 \qquad \text{pOH} = 14.00 - 4.74 = 9.26 \qquad \left[\text{OH}^-\right] = 10^{-9.26} = 5.5\times10^{-10}$$

$$Q = \left[\text{Al}^{3+}\right]\left[\text{OH}^-\right]^3 = (0.010)\left(5.5\times10^{-10}\right)^3 = 1.7\times10^{-30} > 1.3\times10^{-33} = K_{sp} \text{ of Al(OH)}_3$$

Thus, $Al(OH)_3(s)$ should precipitate from this solution.

Complex-Ion Equilibria

51. **(E)** Lead(II) ion forms a complex ion with chloride ion. It forms no such complex ion with nitrate ion. The formation of this complex ion decreases the concentrations of free $Pb^{2+}(aq)$ and free $Cl^-(aq)$. Thus, $PbCl_2$ will dissolve in the HCl(aq) up until the value of the solubility product is exceeded. $Pb^{2+}(aq) + 3Cl^-(aq) \rightleftharpoons [PbCl_3]^-(aq)$

52. **(E)** $Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \left[Zn(NH_3)_4\right]^{2+}(aq) \qquad K_f = 4.1\times10^8$

$NH_3(aq)$ will be least effective in reducing the concentration of the complex ion. In fact, the addition of $NH_3(aq)$ will increase the concentration of the complex ion by favoring a shift of the equilibrium to the right. $NH_4^+(aq)$ will have a similar effect, but not as direct. $NH_3(aq)$ is formed by the hydrolysis of $NH_4^+(aq)$ and, thus, increasing $\left[NH_4^+\right]$ will eventually increase $NH_3(aq)$: $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$. The addition of HCl(aq) will cause the greatest decrease in the concentration of the complex ion. HCl(aq) will react with $NH_3(aq)$ to decrease its concentration (by forming NH_4^+) and this will cause the complex ion equilibrium reaction to shift left toward free aqueous ammonia and $Zn^{2+}(aq)$.

53. **(E)** We substitute the given concentrations directly into the K_f expression to calculate K_f.

$$K_f = \frac{[[Cu(CN)_4^{3-}]}{[Cu^+][CN^-]^4} = \frac{0.0500}{(6.1\times10^{-32})(0.80)^4} = 2.0\times10^{30}$$

54. **(M)** The solution to this problem is organized around the balanced chemical equation. Free $[NH_3]$ is 6.0 M at equilibrium. The size of the equilibrium constant indicates that most copper(II) is present as the complex ion at equilibrium.

Equation:	$Cu^{2+}(aq)$	$+\ 4NH_3(aq)$	$\rightleftharpoons$	$\left[Cu(NH_3)_4\right]^{2+}(aq)$
Initial:	0.10 M	6.00 M		0 M
Change(100 % rxn):	–0.10 M	–0.40 M		+0.10 M
Completion:	0 M	5.60 M		0.10 M
Changes:	$+x$ M	$+4x$ M		$-x$ M
Equil:	x M	$5.60 + 4x$ M		$(0.10 - x)$ M

Let's assume $(5.60 + 4x)$ M ≈ 5.60 M and $(0.10 - x)$ M ≈ 0.10 M

$$K_f = \frac{\left[\left[\mathrm{Cu(NH_3)_4}\right]^{2+}\right]}{\left[\mathrm{Cu^{2+}}\right]\left[\mathrm{NH_3}\right]^4} = 1.1\times10^{13} = \frac{0.10 - x}{x(5.60-4x)^4} \approx \frac{0.10}{(5.60)^4 x} \approx \frac{0.10}{983.\underline{4}x}$$

$$x = \frac{0.10}{983.\underline{4}\times(1.1\times10^{13})} = 9.2\times10^{-18}\ \mathrm{M} = \left[\mathrm{Cu^{2+}}\right] \qquad (x << 0.10\text{, thus the approximation was valid})$$

<u>55.</u> **(M)** We first find the concentration of free metal ion. Then we determine the value of Q_{sp} for the precipitation reaction, and compare its value with the value of K_{sp} to determine whether precipitation should occur.

Equation:	$\mathrm{Ag^+(aq)} +$	$\mathrm{2\ S_2O_3{}^{2-}(aq)}$	$\rightleftharpoons$	$\mathrm{[Ag(S_2O_3)_2]^{3-}(aq)}$
Initial:	0 M	0.76 M		0.048 M
Changes:	$+x$ M	$+2x$ M		$-x$ M
Equil:	x M	$(0.76+2x)$ M		$(0.048-x)$ M

$$K_f = \frac{\left[\left[\mathrm{Ag(S_2O_3)_2}\right]^{3-}\right]}{\left[\mathrm{Ag^+}\right]\left[\mathrm{S_2O_3{}^{2-}}\right]^2} = 1.7\times10^{13} = \frac{0.048-x}{x(0.76+2x)^2} \approx \frac{0.048}{(0.76)^2 x}; x = 4.9\times10^{-15}\mathrm{M} = \left[\mathrm{Ag^+}\right]$$

($x <<$ 0.048 M, thus the approximation was valid.)

$Q_{sp} = \left[\mathrm{Ag^+}\right]\left[\mathrm{I^-}\right] = (4.9\times10^{-15})(2.0) = 9.8\times10^{-15} > 8.5\times10^{-17} = K_{sp}$.

Because $Q_{sp} > K_{sp}$, precipitation of AgI(s) should occur.

56. **(M)** We need to determine $\left[\mathrm{OH^-}\right]$ in this solution, and also the free $\left[\mathrm{Cu^{2+}}\right]$.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{\left[\mathrm{NH_3}\right]}{\left[\mathrm{NH_4{}^+}\right]} = 9.26 + \log\frac{0.10\ \mathrm{M}}{0.10\ \mathrm{M}} = 9.26 \quad \mathrm{pOH} = 14.00 - 9.26 = 4.74$$

$$\left[\mathrm{OH^-}\right] = 10^{-4.74} = 1.8\times10^{-5}\mathrm{M} \qquad \mathrm{Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \left[Cu(NH_3)_4\right]^{2+}(aq)}$$

$$K_f = \frac{\left[\left[\mathrm{Cu(NH_3)_4}\right]^{2+}\right]}{\left[\mathrm{Cu^{2+}}\right]\left[\mathrm{NH_3}\right]^4} = 1.1\times10^{13} = \frac{0.015}{\left[\mathrm{Cu^{2+}}\right]0.10^4}; \quad \left[\mathrm{Cu^{2+}}\right] = \frac{0.015}{1.1\times10^{13}\times0.10^4} = 1.4\times10^{-11}\mathrm{M}$$

Now we determine the value of Q_{sp} and compare it with the value of K_{sp} for $\mathrm{Cu(OH)_2}$.

$Q_{sp} = \left[\mathrm{Cu^{2+}}\right]\left[\mathrm{OH^-}\right]^2 = (1.4\times10^{-11})\times(1.8\times10^{-5})^2 = 4.5\times10^{-21} < 2.2\times10^{-20}$ (K_{sp} for $\mathrm{Cu(OH)_2}$)

Precipitation of $\mathrm{Cu(OH)_2(s)}$ from this solution should not occur.

57. **(M)** We first compute the free $\left[\mathrm{Ag}^{+}\right]$ in the original solution. The size of the complex ion formation equilibrium constant indicates that the reaction lies far to the right, so we form as much complex ion as possible stoichiometrically.

Equation:	$\mathrm{Ag}^{+}(\mathrm{aq})+$	$2\mathrm{NH}_3(\mathrm{aq})$	$\rightleftharpoons$	$\left[\mathrm{Ag}(\mathrm{NH}_3)_2\right]^{+}(\mathrm{aq})$
In soln:	0.10 M	1.00 M		0 M
Form complex:	–0.10 M	–0.20 M		+0.10 M
	0 M	0.80 M		0.10 M
Changes:	$+x$ M	$+2x$ M		$-x$ M
Equil:	x M	$(0.80+2x)$ M		$(0.10-x)$ M

$$K_{\mathrm{f}}=1.6\times10^{7}=\frac{\left[\left[\mathrm{Ag}(\mathrm{NH}_3)_2\right]^{+}\right]}{\left[\mathrm{Ag}^{+}\right]\left[\mathrm{NH}_3\right]^{2}}=\frac{0.10-x}{x(0.80+2x)^{2}}\approx\frac{0.10}{x(0.80)^{2}}\qquad x=\frac{0.10}{1.6\times10^{7}(0.80)^{2}}=9.8\times10^{-9}\ \mathrm{M}.$$

($x <<$ 0.80 M, thus the approximation was valid.)

Thus, $\left[\mathrm{Ag}^{+}\right]=9.8\times10^{-9}$ M. We next determine the $\left[\mathrm{I}^{-}\right]$ that can coexist in this solution without precipitation.

$$K_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{I}^{-}\right]=8.5\times10^{-17}=\left(9.8\times10^{-9}\right)\left[\mathrm{I}^{-}\right];\qquad\left[\mathrm{I}^{-}\right]=\frac{8.5\times10^{-17}}{9.8\times10^{-9}}=8.7\times10^{-9}\,\mathrm{M}$$

Finally, we determine the mass of KI needed to produce this $\left[\mathrm{I}^{-}\right]$

$$\text{mass KI}=1.00\ \text{L soln}\times\frac{8.7\times10^{-9}\,\text{mol I}^{-}}{1\ \text{L soln}}\times\frac{1\,\text{mol KI}}{1\,\text{mol I}^{-}}\times\frac{166.0\ \text{g KI}}{1\,\text{mol KI}}=1.4\times10^{-6}\ \text{g KI}$$

58. **(M)** First we determine $\left[\mathrm{Ag}^{+}\right]$ that can exist with this $\left[\mathrm{Cl}^{-}\right]$. We know that $\left[\mathrm{Cl}^{-}\right]$ will be unchanged because precipitation will not be allowed to occur.

$$K_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=1.8\times10^{-10}=\left[\mathrm{Ag}^{+}\right]0.100\ \mathrm{M};\qquad\left[\mathrm{Ag}^{+}\right]=\frac{1.8\times10^{-10}}{0.100}=1.8\times10^{-9}\ \mathrm{M}$$

We now consider the complex ion equilibrium. If the complex ion's final concentration is x, then the decrease in $\left[\mathrm{NH}_3\right]$ is $2x$, because 2 mol NH_3 react to form each mole of complex ion, as follows. $\mathrm{Ag}^{+}(\mathrm{aq})+2\mathrm{NH}_3(\mathrm{aq})\rightleftharpoons\left[\mathrm{Ag}(\mathrm{NH}_3)_2\right]^{+}(\mathrm{aq})$ We can solve the K_{f} expression for x.

$$K_{\mathrm{f}}=1.6\times10^{7}=\frac{\left[\left[\mathrm{Ag}(\mathrm{NH}_3)_2\right]^{+}\right]}{\left[\mathrm{Ag}^{+}\right]\left[\mathrm{NH}_3\right]^{2}}=\frac{x}{1.8\times10^{-9}(1.00-2x)^{2}}$$

$$x=\left(1.6\times10^{7}\right)\left(1.8\times10^{-9}\right)(1.00-2x)^{2}=0.029\left(1.00-4.00x+4.00x^{2}\right)=0.029-0.12x+0.12x^{2}$$

$0=0.029-1.12x+0.12x^{2}$ We use the quadratic formula roots equation to solve for x.

$$x=\frac{-b\pm\sqrt{b^{2}-4ac}}{2a}=\frac{1.12\pm\sqrt{(1.12)^{2}-4\times0.029\times0.12}}{2\times0.12}=\frac{1.12\pm1.11\underline{4}}{0.24}=9.3,\ 0.025$$

Thus, we can add 0.025 mol $AgNO_3$ (~ 4.4 g $AgNO_3$) to this solution before we see a precipitate of AgCl(s) form.

Precipitation and Solubilities of Metal Sulfides

59. **(M)** We know that $K_{spa} = 3\times10^7$ for MnS and $K_{spa} = 6\times10^2$ for FeS. The metal sulfide will begin to precipitate when $Q_{spa} = K_{spa}$. Let us determine the $\left[H_3O^+\right]$ just necessary to form each precipitate. We assume that the solution is saturated with H_2S, $\left[H_2S\right] = 0.10$ M.

$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2} \qquad [H_3O^+] = \sqrt{\frac{[M^{2+}][H_2S]}{K_{spa}}} = \sqrt{\frac{(0.10\text{ M})(0.10\text{ M})}{3\times10^7}} = 1.8\times10^{-5}\text{ M for MnS}$$

$$\left[H_3O^+\right] = \sqrt{\frac{(0.10\text{ M})(0.10\text{ M})}{6\times10^2}} = 4.1\times10^{-3}\text{ M for FeS}$$

Thus, if the $[H_3O^+]$ is maintained just a bit higher than 1.8×10^{-5} M, FeS will precipitate and $Mn^{2+}(aq)$ will remain in solution. To determine if the separation is complete, we see whether $\left[Fe^{2+}\right]$ has decreased to 0.1% or less of its original value when the solution is held at the aforementioned acidity. Let $\left[H_3O^+\right] = 2.0\times10^{-5}$ M and calculate $\left[Fe^{2+}\right]$.

$$K_{spa} = \frac{\left[Fe^{2+}\right]\left[H_2S\right]}{\left[H_3O^+\right]^2} = 6\times10^2 = \frac{\left[Fe^{2+}\right](0.10\text{ M})}{\left(2.0\times10^{-5}\text{ M}\right)^2}; \quad \left[Fe^{2+}\right] = \frac{\left(6\times10^2\right)\left(2.0\times10^{-5}\right)^2}{0.10} = 2.4\times10^{-6}\text{ M}$$

$$\%\,Fe^{2+}(aq)\text{ remaining} = \frac{2.4\times10^{-6}\text{ M}}{0.10\text{ M}}\times100\% = 0.0024\% \qquad \therefore\text{ Separation is complete.}$$

60. **(M)** Since the cation concentrations are identical, the value of Q_{spa} is the same for each one. It is this value of Q_{spa} that we compare with K_{spa} to determine if precipitation occurs.

$$Q_{spa} = \frac{\left[M^{2+}\right]\left[H_2S\right]}{\left[H_3O^+\right]^2} = \frac{0.05\text{ M}\times0.10\text{ M}}{\left(0.010\text{ M}\right)^2} = 5\times10^1$$

If $Q_{spa} > K_{spa}$, precipitation of the metal sulfide should occur. But, if $Q_{spa} < K_{spa}$, precipitation will not occur.

For CuS, $K_{spa} = 6\times10^{-16} < Q_{spa} = 5\times10^1$ Precipitation of CuS(s) should occur.

For HgS, $K_{spa} = 2\times10^{-32} < Q_{spa} = 5\times10^1$ Precipitation of HgS(s) should occur.

For MnS, $K_{spa} = 3\times10^7 > Q_{spa} = 5\times10^1$ Precipitation of MnS(s) will not occur.

61. (M)

(a) We can calculate $\left[H_3O^+\right]$ in the buffer with the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log\frac{\left[C_2H_3O_2^-\right]}{\left[HC_2H_3O_2\right]} = 4.74 + \log\frac{0.15\,\text{M}}{0.25\,\text{M}} = 4.52 \quad \left[H_3O^+\right] = 10^{-4.52} = 3.0\times10^{-5}\ \text{M}$$

We use this information to calculate a value of Q_{spa} for MnS in this solution and then comparison of Q_{spa} with K_{spa} will allow us to decide if a precipitate will form.

$$Q_{spa} = \frac{\left[Mn^{2+}\right]\left[H_2S\right]}{\left[H_3O^+\right]^2} = \frac{(0.15)(0.10)}{\left(3.0\times10^{-5}\right)^2} = 1.7\times10^7 < 3\times10^7 = K_{spa} \text{ for MnS}$$

Thus, precipitation of MnS(s) will not occur.

(b) We need to change $\left[H_3O^+\right]$ so that

$$Q_{spa} = 3\times10^7 = \frac{(0.15)(0.10)}{\left[H_3O^+\right]^2};\ \left[H_3O^+\right] = \sqrt{\frac{(0.15)(0.10)}{3\times10^7}} \quad [H_3O^+] = 2.2\times10^{-5}\ \text{M} \quad \text{pH} = 4.66$$

This is a more basic solution, which we can produce by increasing the basic component of the buffer solution, namely, the acetate ion. We can find out the necessary acetate ion concentration with the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.66 = 4.74 + \log\frac{[C_2H_3O_2^-]}{0.25\ \text{M}}$$

$$\log\frac{[C_2H_3O_2^-]}{0.25\ \text{M}} = 4.66 - 4.74 = -0.08$$

$$\frac{\left[C_2H_3O_2^-\right]}{0.25\ \text{M}} = 10^{-0.08} = 0.83 \quad \left[C_2H_3O_2^-\right] = 0.83\times0.25\,\text{M} = 0.21\,\text{M}$$

62. (M)

(a) CuS is in the hydrogen sulfide group of qualitative analysis. Its precipitation occurs when 0.3 M HCl is saturated with H_2S. It will certainly precipitate from a (non-acidic) saturated solution of H_2S which has a much higher $\left[S^{2-}\right]$.

$$Cu^{2+}(aq) + H_2S(\text{satd aq}) \longrightarrow CuS(s) + 2H^+(aq)$$

This reaction proceeds to an essentially quantitative extent in the forward direction.

(b) MgS is soluble, according to the solubility rules listed in Chapter 5.

$$Mg^{2+}(aq) + H_2S(\text{satd aq}) \xrightarrow{\text{0.3 M HCl}} \text{no reaction}$$

(c) As in part (a), PbS is in the qualitative analysis hydrogen sulfide group, which precipitates from a 0.3 M HCl solution saturated with H_2S. Therefore, PbS does not dissolve appreciably in 0.3 M HCl. $PbS(s) + HCl\ (0.3M) \longrightarrow \text{no reaction}$

(d) Since ZnS(s) does not precipitate in the hydrogen sulfide group, we conclude that it is soluble in acidic solution.

$ZnS(s) + 2HNO_3(aq) \longrightarrow Zn(NO_3)_2(aq) + H_2S(g)$

Qualitative Cation Analysis

<u>63</u>. **(E)** The purpose of adding hot water is to separate Pb^{2+} from AgCl and Hg_2Cl_2. Thus, the most important consequence would be the absence of a valid test for the presence or absence of Pb^{2+}. In addition, if we add NH_3 first, $PbCl_2$ may form $Pb(OH)_2$. If $Pb(OH)_2$ does form, it will be present with Hg_2Cl_2 in the solid, although $Pb(OH)_2$ will not darken with added NH_3. Thus, we might falsely conclude that Ag^+ is present.

64. **(M)** For $PbCl_2(aq)$, $2[Pb^{2+}] = [Cl^-]$ where s = molar solubility of $PbCl_2$.

Thus $s = [Pb^{2+}]$.

$K_{sp} = [Pb^{2+}][Cl^-]^2 = (s)(2s)^2 = 4s^3 = 1.6\times10^{-5}$; $s = \sqrt[3]{1.6\times10^{-5} \div 4} = 1.6\times10^{-2}$ M $= [Pb^{2+}]$

Both $[Pb^{2+}]$ and $[CrO_4^{\ 2-}]$ are diluted by mixing the two solutions.

$[Pb^{2+}] = 0.016\text{ M} \times \dfrac{1.00\text{ mL}}{1.05\text{ mL}} = 0.015\text{ M}$ $\qquad [CrO_4^{\ 2-}] = 1.0\text{ M} \times \dfrac{0.05\text{ mL}}{1.05\text{ mL}} = 0.048\text{ M}$

$Q_{sp} = [Pb^{2+}][CrO_4^{\ 2-}] = (0.015\text{ M})(0.048\text{ M}) = 7.2\times10^{-4} > 2.8\times10^{-13} = K_{sp}$

Thus, precipitation should occur from the solution described.

<u>65.</u> **(E)**

(a) Ag^+ and/or $Hg_2^{\ 2+}$ are probably present. Both of these cations form chloride precipitates from acidic solutions of chloride ion.

(b) We cannot tell whether Mg^{2+} is present or not. Both MgS and $MgCl_2$ are water soluble.

(c) Pb^{2+} possibly is absent; it is the only cation of those given which forms a precipitate in an acidic solution that is treated with H_2S, and no sulfide precipitate was formed.

(d) We cannot tell whether Fe^{2+} is present. FeS will not precipitate from an acidic solution that is treated with H_2S; the solution must be alkaline for a FeS precipitate to form.

(a) and **(c)** are the valid conclusions.

66. **(E)**

(a) $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$

(b) $Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq)$

(c) $Fe(OH)_3(s) + 3H_3O^+(aq) \longrightarrow Fe^{3+}(aq) + 6H_2O(l)$ or $[Fe(H_2O)_6]^{3+}(aq)$

(d) $Cu^{2+}(aq) + H_2S(aq) \longrightarrow CuS(s) + 2H^+(aq)$

INTEGRATIVE AND ADVANCED EXERCISES

67. **(M)** We determine *s*, the solubility of $CaSO_4$ in a saturated solution, and then the concentration of $CaSO_4$ in ppm in this saturated solution, assuming that the solution's density is 1.00 g/mL.

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = (s)(s) = s^2 = 9.1\times10^{-6} \qquad s = 3.0\times10^{-3}\ M$$

$$\text{ppm } CaSO_4 = 10^6\,\text{g soln} \times \frac{1\ \text{mL}}{1.00\ \text{g}} \times \frac{1\ \text{L soln}}{1000\ \text{mL}} \times \frac{0.0030\ \text{mol } CaSO_4}{1\ \text{L soln}} \times \frac{136.1\ \text{g } CaSO_4}{1\ \text{mol } CaSO_4} = 4.1\times10^2\,\text{ppm}$$

Now we determine the volume of solution remaining after we evaporate the 131 ppm $CaSO_4$ down to a saturated solution (assuming that both solutions have a density of 1.00 g/mL.)

$$\text{volume sat'd soln} = 131\,\text{g } CaSO_4 \times \frac{10^6\ \text{g sat'd soln}}{4.1\times10^2\,\text{g } CaSO_4} \times \frac{1\,\text{mL}}{1.00\,\text{g}} = 3.2\times10^5\ \text{mL}$$

Thus, we must evaporate 6.8 × 10^5 mL of the original 1.000 × 10^6 mL of solution, or 68% of the water sample.

68. **(M)**

(a) First we compute the molar solubility, *s*, of $CaHPO_4 \cdot 2H_2O$.

$$s = \frac{0.32\ \text{g } CaHPO_4\cdot 2H_2O}{1\ \text{L soln}} \times \frac{1\ \text{mol } CaHPO_4\cdot 2H_2O}{172.1\ \text{g } CaHPO_4\cdot\ 2H_2O} = 1.9\times10^{-3}\ M$$

$$K_{sp} = [Ca^{2+}][HPO_4^{2-}] = (s)(s) = s^2 = (1.9\ \times10^{-3})^2 = 3.6\times10^{-6}$$

Thus the values are not quite consistent.

(b) The value of K_{sp} given in the problem is consistent with a smaller value of the molar solubility. The reason is that not all of the solute ends up in solution as HPO_4^{2-} ions. HPO_4^{2-} can act as either an acid or a base in water (see below), but it is base hydrolysis that predominates.

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 4.2\times10^{-13}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2PO_4^-(aq) \qquad K_b = \frac{K_w}{K_2} = 1.6\times10^{-7}$$

69. **(M)** The solutions mutually dilute each other and, because the volumes are equal, the concentrations are halved in the final solution: $[Ca^{2+}]$ = 0.00625 M, $[SO_4^{2-}]$ = 0.00760 M. We cannot assume that either concentration remains constant during the precipitation. Instead, we assume that precipitation proceeds until all of one reagent is used up. Equilibrium is reached from that point.

Equation:	$CaSO_4(s) \rightleftharpoons$	$Ca^{2+}(aq)$	+	$SO_4^{2-}(aq)$	$K_{sp} = 9.1\times10^{-6}$
In soln	–	0.00625 M		0.00760 M	$K_{sp} = [Ca^{2+}][SO_4^{2-}]$
Form ppt	–	-0.00625 M		-0.00625 M	$K_{sp} = (x)(0.00135 + x)$
Not at equil	–	0 M		0.00135 M	$K_{sp} \approx 0.00135\,x$
Changes	–	$+x$ M		$+x$ M	$x = \dfrac{9.1\times10^{-6}}{0.00135} = 6.7\times10^{-3}$ M
Equil:	–	x M		$(0.00135 + x)$ M	{not a reasonable assumption!}

Solving the quadratic $0 = x^2 + (1.35\times10^{-2})x - 9.1\times10^{-6}$ yields $x = 2.4\times10^{-3}$.

$$\%\ \text{unprecipitated } Ca^{2+} = \frac{2.4\times10^{-3}\ M_{\text{final}}}{0.00625\ M_{\text{initial}}}\times100\% = \ 38\%\ \text{unprecipitated}$$

70. **(M)** If equal volumes are mixed, each concentration is reduced to one-half of its initial value. We assume that all of the limiting ion forms a precipitate, and then equilibrium is achieved by the reaction proceeding in the forward direction to a small extent.

Equation:	$BaCO_3(s) \rightleftharpoons$	$Ba^{2+}(aq)$	+	$CO_3^{2-}(aq)$
Orig. soln:	–	0.00050 M		0.0010 M
Form ppt:	–	0 M		0.0005 M
Changes:	–	$+x$ M		$+x$ M
Equil:	–	x M		$(0.0005 + x)$M

$$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.1\times10^{-9} = (x)(0.0005 + x) \approx 0.0005\,x$$

$x = \dfrac{5.1\times10^{-9}}{0.0005} = 1\times10^{-5}$ M The $[Ba^{2+}]$ decreases from 5×10^{-4} M to 1×10^{-5} M.

($x <$ 0.0005 M, thus the approximation was valid.)

$\%\ \text{unprecipitated} = \dfrac{1\times10^{-5}\ M}{5\times10^{-4}\ M}\times100\% = 2\%$ Thus, 98% of the Ba^{2+} is precipitated as $BaCO_3(s)$.

71. **(M)** The pH of the buffer establishes $[H_3O^+] = 10^{-pH} = 10^{-3.00} = 1.0\times10^{-3}$ M.

Now we combine the two equilibrium expressions, and solve the resulting expression for the molar solubility of $Pb(N_3)_2$ in the buffer solution.

$$\mathrm{Pb(N_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ N_3^-(aq)} \qquad K_{sp} = 2.5\times10^{-9}$$

$$\underline{\mathrm{2\ H_3O^+(aq) + 2\ N_3^-(aq) \rightleftharpoons 2\ HN_3(aq) + 2\ H_2O(l)}} \qquad 1/K_a^{\ 2} = \frac{1}{(1.9\times10^{-5})^2} = 2.8\times10^9$$

$$\mathrm{Pb(N_3)_2(s) + 2\ H_3O^+(aq) \rightleftharpoons Pb^{2+}(aq) + 2\ HN_3(aq) + 2\ H_2O\ (l)} \qquad K = K_{sp}\times(1/K_a^{\ 2}) = 7.0$$

	$\mathrm{Pb(N_3)_2(s)}$ +	$\mathrm{2\ H_3O^+(aq)}$ $\rightleftharpoons$	$\mathrm{Pb^{2+}(aq)}$ +	$\mathrm{2\ HN_3(aq)}$ +	$\mathrm{2\ H_2O\ (l)}$
Buffer:	–	0.0010 M	0 M	0 M	–
Dissolving:	–	(buffer)	$+x$ M	$+2x$ M	–
Equilibrium:	–	0.0010 M	x M	$2x$ M	–

$$K = \frac{[\mathrm{Pb^{2+}}][\mathrm{HN_3}]^2}{[\mathrm{H_3O^+}]^2} = 7.0 = \frac{(x)\ (2x)^2}{(0.0010)^2} \qquad 4x^3 = 7.0\,(0.0010)^2 \qquad x = \sqrt[3]{\frac{7.0(0.0010)^2}{4}} = 0.012\ \mathrm{M}$$

Thus, the molar solubility of $\mathrm{Pb(N_3)_2}$ in a pH = 3.00 buffer is 0.012 M.

72. **(M)** We first determine the equilibrium constant of the suggested reaction.

$$\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)} \qquad K_{sp} = 1.8\times10^{-11}$$

$$\mathrm{2\ NH_4^+(aq) + 2\ OH^-(aq) \rightleftharpoons 2\ NH_3(aq) + 2\ H_2O(l)} \qquad 1/K_b^{\ 2} = 1/(1.8\times10^{-5})^2$$

	$\mathrm{Mg(OH)_2(s)}$ +	$\mathrm{2\ NH_4^+(aq)}$ $\rightleftharpoons$	$\mathrm{Mg^{2+}(aq)}$ +	$\mathrm{2\ NH_3(aq)}$ +	$\mathrm{2\ H_2O(l)}$
Initial:	–	1.00 M	0 M	0 M	–
Changes:	–	$-2x$ M	$+x$ M	$+2x$ M	–
Equil:	–	$(1.00\ -2x)$ M	x M	$2x$ M	–

$$K = \frac{K_{sp}}{K_b^{\ 2}} = \frac{1.8\times10^{-11}}{(1.8\times10^{-5})^2} = \frac{[\mathrm{Mg^{2+}}][\mathrm{NH_3}]^2}{[\mathrm{NH_4^+}]^2} = 0.056 = \frac{x(2x)^2}{(1.00-2x)^2} \approx \frac{4x^3}{1.00^2}$$

$$x = \sqrt[3]{\frac{0.056}{4}} = 0.24\ \mathrm{M}$$

Take this as a first approximation and cycle through again. $2x = 0.48$

$$K \approx \frac{4x^3}{(1.00-0.48)^2} = 0.056 \qquad x = \sqrt[3]{\frac{0.056\,(1.00-0.48)^2}{4}} = 0.16\,\mathrm{M}$$

Yet another cycle gives a somewhat more consistent value. $2x = 0.32$

$$K \approx \frac{4x^3}{(1.00-0.32)^2} = 0.056 \qquad x = \sqrt[3]{\frac{0.056\,(1.00-0.38)^2}{4}} = 0.19\,\mathrm{M}$$

Another cycle gives more consistency. $2x = 0.38$

$$K \approx \frac{4x^3}{(1.00-0.38)^2} = 0.056 \qquad x = \sqrt[3]{\frac{0.056\,(1.00-0.38)^2}{4}} = 0.18\,\text{M} = [\text{Mg}^{2+}]$$

The molar solubility of $Mg(OH)_2$ in a 1.00 M NH_4Cl solution is 0.18 M.

73. **(D)** First we determine the value of the equilibrium constant for the cited reaction.

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3{}^{2-}(\text{aq}) \qquad K_{\text{sp}} = 2.8\times10^{-9}$$

$$\text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3{}^{2-}(\text{aq}) \rightleftharpoons \text{H}_2\text{O(l)} + \text{HCO}_3{}^-(\text{aq}) \qquad 1/K_{a2} = 1/4.7\times10^{-11}$$

$$\text{CaCO}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{HCO}_3{}^-(\text{aq}) + \text{H}_2\text{O(l)} \qquad K_{overall} = K_{\text{sp}} \times \left(1/K_{a2}\right)$$

$$K_{overall} = \frac{2.8\times10^{-9}}{4.7\times10^{-11}} = 60$$

Equation:	$CaCO_3(s)$ +	$H_3O^+(aq)$ $\rightleftharpoons$	$Ca^{2+}(aq)$ +	$HCO_3^-(aq)$ +	$H_2O(l)$
Initial:	–	10^{-pH}	0 M	0 M	–
Change:	–	(*buffer*)	$+x$ M	$+x$ M	–
Equil:	–	10^{-pH}	x M	x M	–

In the above set-up, we have assumed that the pH of the solution did not change because of the dissolving of the $CaCO_3(s)$. That is, we have treated the rainwater as if it were a buffer solution.

(a) $$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} = 60. = \frac{x^2}{3\times10^{-6}} \qquad x = \sqrt{60\times3\times10^{-6}} = 1\times10^{-2}\ \text{M} = [\text{Ca}^{2+}]$$

(b) $$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} = 60. = \frac{x^2}{6.3\times10^{-5}} \qquad x = \sqrt{60\times6.3\times10^{-5}} = 6.1\times10^{-2}\ \text{M} = [\text{Ca}^{2+}]$$

74. We use the Henderson-Hasselbalch equation to determine $[H_3O^+]$ in this solution, and then use the K_{sp} expression for MnS to determine $[Mn^{2+}]$ that can exist in this solution without precipitation occurring.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log\frac{0.500\text{ M}}{0.100\text{ M}} = 4.74 + 0.70 = 5.44$$

$$[\text{H}_3\text{O}^+] = 10^{-5.44} = 3.6\times10^{-6}\text{ M}$$

$$\text{MnS(s)} + 2\text{ H}_3\text{O}^+\text{(aq)} \rightleftharpoons \text{Mn}^{2+}\text{(aq)} + \text{H}_2\text{S(aq)} + 2\text{ H}_2\text{O(l)} \qquad K_{spa} = 3\times10^7$$

Note that $[H_2S] = [Mn^{2+}] = s$, the molar solubility of MnS.

$$K_{spa} = \frac{[\text{Mn}^{2+}][\text{H}_2\text{S}]}{[\text{H}_3\text{O}^+]^2} = 3\times10^7 = \frac{s^2}{(3.6\times10^{-6}\text{ M})^2} \qquad s = 0.02\text{ M}$$

$$\text{mass MnS/L} = \frac{0.02\text{ mol Mn}^{2+}}{1\text{ L soln}}\frac{1\text{ mol MnS}}{1\text{ mol Mn}^{2+}}\times\frac{87\text{ g MnS}}{1\text{ mol MnS}} = 2\text{ g MnS/L}$$

75. (M)

(a) The precipitate is likely $Ca_3(PO_4)_2$. Let us determine the %Ca of this compound (by mass)

$$\%\text{Ca} = \frac{3\times 40.078\text{ g Ca}}{310.18\text{ g Ca}_3(\text{PO}_4)_2}\times100\% = 38.763\%\text{ Ca}$$

$$3\,\text{Ca}^{2+}\text{(aq)} + 2\,\text{HPO}_4^{2-}\text{(aq)} \longrightarrow \text{Ca}_3(\text{PO}_4)_2\text{(s)} + 2\,\text{H}^+\text{(aq)}$$

(b) The bubbles are $CO_2(g)$: $\quad CO_2(g) + H_2O(l) \longrightarrow$ “$H_2CO_3(aq)$”

$$\text{Ca}^{2+}\text{(aq)} + \text{H}_2\text{CO}_3\text{(aq)} \longrightarrow \text{CaCO}_3\text{(s)} + 2\text{ H}^+\text{(aq)} \qquad \text{precipitation}$$

$$\text{CaCO}_3\text{(s)} + \text{H}_2\text{CO}_3\text{(aq)} \longrightarrow \text{Ca}^{2+}\text{(aq)} + 2\text{ HCO}_3^-\text{(aq)} \qquad \text{redissolving}$$

76. (D)

(a) A solution of $CO_2(aq)$ has $[CO_3^{2-}] = K_a[H_2CO_3] = 5.6 \times 10^{-11}$. Since $K_{sp} = 2.8 \times 10^{-9}$ for $CaCO_3$, the $[Ca^{2+}]$ needed to form a precipitate from this solution can be computed.

$$[\text{Ca}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = \frac{2.8\times10^{-9}}{5.6\times10^{-11}} = 50.\text{M}$$

This is too high to reach by dissolving $CaCl_2$ in solution. The reason why the technique works is because the $OH^-(aq)$ produced by $Ca(OH)_2$ neutralizes some of the $HCO_3^-(aq)$ from the ionization of $CO_2(aq)$, thereby increasing the $[CO_3^{2-}]$ above a value of 5.6×10^{-11}.

(b) The equation for redissolving can be obtained by combining several equations.

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq) + CO_3^{2-}(aq)} \qquad K_{\mathrm{sp}} = 2.8\times10^{-9}$$

$$\mathrm{CO_3^{2-}(aq) + H_3O^+(aq)} \rightleftharpoons \mathrm{HCO_3^-(aq) + H_2O(l)} \qquad \frac{1}{K_{\mathrm{a2}}} = \frac{1}{5.6\times10^{-11}}$$

$$\underline{\mathrm{CO_2(aq) + 2\ H_2O(l)} \rightleftharpoons \mathrm{HCO_3^-(aq) + H_3O^+(aq)} \qquad K_{\mathrm{a1}} = 4.2\times10^{-7}}$$

$$\mathrm{CaCO_3(s) + CO_2(aq) + H_2O(l)} \rightleftharpoons \mathrm{Ca^{2+}(aq) + 2\,HCO_3^-(aq)} \qquad K = \frac{K_{\mathrm{sp}}\times K_{\mathrm{a1}}}{K_{\mathrm{a2}}}$$

$$K = \frac{(2.8\times10^{-9})(4.2\times10^{-7})}{5.6\times10^{-11}} = 2.1\times10^{-5} = \frac{[\mathrm{Ca^{2+}}][\mathrm{HCO_3^-}]^2}{[\mathrm{CO_2}]}$$

If $\mathrm{CaCO_3}$ is precipitated from 0.005 M $\mathrm{Ca^{2+}(aq)}$ and then redissolved, $[\mathrm{Ca^{2+}}]$ = 0.005 M and $[\mathrm{HCO_3^{2-}}]$ = 2×0.005 M = 0.010 M. We use these values in the above expression to compute $[\mathrm{CO_2}]$.

$$[\mathrm{CO_2}] = \frac{[\mathrm{Ca^{2+}}][\mathrm{HCO_3^-}]^2}{2.1\times10^{-5}} = \frac{(0.005)(0.010)^2}{2.1\times10^{-5}} = 0.02\ \mathrm{M}$$

We repeat the calculation for saturated $\mathrm{Ca(OH)_2}$, in which $[\mathrm{OH^-}] = 2\,[\mathrm{Ca^{2+}}]$, after first determining $[\mathrm{Ca^{2+}}]$ in this solution.

$$K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{OH^-}]^2 = 4\,[\mathrm{Ca^{2+}}] = 5.5\times10^{-6} \qquad [\mathrm{Ca^{2+}}]\ \sqrt[3]{\frac{5.5\times10^{-6}}{4}} = 0.011$$

$$\mathrm{M}[\mathrm{CO_2}] = \frac{[\mathrm{Ca^{2+}}][\mathrm{HCO_3^-}]^2}{2.1\times10^{-5}} = \frac{(0.011)(0.022)^2}{2.1\times10^{-5}} = 0.25\ \mathrm{M}$$

Thus, to redissolve the $\mathrm{CaCO_3}$ requires that $[\mathrm{CO_2}]$ = 0.25 M if the solution initially is saturated $\mathrm{Ca(OH)_2}$, but only 0.02 M $\mathrm{CO_2}$ if the solution initially is 0.005 M $\mathrm{Ca(OH)_2(aq)}$.
A handbook lists the solubility of $\mathrm{CO_2}$ as 0.034 M. Clearly the $\mathrm{CaCO_3}$ produced cannot redissolve if the solution was initially saturated with $\mathrm{Ca(OH)_2(aq)}$.

77. **(M)**
(a)

$$\mathrm{BaSO_4(s)} \rightleftharpoons \mathrm{Ba^{2+}(aq) + SO_4^{2-}(aq)} \qquad K_{\mathrm{sp}} = 1.1\times10^{-10}$$

$$\underline{\mathrm{Ba^{2+}(aq) + CO_3^{2-}(aq)} \rightleftharpoons \mathrm{BaCO_3(s)} \qquad \frac{1}{K_{\mathrm{sp}}} = \frac{1}{5.1\times10^{-9}}}$$

$$\text{Sum}\quad \mathrm{BaSO_4(s) + CO_3^{2-}(aq)} \rightleftharpoons \mathrm{BaCO_3(s) + SO_4^{2-}(aq)} \qquad K_{overall} = \frac{1.1\times10^{-10}}{5.1\times10^{-9}} = 0.0216$$

Initial	–	3 M	–	≈ 0
Equil.	–	(3-x)M	–	x

(where x is the carbonate used up in the reaction)

$$K = \frac{[\mathrm{SO_4^{2-}}]}{[\mathrm{CO_3^{2-}}]} = \frac{x}{3-x} = 0.0216 \text{ and } x = 0.063 \quad \text{Since } 0.063\ \mathrm{M} > 0.050\ \mathrm{M}\text{, the response is yes.}$$

(b)

$$2\text{AgCl(s)} \rightleftharpoons 2\text{Ag}^{+}\text{(aq)} + 2\,\text{Cl}^{-}\text{(aq)} \qquad K_{\text{sp}} = (1.8\times 10^{-10})^{2}$$

$$2\,\text{Ag}^{+}\text{(aq)} + \text{CO}_3^{\,2-}\text{(aq)} \rightleftharpoons \text{Ag}_2\text{CO}_3\text{(s)} \qquad 1/K_{\text{sp}} = \frac{1}{8.5\times 10^{-12}}$$

$$\text{Sum}\quad 2\text{AgCl(s)} + \text{CO}_3^{\,2-}\text{(aq)} \rightleftharpoons \text{Ag}_2\text{CO}_3\text{(s)} + 2\,\text{Cl}^{-}\text{(aq)} \qquad K_{\text{overall}} = \frac{(1.8\times 10^{-10})^{2}}{8.5\times 10^{-12}} = 3.8\times 10^{-9}$$

Initial	–	3 M	–	≈ 0 M
Equil.	–	(3-x)M	–	2x

(where x is the carbonate used up in the reaction)

$$K_{\text{overall}} = \frac{[\text{Cl}^{-}]^{2}}{[\text{CO}_3^{\,2-}]} = \frac{(2x)^{2}}{3\text{-}x} = 3.8\times 10^{-9} \text{ and } x = 5.3\times 10^{-5}\text{ M}$$

Since $2x$, $(2(5.35\times 10^{-5}\text{M}))$, << 0.050 M, the response is no.

(c)

$$\text{MgF}_2\text{(s)} \rightleftharpoons \text{Mg}^{2+}\text{(aq)} + 2\,\text{F}^{-}\text{(aq)} \qquad K_{\text{sp}} = 3.7\times 10^{-8}$$

$$\text{Mg}^{2+}\text{(aq)} + \text{CO}_3^{\,2-}\text{(aq)} \rightleftharpoons \text{MgCO}_3\text{(s)} \qquad 1/K_{\text{sp}} = \frac{1}{3.5\times 10^{-8}}$$

$$\text{sum}\quad \text{MgF}_2\text{(s)} + \text{CO}_3^{\,2-}\text{(aq)} \rightleftharpoons \text{MgCO}_3\text{(s)} + 2\,\text{F}^{-}\text{(aq)} \qquad K_{\text{overall}} = \frac{3.7\times 10^{-8}}{3.5\times 10^{-8}} = 1.1$$

initial	–	3 M	–	0 M
equil.	–	(3-x)M	–	2x

(where x is the carbonate used up in the reaction)

$$K_{\text{overall}} = \frac{[\text{F}^{-}]^{2}}{[\text{CO}_3^{\,2-}]} = \frac{(2x)^{2}}{3-x} = 1.1 \text{ and } x = 0.769\text{M}$$

Since $2x$, $(2(0.769\text{M})) > 0.050$ M, the response is yes.

78. **(D)** For ease of calculation, let us assume that 100 mL, that is, 0.100 L of solution, is to be titrated. We also assume that $[\text{Ag}^{+}] = 0.10$ M in the titrant. In order to precipitate 99.9% of the Br^{-} as AgBr, the following volume of titrant must be added.

$$\text{volume titrant} = 0.999\times 100\text{ mL}\times\frac{0.010\text{ mmol Br}^{-}}{1\text{ mL sample}}\times\frac{1\text{ mmol Ag}^{+}}{1\text{ mmol Br}^{-}}\times\frac{1\text{ mL titrant}}{0.10\text{ mmol Ag}^{+}} = 9.99\text{ mL}$$

We compute $[\text{Ag}^{+}]$ when precipitation is complete.

$$[\text{Ag}^{+}] = \frac{K_{\text{sp}}}{[\text{Br}^{-}]_f} = \frac{5.0\times 10^{-13}}{0.001\times 0.01\,\text{M}} = 5.0\times 10^{-8}\,\text{M}$$

Thus, during the course of the precipitation of AgBr, while 9.99 mL of titrant is added, $[\text{Ag}^{+}]$ increases from *zero* to 5.0×10^{-8} M. $[\text{Ag}^{+}]$ increases from 5.0×10^{-8} M to 1.0×10^{-5} M from the point where AgBr is completely precipitated to the point where Ag_2CrO_4 begins to precipitate. Let us assume, for the purpose of making an initial estimate, that this increase in $[\text{Ag}^{+}]$ occurs while the total volume of the solution is 110 mL (the original 100 mL plus 10 mL of titrant needed to precipitate all the AgBr.) The amount of Ag^+ added during this increase is the difference between the amount present just after AgBr is completely precipitated and the amount present when Ag_2CrO_4 begins to precipitate.

$$\text{amount } Ag^+ \text{ added} = 110\text{ mL} \times \frac{1.0\times10^{-5}\text{ mmol } Ag^+}{1\text{ mL soln}} - 110\text{ mL} \times \frac{5.0\times10^{-8}\text{ mmol } Ag^+}{1\text{ mL soln}}$$
$$= 1.1\times10^{-3}\text{ mmol } Ag^+$$

$$\text{volume added titrant} = 1.1\times10^{-3}\text{ mmol } Ag^+ \times \frac{1\text{ mL titrant}}{0.10\text{ mmol } Ag^+} = 1.1\times10^{-2}\text{ mL titrant}$$

We see that the total volume of solution remains essentially constant. Note that $[Ag^+]$ has increased by more than two powers of ten while the volume of solution increased a very small degree; this is indeed a very rapid rise in $[Ag^+]$, as stated.

79. **(D)** The chemistry of aluminum is complex, however, we can make the following assumptions. Consider the following reactions at various pH:

$$\text{pH} > 7 \quad Al(OH)_3(s) + OH^- \xrightleftharpoons{K_{\text{overall}}=K_f K_{sp} = 1.43} Al(OH)_4^-(aq)$$

$$\text{pH} < 7 \quad Al(OH)_3(s) \xrightleftharpoons{K_{\text{sp}} = 1.3\times10^{-33}} Al^{3+}(aq) + 3\,OH^-$$

For the solubilities in basic solutions, consider the following equilibrium at pH = 13.00 and 11.00.

$$\text{At pH} = 13.00: \quad Al(OH)_3(s) + OH^- \xrightleftharpoons{K_{ov}=K_f K_{sp} = 1.43} Al(OH)_4^-(aq)$$

	$Al(OH)_3(s)$	OH^-	$Al(OH)_4^-(aq)$
Initial :	–	0.10	0
Change:	–	$-x$	$+x$
Equilibrium:	–	$0.10 - x$	x

$$K_f = 1.4\underline{3} = \frac{x}{0.10-x} \approx \frac{x}{0.10} \quad \text{(buffered at pH = 13.00)} \quad x = 0.14\underline{3}\text{ M}$$

$$\text{At pH} = 11.00: \quad K_f = 1.4\underline{3} = \frac{x}{0.0010-x} \approx \frac{x}{0.0010} \quad \text{(buffered at pH = 11)} \quad x = 0.0014\underline{3}\text{ M}$$

Thus, in these two calculations we see that the formation of the aluminate ion $[Al(OH)_4^-]$ is favored at high pH values. Note that the concentration of aluminum(III) increases by a factor of one-hundred when the pH is increased from 11.00 to 13.00, and it will increase further still above pH 13. Now consider the solubility equilibrium established at pH = 3.00, 4.00, and 5.00. These correspond to $[OH^-] = 1.0 \times 10^{-11}$ M, 1.0×10^{-10} M, and 1.0×10^{-9} M, respectively.

$$Al(OH)_3(s) \xrightleftharpoons{K_{\text{sp}} = 1.3\times10^{-33}} Al^{3+}(aq) + 3\,OH^-(aq)$$

At these pH values, $[Al^{3+}]$ in saturated aqueous solutions of $Al(OH)_3$ are

$[Al^{3+}] = 1.3 \times 10^{-33} / (1.0 \times 10^{-11})^3 = 1.3$ M at pH = 3.00

$[Al^{3+}] = 1.3 \times 10^{-33} /(1.0 \times 10^{-10})^3 = 1.3 \times 10^{-3}$ M at pH = 4.00

$[Al^{3+}] = 1.3 \times 10^{-33} /(1.0 \times 10^{-9})^3 = 1.3 \times 10^{-6}$ M at pH = 5.00

These three calculations show that in strongly acidic solutions the concentration of aluminum(III) can be very high and is certainly not limited by the precipitation of $Al(OH)_3(s)$. However, this solubility decreases rapidly as the pH increases beyond pH 4.

At neutral pH 7, a number of equilibria would need to be considered simultaneously, including the self-ionization of water itself. However, the results of just these five calculations do indicate that concentration of aluminum(III) increases at both low and high pH values, with a very low concentration at intermediate pH values around pH 7, thus aluminum(III) concentration as a function of pH is a U-shaped (or V-shaped) curve.

<u>80</u>. (M) We combine the solubility product expression for AgCN(s) with the formation expression for $[Ag(NH_3)_2]^+(aq)$.

$$\text{Solubility:} \quad AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq) \qquad K_{sp} = ?$$

$$\text{Formation:} \quad Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \qquad K_f = 1.6 \times 10^{+7}$$

$$\text{Net reaction:} \quad AgCN(s) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+ + CN^-(aq) \quad K_{overall} = K_{sp} \times K_f$$

$$K_{overall} = \frac{[[Ag(NH_3)_2]^+][CN^-]}{[NH_3]^2} = \frac{(8.8 \times 10^{-6})^2}{(0.200)^2} = 1.9 \times 10^{-9} = K_{sp} \times 1.6 \times 10^{+7}$$

$$K_{sp} = \frac{1.9 \times 10^{-9}}{1.6 \times 10^{+7}} = 1.2 \times 10^{-16}$$

Because of the extremely low solubility of AgCN in the solution, we assumed that $[NH_3]$ was not altered by the formation of the complex ion.

81. We combine the solubility product constant expression for $CdCO_3(s)$ with the formation expression for $[CdI_4]^{2-}(aq)$.

$$\text{Solubility:} \quad CdCO_3(s) \rightleftharpoons Cd^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = 5.2 \times 10^{-12}$$

$$\text{Formation:} \quad Cd^{2+}(aq) + 4\,I^-(aq) \rightleftharpoons [CdI_4]^{2-}(aq) \qquad K_f = ?$$

$$\text{Net reaction:} \quad CdCO_3(s) + 4\,I^-(aq) \rightleftharpoons [CdI_4]^{2-}(aq) + CO_3^{2-}(aq) \qquad K_{overall} = K_{sp} \times K_f$$

$$K_{overall} = \frac{[[CdI_4]^{2-}][CO_3^{2-}]}{[I^-]^4} = \frac{(1.2 \times 10^{-3})^2}{(1.00)^4} = 1.4 \times 10^{-6} = 5.2 \times 10^{-12} K_f$$

$$K_f = \frac{1.4 \times 10^{-6}}{5.2 \times 10^{-12}} = 2.7 \times 10^5$$

Because of the low solubility of CdCO3 in this solution, we assumed that [I–] was not appreciably lowered by the formation of the complex ion.

82. **(M)** We first determine $[Pb^{2+}]$ in this solution, which has $[Cl^-] = 0.10$ M.

$$K_{sp} = 1.6\times10^{-5} = [Pb^{2+}][Cl^-]^2 \qquad [Pb^{2+}] = \frac{K_{sp}}{[Cl^-]^2} = \frac{1.6\times10^{-5}}{(0.10)^2} = 1.6\times10^{-3}\,M$$

Then we use this value of $[Pb^{2+}]$ in the K_f expression to determine $[[PbCl_3]^-]$.

$$K_f = \frac{[[PbCl_3]^-]}{[Pb^{2+}][Cl^-]^3} = 24 = \frac{[[PbCl_3]^-]}{(1.6\times10^{-3})(0.10)^3} = \frac{[[PbCl_3]^-]}{1.6\times10^{-6}}$$

$$[[PbCl_3]^-] = 24\times1.6\times10^{-6} = 3.8\times10^{-5}\,M$$

The solubility of $PbCl_2$ in 0.10 M HCl is the following sum.

solubility = $[Pb^{2+}] + [[PbCl_3]^-] = 1.6\times10^{-3}$ M + 3.8×10^{-5} M = 1.6×10^{-3} M

83. **(M)** Two of the three relationships needed to answer this question are the two solubility product expressions. $1.6\times10^{-8} = [Pb^{2+}][SO_4^{2-}]$ $4.0\times10^{-7} = [Pb^{2+}][S_2O_3^{2-}]$

The third expression required is the electroneutrality equation, which states that the total positive charge concentration must equal the total negative charge concentration:
$[Pb^{2+}] = [SO_4^{2-}] + [S_2O_3^{2-}]$, provided $[H_3O^+] = [OH^-]$.

Or, put another way, there is one Pb^{2+} ion in solution for each SO_4^{2-} ion *and* for each $S_2O_3^{2-}$ ion. We solve each of the first two expressions for the concentration of each anion, substitute these expressions into the electroneutrality expression, and then solve for $[Pb^{2+}]$.

$$[SO_4^{2-}] = \frac{1.6\times10^{-8}}{[Pb^{2+}]} \qquad [S_2O_3^{2-}] = \frac{4.0\times10^{-7}}{[Pb^{2+}]} \qquad [Pb^{2+}] = \frac{1.6\times10^{-8}}{[Pb^{2+}]} + \frac{4.0\times10^{-7}}{[Pb^{2+}]}$$

$$[Pb^{2+}]^2 = 1.6\times10^{-8} + 4.0\times10^{-7} = 4.2\times10^{-7} \qquad [Pb^{2+}] = \sqrt{4.2\times10^{-7}} = 6.5\times10^{-4}\ M$$

84. **(D)** The chemical equations are:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq) \text{ and } \qquad PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Br^-(aq)$$

The two solubility constant expressions, $[Pb^{2+}][Cl^-]^2 = 1.6\times10^{-5}$, $[Pb^{2+}][Br^-]^2 = 4.0\times10^{-5}$ and the condition of electroneutrality, $2\,[Pb^{2+}] = [Cl^-] + [Br^-]$, must be solved simultaneously to determine $[Pb^{2+}]$. (Rearranging the electroneutrality relationship, one obtains: $[Pb^{2+}] = \frac{1}{2}[Cl^-] + \frac{1}{2}[Br^-]$.) First we solve each of the solubility constant expressions for the concentration of the anion. Then we substitute these values into the electroneutrality expression and solve the resulting equation for $[Pb^{2+}]$.

$$[Cl^-] = \sqrt{\frac{1.6\times10^{-5}}{[Pb^{2+}]}} \qquad [Br^-] = \sqrt{\frac{4.0\times10^{-5}}{[Pb^{2+}]}} \qquad 2[Pb^{2+}] = \sqrt{\frac{1.6\times10^{-5}}{[Pb^{2+}]}} + \sqrt{\frac{4.0\times10^{-5}}{[Pb^{2+}]}}$$

$$2\sqrt{[Pb^{2+}]^3} = \sqrt{1.6\times10^{-5}} + \sqrt{4.0\times10^{-5}} = 4.0\times10^{-3} + 6.3\times10^{-3} = 1.03\times10^{-2}$$

$$\sqrt{[Pb^{2+}]^3} = 5.2\times10^{-3} \qquad [Pb^{2+}]^3 = 2.7\times10^{-5} \qquad [Pb^{2+}] = 3.0\times10^{-2}\,M$$

85. **(D) (a)** First let us determine if there is sufficient Ag_2SO_4 to produce a saturated solution, in which $[Ag^+] = 2\,[SO_4^{2-}]$.

$$K_{sp} = 1.4\times10^{-5} = [Ag^+]^2[SO_4^{2-}] = 4[SO_4^{2-}]^3 \quad [SO_4^{2-}] = \sqrt[3]{\frac{1.4\times10^{-5}}{4}} = 0.015\text{ M}$$

$$[SO_4^{2-}] = \frac{2.50\text{ g }Ag_2SO_4}{0.150\text{ L}}\times\frac{1\text{ mol }Ag_2SO_4}{311.8\text{ g }Ag_2SO_4}\times\frac{1\text{ mol }SO_4^{2-}}{1\text{ mol }Ag_2SO_4} = 0.0535\text{ M}$$

Thus, there is more than enough Ag_2SO_4 present to form a saturated solution. Let us now see if AgCl or $BaSO_4$ will precipitate under these circumstances. $[SO_4^{2-}] = 0.015$ M and $[Ag^+] = 0.030$ M.

$Q = [Ag^+][Cl^-] = 0.030 \times 0.050 = 1.5 \times 10^{-3} > 1.8 \times 10^{-10} = K_{sp}$, thus AgCl should precipitate.

$Q = [Ba^{2+}][SO_4^{2-}] = 0.025 \times 0.015 = 3.8 \times 10^{-4} > 1.1 \times 10^{-10} = K_{sp}$, thus $BaSO_4$ should precipitate.

Thus, the net ionic equation for the reaction that will occur is as follows.

$$Ag_2SO_4(s) + Ba^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow BaSO_4(s) + 2\,AgCl(s)$$

(b) Let us first determine if any $Ag_2SO_4(s)$ remains or if it is all converted to $BaSO_4(s)$ and AgCl(s). Thus, we have to solve a limiting reagent problem.

$$\text{amount }Ag_2SO_4 = 2.50\text{ g }Ag_2SO_4\times\frac{1\text{ mol }Ag_2SO_4}{311.8\text{ g }Ag_2SO_4} = 8.02\times10^{-3}\text{ mol }Ag_2SO_4$$

$$\text{amount }BaCl_2 = 0.150\text{ L}\times\frac{0.025\text{ mol }BaCl_2}{1\text{ L soln}} = 3.75\times10^{-3}\text{ mol }BaCl_2$$

Since the two reactants combine in a 1 mole to 1 mole stoichiometric ratio, $BaCl_2$ is the limiting reagent. Since there must be some Ag_2SO_4 present and because Ag_2SO_4 is so much more soluble than either $BaSO_4$ or AgCl, we assume that $[Ag^+]$ and $[SO_4^{2-}]$ are determined by the solubility of Ag_2SO_4. They will have the same values as in a saturated solution of Ag_2SO_4.

$[SO_4^{2-}] = 0.015$ M $\qquad$ $[Ag^+] = 0.030$ M

We use these values and the appropriate K_{sp} values to determine $[Ba^{2+}]$ and $[Cl^-]$.

$$[Ba^{2+}] = \frac{1.1\times10^{-10}}{0.015} = 7.3\times10^{-9}\text{ M} \qquad [Cl^-] = \frac{1.8\times10^{-10}}{0.030} = 6.0\times10^{-9}\text{ M}$$

Since $BaCl_2$ is the limiting reagent, we can use its amount to determine the masses of $BaSO_4$ and AgCl.

$$\text{mass }BaSO_4 = 0.00375\text{ mol }BaCl_2\times\frac{1\text{ mol }BaSO_4}{1\text{ mol }BaCl_2}\times\frac{233.4\text{ g }BaSO_4}{1\text{ mol }BaSO_4} = 0.875\text{ g }BaSO_4$$

$$\text{mass AgCl} = 0.00375\text{ mol }BaCl_2\times\frac{2\text{ mol AgCl}}{1\text{ mol }BaCl_2}\times\frac{143.3\text{ g AgCl}}{1\text{ mol AgCl}} = 1.07\text{ g AgCl}$$

The mass of unreacted Ag_2SO_4 is determined from the initial amount and the amount that reacts with $BaCl_2$.

$$\text{mass } Ag_2SO_4 = \left(0.00802 \text{ mol } Ag_2SO_4 - 0.00375 \text{ mol } BaCl_2 \times \frac{1 \text{ mol } Ag_2SO_4}{1 \text{ mol } BaCl_2}\right) \times \frac{311.8 \text{ g } Ag_2SO_4}{1 \text{ mol } Ag_2SO_4}$$

$$\text{mass } Ag_2SO_4 = 1.33 \text{ g } Ag_2SO_4 \text{ unreacted}$$

Of course, there is some Ag_2SO_4 dissolved in solution. We compute its mass.

$$\text{mass dissolved } Ag_2SO_4 = 0.150 \text{ L} \times \frac{0.0150 \text{ mol } Ag_2SO_4}{1 \text{ L soln}} \times \frac{311.8 \text{ g } Ag_2SO_4}{1 \text{ mol } Ag_2SO_4} = 0.702 \text{ g dissolved}$$

$$\text{mass } Ag_2SO_4(s) = 1.33 \text{ g } - 0.702 \text{ g} = 0.63 \text{ g } Ag_2SO_4(s)$$

86. **(M)** To determine how much NaF must be added, determine what the solubility of BaF_2 is considering that the final concentration of F^- must be 0.030 M.
$K_{sp} = 1\times10^{-6.}$

BaF_2 (s)	$\rightleftharpoons$	Ba^{2+} (aq)	+	$2F^-$ (aq)
		0		0
		$+s$		$+2s$
		s		$2s \rightarrow (0.030 \text{ M})$

$$K_{sp} = 1\times10^{-6.} = (s)(0.030)^2 = s(9.0\times10^{-4}); \text{Therefore, } s = 0.0011 \text{ M}.$$

Since s is 0.0011 M, the F^- contribution from BaF_2 considering the common ion effect exerted by NaF is 0.0022 M. Therefore, the total number of moles of NaF in a 1 L solution required is therefore 0.0278 moles.

To determine how much BaF_2 precipitates, we must first determine what the value of s is for a saturated solution in absence of the common ion effect. That is,

$$K_{sp} = 1\times10^{-6.} = (s)(2s)^2 = 4s^3; \text{Therefore, } s = 0.0063 \text{ M}.$$

Since in absence of the common ion effect from NaF the solubility of BaF_2 is 0.0063 M, and with NaF the solubility is 0.0011, the difference between the two (0.0063 – 0.0011 = 0.0052 M) has to be precipitated. The mass of the precipitate is therefore:

$$\text{mass of } BaF_2 = \frac{0.0052 \text{ mol } BaF_2}{1 \text{ L solution}} \times \frac{175.3 \text{ g } BaF_2}{1 \text{ mol } BaF_2} = 0.91 \text{ g}$$

FEATURE PROBLEMS

87. **(M)** $\left[\mathrm{Ca}^{2+}\right]=\left[\mathrm{SO_4}^{2-}\right]$ in the saturated solution. Let us first determine the amount of $\mathrm{H_3O^+}$ in the 100.0 mL diluted effluent. $\mathrm{H_3O^+(aq)+NaOH(aq)\longrightarrow 2H_2O(l)+Na^+(aq)}$

$$\text{mmol } \mathrm{H_3O^+} = 100.0\text{ mL}\times\frac{8.25\text{ mL base}}{10.00\text{ mL sample}}\times\frac{0.0105\text{ mmol NaOH}}{1\text{ mL base}}\times\frac{1\text{ mmol } \mathrm{H_3O^+}}{1\text{ mmol NaOH}}$$

$$= 0.866\text{ mmol } \mathrm{H_3O^+(aq)}$$

Now we determine $\left[\mathrm{Ca}^{2+}\right]$ in the original 25.00 mL sample, remembering that $2\mathrm{H_3O^+}$ were produced for each Ca^{2+}.

$$\left[\mathrm{Ca}^{2+}\right]=\frac{0.866\text{ mmol } \mathrm{H_3O^+(aq)}\times\dfrac{1\text{ mmol } \mathrm{Ca}^{2+}}{2\text{ mmol } \mathrm{H_3O^+}}}{25.00\text{ mL}}=0.0173\text{ M}$$

$K_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}\right]\left[\mathrm{SO_4}^{2-}\right]=(0.0173)^2=3.0\times10^{-4}$; the K_{sp} for $\mathrm{CaSO_4}$ is 9.1×10^{-6} in Appendix D.

88. **(D)**

(a) We assume that there is little of each ion present in solution at equilibrium (that this is a simple stoichiometric calculation). This is true because the *K* value for the titration reaction is very large. $K_{\text{titration}} = 1/K_{\text{sp(AgCl)}} = 5.6\times10^{9}$. We stop the titration when just enough silver ion has been added. $\mathrm{Ag^+(aq)+Cl^-(aq)\longrightarrow AgCl(s)}$

$$V = 100.0\text{ mL}\times\frac{29.5\text{ mg Cl}^-}{1000\text{ mL}}\times\frac{1\text{ mmol Cl}^-}{35.45\text{ mg Cl}^-}\times\frac{1\text{ mmol Ag}^+}{1\text{ mmol Cl}^-}\times\frac{1\text{ mL}}{0.01000\text{ mmol AgNO}_3}$$

$$= 8.32\text{ mL}$$

(b) We first calculate the concentration of each ion as the consequence of dilution. Then we determine the $[\mathrm{Ag^+}]$ from the value of K_{sp}.

$$\text{initial }\left[\mathrm{Ag^+}\right]=0.01000\text{ M}\times\frac{8.32\text{ mL added}}{108.3\text{ mL final volume}}=7.68\times10^{-4}\text{ M}$$

$$\text{initial }\left[\mathrm{Cl^-}\right]=\frac{29.5\text{ mg Cl}^-\times\dfrac{1\text{ mmol Cl}^-}{35.45\text{ mg Cl}^-}}{1000\text{ mL}}\times\frac{100.0\text{ mL taken}}{108.3\text{ mL final volume}}=7.68\times10^{-4}\text{ M}$$

The slight excess of each ion will precipitate until the solubility constant is satisfied.

$$\left[\mathrm{Ag^+}\right]=\left[\mathrm{Cl^-}\right]=\sqrt{K_{\mathrm{sp}}}=\sqrt{1.8\times10^{-10}}=1.3\times10^{-5}\text{ M}$$

(c) If we want $\mathrm{Ag_2CrO_4}$ to appear just when AgCl has completed precipitation, $\left[\mathrm{Ag^+}\right]=1.3\times10^{-5}$ M. We determine $\left[\mathrm{CrO_4}^{2-}\right]$ from the K_{sp} expression.

$$K_{sp} = \left[Ag^+\right]^2\left[CrO_4^{\ 2-}\right] = 1.1\times10^{-12} = \left(1.3\times10^{-5}\right)^2\left[CrO_4^{\ 2-}\right]; \quad \left[CrO_4^{\ 2-}\right] = \frac{1.1\times10^{-12}}{\left(1.3\times10^{-5}\right)^2} = 0.0065\text{ M}$$

(d) If $\left[CrO_4^{\ 2-}\right]$ were greater than the answer just computed for part (c), Ag_2CrO_4 would appear before all Cl^- had precipitated, leading to a false early endpoint. We would calculate a falsely low $\left[Cl^-\right]$ for the original solution.

If $\left[CrO_4^{\ 2-}\right]$ were less than computed in part 3, Ag_2CrO_4 would appear somewhat after all Cl^- had precipitated, leading one to conclude there was more Cl^- in solution than actually was the case.

(e) If it was Ag^+ that was being titrated, it would react immediately with the $CrO_4^{\ 2-}$ in the sample, forming a red-orange precipitate. This precipitate would not likely dissolve, and thus, very little if any AgCl would form. There would be no visual indication of the endpoint.

89. **(D)**

(a) We need to calculate the $\left[Mg^{2+}\right]$ in a solution that is saturated with $Mg(OH)_2$.

$$K_{sp} = 1.8\times10^{-11} = \left[Mg^{2+}\right]\left[OH^-\right]^2 = (s)(2s)^2 = 4s^3$$

$$s = \sqrt[3]{\frac{1.8\times10^{-11}}{4}} = 1.7\times10^{-4}\text{ M} = [Mg^{2+}]$$

(b) Even though water has been added to the original solution, it remains saturated (it is in equilibrium with the undissolved solid $Mg(OH)_2$). $\left[Mg^{2+}\right] = 1.7\times10^{-4}$ M.

(c) Although HCl(aq) reacts with OH^-, it will not react with Mg^{2+}. The solution is simply a more dilute solution of Mg^{2+}.

$$\left[Mg^{2+}\right] = 1.7\times10^{-4}\text{ M}\times\frac{100.0\text{ mL initial volume}}{(100.0+500.)\text{ mL final volume}} = 2.8\times10^{-5}\text{ M}$$

(d) In this instance, we have a dual dilution to a 275.0 mL total volume, followed by a common-ion scenario.

$$\text{initial}\left[Mg^{2+}\right] = \frac{\left(25.00\text{ mL}\times\frac{1.7\times10^{-4}\text{ mmol }Mg^{2+}}{1\text{ mL}}\right)+\left(250.0\text{ mL}\times\frac{0.065\text{ mmol }Mg^{2+}}{1\text{ mL}}\right)}{275.0\text{ mL total volume}}$$

$$= 0.059\text{ M}$$

$$\text{initial}\left[OH^-\right] = \frac{25.00\text{ mL}\times\frac{1.7\times10^{-4}\text{ mmol }Mg^{2+}}{1\text{ mL}}\times\frac{2\text{ mmol }OH^-}{1\text{ mmol }Mg^{2+}}}{275.0\text{ mL total volume}} = 3.1\times10^{-5}\text{ M}$$

Let's see if precipitation occurs.

$$Q_{sp} = \left[\mathrm{Mg^{2+}}\right]\left[\mathrm{OH^-}\right]^2 = (0.059)\left(3.1\times10^{-5}\right)^2 = 5.7\times10^{-11} > 1.8\times10^{-11} = K_{sp}$$

Thus, precipitation does occur, but very little precipitate forms. If $\left[\mathrm{OH^-}\right]$ goes down by $1.4\times10^{-5}\ \mathrm{M}$ (which means that $\left[\mathrm{Mg^{2+}}\right]$ drops by $0.7\times10^{-5}\,\mathrm{M}$), then

$\left[\mathrm{OH^-}\right] = 1.7\times10^{-5}\,\mathrm{M}$ and

$\left[\mathrm{Mg^{2+}}\right] = \left(0.059\ \mathrm{M} - 0.7\times10^{-5}\ \mathrm{M} =\right)0.059\ \mathrm{M}$, then $Q_{sp} < K_{sp}$ and precipitation will stop. Thus, $\left[\mathrm{Mg^{2+}}\right] = 0.059\ \mathrm{M}$.

(e) Again we have a dual dilution, now to a 200.0 mL final volume, followed by a common-ion scenario.

$$\text{initial}\left[\mathrm{Mg^{2+}}\right] = \frac{50.00\ \mathrm{mL}\times\dfrac{1.7\times10^{-4}\ \mathrm{mmol\,Mg^{2+}}}{1\ \mathrm{mL}}}{200.0\ \mathrm{mL\ total\ volume}} = 4.3\times10^{-5}\ \mathrm{M}$$

$$\text{initial}\left[\mathrm{OH^-}\right] = 0.150\ \mathrm{M}\times\frac{150.0\ \mathrm{mL\ initial\ volume}}{200.0\ \mathrm{mL\ total\ volume}} = 0.113\ \mathrm{M}$$

Now it is evident that precipitation will occur. Next we determine the $\left[\mathrm{Mg^{2+}}\right]$that can exist in solution with $0.113\ \mathrm{M\ OH^-}$. It is clear that $\left[\mathrm{Mg^{2+}}\right]$ will drop dramatically to satisfy the K_{sp} expression but the larger value of $\left[\mathrm{OH^-}\right]$ will scarcely be affected.

$$K_{sp} = \left[\mathrm{Mg^{2+}}\right]\left[\mathrm{OH^-}\right]^2 = 1.8\times10^{-11} = \left[\mathrm{Mg^{2+}}\right](0.0113\ \mathrm{M})^2$$

$$\left[\mathrm{Mg^{2+}}\right] = \frac{1.8\times10^{-11}}{(0.113)^2} = 1.4\times10^{-9}\ \mathrm{M}$$

SELF-ASSESSMENT EXERCISES

90. (E)

(a) K_{sp}: The solubility product constant, which is the constant for the equilibrium established between a solid solute and its ions in a saturated solution

(b) K_f: The formation constant of a complex ion, which is the equilibrium constant describing the formation of a complex ion from a central ion (typically a metal cation) and the ligands that attach to it

(c) Q_{sp}: The ion product, which is the product of concentrations of the constituent ions of a compound, and is used to determine if they meet the precipitation criteria or not.

(d) Complex ion: A polyatomic cation or anion composed of a central metal ion to which other groups (molecules or ions) called ligands are coordinated/attached to.

91. (E)

(a) Common-ion effect in solubility equilibrium: Where the solubility of a sparingly soluble compound is suppressed by the presence of a quantity (often large) of one of the compound's ions from another source

(b) Fractional precipitation: A technique in which two or more ions in solution, each capable of being precipitated by the same reagent, are separated by the proper use of that reagent: One ion is precipitated, while the other(s) remains in solution.

(c) Ion-pair formation: Pair of ions held loosely together by electrostatic interactions in water

(d) Qualitative cation analysis: A qualitative method that is used to identify various the cations present in a solution by stepwise addition of various anions in order to selectively precipitate out various cations in steps.

92. (E)

(a) Solubility and solubility product constant: Solubility is the number of moles of a precipitate dissolved in a certain mass of water (or some other solvent.) The solubility product constant is the constant for the equilibrium established between a solid solute and its ions in a saturated solution.

(b) Common–ion effect and salt effect: The common ion effect is a consequence of Le Châtelier's principle, where the equilibrium concentration of all ions resulting from the dissolution of a sparingly soluble precipitate is reduced because a large amount of one (or more) of the ions from another source is present. The salt effect is the presence of a large quantity of ions from a very soluble salt which slightly increases the solubility of a sparingly soluble precipitate.

(c) Ion pair and ion product: An ion pair comprises two oppositely charged ions held together by electrostatic forces. The ion product (Q_{sp}) is the product of concentrations of the constituent ions of a compound, and is used to determine if they meet the precipitation criteria or not.

93. **(E)** The answer is (d). See the reasoning below.
(a) Wrong, because the stoichiometry is wrong
(b) Wrong, because $K_{sp} = [Pb^{2+}]\cdot[I^-]^2$
(c) Wrong, because $[Pb^{2+}] = K_{sp}/[I^-]^2$
(d) Correct because of the $[Pb^{2+}]$:$2[I^-]$ stoichiometry

94. **(E)** The answer is (a). $BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$. If Na_2SO_4 is added, the common–ion effect forces the equilibrium to the left and reduces $[Ba^{2+}]$.

95. **(E)** The answer is (c). Choices (b) and (d) reduce solubility because of the common–ion effect. In the case of choice (c), the diverse non-common–ion effect or the "salt effect" causes more Ag_2CrO_4 to dissolve.

96. **(E)** The answer is (b). The sulfate salt of Cu is soluble, whereas the Pb salt is insoluble.

97. **(M)** The answers are (c) and (d). Adding NH_3 causes the solution to become basic (adding OH^-). Mg, Fe, Cu, and Al all have insoluble hydroxides. However, only Cu can form a complex ion with NH_3, which is soluble. In the case of $(NH_4)_2SO_4$, it is slightly acidic and dissolved readily in a base.

98. **(M)** The answer is (a). $CaCO_3$ is slightly basic, so it is more soluble in an acid. The only option for an acid given is NH_4Cl.

99. **(M)** The answer is (c). Referring to Figure 18-7, it is seen that ammonia is added to an aqueous H_2S solution to precipitate more metal ions. Since ammonia is a base, increasing the pH should cause more precipitation.

100. **(M)**
(a) $H_2C_2O_4$ is a moderately strong acid, so it is more soluble in a basic solution.
(b) $MgCO_3$ is slightly basic, so it is more soluble in an acidic solution.
(c) CdS is more soluble in acidic solutions, but the solubility is still so small that it is essentially insoluble even in acidic solutions.
(d) KCl is a neutral salt, and therefore its solubility is independent of pH.
(e) $NaNO_3$ is a neutral salt, and therefore its solubility is independent of pH.
(f) $Ca(OH)_2$, a strong base, is more soluble in an acidic solution.

101. **(E)** The answer is NH_3. NaOH(aq) precipitates both, and HCl(aq) precipitates neither. $Mg(OH)_2$ precipitates from an NH_3(aq) solution but forms the soluble complex $Cu(NH_3)_4(OH)_2$.

102. **(D)** $Al(OH)_3$ will precipitate. To demonstrate this, the pH of the acetate buffer needs to be determined first, from which the OH^- can be determined. The OH^- concentration can be used to calculate Q_{sp}, which can then be compared to K_{sp} to see if any $Al(OH)_3$ will precipitate. This is shown below:

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{\left[\mathrm{Ac^-}\right]}{\left[\mathrm{HAc}\right]} = -\log\left(1.8\times10^{-5}\right) + \log\frac{0.35\ \mathrm{M}}{0.45\ \mathrm{M}} = 4.65$$

$$[\mathrm{OH^-}] = 10^{-(14-\mathrm{pH})} = 4.467\times10^{-10}\ \mathrm{M}$$

$$\mathrm{Al(OH)_3} \rightleftharpoons \mathrm{Al^{3+}} + 3\mathrm{OH^-}$$

$$Q_{\mathrm{sp}} = (s)(3s)^3$$

$$Q_{\mathrm{sp}} = (0.275)\left(4.467\times10^{-10}\right)^3 = 2.45\times10^{-29}$$

$Q_{\mathrm{sp}} > K_{\mathrm{sp}}$, therefore there will be precipitation.

103. **(E)** The answer is (b). Based on solubility rules, $Cu_3(PO_4)_2$ is the only species that is sparingly soluble in water.

104. **(M)** The answer is (d). The abbreviated work shown for each part calculates the molar solubility (*s*) for all the salts. They all follow the basic outlined below:

$$\mathrm{M_xA_y} \rightleftharpoons \mathrm{xM} + \mathrm{yA}$$

$$\mathrm{K_{sp}} = (\mathrm{x}\cdot\mathrm{s})^{\mathrm{x}}\cdot(\mathrm{y}\cdot\mathrm{s})^{\mathrm{y}}$$

and we solve for s.

(a) $\mathrm{MgF_2} \rightleftharpoons \mathrm{Mg^{2+}} + 2\mathrm{F^-}$

$3.7\times10^{-8} = \mathrm{s}\cdot(2\mathrm{s})^2 = 4\mathrm{s}^3$

$\mathrm{s} = 2.1\times10^{-3}\mathrm{M}$

(b) $\mathrm{MgCO_3} \rightleftharpoons \mathrm{Mg^{2+}} + \mathrm{CO_3^{2-}}$

$3.5\times10^{-8} = \mathrm{s}\cdot\mathrm{s}$

$\mathrm{s} = 1.9\times10^{-4}\mathrm{M}$

(c) $\mathrm{Mg_3(PO_4)_2} \rightleftharpoons 3\mathrm{Mg^{2+}} + 2\mathrm{PO_4^{3-}}$

$1\times10^{-25} = (3\mathrm{s})^3\cdot(2\mathrm{s})^2 = 108\mathrm{s}^5$

$\mathrm{s} = 3.9\times10^{-6}\mathrm{M}$

(d) $\mathrm{Li_3PO_4} \rightleftharpoons 3\mathrm{Li^+} + \mathrm{PO_4^{3-}}$

$3.2\times10^{-9} = (3\mathrm{s})^3\cdot\mathrm{s} = 27\mathrm{s}^4$

$\mathrm{s} = 3.3\times10^{-3}\mathrm{M}$

105. **(E)** The answer is (b). This is due to the “salt effect.” The more moles of salt there are available, the greater the solubility. For (b), there are 0.300 moles of ions (3×0.100 M $Na_2S_2O_3$).

106. **(E)** It will decrease the amount of precipitate. Since all salts of NO_3^- are highly soluble and Ag^+ and Hg^{2+} salts of I^- are not, anything that forms a soluble complex ion with Ag^+ and Hg^{2+} will reduce the amount of those ions available for precipitation with I^- and therefore will reduce the amount of precipitate.

107. **(M)** No precipitate will form. To demonstrate this, one has to calculate $[Ag^+]$, and then, using $[I^-]$, determine the Q_{sp} and compare it to K_{sp} of AgI.

Since K_f is for the formation of the complex ion $Ag(CN)_2^-$, its inverse is for the dissociation of $Ag(CN)_2^-$ to Ag^+ and CN^-.

$$K_{dis} = 1/K_f = 1/5.6\times10^{18} = 1.786\times10^{-19}$$

The dissociation of $Ag(CN)_2^-$ is as follows:

$$Ag(CN)_2^-(aq) \rightleftharpoons Ag^+ + 2CN^-$$

$$K_{dis} = \frac{x(1.05+\cancel{x})}{(0.012-\cancel{x})} = 1.786\times10^{-19}$$

We can simplify the calculations by noting that x is very small in relation to $[Ag^+]$ and $[CN^-]$. Therefore, $x = 1.70\times10^{-19}$ M.

Dissociation of AgI is as follows:

$$AgI \rightleftharpoons Ag^+ + I^-$$

$$Q_{sp} = (1.7\times10^{-19})(2.0) = 3.4\times10^{-19}$$

Since $Q_{sp} < K_{sp}$, no precipitate will form.

108. **(M)** In both cases, the dissolution reaction is similar to reaction (18.5), for which $K = K_f \times K_{sp}$. This is an exceedingly small quantity for (a) but large for (b). $CuCO_3$ is soluble in $NH_3(aq)$ and CuS(s) is not.

109. **(M)** In this chapter, the concept of solubility of sparingly soluble precipitates is the overarching concept. Deriving from this overall concept is the dissociation constant for the precipitate, K_{sp} and molar solubility. Also emanating from the solubility concept are factors that affect solubility: the common ion–effect, the salt effect, the effects of pH on solubility, and formation of complex ions. Take a look at the subsection headings and problems for more refining of the general and specific concepts.

CHAPTER 19

SPONTANEOUS CHANGE: ENTROPY AND GIBBS ENERGY

PRACTICE EXAMPLES

1A **(E)** In general, $\Delta S > 0$ if $\Delta n_{\text{gas}} > 0$. This is because gases are very dispersed compared to liquids or solids; (gases possess large entropies). Recall that Δn_{gas} is the difference between the sum of the stoichiometric coefficients of the gaseous products and a similar sum for the reactants.

(a) $\Delta n_{\text{gas}} = 2 + 0 - (2 + 1) = -1$. One mole of gas is consumed here. We predict $\Delta S < 0$.

(b) $\Delta n_{\text{gas}} = 1 + 0 - 0 = +1$. Since one mole of gas is produced, we predict $\Delta S > 0$.

1B **(E) (a)** The outcome is uncertain in the reaction between ZnS(s) and $\mathrm{Ag_2O(s)}$. We have used Δn_{gas} to estimate the sign of entropy change. There is no gas involved in this reaction and thus our prediction is uncertain.

(b) In the chlor-alkali process the entropy increases because two moles of gas have formed where none were originally present ($\Delta n_{gas} = (1 + 1 + 0) - (0 + 0) = 2$

2A **(E)** For a vaporization, $\Delta G^{\circ}_{\text{vap}} = 0 = \Delta H^{\circ}_{\text{vap}} - T\Delta S^{\circ}_{\text{vap}}$. Thus, $\Delta S^{\circ}_{\text{vap}} = \Delta H^{\circ}_{\text{vap}} / T_{\text{vap}}$.

We substitute the given values. $\Delta S^{\circ}_{\text{vap}} = \dfrac{\Delta H^{\circ}_{\text{vap}}}{T_{\text{vap}}} = \dfrac{20.2 \text{ kJ mol}^{-1}}{(-29.79 + 273.15)\text{ K}} = 83.0 \text{ J mol}^{-1}\text{ K}^{-1}$

2B **(E)** For a phase change, $\Delta G^{\circ}_{\text{tr}} = 0 = \Delta H^{\circ}_{\text{tr}} - T\Delta S^{\circ}_{\text{tr}}$. Thus, $\Delta H^{\circ}_{\text{tr}} = T\Delta S^{\circ}_{\text{tr}}$. We substitute in the given values. $\Delta H^{\circ}_{\text{tr}} = T\Delta S^{\circ}_{\text{tr}} = (95.5 + 273.2)\text{ K} \times 1.09 \text{ J mol}^{-1}\text{ K}^{-1} = 402 \text{ J/mol}$

3A **(M)** The entropy change for the reaction is expressed in terms of the standard entropies of the reagents.

$$\Delta S^{\circ} = 2S^{\circ}[\mathrm{NH_3(g)}] - S^{\circ}[\mathrm{N_2(g)}] - 3S^{\circ}[\mathrm{H_2(g)}]$$
$$= 2\times 192.5 \text{ J mol}^{-1}\text{K}^{-1} - 191.6 \text{ J mol}^{-1}\text{ K}^{-1} - 3\times 130.7 \text{ J mol}^{-1}\text{ K}^{-1} = -198.7 \text{ J mol}^{-1}\text{ K}^{-1}$$

Thus to form *one* mole of $\mathrm{NH_3(g)}$, the standard entropy change is $-99.4 \text{ J mol}^{-1}\text{ K}^{-1}$

3B **(M)** The entropy change for the reaction is expressed in terms of the standard entropies of the reagents.

$$\Delta S^\circ = S^\circ[\mathrm{NO(g)}] + S^\circ[\mathrm{NO_2(g)}] - S^\circ[\mathrm{N_2O_3(g)}]$$

$$138.5\ \mathrm{J\ mol^{-1}\ K^{-1}} = 210.8\ \mathrm{J\ mol^{-1}\ K^{-1}} + 240.1\ \mathrm{J\ mol^{-1}\ K^{-1}} - S^\circ[\mathrm{N_2O_3(g)}]$$

$$= 450.9\ \mathrm{J\ mol^{-1}\ K^{-1}} - S^\circ[\mathrm{N_2O_3(g)}]$$

$$S^\circ[\mathrm{N_2O_3(g)}] = 450.9\ \mathrm{J\ mol^{-1}\ K^{-1}} - 138.5\ \mathrm{J\ mol^{-1}\ K^{-1}} = 312.4\ \mathrm{J\ mol^{-1}\ K}$$

4A **(E) (a)** Because $\Delta n_{\mathrm{gas}} = 2 - (1+3) = -2$ for the synthesis of ammonia, we would predict $\Delta S < 0$ for the reaction. We already know that $\Delta H < 0$. Thus, the reaction falls into case 2, namely, a reaction that is spontaneous at low temperatures and non-spontaneous at high temperatures.

(b) For the formation of ethylene $\Delta n_{\mathrm{gas}} = 1 - (2+0) = -1$ and thus $\Delta S < 0$. We are given that $\Delta H > 0$ and, thus, this reaction corresponds to case 4, namely, a reaction that is non-spontaneous at all temperatures.

4B **(E) (a)** Because $\Delta n_{\mathrm{gas}} = +1$ for the decomposition of calcium carbonate, we would predict $\Delta S > 0$ for the reaction, favoring the reaction at high temperatures. High temperatures also favor this endothermic $(\Delta H^\circ > 0)$ reaction.

(b) The "roasting" of ZnS(s) has $\Delta n_{\mathrm{gas}} = 2 - 3 = -1$ and, thus, $\Delta S < 0$. We are given that $\Delta H < 0$; thus, this reaction corresponds to case 2, namely, a reaction that is spontaneous at low temperatures, and non-spontaneous at high ones.

5A **(E)** The expression $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is used with $T = 298.15\ \mathrm{K}$.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -1648\ \mathrm{kJ} - 298.15\ \mathrm{K} \times (-549.3\ \mathrm{J\ K^{-1}}) \times (1\ \mathrm{kJ}/1000\ \mathrm{J})$$

$$= -1648\ \mathrm{kJ} + 163.8\ \mathrm{kJ} = -1484\ \mathrm{kJ}$$

5B **(M)** We just need to substitute values from Appendix D into the supplied expression.

$$\Delta G^\circ = 2\Delta G_f^\circ[\mathrm{NO_2(g)}] - 2\Delta G_f^\circ[\mathrm{NO(g)}] - \Delta G_f^\circ[\mathrm{O_2(g)}]$$

$$= 2 \times 51.31\ \mathrm{kJ\ mol^{-1}} - 2 \times 86.55\ \mathrm{kJ\ mol^{-1}} - 0.00\ \mathrm{kJ\ mol^{-1}} = -70.48\ \mathrm{kJ\ mol^{-1}}$$

6A **(M)** Pressures of gases and molarities of solutes in aqueous solution appear in thermodynamic equilibrium constant expressions. Pure solids and liquids (including solvents) do not appear.

(a) $K = \dfrac{P_{SiCl_4}}{P_{Cl_2}^2} = K_p$ **(b)** $K = \dfrac{[\mathrm{HOCl}][\mathrm{H^+}][\mathrm{Cl^-}]}{P_{Cl_2}}$

$K = K_p$ for (a) because all terms in the K expression are gas pressures.

6B **(M)** We need the balanced chemical equation in order to write the equilibrium constant expression. We start by translating names into formulas.

$$\mathrm{PbS(s)+HNO_3(aq)\rightarrow Pb(NO_3)_2(aq)+S(s)+NO(g)}$$

The equation then is balanced with the ion-electron method.

$$\text{oxidation}:\{\mathrm{PbS(s)\rightarrow Pb^{2+}(aq)+S(s)+2e^-}\quad\}\times 3$$

$$\text{reduction}:\{\mathrm{NO_3^-(aq)+4H^+(aq)+3e^-\rightarrow NO(g)+2H_2O(l)}\quad\}\times 2$$

$$\text{net ionic}:\mathrm{3\,PbS(s)+2NO_3^-(aq)+8H^+(aq)\rightarrow 3Pb^{2+}(aq)+3S(s)+2NO(g)+4H_2O(l)}$$

In writing the thermodynamic equilibrium constant, recall that neither pure solids (PbS(s) and S(s)) nor pure liquids $(\mathrm{H_2O(l)})$ appear in the thermodynamic equilibrium constant expression. Note also that we have written $\mathrm{H^+(aq)}$ here for brevity even though we understand that $\mathrm{H_3O^+(aq)}$ is the acidic species in aqueous solution.

$$K=\frac{[Pb^{2+}]^3\,p_{NO}^2}{[NO_3^-]^2[H^+]^8}$$

7A **(M)** Since the reaction is taking place at 298.15 K, we can use standard free energies of formation to calculate the standard free energy change for the reaction:

$$\mathrm{N_2O_4(g)\ \rightleftharpoons\ 2\,NO_2(g)}$$

$$\Delta G^\circ=2\Delta G_f^\circ\left[\mathrm{NO_2(g)}\right]-\Delta G_f^\circ\left[\mathrm{N_2O_4(g)}\right]=2\times 51.31\ \text{kJ/mol}-97.89\ \text{kJ/mol}=+4.73\,\text{kJ}$$

ΔG^{o}_{rxn} = +4.73 kJ . Thus, the forward reaction is non-spontaneous as written at 298.15 K.

7B **(M)** In order to answer this question we must calculate the reaction quotient and compare it to the K_p value for the reaction:

$$\mathrm{N_2O_4(g)\ \rightleftharpoons\ 2\,NO_2(g)}\qquad Q_p=\frac{(0.5)^2}{0.5}=0.5$$

0.5 bar 0.5 bar

ΔG^{o}_{rxn} = +4.73 kJ = $-RT\ln K_p$; 4.73 kJ/mol = $-(8.3145\times 10^{-3}$ kJ/K·mol)(298.15 K)lnK_p

Therefore, K_p = 0.148. Since Q_p is greater than K_p, we can conclude that the reverse reaction will proceed spontaneously, i.e. NO_2 will spontaneously convert into N_2O_4.

8A **(D)** We first determine the value of ΔG° and then set $\Delta G^\circ=-RT\ln K$ to determine K.

$$\Delta G=\Delta G_f^\circ\left[\mathrm{Ag^+(aq)}\right]+\Delta G_f^\circ[\mathrm{I^-(aq)}]-\Delta G_f^\circ\left[\mathrm{AgI(s)}\right]$$

$$=[(77.11-51.57)-(-66.19)]\ \text{kJ/mol}=+91.73$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = -\frac{-91.73\text{ kJ/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}\times 298.15\text{ K}}\times\frac{1000\text{ J}}{1\text{ kJ}} = -37.00$$

$$K = \mathrm{e}^{-37.00} = 8.5\times 10^{-17}$$

This is precisely equal to the value for the K_{sp} of AgI listed in Appendix D.

8B **(D)** We begin by translating names into formulas.

$MnO_2(s) + HCl(aq) \rightarrow Mn^{2+}(aq) + Cl_2(aq)$ Then we produce a balanced net ionic equation with the ion-electron method.

$$\text{oxidation}: 2\,Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

$$\text{reduction}: MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$$

$$\text{net ionic}: MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$

Next we determine the value of ΔG° for the reaction and then the value of K.

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\left[Mn^{2+}(aq)\right] + \Delta G_f^\circ\left[Cl_2(g)\right] + 2\Delta G_f^\circ\left[H_2O(l)\right]\\ &\quad - \Delta G_f^\circ\left[MnO_2(s)\right] - 4\Delta G_f^\circ\left[H^+(aq)\right] - 2\Delta G_f^\circ\left[Cl^-(aq)\right]\\ &= -228.1\text{ kJ} + 0.0\text{ kJ} + 2\times(-237.1\text{ kJ})\\ &\quad -(-465.1\text{ kJ}) - 4\times 0.0\text{ kJ} - 2\times(-131.2\text{ kJ}) = +25.2\text{ kJ}\end{aligned}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(+25.2\times 10^3\text{ J mol}^{-1})}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}\times 298.15\ K} = -10.1\underline{7} \qquad K = \mathrm{e}^{-10.2} = 4\times 10^{-5}$$

Because the value of K is so much smaller than unity, we do not expect an appreciable forward reaction.

9A **(M)** We set equal the two expressions for ΔG° and solve for the absolute temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \qquad \Delta H^\circ = T\Delta S^\circ - RT\ln K = T\left(\Delta S^\circ - R\ln K\right)$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K} = \frac{-114.1\times 10^3\text{ J/mol}}{\left[-146.4 - 8.3145\ \ln(150)\right]\text{J mol}^{-1}\text{ K}^{-1}} = 607\text{ K}$$

9B **(D)** We expect the value of the equilibrium constant to increase as the temperature decreases since this is an exothermic reaction and exothermic reactions will have a larger equilibrium constant (shift right to form more products), as the temperature decreases. Thus, we expect K to be larger than 1000, which is its value at 4.3×10^2 K.

(a) The value of the equilibrium constant at 25° C is obtained directly from the value of ΔG°, since that value is also for 25°C. Note:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -77.1\text{ kJ/mol} - 298.15\text{ K}\left(-0.1213\text{ kJ/mol}\cdot\text{K}\right) = -40.9\text{ kJ/mol}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-40.9\times 10^3\text{ J mol}^{-1})}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}\times 298.15\text{ K}} = 16.5 \qquad K = \mathrm{e}^{+16.5} = 1.5\times 10^7$$

(b) First, we solve for ΔG° at $75^{\circ}\text{C} = 348\text{ K}$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -77.1\ \frac{\text{kJ}}{\text{mol}} \times \frac{1000\text{ J}}{1\text{ kJ}} - \left(348.15\text{ K} \times \left(-121.3 \frac{\text{J}}{\text{mol K}}\right)\right)$$

$$= -34.87 \times 10^{3}\text{ J/mol}$$

Then we use this value to obtain the value of the equilibrium constant, as in part (a).

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-(-34.87 \times 10^{3}\text{ J mol}^{-1})}{8.3145\text{ J mol}^{-1}\text{ K}^{-1} \times 348.15\text{ K}} = 12.05 \qquad K = \text{e}^{+12.05} = 1.7 \times 10^{5}$$

As expected, K for this exothermic reaction decreases with increasing temperature.

10A **(M)** We use the value of $K_{\text{p}} = 9.1 \times 10^{2}$ at 800 K and $\Delta H^{o} = -1.8 \times 10^{5}\text{ J / mol}$, for the appropriate terms, in the van't Hoff equation.

$$\ln \frac{5.8 \times 10^{-2}}{9.1 \times 10^{2}} = \frac{-1.8 \times 10^{5}\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}} \left(\frac{1}{800\text{ K}} - \frac{1}{T\text{ K}}\right) = -9.66; \quad \frac{1}{T} = \frac{1}{800} - \frac{9.66 \times 8.3145}{1.8 \times 10^{5}}$$

$$1/T = 1.25 \times 10^{-3} - 4.5 \times 10^{-4} = 8.0 \times 10^{-4} \qquad T = 1240\text{ K} \approx 970^{\circ}\text{C}$$

This temperature is an estimate because it is an extrapolated point beyond the range of the data supplied.

10B **(M)** The temperature we are considering is $235^{\circ}\text{C} = 508\text{ K}$. We substitute the value of $K_{\text{p}} = 9.1 \times 10^{2}$ at 800 K and $\Delta H^{o} = -1.8 \times 10^{5}$ J/mol, for the appropriate terms, in the van't Hoff equation.

$$\ln \frac{K_{\text{p}}}{9.1 \times 10^{2}} = \frac{-1.8 \times 10^{5}\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}} \left(\frac{1}{800\text{ K}} - \frac{1}{508\text{ K}}\right) = +15_{.6}; \quad \frac{K_{\text{p}}}{9.1 \times 10^{2}} = \text{e}^{+15_{.6}} = 6 \times 10^{6}$$

$$K_{\text{p}} = 6 \times 10^{6} \times 9.1 \times 10^{2} = 5 \times 10^{9}$$

INTEGRATIVE EXAMPLE

11A **(D)** The value of ΔG^{o} can be calculated by finding the value of the equilibrium constant K_p at 25 °C. The equilibrium constant for the reaction is simply given by $K_{p} = p\{N_{2}O_{5}(g)\}$.

The vapor pressure of $N_2O_5(g)$ can be determined from the Clausius-Clapeyron eqution, which is a specialized version of the van’t Hoff equation.

Stepwise approach:

We first determine the value of ΔH_{sub}.

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{sub}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \ln \frac{760\text{ mmHg}}{100\text{ mmHg}} = \frac{\Delta H_{sub}}{8.314\text{Jmol}^{-1}\text{K}^{-1}} \left(\frac{1}{7.5 + 273.15} - \frac{1}{32.4 + 273.15}\right)$$

$$\Delta H_{sub} = \frac{2.028}{3.49 \times 10^{-5}} = 5.81 \times 10^{4}\text{ J/mol}$$

Using the same formula, we can now calculate the vapor pressure of N_2O_5 at 25 °C.

$$\ln\frac{p_3}{100\text{ mmHg}}=\frac{5.81\times10^4\text{ J/mol}}{8.314\text{Jmol}^{-1}\text{K}^{-1}}\left(\frac{1}{280.7}-\frac{1}{298.2}\right)=1.46\Rightarrow\frac{p_3}{100\text{ mmHg}}=e^{1.46}=4.31$$

$$p_3=4.31\times100\text{mmHg}\times\frac{1\text{ atm}}{760\text{ mmHg}}=0.567\text{atm}=K_p$$

$$\Delta G^o=-RT\ln K_p=-(8.314\times10^{-3}\text{kJmol}^{-1}\text{K}^{-1}\times298.15\text{K})\ln(0.567)=1.42\text{kJ/mol}$$

Conversion pathway approach:

$$\ln\frac{p_2}{p_1}=\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\Rightarrow\Delta H_{sub}=\frac{R\ln\dfrac{p_2}{p_1}}{\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)}$$

$$\Delta H_{sub}=\frac{8.314\text{Jmol}^{-1}\text{K}^{-1}\times\ln\dfrac{760\text{mmHg}}{100\text{mmHg}}}{\left(\dfrac{1}{7.5+273.15}-\dfrac{1}{32.4+273.15}\right)}=\frac{2.028}{3.49\times10^{-5}}\text{Jmol}^{-1}=5.81\times10^4\text{Jmol}^{-1}$$

$$\ln\frac{p_3}{p_1}=\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\Rightarrow p_3=p_1e^{\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$p_3=100\,mmHg\times e^{\frac{5.81\times10^4\text{ Jmol}^{-1}}{8.314\text{JK}^{-1}\text{mol}^{-1}}\left(\frac{1}{280.7}-\frac{1}{298.2}\right)\text{K}^{-1}}=431\text{mmHg}\times\frac{1\text{atm}}{760\text{mmHg}}=0.567\text{atm}=K_p$$

$$\Delta G^o=-RT\ln K_p=-(8.314\times10^{-3}\text{kJmol}^{-1}\text{K}^{-1}\times298.15\text{K})\ln(0.567)=1.42\text{kJ/mol}$$

11B **(D)** The standard entropy change for the reaction (ΔS^o) can be calculated from the known values of ΔH^o and ΔG^o.

Stepwise approach:

$$\Delta G^o=\Delta H^o-T\Delta S^o\Rightarrow\Delta S^o=\frac{\Delta H^o-\Delta G^o}{T}=\frac{-454.8\text{kJmol}^{-1}-(-323.1\text{kJmol}^{-1})}{298.15\text{K}}=-441.7\text{JK}^{-1}\text{mol}^{-1}$$

Plausible chemical reaction for the production of ethylene glycol can also be written as:

$$\text{2C(s)+3H}_2\text{(g)+O}_2\text{(g)}\longrightarrow\text{CH}_2\text{OHCH}_2\text{OH(l)}$$

Since $\Delta S^o=\sum\{S^o_{products}\}-\sum\{S^o_{reac\tan ts}\}$ it follows that:

$$\Delta S^o_{rxn}=S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)})-[2\times S^o(\text{C(s)})+3\times S^o(\text{H}_2\text{(g)})+S^o(\text{O}_2\text{(g)})]$$

$$-441.7\text{JK}^{-1}\text{mol}^{-1}=S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)})-[2\times5.74\text{JK}^{-1}\text{mol}^{-1}+3\times130.7\text{JK}^{-1}\text{mol}^{-1}+205.1\text{JK}^{-1}\text{mol}^{-1}]$$

$$S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)})=-441.7\text{JK}^{-1}\text{mol}^{-1}+608.68\text{JK}^{-1}\text{mol}^{-1}=167\text{JK}^{-1}\text{mol}^{-1}$$

Conversion pathway approach:

$$\Delta G^o = \Delta H^o - T\Delta S^o \Rightarrow \Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-454.8\text{kJmol}^{-1} - (-323.1\text{kJmol}^{-1})}{298.15\text{K}} = -441.7\text{JK}^{-1}\text{mol}^{-1}$$

$$-441.7\text{JK}^{-1}\text{mol}^{-1} = S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)}) - [2 \times 5.74\text{JK}^{-1}\text{mol}^{-1} + 3 \times 130.7\text{JK}^{-1}\text{mol}^{-1} + 205.1\text{JK}^{-1}\text{mol}^{-1}]$$

$$S^o(\text{CH}_2\text{OHCH}_2\text{OH(l)}) = -441.7\text{JK}^{-1}\text{mol}^{-1} + 608.68\text{JK}^{-1}\text{mol}^{-1} = 167\text{JK}^{-1}\text{mol}^{-1}$$

EXERCISES

Spontaneous Change and Entropy

1. **(E) (a)** The freezing of ethanol involves a *decrease* in the entropy of the system. There is a reduction in mobility and in the number of forms in which their energy can be stored when they leave the solution and arrange themselves into a crystalline state.

(b) The sublimation of dry ice involves converting a solid that has little mobility into a highly dispersed vapor which has a number of ways in which energy can be stored (rotational, translational). Thus, the entropy of the system *increases* substantially.

(c) The burning of rocket fuel involves converting a liquid fuel into the highly dispersed mixture of the gaseous combustion products. The entropy of the system *increases* substantially.

2. **(E)** Although there is a substantial change in entropy involved in **(a)** changing H_2O (1iq., 1 atm) to H_2O (g, 1 atm), it is not as large as **(c)** converting the liquid to a gas at 10 mmHg. The gas is more dispersed, (less ordered), at lower pressures. In **(b),** if we start with a solid and convert it to a gas at the lower pressure, the entropy change should be even larger, since a solid is more ordered (concentrated) than a liquid. Thus, in order of increasing ΔS, the processes are: **(a)** $<$ **(c)** $<$ **(b)**.

3. **(E)** The first law of thermodynamics states that energy is neither created nor destroyed (thus, "The energy of the universe is constant"). A consequence of the second law of thermodynamics is that entropy of the universe increases for all spontaneous, that is, naturally occurring, processes (and therefore, "the entropy of the universe increases toward a maximum").

4. **(E)** When pollutants are produced they are usually dispersed throughout the environment. These pollutants thus start in a relatively compact form and end up dispersed throughout a large volume mixed with many other substances. The pollutants are highly dispersed, thus, they have a high entropy. Returning them to their original compact form requires reducing this entropy, which is a highly non-spontaneous process. If we have had enough foresight to retain these pollutants in a reasonably compact form, such as disposing of them in a *secure* landfill, rather than dispersing them in the atmosphere or in rivers and seas, the task of permanently removing them from the environment, and perhaps even converting them to useful forms, would be considerably easier.

5. **(E) (a)** Increase in entropy because a gas has been created from a liquid, a condensed phase.

(b) Decrease in entropy as a condensed phase, a solid, is created from a solid and a gas.

(c) For this reaction we cannot be certain of the entropy change. Even though the number of moles of gas produced is the same as the number that reacted, we cannot conclude that the entropy change is zero because not all gases have the same molar entropy.

(d) $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$ Decrease in entropy since five moles of gas with high entropy become only four moles of gas, with about the same quantity of entropy per mole.

6. **(E) (a)** At 75° C, 1 mol H_2O (g, 1 atm) has a greater entropy than 1 mol H_2O (1iq., 1 atm) since a gas is much more dispersed than a liquid.

(b) $50.0 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.8 \text{ g Fe}} = 0.896$ mol Fe has a higher entropy than 0.80 mol Fe, both (s) at 1 atm and 5° C, because entropy is an extensive property that depends on the amount of substance present.

(c) 1 mol Br_2 (1iq., 1 atm, 8° C) has a higher entropy than 1 mol Br_2 (s, 1atm, -8° C) because solids are more ordered (concentrated) substances than are liquids, and furthermore, the liquid is at a higher temperature.

(d) 0.312 mol SO_2 (g, 0.110 atm, 32.5° C) has a higher entropy than 0.284 mol O_2 (g, 15.0 atm, 22.3° C) for at least three reasons. First, entropy is an extensive property that depends on the amount of substance present (more moles of SO_2 than O_2). Second, entropy increases with temperature (temperature of SO_2 is greater than that for O_2. Third, entropy is greater at lower pressures (the O_2 has a much higher pressure). Furthermore, entropy generally is higher per mole for more complicated molecules.

7. **(E) (a)** Negative; A liquid (moderate entropy) combines with a solid to form another solid.

(b) Positive; One mole of high entropy gas forms where no gas was present before.

(c) Positive; One mole of high entropy gas forms where no gas was present before.

(d) Uncertain; The number of moles of gaseous products is the same as the number of moles of gaseous reactants.

(e) Negative; Two moles of gas (and a solid) combine to form just one mole of gas.

8. **(M)** The entropy of formation of a compound would be the difference between the absolute entropy of one mole of the compound and the sum of the absolute entropies of the appropriate amounts of the elements constituting the compound, with each species in its most stable form.

Stepwise approach:
It seems as though $CS_2(1)$ would have the highest molar entropy of formation of the compounds listed, since it is the only substance whose formation does not involve the consumption of high entropy gaseous reactants. This prediction can be checked by determining ΔS_f^o values from the data in Appendix D:

(a) $C(\text{graphite}) + 2H_2(g) \rightleftharpoons CH_4(g)$

$$\Delta S_f^o[CH_4(g)] = S^o[CH_4(g)] - S^o[C(\text{graphite})] - 2S^o[H_2(g)]$$
$$= 186.3\ \text{J mol}^{-1}\text{K}^{-1} - 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 2 \times 130.7\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= -80.8\ \text{J mol}^{-1}\text{K}^{-1}$$

(b) $2C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons CH_3CH_2OH(l)$

$$\Delta S_f^o[CH_3CH_2OH(l)] = S^o[CH_3CH_2OH(l)] - 2S^o[C(\text{graphite})] - 3S^o[H_2(g)] - \frac{1}{2}S^o[O_2(g)]$$
$$= 160.7\,\text{J mol}^{-1}\,\text{K}^{-1} - 2\times 5.74\ \text{J mol}^{-1}\,\text{K}^{-1} - 3\times 130.7\ \text{J mol}^{-1}\,\text{K}^{-1} - \tfrac{1}{2}\times 205.1\text{J mol}^{-1}\text{K}^{-1}$$
$$= -345.4\ \text{J mol}^{-1}\,\text{K}^{-1}$$

(c) $C(\text{graphite}) + 2S(\text{rhombic}) \rightleftharpoons CS_2(l)$

$$\Delta S_f^\circ[CS_2(l)] = S^o[CS_2(l)] - S^o[C(\text{graphite})] - 2S^o[S(\text{rhombic})]$$
$$= 151.3\ \text{J mol}^{-1}\ \text{K}^{-1} - 5.74\ \text{J mol}^{-1}\,\text{K}^{-1} - 2\times 31.80\ \text{J mol}^{-1}\,\text{K}^{-1}$$
$$= 82.0\ \text{J mol}^{-1}\,\text{K}^{-1}$$

Conversion pathway approach:
CS_2 would have the highest molar entropy of formation of the compounds listed, because it is the only substance whose formation does not involve the consumption of high entropy gaseous reactants.

(a) $C(\text{graphite}) + 2H_2(g) \rightleftharpoons CH_4(g)$

$$\Delta S_f^o[CH_4(g)] = 186.3\ \text{J mol}^{-1}\text{K}^{-1} - 5.74\ \text{J mol}^{-1}\text{K}^{-1} - 2\times 130.7\ \text{J mol}^{-1}\text{K}^{-1}$$
$$= -80.8\ \text{J mol}^{-1}\text{K}^{-1}$$

(b) $2C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons CH_3CH_2OH(l)$

$$\Delta S_f^o[CH_3CH_2OH(l)] = (160.7 - 2\times 5.74 - 3\times 130.7 - \tfrac{1}{2}\times 205.1)\text{J mol}^{-1}\,\text{K}^{-1}$$
$$= -345.4\ \text{J mol}^{-1}\,\text{K}^{-1}$$

(c) $C(\text{graphite}) + 2S(\text{rhombic}) \rightleftharpoons CS_2(l)$

$$\Delta S_f^\circ[CS_2(l)] = 151.3\,\text{J mol}^{-1}\ \text{K}^{-1} - 5.74\,\text{J mol}^{-1}\,\text{K}^{-1} - 2\times 31.80\,\text{J mol}^{-1}\,\text{K}^{-1}$$
$$= 82.0\ \text{J mol}^{-1}\,\text{K}^{-1}$$

Phase Transitions

9. **(M) (a)** $\Delta H^\circ_{\text{vap}} = \Delta H^\circ_{\text{f}}[\text{H}_2\text{O(g)}] - \Delta H^\circ_{\text{f}}[\text{H}_2\text{O(l)}] = -241.8 \text{ kJ/mol} - (-285.8\,\text{kJ/mol})$
$= +44.0 \text{ kJ/mol}$

$$\Delta S^\circ_{\text{vap}} = S^\text{o}\left[\text{H}_2\text{O}(\text{g})\right] - S^\text{o}\left[\text{H}_2\text{O}(\text{l})\right] = 188.8 \text{ J mol}^{-1}\text{ K}^{-1} - 69.91 \text{ J mol}^{-1}\text{K}^{-1}$$
$$= 118.9 \text{ J mol}^{-1}\text{K}^{-1}$$

There is an alternate, but incorrect, method of obtaining $\Delta S^\circ_{\text{vap}}$.

$$\Delta S^\circ_{\text{vap}} = \frac{\Delta H^\circ_{\text{vap}}}{T} = \frac{44.0\times10^3 \text{ J/mol}}{298.15\,\text{K}} = 148 \text{ J mol}^{-1}\text{ K}^{-1}$$

This method is invalid because the temperature in the denominator of the equation must be the temperature at which the liquid-vapor transition is at equilibrium. Liquid water and water vapor at 1 atm pressure (standard state, indicated by $^\circ$) are in equilibrium only at $100^\circ\text{ C} = 373\text{ K}$.

(b) The reason why $\Delta H^\circ_{\text{vap}}$ is different at 25° C from its value at 100° C has to do with the heat required to bring the reactants and products down to 298 K from 373 K. The specific heat of liquid water is higher than the heat capacity of steam. Thus, more heat is given off by lowering the temperature of the liquid water from 100° C to 25° C than is given off by lowering the temperature of the same amount of steam. Another way to think of this is that hydrogen bonding is more disrupted in water at 100°C than at 25°C (because the molecules are in rapid—thermal—motion), and hence, there is not as much energy needed to convert liquid to vapor (thus $\Delta H^\circ_{\text{vap}}$ has a smaller value at 100° C. The reason why $\Delta S^\circ_{\text{vap}}$ has a larger value at 25° C than at 100° C has to do with dispersion. A vapor at 1 atm pressure (the case at both temperatures) has about the same entropy. On the other hand, liquid water is more disordered (better able to disperse energy) at higher temperatures since more of the hydrogen bonds are disrupted by thermal motion. (The hydrogen bonds are totally disrupted in the two vapors).

10. **(M)** In this problem we are given standard enthalpies of the formation (ΔH^o_f) of liquid and gas pentane at 298.15 K and asked to estimate the normal boiling point of pentane, ΔG^o_{vap} and furthermore comment on the significance of the sign of ΔG^o_{vap}. The general strategy in solving this problem is to first determine ΔH^o_{vap} from the known enthalpies of formation. Trouton's rule can then be used to determine the normal boiling point of pentane. Lastly, $\Delta G^o_{vap,298K}$ can be calculated using $\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}}$.

Stepwise approach:

Calculate ΔH^{o}_{vap} from the known values of ΔH^{o}_{f} (part a):

$$C_5H_{12}(l) \rightleftharpoons C_5H_{12}(g)$$

$$\Delta H^{o}_{f} \quad -173.5 \text{ kJmol}^{-1} \qquad -146.9 \text{ kJmol}^{-1}$$

$$\Delta H^{o}_{vap} = -146.9 - (-173.5)\text{kJmol}^{-1} = 26.6\text{kJmol}^{-1}$$

Determine normal boiling point using Trouton's rule (part a):

$$\Delta S^{o}_{vap} = \frac{\Delta H^{o}_{vap}}{T_{nbp}} = 87\text{Jmol}^{-1}\text{K}^{-1}$$

$$T_{nbp} = \frac{\Delta H^{o}_{vap}}{\Delta S^{o}_{vap}} = \frac{26.6kJmol^{-1}}{\frac{87kJK^{-1}mol^{-1}}{1000}} = 306K$$

$$T_{nbp} = 32.9^{o}C$$

Use $\Delta G^{\circ}_{\text{vap}} = \Delta H^{\circ}_{\text{vap}} - T\Delta S^{\circ}_{\text{vap}}$ to calculate $\Delta G^{\circ}_{\text{vap,298K}}$ (part b):

$$\Delta G^{\circ}_{\text{vap}} = \Delta H^{\circ}_{\text{vap}} - T\Delta S^{\circ}_{\text{vap}}$$

$$\Delta G^{\circ}_{\text{vap,298K}} = 26.6\text{kJmol}^{-1} - 298.15K \times \frac{87\text{kJmol}^{-1}\text{K}^{-1}}{1000}$$

$$\Delta G^{\circ}_{\text{vap,298K}} = 0.66\text{kJmol}^{-1}$$

Comment on the value of $\Delta G^{\circ}_{\text{vap,298K}}$ (part c):

The positive value of $\Delta G^{\circ}_{\text{vap}}$ indicates that normal boiling (having a vapor pressure of 1.00 atm) for pentane should be non-spontaneous (will not occur) at 298. The vapor pressure of pentane at 298 K should be less than 1.00 atm.

Conversion pathway approach:

$$C_5H_{12}(l) \rightleftharpoons C_5H_{12}(g)$$

$$\Delta H^{o}_{f} \quad -173.5 \text{ kJmol}^{-1} \qquad -146.9 \text{ kJmol}^{-1}$$

$$\Delta H^{o}_{vap} = -146.9 - (-173.5)\text{kJmol}^{-1} = 26.6\text{kJmol}^{-1}$$

$$\Delta S^{o}_{vap} = \frac{\Delta H^{o}_{vap}}{T_{nbp}} = 87\text{Jmol}^{-1}\text{K}^{-1} \Rightarrow T_{nbp} = \frac{\Delta H^{o}_{vap}}{\Delta S^{o}_{vap}} = \frac{26.6\text{kJmol}^{-1}}{\frac{87\text{kJK}^{-1}\text{mol}^{-1}}{1000}} = 306K$$

$$\Delta G^{\circ}_{\text{vap}} = \Delta H^{\circ}_{\text{vap}} - T\,\Delta S^{\circ}_{\text{vap}} = 26.6\text{kJmol}^{-1} - 298.15K \times \frac{87\text{kJmol}^{-1}\text{K}^{-1}}{1000} = 0.66\text{kJmol}^{-1}$$

11. **(M)** Trouton's rule is obeyed most closely by liquids that do not have a high degree of order within the liquid. In both HF and CH_3OH, hydrogen bonds create considerable order within the liquid. In $C_6H_5CH_3$, the only attractive forces are non-directional London forces, which have no preferred orientation as hydrogen bonds do. Thus, of the three choices, liquid $C_6H_5CH_3$ would most closely follow Trouton's rule.

12. **(E)** $\Delta H^\circ_{\text{vap}} = \Delta H^\circ_{\text{f}}[\text{Br}_2(\text{g})] - \Delta H^\circ_{\text{f}}[\text{Br}_2(\text{l})] \approx 30.91 \text{ kJ/mol} - 0.00 \text{ kJ/mol} = 30.91 \text{ kJ/mol}$

$$\Delta S^\circ_{\text{vap}} = \frac{\Delta H^\circ_{\text{vap}}}{T_{\text{vap}}} \approx 87 \text{ J mol}^{-1} \text{ K}^{-1} \text{ or } \quad T_{\text{vap}} = \frac{\Delta H^\circ_{\text{vap}}}{\Delta S^\circ_{\text{vap}}} \approx \frac{30.91\times10^3 \text{ J/mol}}{87 \text{ J mol}^{-1}\text{K}^{-1}} = 3.5\times10^2 \text{ K}$$

The accepted value of the boiling point of bromine is $58.8^\circ\text{C} = 332 \text{ K} = 3.32\times10^2 \text{ K}$. Thus, our estimate is in reasonable agreement with the measured value.

13. **(M)** The liquid water-gaseous water equilibrium $\text{H}_2\text{O (l, 0.50 atm)} \rightleftharpoons \text{H}_2\text{O (g, 0.50 atm)}$ can only be established at <u>one temperature</u>, namely the boiling point for water under 0.50 atm external pressure. We can estimate the boiling point for water under 0.50 atm external pressure by using the Clausius-Clapeyron equation:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H^o_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

We know that at 373 K, the pressure of water vapor is 1.00 atm. Let's make P_1 = 1.00 atm, P_2 = 0.50 atm and T_1 = 373 K. Thus, the boiling point under 0.50 atm pressure is T_2. To find T_2 we simply insert the appropriate information into the Clausius-Clapeyron equation and solve for T_2:

$$\ln\frac{0.50 \text{ atm}}{1.00 \text{ atm}} = \frac{40.7 \text{ kJ mol}^{-1}}{8.3145\times10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)$$

$$-1.4\underline{16} \times 10^{-4} \text{K} = \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right)$$

Solving for T_2 we find a temperature of 354 K or 81°C. Consequently, to achieve an equilibrium between gaseous and liquid water under 0.50 atm pressure, the temperature must be set at 354 K.

14. **(M)** Figure 12-19 (phase diagram for carbon dioxide) shows that at –60°C and under 1 atm of external pressure, carbon dioxide exists as a gas. In other words, neither solid nor liquid CO_2 can exist at this temperature and pressure. Clearly, of the three phases, gaseous CO_2 must be the most stable and, hence, have the lowest free energy when T = –60 °C and P_{ext} = 1.00 atm.

Gibbs Energy and Spontaneous Change

15. **(E)** Answer (b) is correct. Br—Br bonds are broken in this reaction, meaning that it is endothermic, with $\Delta H > 0$. Since the number of moles of gas increases during the reaction, $\Delta S > 0$. And, because $\Delta G = \Delta H - T\,\Delta S$, this reaction is non-spontaneous ($\Delta G > 0$) at low temperatures where the ΔH term predominates and spontaneous ($\Delta G < 0$) at high temperatures where the $T\,\Delta S$ term predominates.

16. **(E)** Answer (d) is correct. A reaction that proceeds only through electrolysis is a reaction that is non-spontaneous. Such a reaction has $\Delta G > 0$.

17. **(E) (a)** $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} < 0$ (since $\Delta n_{\text{gas}} < 0$) for this reaction. Thus, this reaction is case 2 of Table 19-1. It is spontaneous at low temperatures and non-spontaneous at high temperatures.

(b) We are unable to predict the sign of ΔS° for this reaction, since $\Delta n_{\text{gas}} = 0$. Thus, no strong prediction as to the temperature behavior of this reaction can be made. Since $\Delta H^{o} > 0$, we can, however, conclude that the reaction will be non-spontaneous at low temperatures.

(c) $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$ (since $\Delta n_{\text{gas}} > 0$) for this reaction. This is case 3 of Table 19-1. It is non-spontaneous at low temperatures, but spontaneous at high temperatures.

18. **(E) (a)** $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} < 0$ (since $\Delta n_{\text{gas}} < 0$) for this reaction. This is case 4 of Table 19-1. It is non-spontaneous at all temperatures.

(b) $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} > 0$ (since $\Delta n_{\text{gas}} > 0$) for this reaction. This is case 1 of Table 19-1. It is spontaneous at all temperatures.

(c) $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} < 0$ (since $\Delta n_{\text{gas}} < 0$) for this reaction. This is case 2 of Table 19-1. It is spontaneous at low temperatures and non-spontaneous at high temperatures.

19. **(E)** First of all, the process is clearly spontaneous, and therefore $\Delta G < 0$. In addition, the gases are more dispersed when they are at a lower pressure and therefore $\Delta S > 0$. We also conclude that $\Delta H = 0$ because the gases are ideal and thus there are no forces of attraction or repulsion between them.

20. **(E)** Because an ideal solution forms spontaneously, $\Delta G < 0$. Also, the molecules of solvent and solute that are mixed together in the solution are in a more dispersed state than the separated solvent and solute. Therefore, $\Delta S > 0$. However, in an ideal solution, the attractive forces between solvent and solute molecules equal those forces between solvent molecules and those between solute molecules. Thus, $\Delta H = 0$. There is no net energy of interaction.

21. **(M) (a)** An exothermic reaction (one that gives off heat) may not occur spontaneously if, at the same time, the system becomes more ordered (concentrated) that is, $\Delta S^{\circ} < 0$. This is particularly true at a high temperature, where the $T\Delta S$ term dominates the ΔG expression. An example of such a process is freezing water (clearly exothermic because the reverse process, melting ice, is endothermic), which is not spontaneous at temperatures above $0\ ^{\circ}\text{C}$.

(b) A reaction in which $\Delta S > 0$ need not be spontaneous if that process also is endothermic. This is particularly true at low temperatures, where the ΔH term dominates the ΔG expression. An example is the vaporization of water (clearly an endothermic process, one that requires heat, and one that produces a gas, so $\Delta S > 0$), which is not spontaneous at low temperatures, that is, below $100\ ^\circ\text{C}$ (assuming P_{ext} = 1.00 atm).

22. **(M)** In this problem we are asked to explain whether the reaction AB(g)→A(g)+B(g) is always going to be spontaneous at high rather than low temperatures. In order to answer this question, we need to determine the signs of ΔH, ΔS and consequently ΔG. Recall that $\Delta G = \Delta H - T\Delta S$.

Stepwise approach:

Determine the sign of *ΔS*:

We are generating two moles of gas from one mole. The randomness of the system increases and ΔS must be greater than zero.

Determine the sign of *ΔH*:

In this reaction, we are breaking A-B bond. Bond breaking requires energy, so the reaction must be endothermic. Therefore, ΔH is also greater than zero.

Use $\Delta G = \Delta H - T\Delta S$ to determine the sign of ΔG:

$\Delta G = \Delta H - T\Delta S$. Since ΔH is positive and ΔS is positive there will be a temperature at which $T\Delta S$ will become greater than ΔH. The reaction will be favored at high temperatures and disfavored at low temperatures.

Conversion pathway approach:

ΔS for the reaction is greater than zero because we are generating two moles of gas from one mole. ΔH for the reaction is also greater than zero because we are breaking A-B (bond breaking requires energy). Because $\Delta G = \Delta H - T\Delta S$, there will be a temperature at which $T\Delta S$ will become greater than ΔH. The reaction will be favored at high temperatures and disfavored at low temperatures.

Standard Gibbs Energy Change

23. (M)

$$\Delta H^\circ = \Delta H_f^\circ\left[\text{NH}_4\text{Cl}(\text{s})\right] - \Delta H_f^\circ\left[\text{NH}_3(\text{g})\right] - \Delta \text{H}_f^\circ\left[\text{HCl}(\text{g})\right]$$

$$= -314.4\ \text{kJ/mol} - (-46.11\ \text{kJ/mol} - 92.31\ \text{kJ/mol}) = -176.0\ \text{kJ/mol}$$

$$\Delta G^\circ = \Delta G_f^\circ\left[\text{NH}_4\text{Cl}(\text{s})\right] - \Delta G_f^\circ\left[\text{NH}_3(\text{g})\right] - \Delta G_f^\circ\left[\text{HCl}(\text{g})\right]$$

$$= -202.9\ \text{kJ/mol} - (-16.48\ \text{kJ/mol} - 95.30\ \text{kJ/mol}) = -91.1\ \text{kJ/mol}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-176.0\ \text{kJ/mol} + 91.1\ \text{kJ/mol}}{298\ \text{K}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = -285\ \text{J mol}^{-1}$$

24. **(M) (a)**

$$\Delta G^\circ = \Delta G_f^\circ\left[\text{C}_2\text{H}_6(\text{g})\right] - \Delta G_f^\circ\left[\text{C}_2\text{H}_2(\text{g})\right] - 2\Delta G_f^\circ\left[\text{H}_2(\text{g})\right]$$

$$= -32.82\ \text{kJ/mol} - 209.2\ \text{kJ/mol} - 2(0.00\ \text{kJ/mol}) = -242.0\ \text{kJ/mol}$$

(b)

$$\Delta G^\circ = 2\Delta G_f^\circ\left[\text{SO}_2(\text{g})\right] + \Delta G_f^\circ\left[\text{O}_2(\text{g})\right] - 2\Delta G_f^\circ\left[\text{SO}_3(\text{g})\right]$$

$$= 2(-300.2\ \text{kJ/mol}) + 0.00\ \text{kJ/mol} - 2(-371.1\ \text{kJ/mol}) = +141.8\ \text{kJ/mol}$$

(c) $$\Delta G^{\circ} = 3\Delta G_f^{\circ}\left[\mathrm{Fe(s)}\right] + 4\Delta G_f^{\circ}\left[\mathrm{H_2O(g)}\right] - \Delta G_f^{\circ}\left[\mathrm{Fe_3O_4(s)}\right] - 4\Delta G_f^{\circ}\left[\mathrm{H_2(g)}\right]$$
$$= 3(0.00\ \text{kJ/mol}) + 4(-228.6\ \text{kJ/mol}) - (-1015\ \text{kJ/mol}) - 4(0.00\ \text{kJ/mol}) = 101\ \text{kJ/mol}$$

(d) $$\Delta G^{\circ} = 2\Delta G_f^{\circ}\left[\mathrm{Al^{3+}(aq)}\right] + 3\Delta G_f^{\circ}\left[\mathrm{H_2(g)}\right] - 2\Delta G_f^{\circ}\left[\mathrm{Al(s)}\right] - 6\Delta G_f^{\circ}\left[\mathrm{H^+(aq)}\right]$$
$$= 2(-485\ \text{kJ/mol}) + 3(0.00\ \text{kJ/mol}) - 2(0.00\text{kJ/mol}) - 6(0.00\ \text{kJ/mol}) = -970.\ \text{kJ/mol}$$

25. **(M) (a)** $$\Delta S^{\circ} = 2S^{\circ}\left[\mathrm{POCl_3(l)}\right] - 2S^{\circ}\left[\mathrm{PCl_3(g)}\right] - S^{\circ}\left[\mathrm{O_2(g)}\right]$$
$$= 2(222.4\ \text{J/K}) - 2(311.7\ \text{J/K}) - 205.1\ \text{J/K} = -383.7\ \text{J/K}$$
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -620.2\times10^3\ \text{J} - (298\ \text{K})(-383.7\ \text{J/K}) = -506\times10^3\ \text{J} = -506\ \text{kJ}$$

(b) The reaction proceeds spontaneously in the forward direction when reactants and products are in their standard states, because the value of ΔG° is less than zero.

26. **(M) (a)** $$\Delta S^{\circ} = S^{\circ}\left[\mathrm{Br_2(l)}\right] + 2S^{\circ}\left[\mathrm{HNO_2(aq)}\right] - 2S^{\circ}\left[\mathrm{H^+(aq)}\right] - 2S^{\circ}\left[\mathrm{Br^-(aq)}\right] - 2S^{\circ}\left[\mathrm{NO_2(g)}\right]$$
$$= 152.2\ \text{J/K} + 2(135.6\ \text{J/K}) - 2(0\ \text{J/K}) - 2(82.4\ \text{J/K}) - 2(240.1\ \text{J/K}) = -221.6\ \text{J/K}$$
$$\Delta G^{\circ} = \Delta H^{\circ} - T\,\Delta S^{\circ} = -61.6\times10^3\text{J} - (298\text{K})(-221.6\ \text{J/K}) = +4.4\times10^3\ \text{J} = +4.4\,\text{kJ}$$

(b) The reaction does not proceed spontaneously in the forward direction when reactants and products are in their standard states, because the value of ΔG° is greater than zero.

27. **(M)** We combine the reactions in the same way as for any Hess's law calculations.

(a)
$$\begin{array}{ll} \mathrm{N_2O(g)} \rightarrow \mathrm{N_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} & \Delta G^{\circ} = -\tfrac{1}{2}(+208.4\,\text{kJ}) = -104.2\,\text{kJ} \\ \mathrm{N_2(g)} + 2\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{NO_2(g)} & \Delta G^{\circ} = +102.6\,\text{kJ} \\ \hline \text{Net: } \mathrm{N_2O(g)} + \tfrac{3}{2}\mathrm{O_2(g)} \rightarrow 2\mathrm{NO_2(g)} & \Delta G^{\circ} = -104.2 + 102.6 = -1.6\ \text{kJ} \end{array}$$

This reaction reaches an equilibrium condition, with significant amounts of all species being present. This conclusion is based on the relatively small absolute value of ΔG°.

(b)
$$\begin{array}{ll} 2\mathrm{N_2(g)} + 6\mathrm{H_2(g)} \rightarrow 4\mathrm{NH_3(g)} & \Delta G^{\circ} = 2(-33.0\ \text{kJ}) = -66.0\ \text{kJ} \\ 4\mathrm{NH_3(g)} + 5\mathrm{O_2(g)} \rightarrow 4\mathrm{NO(g)} + 6\mathrm{H_2O(l)} & \Delta G^{\circ} = -1010.5\ \text{kJ} \\ 4\mathrm{NO(g)} \rightarrow 2\mathrm{N_2(g)} + 2\mathrm{O_2(g)} & \Delta G^{\circ} = -2(+173.1\ \text{kJ}) = -346.2\ \text{kJ} \\ \hline \text{Net: } 6\mathrm{H_2(g)} + 3\mathrm{O_2(g)} \rightarrow 6\mathrm{H_2O(l)} & \Delta G^{\circ} = -66.0\,\text{kJ} - 1010.5\,\text{kJ} - 346.2\,\text{kJ} = -1422.7\,\text{kJ} \end{array}$$

This reaction is three times the desired reaction, which therefore has $\Delta G^{\circ} = -1422.7\ \text{kJ} \div 3 = -474.3\ \text{kJ}$.

The large negative ΔG° value indicates that this reaction will go to completion at $25^{\circ}\mathrm{C}$.

(c)

$$\begin{array}{ll}
4NH_3(g)+5O_2(g)\rightarrow 4NO(g)+6H_2O(l) & \Delta G^o = -1010.5\text{ kJ} \\
4NO(g)\rightarrow 2N_2(g)+2O_2(g) & \Delta G^o = -2(+173.1\text{ kJ}) = -346.2\text{ kJ} \\
2N_2(g)+O_2(g)\rightarrow 2N_2O(g) & \Delta G^o = +208.4\text{ kJ} \\
\hline
4NH_3(g)+4O_2(g)\rightarrow 2N_2O(g)+6H_2O(l) & \Delta G^o = -1010.5\text{ kJ} - 346.2\text{ kJ} + 208.4\text{ kJ} \\
 & = -1148.3\text{ kJ}
\end{array}$$

This reaction is twice the desired reaction, which, therefore, has ΔG^o = -574.2 kJ. The very large negative value of the ΔG^o for this reaction indicates that it will go to completion.

28. **(M)** We combine the reactions in the same way as for any Hess's law calculations.

(a)

$$\begin{array}{ll}
COS(g)+2CO_2(g)\rightarrow SO_2(g)+3CO(g) & \Delta G^o = -(-246.4\text{ kJ}) = +246.6\text{ kJ} \\
2CO(g)+2H_2O(g)\rightarrow 2CO_2(g)+2H_2(g) & \Delta G^o = 2(-28.6\text{ kJ}) = -57.2\text{ kJ} \\
\hline
\end{array}$$

$$COS(g)+2H_2O(g)\rightarrow SO_2(g)+CO(g)+2H_2(g) \quad \Delta G^o = +246.6 - 57.2 = +189.4\text{ kJ}$$

This reaction is spontaneous in the reverse direction, because of the large positive value of ΔG^o

(b)

$$\begin{array}{ll}
COS(g)+2CO_2(g)\rightarrow SO_2(g)+3CO(g) & \Delta G^o = -(-246.4\text{ kJ}) = +246.6\text{ kJ} \\
3CO(g)+3H_2O(g)\rightarrow 3CO_2(g)+3H_2(g) & \Delta G^o = 3(-28.6\text{ kJ}) = -85.8\text{ kJ} \\
\hline
COS(g)+3H_2O(g)\rightarrow CO_2(g)+SO_2(g)+3H_2(g) & \Delta G^o = +246.6 - 85.8 = +160.8\text{ kJ}
\end{array}$$

This reaction is spontaneous in the reverse direction, because of the large positive value of ΔG^o.

(c)

$$\begin{array}{ll}
COS(g)+H_2(g)\rightarrow CO(g)+H_2S(g) & \Delta G^o = -(+1.4)\text{ kJ} \\
CO(g)+H_2O(g)\rightarrow CO_2(g)+H_2(g) & \Delta G^o = -28.6\text{ kJ} = -28.6\text{ kJ} \\
\hline
COS(g)+H_2O(g)\rightarrow CO_2(g)+H_2S(g) & \Delta G^o = -1.4\text{ kJ} - 28.6\text{ kJ} = -30.0\text{ kJ}
\end{array}$$

The negative value of the ΔG^o for this reaction indicates that it is spontaneous in the forward direction.

29. **(D)** The combustion reaction is : $C_6H_6(l)+\frac{15}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(\text{g or l})$

(a)

$$\begin{aligned}
\Delta G^o &= 6\Delta G_f^\circ[CO_2(g)] + 3\Delta G_f^\circ[H_2O(l)] - \Delta G_f^\circ[C_6H_6(l)] - \tfrac{15}{2}\Delta G_f^\circ[O_2(g)] \\
&= 6(-394.4\text{ kJ}) + 3(-237.1\text{ kJ}) - (+124.5\text{ kJ}) - \tfrac{15}{2}(0.00\text{ kJ}) = -3202\text{ kJ}
\end{aligned}$$

(b)

$$\begin{aligned}
\Delta G^o &= 6\Delta G_f^\circ[CO_2(g)] + 3\Delta G_f^\circ[H_2O(g)] - \Delta G_f^\circ[C_6H_6(l)] - \tfrac{15}{2}\Delta G_f^\circ[O_2(g)] \\
&= 6(-394.4\text{ kJ}) + 3(-228.6\text{ kJ}) - (+124.5\text{ kJ}) - \tfrac{15}{2}(0.00\text{ kJ}) = -3177\text{ kJ}
\end{aligned}$$

We could determine the difference between the two values of ΔG^{o} by noting the difference between the two products: $3H_2O(l) \rightarrow 3H_2O(g)$ and determining the value of ΔG^{o} for this difference:

$$\Delta G^{\mathrm{o}} = 3\Delta G_{\mathrm{f}}^{\circ}\left[H_2O(g)\right] - 3\Delta G_{\mathrm{f}}^{\circ}\left[H_2O(l)\right] = 3\left[-228.6-(-237.1)\right] \text{ kJ} = 25.5 \text{ kJ}$$

30. **(M)** We wish to find the value of the ΔH^{o} for the given reaction: $F_2(g) \rightarrow 2\,F(g)$

$$\Delta S^{\mathrm{o}} = 2S^{\mathrm{o}}\left[F(g)\right] - S^{\mathrm{o}}\left[F_2(g)\right] = 2\left(158.8 \text{ J K}^{-1}\right) - \left(202.8 \text{ J K}^{-1}\right) = +114.8 \text{ J K}^{-1}$$

$$\Delta H^{\mathrm{o}} = \Delta G^{\mathrm{o}} + T\Delta S^{\mathrm{o}} = 123.9\times10^{3}\text{ J} + \left(298 \text{ K}\times 114.8 \text{ J/K}\right) = 158.1 \text{ kJ/mole of bonds}$$

The value in Table 10.3 is 159 kJ/mol, which is in quite good agreement with the value found here.

31. **(M)** **(a)** $\Delta S^{o}_{rxn} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$

$= [1 \text{ mol} \times 301.2 \text{ J K}^{-1}\text{mol}^{-1} + 2 \text{ mol} \times 188.8 \text{ J K}^{-1}\text{mol}^{-1}] - [2 \text{ mol} \times 247.4 \text{ J K}^{-1}\text{mol}^{-1} + 1 \text{ mol} \times 238.5 \text{ J K}^{-1}\text{mol}^{-1}] = -54.5 \text{ J K}^{-1}$

$\Delta S^{o}_{rxn} = = -0.0545 \text{ kJ K}^{-1}$

(b) $\Delta H^{o}_{rxn} = \Sigma$(bonds broken in reactants (kJ/mol)) $-\Sigma$(bonds broken in products(kJ/ mol))

$= [4 \text{ mol} \times (389 \text{ kJ mol}^{-1})_{\text{N-H}} + 4 \text{ mol} \times (222 \text{ kJ mol}^{-1})_{\text{O-F}}] - [4 \text{ mol} \times (301 \text{ kJ mol}^{-1})_{\text{N-F}} + 4 \text{ mol} \times (464 \text{ kJ mol}^{-1})_{\text{O-H}}]$

$\Delta H^{o}_{rxn} = -616 \text{ kJ}$

(c) $\Delta G^{o}_{rxn} = \Delta H^{o}_{rxn} - T\Delta S^{o}_{rxn} = -616 \text{ kJ} - 298 \text{ K}(-0.0545 \text{ kJ K}^{-1}) = -600 \text{ kJ}$

Since the ΔG^{o}_{rxn} is negative, the reaction is spontaneous, and hence feasible (at 25 °C). Because both the entropy and enthalpy changes are *negative*, this reaction will be more highly favored at low temperatures (i.e., the reaction is enthalpy driven)

32. **(D)** In this problem we are asked to find ΔG° at 298 K for the decomposition of ammonium nitrate to yield dinitrogen oxide gas and liquid water. Furthermore, we are asked to determine whether the decomposition will be favored at temperatures above or below 298 K. In order to answer these questions, we first need the balanced chemical equation for the process. From the data in Appendix D, we can determine $\Delta H^{\circ}_{\text{rxn}}$ and $\Delta S^{\circ}_{\text{rxn}}$. Both quantities will be required to determine $\Delta G^{\circ}_{\text{rxn}}$ ($\Delta G^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T\Delta S^{\circ}_{\text{rxn}}$). Finally the magnitude of $\Delta G^{\circ}_{\text{rxn}}$ as a function of temperature can be judged depending on the values of $\Delta H^{\circ}_{\text{rxn}}$ and $\Delta S^{\circ}_{\text{rxn}}$.

Stepwise approach:

First we need the balanced chemical equation for the process:

$$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$$

Now we can determine $\Delta H^{\circ}_{\text{rxn}}$ by utilizing ΔH_f^{o} values provided in Appendix D:

	$NH_4NO_3(s)$	$\xrightarrow{\Delta}$	$N_2O(g)$	+	$2H_2O(l)$
ΔH_f^{o}	-365.6 kJmol^{-1}		82.05 kJmol^{-1}		-285.6 kJmol^{-1}

$$\Delta H^{\circ}_{\text{rxn}} = \Sigma\Delta H_{\text{f}}^{\circ}{}_{\text{products}} - \Sigma\Delta H_{\text{f}}^{\circ}{}_{\text{reactants}}$$

$$\Delta H^{\circ}_{\text{rxn}} = [2 \text{ mol}(-285.8 \text{ kJ mol}^{-1}) + 1 \text{ mol}(82.05 \text{ kJ mol}^{-1})] - [1 \text{ mol } (-365.6 \text{ kJ mol}^{-1})]$$

$\Delta H^\circ_{rxn} = -124.0$ kJ

Similarly, ΔS°_{rxn} can be calculated utilizing S° values provided in Appendix D

$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$

S^o 15.1 $Jmol^{-1}K^{-1}$ 219.9 $Jmol^{-1}K^{-1}$ 69.91 $Jmol^{-1}K^{-1}$

$\Delta S^\circ_{rxn} = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

$\Delta S^\circ_{rxn} = [2 \text{ mol} \times 69.91 \text{ J K}^{-1}\text{mol}^{-1} + 1 \text{ mol} \times 219.9 \text{ J K}^{-1}\text{mol}^{-1}] - [1 \text{ mol} \times 151.1 \text{ J K}^{-1}\text{mol}^{-1}]$

$\Delta S^\circ_{rxn} = 208.6 \text{ J K}^{-1} = 0.2086 \text{ kJ K}^{-1}$

To find ΔG°_{rxn} we can either utilize ΔG°_f values provided in Appendix D or $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$:

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = -124.0 \text{ kJ} - 298.15 \text{ K} \times 0.2086 \text{ kJK}^{-1}$

$\Delta G^\circ_{rxn} = -186.1$ kJ

Magnitude of ΔG°_{rxn} as a function of temperature can be judged depending on the values of ΔH°_{rxn} and ΔS°_{rxn}:

Since ΔH°_{rxn} is negative and ΔS°_{rxn} is positive, the decomposition of ammonium nitrate is spontaneous at all temperatures. However, as the temperature increases, the $T\Delta S$ term gets larger and as a result, the decomposition reaction shift towards producing more products. Consequently, we can say that the reaction is more highly favored above 298 K (it will also be faster at higher temperatures)

Conversion pathway approach:

From the balanced chemical equation for the process

$NH_4NO_3(s) \xrightarrow{\Delta} N_2O(g) + 2H_2O(l)$

we can determine ΔH°_{rxn} and ΔS°_{rxn} by utilizing ΔH^o_f and S° values provided in Appendix D:

$\Delta H^\circ_{rxn} = [2 \text{ mol}(-285.8 \text{ kJ mol}^{-1}) + 1 \text{ mol}(82.05 \text{ kJ mol}^{-1})] - [1 \text{ mol } (-365.6 \text{ kJ mol}^{-1})]$

$\Delta H^\circ_{rxn} = -124.0$ kJ

$\Delta S^\circ_{rxn} = [2 \text{ mol} \times 69.91 \text{ J K}^{-1}\text{mol}^{-1} + 1 \text{ mol} \times 219.9 \text{ J K}^{-1}\text{mol}^{-1}] - [1 \text{ mol} \times 151.1 \text{ J K}^{-1}\text{mol}^{-1}]$

$\Delta S^\circ_{rxn} = 208.6 \text{ J K}^{-1} = 0.2086 \text{ kJ K}^{-1}$

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = -124.0 \text{ kJ} - 298.15 \text{ K} \times 0.2086 \text{ kJK}^{-1}$

$\Delta G^\circ_{rxn} = -186.1$ kJ

Since ΔH°_{rxn} is negative and ΔS°_{rxn} is positive, the decomposition of ammonium nitrate is spontaneous at all temperatures. However, as the temperature increases, the $T\Delta S$ term gets larger and as a result, the decomposition reaction shift towards producing more products. The reaction is highly favored above 298 K (it will also be faster).

The Thermodynamic Equilibrium Constant

33. **(E)** In all three cases, $K_{eq} = K_p$ because only gases, pure solids, and pure liquids are present in the chemical equations. There are no factors for solids and liquids in K_{eq} expressions, and gases appear as partial pressures in atmospheres. That makes K_{eq} the same as K_p for these three reactions.

We now recall that $K_p = K_c(RT)^{\Delta n}$. Hence, in these three cases we have:

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta n_{gas} = 2-(2+1) = -1$; $K = K_p = K_c(RT)^{-1}$

(b) $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$; $\Delta n_{gas} = 1-(\frac{1}{2}+\frac{1}{2}) = 0$; $K = K_p = K_c$

(c) $NH_4HCO_3(s) \rightleftharpoons NH_3(g) + CO_2(g) + H_2O(l)$;

$\Delta n_{gas} = 2-(0) = +2$ $K = K_p = K_c(RT)^2$

34. (M) (a) $K = \dfrac{P\{H_2(g)\}^4}{P\{H_2O(g)\}^4}$

(b) Terms for both solids, Fe(s) and $Fe_3O_4(s)$, are properly excluded from the thermodynamic equilibrium constant expression. (Actually, each solid has an activity of 1.00.) Thus, the equilibrium partial pressures of both $H_2(g)$ and $H_2O(g)$ do not depend on the amounts of the two solids present, as long as some of each solid is present. One way to understand this is that any chemical reaction occurs on the surface of the solids, and thus is unaffected by the amount present.

(c) We can produce $H_2(g)$ from $H_2O(g)$ without regard to the proportions of Fe(s) and $Fe_3O_4(s)$ with the qualification, that there must always be some Fe(s) present for the production of $H_2(g)$ to continue.

35. (M) In this problem we are asked to determine the equilibrium constant and the change in Gibbs free energy for the reaction between carbon monoxide and hydrogen to yield methanol. The equilibrium concentrations of each reagent at 483K were provided. We proceed by first determining the equilibrium constant. Gibbs free energy can be calculated using $\Delta G^o = -RT\ln K$.

Stepwise approach:

First determine the equilibrium constant for the reaction at 483K:

$$CO(g)+2H_2(g) \rightleftharpoons CH_3OH(g)$$

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911\times 0.0822^2} = 14.5$$

Now use $\Delta G^o = -RT\ln K$ to calculate the change in Gibbs free energy at 483 K:

$$\Delta G^o = -RT\ln K$$

$$\Delta G^o = -8.314\times 483\times \ln(14.5)\text{Jmol}^{-1} = -1.1\times 10^4\text{Jmol}^{-1}$$

$$\Delta G^o = -11\text{kJmol}^{-1}$$

Conversion pathway approach:

$$K = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{0.00892}{0.0911\times 0.0822^2} = 14.5$$

$$\Delta G^o = -RT\ln K = -8.314\times 483\times \ln(14.5)\text{Jmol}^{-1} = -1.1\times 10^4\text{Jmol}^{-1}$$

$$\Delta G^o = -11\text{kJmol}^{-1}$$

36. **(M)** Gibbs free energy for the reaction ($\Delta G^o = \Delta H^o - T\Delta S^o$) can be calculated using ΔH_f^o and S^o values for CO(g), H_2(g) and CH_3OH(g) from Appendix D.

$$\Delta H^o = \Delta H_f^o(\mathrm{CH_3OH(g)}) - [\Delta H_f^o(\mathrm{CO(g)}) + 2\Delta H_f^o(\mathrm{H_2(g)}]$$

$$\Delta H^o = -200.7\mathrm{kJmol^{-1}} - (-110.5\mathrm{kJmol^{-1}} + 0\mathrm{kJmol^{-1}}) = -90.2\mathrm{kJmol^{-1}}$$

$$\Delta S^o = S^o(\mathrm{CH_3OH(g)}) - [S^o(\mathrm{CO(g)}) + 2S^o(\mathrm{H_2(g)}]$$

$$\Delta S^o = 239.8\mathrm{JK^{-1}mol^{-1}} - (197.7\mathrm{JK^{-1}mol^{-1}} + 2\times 130.7\mathrm{JK^{-1}mol^{-1}}) = -219.3\mathrm{JK^{-1}mol^{-1}}$$

$$\Delta G^o = -90.2\mathrm{kJmol^{-1}} - \frac{483K\times(-219.3)\mathrm{kJK^{-1}mol^{-1}}}{1000} = 15.7\mathrm{kJmol^{-1}}$$

Equilibrium constant for the reaction can be calculated using $\Delta G^o = -RT\ln K$

$$\ln K = \frac{-\Delta G^o}{RT} \Rightarrow \ln K = \frac{-15.7\times 1000\,Jmol^{-1}}{8.314\,JK^{-1}mol^{-1}\times 483K} = -3.9 \Rightarrow K = e^{-3.9} = 2.0\times 10^{-2}$$

The values are different because in this case, the calculated K is the thermodynamic equilibrium constant that represents the reactants and products in their standard states. In Exercise 35, the reactants and products were not in their standard states.

Relationships Involving ΔG, ΔG^{o}, Q and K

37. **(M)** $\Delta G^o = 2\Delta G_f^\circ\left[\mathrm{NO(g)}\right] - \Delta G_f^\circ\left[\mathrm{N_2O(g)}\right] - 0.5\,\Delta G_f^\circ\left[\mathrm{O_2(g)}\right]$

$$= 2(86.55\text{ kJ/mol}) - (104.2\text{ kJ/mol}) - 0.5(0.00\text{ kJ/mol}) = 68.9\text{ kJ/mol}$$

$$= -RT\ln K_p = -\left(8.3145\times10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1}\right)(298\text{ K})\ln K_p$$

$$\ln K_p = -\frac{68.9\text{ kJ/mol}}{8.3145\times10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1}\times 298\text{ K}} = -27.8 \qquad K_p = e^{-27.8} = 8\times10^{-13}$$

38. **(M) (a)** $\Delta G^o = 2\Delta G_f^\circ\left[\mathrm{N_2O_5(g)}\right] - 2\Delta G_f^\circ\left[\mathrm{N_2O_4(g)}\right] - \Delta G_f^\circ\left[\mathrm{O_2(g)}\right]$

$$= 2(115.1\text{ kJ/mol}) - 2(97.89\text{ kJ/mol}) - (0.00\text{ kJ/mol}) = 34.4\text{ kJ/mol}$$

(b) $\Delta G^o = -RT\ln K_p \qquad \ln K_p = -\dfrac{\Delta G^o}{RT} = -\dfrac{34.4\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}\times 298\text{K}} = -13.9$

$$K_p = e^{-13.9} = 9\times10^{-7}$$

39. **(M)** We first balance each chemical equation, then calculate the value of ΔG^o with data from Appendix D, and finally calculate the value of K_{eq} with the use of $\Delta G^o = -RT\ln K$.

(a) $\mathrm{4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(s)}$

$$\Delta G^o = 2\Delta G_f^\circ\left[\mathrm{H_2O(g)}\right] + 2\Delta G_f^\circ\left[\mathrm{Cl_2(g)}\right] - 4\Delta G_f^\circ\left[\mathrm{HCl(g)}\right] - \Delta G_f^\circ\left[\mathrm{O_2(g)}\right]$$

$$= 2\times\left(-228.6\frac{\text{kJ}}{\text{mol}}\right) + 2\times 0\frac{\text{kJ}}{\text{mol}} - 4\times\left(-95.30\frac{\text{kJ}}{\text{mol}}\right) - 0\frac{\text{kJ}}{\text{mol}} = -76.0\ \frac{\text{kJ}}{\text{mol}}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{+76.0\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}\times 298\text{ K}} = +30.7 \qquad K = e^{+30.7} = 2\times10^{13}$$

(b) $3Fe_2O_3(s) + H_2(g) \rightleftharpoons 2Fe_3O_4(s) + H_2O(g)$

$$\begin{aligned}\Delta G^o &= 2\Delta G_f^\circ\left[Fe_3O_4(s)\right] + \Delta G_f^\circ\left[H_2O(g)\right] - 3\Delta G_f^\circ\left[Fe_2O_3(s)\right] - \Delta G_f^\circ\left[H_2(g)\right]\\ &= 2\times(-1015 \text{ kJ/mol}) - 228.6 \text{ kJ/mol} - 3\times(-742.2 \text{ kJ/mol}) - 0.00 \text{ kJ/mol}\\ &= -32 \text{ kJ/mol}\end{aligned}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{32\times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1}\times 298 \text{ K}} = 13; \quad K = e^{+13} = 4\times 10^5$$

(c) $2Ag^+(aq) + SO_4{}^{2-}(aq) \rightleftharpoons Ag_2SO_4(s)$

$$\begin{aligned}\Delta G^o &= \Delta G_f^\circ\left[Ag_2SO_4(s)\right] - 2\Delta G_f^\circ\left[Ag^+(aq)\right] - \Delta G_f^\circ\left[SO_4^{2-}(aq)\right]\\ &= -618.4\text{ kJ/mol} - 2\times 77.11\text{ kJ/mol} - (-744.5\text{ kJ/mol}) = -28.1\text{ kJ/mol}\end{aligned}$$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{28.1\times 10^3 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1}\times 298 \text{ K}} = 11.3; \; K = e^{+11.3} = 8\times 10^4$$

40. **(E)**
$$\begin{aligned}\Delta S^o &= S^o\{CO_2(g)\} + S^o\{H_2(g)\} - S^o\{CO(g)\} - S^o\{H_2O(g)\}\\ &= 213.7 \text{ J mol}^{-1}\text{ K}^{-1} + 130.7 \text{ J mol}^{-1}\text{ K}^{-1} - 197.7 \text{ J mol}^{-1}\text{ K}^{-1} - 188.8 \text{ J mol}^{-1}\text{K}^{-1}\\ &= -42.1 \text{ J mol}^{-1}\text{ K}^{-1}\end{aligned}$$

41. **(M)** In this problem we need to determine in which direction the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is spontaneous when the partial pressure of SO_2, O_2, and SO_3 are 1.0×10^{-4}, 0.20 and 0.10 atm, respectively. We proceed by first determining the standard free energy change for the reaction (ΔG^o) using tabulated data in Appendix D. Change in Gibbs free energy for the reaction (ΔG) is then calculated by employing the equation $\Delta G = \Delta G^o + RT\ln Q_p$, where Q_p is the reaction quotient. Based on the sign of ΔG, we can determine in which direction is the reaction spontaneous.

Stepwise approach:

First determine ΔG^o for the reaction using data in Appendix D:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$\Delta G^o = 2\Delta G_f^o\left[SO_3(g)\right] - 2\Delta G_f^o\left[SO_2(g)\right] - \Delta G_f^o\left[O_2(g)\right]$$

$$\Delta G^o = 2\times(-371.1 \text{ kJ/mol}) - 2\times(-300.2 \text{ kJ/mol}) - 0.0 \text{ kJ/mol}$$

$$\Delta G^o = -141.8\text{kJ}$$

Calculate ΔG by employing the equation $\Delta G = \Delta G^o + RT\ln Q_p$, where Q_p is the reaction quotient:

$$\Delta G = \Delta G^o + RT\ln Q_p$$

$$Q_p = \frac{P\{SO_3(g)\}^2}{P\{O_2(g)\}P\{SO_2(g)\}^2}$$

$$Q_p = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})(1.0\times10^{-4} \text{ atm})^2} = 5.0\times10^6$$

ΔG = –141.8 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(5.0 × 10^6)

ΔG = –141.8 kJ + 38.2 kJ = –104 kJ.

Examine the sign of ΔG to decide in which direction is the reaction spontaneous: Since ΔG is negative, the reaction is spontaneous in the forward direction.

Conversion pathway approach:

$$\Delta G^o = 2\Delta G_f^o[SO_3(g)] - 2\Delta G_f^o[SO_2(g)] - \Delta G_f^o[O_2(g)]$$

$$\Delta G^o = 2 \times (-371.1 \text{ kJ/mol}) - 2 \times (-300.2 \text{ kJ/mol}) - 0.0 \text{ kJ/mol}=-141.8\text{kJ}$$

$$\Delta G = \Delta G^o + RT \ln Q_p$$

$$Q_p = \frac{P\{SO_3(g)\}^2}{P\{O_2(g)\}P\{SO_2(g)\}^2} = \frac{(0.10 \text{ atm})^2}{(0.20 \text{ atm})(1.0 \times 10^{-4} \text{ atm})^2} = 5.0 \times 10^6$$

ΔG = –141.8 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(5.0 × 10^6)=-104 kJ.

Since ΔG is negative, the reaction is spontaneous in the forward direction.

42. **(M)** We begin by calculating the standard free energy change for the reaction:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$\Delta G^\circ = 2\Delta G_f^\circ[HCl(g)] - \Delta G_f^\circ[Cl_2(g)] - \Delta G_f^\circ[H_2(g)]$$
$$= 2\times(-95.30 \text{ kJ/mol}) - 0.0 \text{ kJ/mol} - 0.0 \text{ kJ/mol} = -190.6 \text{ kJ}$$

Now we can calculate ΔG by employing the equation $\Delta G = \Delta G^o + RT \ln Q_p$, where

$$Q_p = \frac{P\{HCl(g)\}^2}{P\{H_2(g)\}P\{Cl_2(g)\}} \; ; \; Q_p = \frac{(0.5 \text{ atm})^2}{(0.5 \text{ atm})(0.5 \text{ atm})} = 1$$

ΔG = –190.6 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(1)

ΔG = –190.6 kJ + 0 kJ = –190.6 kJ.

Since ΔG is negative, the reaction is spontaneous in the forward direction.

<u>43.</u> **(M)** In order to determine the direction in which the reaction is spontaneous, we need to calculate the non-standard free energy change for the reaction. To accomplish this, we will employ the equation $\Delta G = \Delta G^o + RT \ln Q_c$, where

$$Q_c = \frac{[H_3O^+(aq)]\,[CH_3CO_2^-(aq)]}{[CH_3CO_2H(aq)]} \; ; \; Q_c = \frac{(1.0\times10^{-3} \text{ M})^2}{(0.10 \text{ M})} = 1.0\times10^{-5}$$

ΔG = 27.07 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(1.0 × 10^{-5})

ΔG = 27.07 kJ + (–28.53 kJ) = –1.46 kJ.

Since ΔG is negative, the reaction is spontaneous in the forward direction.

44. **(M)** As was the case for exercise 39, we need to calculate the non-standard free energy change for the reaction. Once again, we will employ the equation $\Delta G = \Delta G^{\circ} + RT \ln Q$, but this time

$$Q_c = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]}\ ;\ Q_c = \frac{\left(1.0\times10^{-3}\ M\right)^2}{(0.10\ M)} = 1.0\times10^{-5}$$

ΔG = 29.05 kJ + (8.3145 × 10^{-3} kJ/K·mol)(298 K)ln(1.0 × 10^{-5})

ΔG = 29.05 kJ + (–28.53 kJ) = 0.52 kJ.

Since ΔG is positive, the reaction is spontaneous in the reverse direction.

45. **(E)** The relationship $\Delta S^{\circ} = (\Delta G^{\circ} - \Delta H^{\circ})/T$ (Equation (b)) is incorrect. Rearranging this equation to put ΔG° on one side by itself gives $\Delta G^{\circ} = \Delta H^{\circ} + T\Delta S^{\circ}$. This equation is not valid. The $T\Delta S^{\circ}$ term should be subtracted from the ΔH° term, not added to it.

46. **(E)** The ΔG° value is a powerful thermodynamic parameter because it can be used to determine the equilibrium constant for the reaction at each and every chemically reasonable temperature via the equation $\Delta G^{\circ} = -RT \ln K$.

47. **(M) (a)** To determine K_p we need the equilibrium partial pressures. In the ideal gas law, each partial pressure is defined by $P = nRT/V$. Because R, T, and V are the same for each gas, and because there are the same number of partial pressure factors in the numerator as in the denominator of the K_p expression, we can use the ratio of amounts to determine K_p.

$$K_p = \frac{P\{CO(g)\}\,P\{H_2O(g)\}}{P\{CO_2(g)\}\,P\{H_2(g)\}} = \frac{n\{CO(g)\}\,n\{H_2O(g)\}}{n\{CO_2(g)\}\,n\{H_2(g)\}} = \frac{0.224\text{ mol CO}\times 0.224\text{ mol H}_2\text{O}}{0.276\text{ mol CO}_2\times 0.276\text{ mol H}_2} = 0.659$$

(b) $\Delta G^{\circ}_{1000K} = -RT\ \ln\ K_p = -8.3145\text{ J mol}^{-1}\text{K}^{-1}\times 1000.\text{ K}\times\ln(0.659)$

$= 3.467\times10^3\text{ J/mol} = 3.467\text{ kJ/mol}$

(c)

$$Q_p = \frac{0.0340\text{ mol CO}\times 0.0650\text{ mol H}_2\text{O}}{0.0750\text{ mol CO}_2\times 0.095\text{ mol H}_2} = 0.31 < 0.659 = K_p$$

Since Q_p is smaller than K_p, the reaction will proceed to the right, forming products, to attain equilibrium, i.e., $\Delta G = 0$.

48. **(M) (a)** We know that $K_p = K_c(RT)^{\Delta n}$. For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta n_{gas} = 2-(2+1) = -1$, and therefore a value of K_p can be obtained.

$$K_p = K_c\left(RT\right)^{-1} = \frac{2.8\times10^2}{\dfrac{0.08206\text{ L atm}}{\text{mol K}}\times 1000\text{ K}} = 3.41 = K$$

We recognize that $K = K_p$ since all of the substances involved in the reaction are gases. We can now evaluate ΔG°.

$$\Delta G^{\circ} = -RT\ \ln\ K_{\text{eq}} = -\frac{8.3145\ \text{J}}{\text{mol}\ \ \text{K}} \times 1000\ \text{K} \times \ln(3.41) = -1.02\times10^{4}\ \text{J/mol} = -10.2\ \text{kJ/mol}$$

(b) We can evaluate Q_c for this situation and compare the value with that of $K_c = 2.8\times10^2$ to determine the direction of the reaction to reach equilibrium.

$$Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{\left(\dfrac{0.72\ \text{mol SO}_3}{2.50\ \text{L}}\right)^2}{\left(\dfrac{0.40\ \text{mol SO}_2}{2.50\ \text{L}}\right)^2 \times \left(\dfrac{0.18\ \text{mol O}_2}{2.50\ \text{L}}\right)} = 45 < 2.8\times10^2 = K_c$$

Since Q_c is smaller than K_c the reaction will shift right, producing sulfur trioxide and consuming sulfur dioxide and molecular oxygen, until the two values are equal.

49. **(M) (a)** $K = K_c$

$$\Delta G^{\circ} = -RT\ \ln\ K_{\text{eq}} = -\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(445+273\right)\text{K}\ \ln\ 50.2 = -23.4\ \text{kJ}$$

(b) $K = K_p = K_c\left(RT\right)^{\Delta n_g} = 1.7\times10^{-13}\left(0.0821\times298\right)^{1/2} = 8.4\times10^{-13}$

$$\Delta G^{\circ} = -RT\ \ln\ K_p = -\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(298\ \text{K}\right)\ \ln\ \left(8.4\times10^{-13}\right)$$

$\Delta G^{\circ} = +68.9$ kJ/mol

(c) $K = K_p = K_c\left(RT\right)^{\Delta n} = 4.61\times10^{-3}\left(0.08206\times298\right)^{+1} = 0.113$

$$\Delta G^{\circ} = -RT\ \ln\ K_p = -\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(298\text{K}\right)\ln\left(0.113\right) = +5.40\ \text{kJ/mol}$$

(d) $K = K_c = 9.14\times10^{-6}$

$$\Delta G^{\circ} = -RT\ \ln\ K_c = -\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}\right)\left(298\ \text{K}\right)\ln\left(9.14\times10^{-6}\right)$$

$\Delta G^{\circ} = +28.7$ kJ/mol

50. **(M) (a)** The first equation involves the formation of one mole of $\text{Mg}^{2+}(\text{aq})$ from $\text{Mg(OH)}_2(\text{s})$ and $2\text{H}^+(\text{aq})$, while the second equation involves the formation of only half-a-mole of $\text{Mg}^{2+}(\text{aq})$. We would expect a free energy change of half the size if only half as much product is formed.

(b) The value of K for the first reaction is the square of the value of K for the second reaction. The equilibrium constant expressions are related in the same fashion.

$$K_1 = \frac{\left[\text{Mg}^{2+}\right]}{\left[\text{H}^+\right]^2} = \left(\frac{\left[\text{Mg}^{2+}\right]^{1/2}}{\left[\text{H}^+\right]}\right)^2 = \left(K_2\right)^2$$

(c) The equilibrium solubilities will be the same regardless which expression is used. The equilibrium conditions (solubilities in this instance) are the same no matter how we choose to express them in an equilibrium constant expression.

51. **(E)** $\Delta G^{\circ} = -RT \ln K_{\mathrm{p}} = -\left(8.3145\times10^{-3}\ \text{kJ mol}^{-1}\text{K}^{-1}\right)\left(298\,\text{K}\right)\ln\left(6.5\times10^{11}\right) = -67.4\ \text{kJ/mol}$

$$\mathrm{CO(g)} + \mathrm{Cl_2(g)} \rightarrow \mathrm{COCl_2(g)} \qquad \Delta G^{\circ} = -67.4\,\text{kJ/mol}$$

$$\mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)} \qquad \Delta G_{\mathrm{f}}^{\circ} = -137.2\ \text{kJ/mol}$$

$$\mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{Cl_2(g)} \rightarrow \mathrm{COCl_2(g)} \qquad \Delta G_{\mathrm{f}}^{\circ} = -204.6\ \text{kJ/mol}$$

$\Delta G_{\mathrm{f}}^{\circ}$ of $\mathrm{COCl_2(g)}$ given in Appendix D is -204.6 kJ/mol, thus the agreement is excellent.

52. **(M)** In each case, we first determine the value of ΔG° for the solubility reaction. From that, we calculate the value of the equilibrium constant, K_{sp}, for the solubility reaction.

(a) $\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)}$

$$\Delta G^{\circ} = \Delta G_{\mathrm{f}}^{\circ}\left[\mathrm{Ag^+(aq)}\right] + \Delta G_{\mathrm{f}}^{\circ}\left[\mathrm{Br^-(aq)}\right] - \Delta G_{\mathrm{f}}^{\circ}\left[\mathrm{AgBr(s)}\right]$$

$$= 77.11\ \text{kJ/mol} - 104.0\ \text{kJ/mol} - \left(-96.90\ \text{kJ/mol}\right) = +70.0\ \text{kJ/mol}$$

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-70.0\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times 298.15\ \text{K}} = -28.2; \qquad K_{\mathrm{sp}} = e^{-28.2} = 6\times10^{-13}$$

(b) $\mathrm{CaSO_4(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + \mathrm{SO_4^{\,2-}(aq)}$

$$\Delta G^{\circ} = \Delta G_{\mathrm{f}}^{\,\circ}\left[\mathrm{Ca^{2+}(aq)}\right] + \Delta G_{\mathrm{f}}^{\,\circ}\left[\mathrm{SO_4^{\,2-}(aq)}\right] - \Delta G_{\mathrm{f}}^{\,\circ}\left[\mathrm{CaSO_4(s)}\right]$$

$$= -553.6\ \text{kJ/mol} - 744.5\ \text{kJ/mol} - \left(-1332\ \text{kJ/mol}\right) = +34\ \text{kJ/mol}$$

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-34\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times 298.15\ \text{K}} = -14; \qquad K_{\mathrm{sp}} = e^{-14} = 8\times10^{-7}$$

(c) $\mathrm{Fe(OH)_3(s)} \rightleftharpoons \mathrm{Fe^{3+}(aq)} + 3\mathrm{OH^-(aq)}$

$$\Delta G^{\circ} = \Delta G_{\mathrm{f}}^{\circ}\left[\mathrm{Fe^{3+}(aq)}\right] + 3\,\Delta G_{\mathrm{f}}^{\circ}\left[\mathrm{OH^-(aq)}\right] - \Delta G_{\mathrm{f}}^{\circ}\left[\mathrm{Fe(OH)_3(s)}\right]$$

$$= -4.7\ \text{kJ/mol} + 3\times\left(-157.2\ \text{kJ/mol}\right) - \left(-696.5\ \text{kJ/mol}\right) = +220.2\ \text{kJ/mol}$$

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-220.2\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times 298.15\ \text{K}} = -88.83 \qquad K_{\mathrm{sp}} = e^{-88.83} = 2.6\times10^{-39}$$

53. **(M)(a)** We can determine the equilibrium partial pressure from the value of the equilibrium constant.

$$\Delta G^{\circ} = -RT\ln K_{\mathrm{p}} \qquad \ln K_{\mathrm{p}} = -\frac{\Delta G^{\circ}}{RT} = -\frac{58.54\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\text{K}^{-1}\times 298.15\ \text{K}} = -23.63$$

$$K_{\mathrm{p}} = P\{\mathrm{O_2(g)}\}^{1/2} = e^{-23.63} = 5.5\times10^{-11} \qquad P\{\mathrm{O_2(g)}\} = \left(5.5\times10^{-11}\right)^{2} = 3.0\times10^{-21}\,\text{atm}$$

(b) Lavoisier did two things to increase the quantity of oxygen that he obtained. First, he ran the reaction at a high temperature, which favors the products (i.e., the side with molecular oxygen.) Second, the molecular oxygen was removed immediately after it was formed, which causes the equilibrium to shift to the right continuously (the shift towards products as result of the removal of the O_2 is an example of Le Châtelier's principle).

54. **(D) (a)** We determine the values of ΔH^o and ΔS^o from the data in Appendix D, and then the value of ΔG^o at $25^\circ\text{ C} = 298\text{ K}$.

$$\Delta H^o = \Delta H_f^\circ\left[CH_3OH(g)\right] + \Delta H_f^\circ\left[H_2O(g)\right] - \Delta H_f^\circ\left[CO_2(g)\right] - 3\,\Delta H_f^\circ\left[H_2(g)\right]$$

$$= -200.7\text{ kJ/mol} + (-241.8\text{ kJ/mol}) - (-393.5\text{ kJ/mol}) - 3\,(0.00\text{ kJ/mol}) = -49.0\text{ kJ/mol}$$

$$\Delta S^o = S^o\left[CH_3OH(g)\right] + S^o\left[H_2O(g)\right] - S^o\left[CO_2(g)\right] - 3\,S^o\left[H_2(g)\right]$$

$$= (239.8 + 188.8 - 213.7 - 3\times 130.7)\text{ J mol}^{-1}\text{K}^{-1} = -177.2\text{ J mol}^{-1}\text{K}^{-1}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o = -49.0\text{ kJ/mol} - 298\text{ K}\left(-0.1772\text{ kJ mol}^{-1}\text{K}^{-1}\right) = +3.81\text{ kJ/mol}$$

Because the value of ΔG^o is positive, this reaction does not proceed in the forward direction at 25° C.

(b) Because the value of ΔH^o is negative and that of ΔS^o is negative, the reaction is *non-spontaneous* at high temperatures, if reactants and products are *in their standard states*. The reaction will proceed slightly in the forward direction, however, to produce an equilibrium mixture with small quantities of $CH_3OH(g)$ and $H_2O(g)$. Also, because the forward reaction is exothermic, this reaction is favored by lowering the temperature. That is, the value of K increases with decreasing temperature.

(c)

$$\Delta G^o_{500K} = \Delta H^o - T\,\Delta S^o = -49.0\text{ kJ/mol} - 500.\text{K}\left(-0.1772\text{ kJ mol}^{-1}\text{K}^{-1}\right) = 39.6\text{ kJ/mol}$$

$$= 39.6\times 10^3\text{ J/mol} = -RT\ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-39.6\times 10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{K}^{-1}\times 500.\text{ K}} = -9.53; \quad K_p = e^{-9.53} = 7.3\times 10^{-5}$$

(d)

Reaction:	$CO_2(g)+$	$3H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$	$+H_2O(g)$
Initial:	1.00 atm	1.00 atm		0 atm	0 atm
Changes:	$-x$ atm	$-3x$ atm		$+x$ atm	$+x$ atm
Equil:	$(1.00-x)$ atm	$(1.00-3x)$ atm		x atm	x atm

$$K_p = 7.3\times 10^{-5} = \frac{P\{CH_3OH\}P\{H_2O\}}{P\{CO_2\}P\{H_2\}^3} = \frac{x\cdot x}{(1.00-x)(1.00-3x)^3} \approx x^2$$

$x = \sqrt{7.3\times 10^{-5}} = 8.5\times 10^{-3}\text{ atm} = P\{CH_3OH\}$ Our assumption, that $3x \ll 1.00$ atm, is valid.

ΔG^o and K as Function of Temperature

55 **(M)(a)** $\Delta S^o = S^o\left[Na_2CO_3(s)\right] + S^o\left[H_2O(l)\right] + S^o\left[CO_2(g)\right] - 2S^o\left[NaHCO_3(s)\right]$

$$= 135.0\,\frac{\text{J}}{\text{K mol}} + 69.91\,\frac{\text{J}}{\text{K mol}} + 213.7\,\frac{\text{J}}{\text{K mol}} - 2\left(101.7\,\frac{\text{J}}{\text{K mol}}\right) = +215.2\,\frac{\text{J}}{\text{K mol}}$$

(b) $$\Delta H^{\circ} = \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{Na_2CO_3(s)}\right] + \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{H_2O(l)}\right] + \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{CO_2(g)}\right] - 2\Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{NaHCO_3(s)}\right]$$

$$= -1131\frac{\mathrm{kJ}}{\mathrm{mol}} - 285.8\frac{\mathrm{kJ}}{\mathrm{mol}} - 393.5\frac{\mathrm{kJ}}{\mathrm{mol}} - 2\left(-950.8\frac{\mathrm{kJ}}{\mathrm{mol}}\right) = +91\frac{\mathrm{kJ}}{\mathrm{mol}}$$

(c) $$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 91\ \mathrm{kJ/mol} - (298\ \mathrm{K})\left(215.2\times10^{-3}\ \mathrm{kJ\ mol^{-1}K^{-1}}\right)$$

$$= 91\ \mathrm{kJ/mol} - 64.13\ \mathrm{kJ/mol} = 27\ \mathrm{kJ/mol}$$

(d) $$\Delta G^{\circ} = -RT\ln K \qquad \ln K = -\frac{\Delta G^{\circ}}{RT} = -\frac{27\times10^{3}\ \mathrm{J/mol}}{8.3145\,\mathrm{J\ mol^{-1}K^{-1}}\times298\,\mathrm{K}} = -10.\underline{9}$$

$$K = \mathrm{e}^{-10.9} = 2\times10^{-5}$$

56. **(M) (a)** $$\Delta S^{\circ} = S^{\circ}\left[\mathrm{CH_3CH_2OH(g)}\right] + S^{\circ}\left[\mathrm{H_2O(g)}\right] - S^{\circ}\left[\mathrm{CO(g)}\right] - 2S^{\circ}\left[\mathrm{H_2\,(g)}\right] - S^{\circ}\left[\mathrm{CH_3OH(g)}\right]$$

$$\Delta S^{\circ} = 282.7\ \frac{\mathrm{J}}{\mathrm{K\ mol}} + 188.8\ \frac{\mathrm{J}}{\mathrm{K\ mol}} - 197.7\frac{\mathrm{J}}{\mathrm{K\ mol}} - 2\left(130.7\ \frac{\mathrm{J}}{\mathrm{K\ mol}}\right) - 239.8\ \frac{\mathrm{J}}{\mathrm{K\ mol}}$$

$$\Delta S^{\circ} = -227.4\ \frac{\mathrm{J}}{\mathrm{K\ mol}}$$

$$\Delta H^{\circ} = \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{CH_3CH_2OH(g)}\right] + \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{H_2O(g)}\right] - \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{CO(g)}\right] - 2\Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{H_2\,(g)}\right] - \Delta H_{\mathrm{f}}^{\circ}\left[\mathrm{CH_3OH(g)}\right]$$

$$\Delta H^{\circ} = -235.1\frac{\mathrm{kJ}}{\mathrm{mol}} - 241.8\frac{\mathrm{kJ}}{\mathrm{mol}} - \left(-110.5\frac{\mathrm{kJ}}{\mathrm{mol}}\right) - 2\left(0.00\frac{\mathrm{kJ}}{\mathrm{mol}}\right) - \left(-200.7\frac{\mathrm{kJ}}{\mathrm{mol}}\right)$$

$$\Delta H^{\circ} = -165.7\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^{\circ} = -165.7\frac{\mathrm{kJ}}{\mathrm{mol}} - (298\mathrm{K})\left(-227.4\times10^{-3}\ \frac{\mathrm{kJ}}{\mathrm{K\,mol}}\right) = -165.4\frac{\mathrm{kJ}}{\mathrm{mol}} + 67.8\frac{\mathrm{kJ}}{\mathrm{mol}} = -97.9\frac{\mathrm{kJ}}{\mathrm{mol}}$$

(b) $\Delta H^{\circ} < 0$ for this reaction. Thus it is favored at low temperatures. Also, because $\Delta n_{\mathrm{gas}} = +2 - 4 = -2$, which is less than zero, the reaction is favored at high pressures.

(c) First we assume that neither ΔS° nor ΔH° varies significantly with temperature. Then we compute a value for ΔG° at 750 K. From this value of ΔG°, we compute a value for K_{p}.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -165.7\,\mathrm{kJ/mol} - (750.\mathrm{K})\left(-227.4\times10^{-3}\,\mathrm{kJ\ mol^{-1}\ K^{-1}}\right)$$

$$= -165.7\,\mathrm{kJ/mol} + 170.6\,\mathrm{kJ/mol} = +4.9\mathrm{kJ/mol} = -RT\ln K_{\mathrm{p}}$$

$$\ln K_{\mathrm{p}} = -\frac{\Delta G^{\circ}}{RT} = -\frac{4._{9}\times10^{3}\ \mathrm{J/mol}}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}\times750.\mathrm{K}} = -0.79 \qquad K_{\mathrm{p}} = \mathrm{e}^{-0.79} = 0.5$$

57. **(E)** In this problem we are asked to determine the temperature for the reaction between iron(III) oxide and carbon monoxide to yield iron and carbon dioxide given ΔG^{o}, ΔH^{o}, and ΔS^{o}. We proceed by rearranging $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ in order to express the temperature as a function of ΔG^{o}, ΔH^{o}, and ΔS^{o}.

Stepwise approach:

Rearrange $\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$ in order to express T as a function of ΔG^{o}, ΔH^{o}, and ΔS^{o}:

$$\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$$

$$T\Delta S^{\circ}=\Delta H^{\circ}-\Delta G^{\circ}$$

$$T=\frac{\Delta H^{\circ}-\Delta G^{\circ}}{\Delta S^{\circ}}$$

Calculate T:

$$T=\frac{-24.8\times 10^{3}\text{ J}-\left(-45.5\times 10^{3}\text{ J}\right)}{15.2\text{ J/K}}=1.36\times 10^{3}\text{ K}$$

Conversion pathway approach:

$$\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}\Rightarrow T=\frac{\Delta H^{\circ}-\Delta G^{\circ}}{\Delta S^{\circ}}=\frac{-24.8\times 10^{3}\text{ J}-\left(-45.5\times 10^{3}\text{ J}\right)}{15.2\text{ J/K}}=1.36\times 10^{3}\text{ K}$$

58. **(E)** We use the van't Hoff equation with $\Delta H^{\circ}=-1.8\times 10^{5}$ J/mol, $T_1=800.$ K, $T_2=100.^{\circ}\text{C}=373\text{K}$, and $K_1=9.1\times 10^{2}$.

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{-1.8\times 10^{5}\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{800\text{ K}}-\frac{1}{373\text{K}}\right)=31$$

$$\frac{K_2}{K_1}=e^{31}=2.\underline{9}\times 10^{13}=\frac{K_2}{9.1\times 10^{2}}\qquad K_2=\left(2.\underline{9}\times 10^{13}\right)\left(9.1\times 10^{2}\right)=3\times 10^{16}$$

59. **(M)** We first determine the value of ΔG° at 400°C, from the values of ΔH° and ΔS°, which are calculated from information listed in Appendix D.

$$\Delta H^{\circ}=2\Delta H_f^{\circ}\left[\text{NH}_3(\text{g})\right]-\Delta H_f^{\circ}\left[\text{N}_2(\text{g})\right]-3\Delta H_f^{\circ}\left[\text{H}_2(\text{g})\right]$$

$$=2(-46.11\text{kJ/mol})-(0.00\text{kJ/mol})-3(0.00\text{ kJ/mol})=-92.22\text{kJ/mol N}_2$$

$$\Delta S^{\circ}=2S^{\circ}\left[\text{NH}_3(\text{g})\right]-S^{\circ}\left[\text{N}_2(\text{g})\right]-3S^{\circ}\left[\text{H}_2(\text{g})\right]$$

$$=2\left(192.5\text{ J mol}^{-1}\text{ K}^{-1}\right)-\left(191.6\text{ J mol}^{-1}\text{ K}^{-1}\right)-3\left(130.7\text{ J mol}^{-1}\text{ K}^{-1}\right)=-198.7\text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta G^{\circ}=\Delta H^{\circ}-T\,\Delta S^{\circ}=-92.22\text{ kJ/mol}-673\text{ K}\times\left(-0.1987\text{ kJ mol}^{-1}\text{ K}^{-1}\right)$$

$$=+41.51\text{ kJ/mol}=-RT\ln K_p$$

$$\ln K_p=\frac{-\Delta G^{\circ}}{RT}=\frac{-41.51\times 10^{3}\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{K}^{-1}\times 673\text{K}}=-7.42;\quad K_p=e^{-7.42}=6.0\times 10^{-4}$$

60. **(M) (a)** $$\Delta H^\circ = \Delta H_f^\circ\left[CO_2(g)\right] + \Delta H_f^\circ\left[H_2(g)\right] - \Delta H_f^\circ\left[CO(g)\right] - \Delta H_f^\circ\left[H_2O(g)\right]$$
$$= -393.5\text{ kJ/mol} - 0.00\text{ kJ/mol} - (-110.5\text{ kJ/mol}) - (-241.8\text{ kJ/mol}) = -41.2\text{ kJ/mol}$$

$$\Delta S^\circ = S^\circ\left[CO_2(g)\right] + S^\circ\left[H_2(g)\right] - S^\circ\left[CO(g)\right] - S^\circ\left[H_2O(g)\right]$$
$$= 213.7\text{ J mol}^{-1}\text{ K}^{-1} + 130.7\text{ J mol}^{-1}\text{ K}^{-1} - 197.7\text{ J mol}^{-1}\text{ K}^{-1} - 188.8\text{ J mol}^{-1}\text{ K}^{-1}$$
$$= -42.1\text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o = -41.2\text{kJ/mol} - 298.15\text{K} \times (-42.1 \times 10^{-3})\text{kJ/molK}$$
$$\Delta G^o = -41.2\text{kJ/mol} + 12.6\text{kJ/mol} = -28.6\text{kJ/mol}$$

(b) $$\Delta G^\circ = \Delta H^\circ - T\ \Delta S^\circ = -41.2\text{ kJ/mol} - (875\text{ K})(-42.1 \times 10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1})$$
$$= -41.2\text{ kJ/mol} + 36.8\text{ kJ/mol} = -4.4\text{ kJ/mol} = -RT\ \ln K_p$$
$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{-4.4 \times 10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{K}^{-1} \times 875\text{K}} = +0.60 \qquad K_p = e^{+0.60} = 1.8$$

61. **(M)** We assume that both ΔH° and ΔS° are constant with temperature.
$$\Delta H^\circ = 2\Delta H_f^\circ\left[SO_3(g)\right] - 2\Delta H_f^\circ\left[SO_2(g)\right] - \Delta H_f^\circ\left[O_2(g)\right]$$
$$= 2(-395.7\text{ kJ/mol}) - 2(-296.8\text{ kJ/mol}) - (0.00\text{ kJ/mol}) = -197.8\text{ kJ/mol}$$
$$\Delta S^\circ = 2S^\circ\left[SO_3(g)\right] - 2S^\circ\left[SO_2(g)\right] - S^\circ\left[O_2(g)\right]$$
$$= 2(256.8\text{ J mol}^{-1}\text{ K}^{-1}) - 2(248.2\text{ J mol}^{-1}\text{ K}^{-1}) - (205.1\text{ J mol}^{-1}\text{ K}^{-1})$$
$$= -187.9\text{ J mol}^{-1}\text{ K}^{-1}$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \qquad \Delta H^\circ = T\Delta S^\circ - RT\ln K \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K}$$
$$T = \frac{-197.8 \times 10^3\text{ J/mol}}{-187.9\text{ J mol}^{-1}\text{ K}^{-1} - 8.3145\text{ J mol}^{-1}\text{ K}^{-1}\ \ln(1.0 \times 10^6)} \approx 650\text{ K}$$

This value compares very favorably with the value of $T = 6.37 \times 10^2$ that was obtained in Example 19-10.

62. **(E)** We use the van't Hoff equation to determine the value of ΔH° ($448^\circ\text{ C} = 721\text{ K}$ and $350^\circ\text{ C} = 623\text{ K}$).
$$\ln\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \ln\frac{50.0}{66.9} = -0.291 = \frac{\Delta H^\circ}{R}\left(\frac{1}{623} - \frac{1}{721}\right) = \frac{\Delta H^\circ}{R}(2.2 \times 10^{-4})$$
$$\frac{\Delta H^\circ}{R} = \frac{-0.291}{2.2 \times 10^{-4}\ \text{K}^{-1}} = -1.3 \times 10^3\ \text{K};$$
$$\Delta H^\circ = -1.3 \times 10^3\text{K} \times 8.3145\text{ J K}^{-1}\text{ mol}^{-1} = -11 \times 10^3\text{J mol}^{-1} = -11\text{ kJ mol}^{-1}$$

63. **(M) (a)** $\ln\frac{K_2}{K_1}=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{57.2\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{298\text{ K}}-\frac{1}{273\text{ K}}\right)=-2.11$

$$\frac{K_2}{K_1}=\mathrm{e}^{-2.11}=0.121 \qquad K_2=0.121\times0.113=0.014\text{ at }273\text{ K}$$

(b) $\ln\frac{K_2}{K_1}=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{57.2\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{T_1}-\frac{1}{298\text{ K}}\right)=\ln\frac{0.113}{1.00}=-2.180$

$$\left(\frac{1}{T_1}-\frac{1}{298\text{K}}\right)=\frac{-2.180\times8.3145}{57.2\times10^3}\text{K}^{-1}=-3.17\times10^{-4}\text{K}^{-1}$$

$$\frac{1}{T_1}=\frac{1}{298}-3.17\times10^{-4}=3.36\times10^{-3}-3.17\times10^{-4}=3.04\times10^{-3}\text{ K}^{-1};\quad T_1=329\text{ K}$$

64. **(D)** First we calculate ΔG° at 298 K to obtain a value for K_{eq} at that temperature.

$$\Delta G^\circ=2\Delta G_f^\circ\left[\text{NO}_2(\text{g})\right]-2\Delta G_f^\circ\left[\text{NO}(\text{g})\right]-\Delta G_f^\circ\left[\text{O}_2(\text{g})\right]$$
$$=2(51.31\text{ kJ/mol})-2(86.55\text{ kJ/mol})-0.00\text{ kJ/mol}=-70.48\text{ kJ/mol}$$

$$\ln K=\frac{-\Delta G^\circ}{RT}=-\frac{-70.48\times10^3\text{ J/mol K}}{\frac{8.3145\text{ J}}{\text{mol K}}\times298.15\text{ K}}=28.43 \qquad K=\mathrm{e}^{28.43}=2.2\times10^{12}$$

Now we calculate ΔH° for the reaction, which then will be inserted into the van't Hoff equation.

$$\Delta H^\circ=2\Delta H_f^\circ\left[\text{NO}_2(\text{g})\right]-2\Delta H_f^\circ\left[\text{NO}(\text{g})\right]-\Delta H_f^\circ\left[\text{O}_2(\text{g})\right]$$
$$=2(33.18\text{ kJ/mol})-2(90.25\text{ kJ/mol})-0.00\text{ kJ/mol}=-114.14\text{ kJ/mol}$$

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{-114.14\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{298\text{ K}}-\frac{1}{373\text{ K}}\right)=-9.26$$

$$\frac{K_2}{K_1}=\mathrm{e}^{-9.26}=9.5\times10^{-5};\quad K_2=9.5\times10^{-5}\times2.2\times10^{12}=2.1\times10^8$$

Another way to find K at 100 °C is to compute $\Delta H^\circ\left(-114.14\text{ kJ/mol}\right)$ from ΔH_f° values and $\Delta S^\circ\left(-146.5\text{ J mol}^{-1}\text{ K}^{-1}\right)$ from S° values. Then determine $\Delta G^\circ(-59.5\text{ kJ/mol})$, and find K_p with the expression $\Delta G^\circ=-RT\ln K_p$. Not surprisingly, we obtain the same result, $K_p=2.2\times10^8$.

65. **(M)** First, the van't Hoff equation is used to obtain a value of ΔH°. $200^\circ\text{C}=473\text{K}$ and $260^\circ\text{C}=533\text{K}$.

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\ln\frac{2.15\times10^{11}}{4.56\times10^8}=6.156=\frac{\Delta H^\circ}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{533\text{K}}-\frac{1}{473\text{ K}}\right)$$

$$6.156=-2.9\times10^{-5}\Delta H^\circ \qquad \Delta H^\circ=\frac{6.156}{-2.9\times10^{-5}}=-2.1\times10^5\text{J / mol}=-2.1\times10^2\text{kJ / mol}$$

Another route to ΔH^o is the combination of standard enthalpies of formation.

$$\mathrm{CO(g)} + 3\mathrm{H_2(g)} \rightleftharpoons \mathrm{CH_4(g)} + \mathrm{H_2O(g)}$$

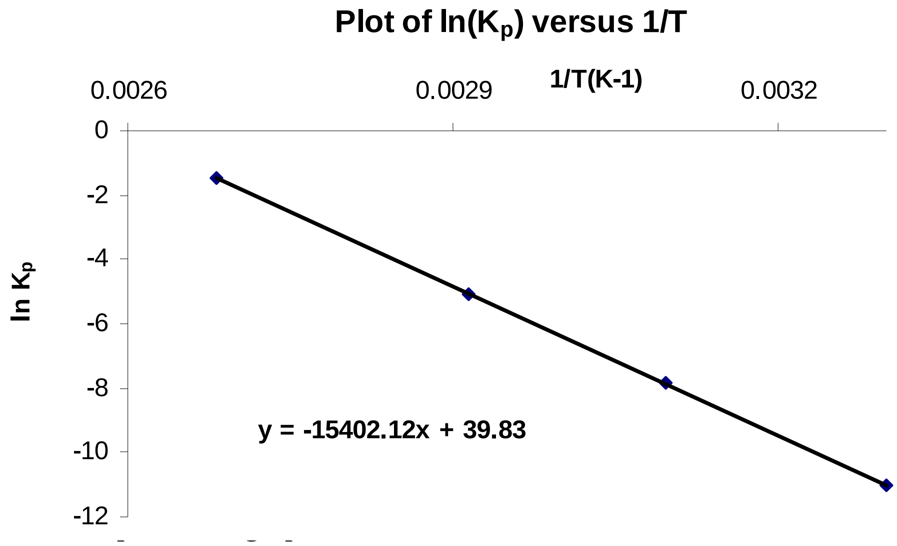
$$\Delta H^o = \Delta H_f^\circ[\mathrm{CH_4(g)}] + \Delta H_f^\circ[\mathrm{H_2O(g)}] - \Delta H_f^\circ[\mathrm{CO(g)}] - 3\Delta H_f^\circ[\mathrm{H_2(g)}]$$

$$= -74.81\ \text{kJ/mol} - 241.8\ \text{kJ/mol} - (-110.5) - 3\times 0.00\ \text{kJ/mol} = -206.1\ \text{kJ/mol}$$

Within the precision of the data supplied, the results are in good agreement.

66. **(D) (a)**

$t, ^\circ\mathrm{C}$	T, K	$1/T, \mathrm{K}^{-1}$	K_p	$\ln K_p$
30.	303	3.30×10^{-3}	1.66×10^{-5}	-11.006
50.	323	3.10×10^{-3}	3.90×10^{-4}	-7.849
70.	343	2.92×10^{-3}	6.27×10^{-3}	-5.072
100.	373	2.68×10^{-3}	2.31×10^{-1}	-1.465



$$\Delta H^o = -(8.3145\ \mathrm{J\ mol^{-1}K^{-1}})(-1.54\times10^4\ \mathrm{K}) = 128\times10^3\ \mathrm{J/mol} = 128\ \mathrm{kJ/mol}$$

(b) When the total pressure is 2.00 atm, and both gases have been produced from $\mathrm{NaHCO_3(s)}$,

$$P\{\mathrm{H_2O(g)}\} = P\{\mathrm{CO_2(g)}\} = 1.00\ \text{atm}$$

$$K_p = P\{\mathrm{H_2O(g)}\}P\{\mathrm{CO_2(g)}\} = (1.00)(1.00) = 1.00$$

Thus, $\ln K_p = \ln(1.00) = 0.000$. The corresponds to $1/T = 2.59\times10^{-3}\ \mathrm{K}^{-1}$;
$T = 386\ \mathrm{K}$.
We can compute the same temperature from the van't Hoff equation.

$$\ln\frac{K_2}{K_1}=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{128\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{T_1}-\frac{1}{303\text{ K}}\right)=\ln\frac{1.66\times10^{-5}}{1.00}=-11.006$$

$$\left(\frac{1}{T_1}-\frac{1}{303\text{ K}}\right)=\frac{-11.006\times8.3145}{128\times10^3}\text{ K}^{-1}=-7.15\times10^{-4}\text{ K}^{-1}$$

$$\frac{1}{T_1}=\frac{1}{303}-7.15\times10^{-4}=3.30\times10^{-3}-7.15\times10^{-4}=2.59\times10^{-3}\text{ K}^{-1};\quad T_1=386\text{ K}$$

This temperature agrees well with the result obtained from the graph.

Coupled Reactions

67. **(E) (a)** We compute ΔG° for the given reaction in the following manner

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{TiCl}_4(\text{l})]+\Delta H_f^\circ[\text{O}_2(\text{g})]-\Delta H_f^\circ[\text{TiO}_2(\text{s})]-2\Delta H_f^\circ[\text{Cl}_2(\text{g})]\\ &= -804.2\text{ kJ/mol}+0.00\text{ kJ/mol}-(-944.7\text{ kJ/mol})-2(0.00\text{ kJ/mol})\\ &= +140.5\text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{TiCl}_4(\text{l})]+S^\circ[\text{O}_2(\text{g})]-S^\circ[\text{TiO}_2(\text{s})]-2S^\circ[\text{Cl}_2(\text{g})]\\ &= 252.3\text{ J mol}^{-1}\text{ K}^{-1}+205.1\text{ J mol}^{-1}\text{ K}^{-1}-\left(50.33\text{ J mol}^{-1}\text{ K}^{-1}\right)-2\left(223.1\text{ J mol}^{-1}\text{ K}^{-1}\right)\\ &= -39.1\text{ J mol}^{-1}\text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\,\Delta S^\circ = +140.5\text{ kJ/mol}-(298\text{ K})\left(-39.1\times10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1}\right)\\ &= +140.5\text{ kJ/mol}+11.6\text{ kJ/mol}=+152.1\text{ kJ/mol}\end{aligned}$$

Thus the reaction is non-spontaneous at 25° C. (we also could have used values of ΔG_f° to calculate ΔG°).

(b) For the cited reaction, $\Delta G^\circ = 2\Delta G_f^\circ[\text{CO}_2(\text{g})]-2\Delta G_f^\circ[\text{CO(g)}]-\Delta G_f^\circ[\text{O}_2(\text{g})]$

$$\Delta G^\circ = 2(-394.4\text{ kJ/mol})-2(-137.2\text{ kJ/mol})-0.00\text{ kJ/mol}=-514.4\text{ kJ/mol}$$

Then we couple the two reactions.

$$\begin{array}{ll}\text{TiO}_2(\text{s})+2\text{Cl}_2(\text{g})\longrightarrow\text{TiCl}_4(\text{l})+\text{O}_2(\text{g}) & \Delta G^\circ=+152.1\text{ kJ/mol}\\ 2\text{CO(g)}+\text{O}_2(\text{g})\longrightarrow2\text{CO}_2(\text{g}) & \Delta G^\circ=-514.4\text{ kJ/mol}\\ \hline \text{TiO}_2(\text{s})+2\text{Cl}_2(\text{g})+2\text{CO(g)}\longrightarrow\text{TiCl}_4(\text{l})+2\text{CO}_2(\text{g});\Delta G^\circ & =-362.3\text{ kJ/mol}\end{array}$$

The coupled reaction has $\Delta G^\circ < 0$, and, therefore, is spontaneous.

68. **(E)** If $\Delta G^{\circ} < 0$ for the sum of coupled reactions, the reduction of the oxide with carbon is spontaneous.

(a)

$$\mathrm{NiO(s)} \rightarrow \mathrm{Ni(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \qquad \Delta G^{\circ} = +115\ \mathrm{kJ}$$

$$\mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)} \qquad \Delta G^{\circ} = -250\ \mathrm{kJ}$$

$$\text{Net}: \mathrm{NiO}(s) + \mathrm{C(s)} \rightarrow \mathrm{Ni(s)} + \mathrm{CO(g)} \qquad \Delta G^{\circ} = +115\ \mathrm{kJ} - 250\ \mathrm{kJ} = -135\ \mathrm{kJ}$$

Therefore the coupled reaction is spontaneous

(b)

$$\mathrm{MnO(s)} \rightarrow \mathrm{Mn(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \qquad \Delta G^{\circ} = +280\ \mathrm{kJ}$$

$$\mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)} \qquad \Delta G^{\circ} = -250\ \mathrm{kJ}$$

$$\text{Net}: \mathrm{MnO(s)} + \mathrm{C(s)} \longrightarrow \mathrm{Mn(s)} + \mathrm{CO(g)} \qquad \Delta G^{\circ} = +280\ \mathrm{kJ} - 250\ \mathrm{kJ} = +30\ \mathrm{kJ}$$

Therefore the coupled reaction is non-spontaneous

(c)

$$\mathrm{TiO_2(s)} \longrightarrow \mathrm{Ti(s)} + \mathrm{O_2(g)} \qquad \Delta G^{\circ} = +630\ \mathrm{kJ}$$

$$2\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow 2\mathrm{CO(g)} \qquad \Delta G^{\circ} = 2(-250\ \mathrm{kJ}) = -500\ \mathrm{kJ}$$

$$\text{Net}: \mathrm{TiO_2(s)} + 2\mathrm{C(s)} \longrightarrow \mathrm{Ti(s)} + 2\mathrm{CO(g)} \qquad \Delta G^{\circ} = +630\ \mathrm{kJ} - 500\ \mathrm{kJ} = +130\ \mathrm{kJ}$$

Therefore the coupled reaction is non-spontaneous

69. **(E)** In this problem we need to determine if the phosphorylation of arginine with ATP is a spontaneous reaction. We proceed by coupling the two given reactions in order to calculate ΔG_t^o for the overall reaction. The sign of ΔG_t^o can then be used to determine whether the reaction is spontaneous or not.

Stepwise approach:

First determine ΔG_t^o for the coupled reaction:

$$\mathrm{ATP+H_2O \longrightarrow ADP+P} \qquad \Delta G_t^o = -31.5\mathrm{kJmol^{-1}}$$

$$\mathrm{arginine+P \longrightarrow phosphorarginine+H_2O} \qquad \Delta G_t^o = -33.2\mathrm{kJmol^{-1}}$$

$$\mathrm{ATP+arginine \longrightarrow phosphorarginine+ADP}$$

$$\Delta G^o = (-31.5 + 33.2)\mathrm{kJmol^{-1}} = 1.7\mathrm{kJmol^{-1}}$$

Examine the sign of ΔG_t^o:

$\Delta G_t^o > 0$. Therefore, the reaction is not spontaneous.

Conversion pathway approach:

ΔG_t^o for the coupled reaction is:

$$\mathrm{ATP+arginine \longrightarrow phosphorarginine+ADP}$$

$$\Delta G^o = (-31.5 + 33.2)\mathrm{kJmol^{-1}} = 1.7\mathrm{kJmol^{-1}}$$

Since $\Delta G_t^o > 0$, the reaction is not spontaneous.

70. **(E)** By coupling the two reactions, we obtain:

$$\text{Glu}^- + \text{NH}_4^+ \longrightarrow \text{Gln} + \text{H}_2\text{O} \qquad \Delta G_t^o = 14.8\,\text{kJmol}^{-1}$$

$$\text{ATP} + \text{H}_2\text{O} \longrightarrow \text{ADP} + \text{P} \qquad \Delta G_t^o = -31.5\,\text{kJmol}^{-1}$$

$$\text{Glu}^- + \text{NH}_4^+ + \text{ATP} \longrightarrow \text{Gln} + \text{ADP} + \text{P} \qquad \Delta G^o = (14.8 - 31.5)\,\text{kJmol}^{-1} = -16.7\,\text{kJmol}^{-1}$$

Therefore, the reaction is spontaneous.

INTEGRATIVE AND ADVANCED EXERCISES

71. (M) (a) The normal boiling point of mercury is that temperature at which the mercury vapor pressure is 1.00 atm, or where the equilibrium constant for the vaporization equilibrium reaction has a numerical value of 1.00. This is also the temperature where $\Delta G° = 0$, since $\Delta G° = -RT\ln K_{\text{eq}}$ and $\ln(1.00) = 0$.

$$\text{Hg(l)} \rightleftharpoons \text{Hg(g)}$$

$$\Delta H° = \Delta H°_{\text{f}}\,[\text{Hg(g)}] - \Delta H°_{\text{f}}\,[\text{Hg(l)}] = 61.32\,\text{kJ/mol} - 0.00\,\text{kJ/mol} = 61.32\,\text{kJ/mol}$$

$$\Delta S° = S°[\text{Hg(g)}] - S°[\text{Hg(l)}] = 175.0\,\text{J mol}^{-1}\,\text{K}^{-1} - 76.02\,\text{J mol}^{-1}\,\text{K}^{-1} = 99.0\,\text{J mol}^{-1}\,\text{K}^{-1}$$

$$0 = \Delta H° - T\,\Delta S° = 61.32 \times 10^3\ \text{J/mol} - T \times 99.0\,\text{J mol}^{-1}\,\text{K}^{-1}$$

$$T = \frac{61.32 \times 10^3\ \text{J/mol}}{99.0\,\text{J mol}^{-1}\,\text{K}^{-1}} = 619\,\text{K}$$

(b) The vapor pressure in atmospheres is the value of the equilibrium constant, which is related to the value of the free energy change for formation of Hg vapor.

$$\Delta G°_{\text{f}}\ [\text{Hg(g)}] = 31.82\,\text{kJ/mol} = -RT\ln K_{\text{eq}}$$

$$\ln K = \frac{-31.82 \times 10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298.15\,\text{K}} = -12.84 \qquad K = \text{e}^{-12.84} = 2.65 \times 10^{-6}\ \text{atm}$$

Therefore, the vapor pressure of Hg at 25ºC is 2.65×10^{-6} atm.

72. (M) (a) **TRUE;** It is the change in free energy for a process in which reactants and products are all in their standard states (regardless of whatever states might be mentioned in the statement of the problem). When liquid and gaseous water are each at 1 atm at 100 °C (the normal boiling point), they are in equilibrium, so that $\Delta G = \Delta G° = 0$ is only true when the difference of the standard free energies of products and reactants is zero. A reaction with $\Delta G° = 0$ would be at equilibrium when products and reactants were all present under standard state conditions and the pressure of H_2O(g) = 2.0 atm is not the standard pressure for H_2O(g).

(b) **FALSE;** $\Delta G \neq 0$. The system is not at equilibrium.

(c) FALSE; $\varDelta G°$ can have only one value at any given temperature, and that is the value corresponding to all reactants and products in their standard states, so at the normal boiling point $\varDelta G° = 0$ [as was also the case in answering part (a)]. Water will not vaporize spontaneously under standard conditions to produce water vapor with a pressure of 2 atmospheres.

(d) TRUE; $\Delta G > 0.$ The process of transforming water to vapor at 2.0 atm pressure at 100°C is not a spontaneous process; the condensation (reverse) process is spontaneous. (i.e. for the system to reach equilibrium, some $H_2O(l)$ must form)

<u>73</u>. (D) $\Delta G° = +\tfrac{1}{2}\Delta G°_f\,[\mathrm{Br_2(g)}] + \tfrac{1}{2}\Delta G°_f\,[\mathrm{Cl_2(g)}] - \Delta G°_f\,[\mathrm{BrCl(g)}]$

$$= +\tfrac{1}{2}(3.11\,\mathrm{kJ/mol}) + \tfrac{1}{2}(0.00\,\mathrm{kJ/mol}) - (-0.98\,\mathrm{kJ/mol}) = +2.54\,\mathrm{kJ/mol} = -RT\ln K_p$$

$$\ln K_p = -\frac{\Delta G°}{RT} = -\frac{2.54\times10^3\ \mathrm{J/mol}}{8.3145\,\mathrm{J\,mol^{-1}\,K^{-1}}\times 298.15\,\mathrm{K}} = -1.02 \qquad K_p = e^{-1.02} = 0.361$$

For ease of solving the problem, we double the reaction, which squares the value of the equilibrium constant. $K_{eq} = (0.357)^2 = 0.130$

Reaction:	$2\,\mathrm{BrCl(g)}$	$\rightleftharpoons$	$\mathrm{Br_2(g)}$	$+$	$\mathrm{Cl_2(g)}$
Initial:	$1.00\,\mathrm{mol}$		$0\,\mathrm{mol}$		$0\,\mathrm{mol}$
Changes:	$-2x\,\mathrm{mol}$		$+x\,\mathrm{mol}$		$+x\,\mathrm{mol}$
Equil:	$(1.00-2x)\mathrm{mol}$		$x\,\mathrm{mol}$		$x\,\mathrm{mol}$

$$K_p = \frac{P\{\mathrm{Br_2(g)}\}P\{\mathrm{Cl_2(g)}\}}{P\{\mathrm{BrCl(g)}\}^2} = \frac{[n\{\mathrm{Br_2(g)}\}RT/V][n\{\mathrm{Cl_2(g)}\}RT/V]}{[n\{\mathrm{BrCl(g)}\}RT/V]^2} = \frac{n\{\mathrm{Br_2(g)}\}n\{\mathrm{Cl_2(g)}\}}{n\{\mathrm{BrCl(g)}\}^2}$$

$$= \frac{x^2}{(1.00-2x)^2} = (0.361)^2 \qquad \frac{x}{1.00-2x} = 0.361 \qquad x = 0.361 - 0.722\,x$$

$$x = \frac{0.361}{1.722} = 0.210\,\mathrm{mol\,Br_2} = 0.210\,\mathrm{mol\,Cl_2} \qquad 1.00 - 2x = 0.580\,\mathrm{mol\,BrCl}$$

74. (M) First we determine the value of K_p for the dissociation reaction. If $I_2(g)$ is 50% dissociated, then for every mole of undissociated $I_2(g)$, one mole of $I_2(g)$ has dissociated, producing two moles of I(g). Thus, the partial pressure of I(g) is twice the partial pressure of $I_2(g)$ ($\mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{I(g)}$).

$$P_{\mathrm{total}} = 1.00\,\mathrm{atm} = P_{\mathrm{I_2(g)}} + P_{\mathrm{I(g)}} = P_{\mathrm{I_2(g)}} + 2\times P_{\mathrm{I_2(g)}} = 3\,P_{\mathrm{I_2(g)}} \qquad P_{\mathrm{I_2(g)}} = 0.333\,\mathrm{atm}$$

$$K_p = \frac{{P_{\mathrm{I(g)}}}^2}{P_{\mathrm{I_2(g)}}} = \frac{(0.667)^2}{0.333} = 1.34 \qquad \ln K_p = 0.293$$

$$\Delta H° = 2\,\Delta H°_f\,[\mathrm{I(g)}] - \Delta H°_f\,[\mathrm{I_2(g)}] = 2\times106.8\,\mathrm{kJ/mol} - 62.44\,\mathrm{kJ/mol} = 151.2\,\mathrm{kJ/mol}$$

$$\Delta S° = 2\,S°[\mathrm{I(g)}] - S°[\mathrm{I_2(g)}] = 2\times180.8\,\mathrm{J\,mol^{-1}\,K^{-1}} - 260.7\,\mathrm{J\,mol^{-1}\,K^{-1}} = 100.9\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

Now we equate two expressions for $\Delta G°$ and solve for *T*.

$$\Delta G° = \Delta H° - T\,\Delta S° = -RT\,\ln K_p = 151.2\times10^3 - 100.9T = -8.3145\times T\times 0.293$$

$$151.2\times10^3 = 100.9T - 2.44T = 98.4T \qquad T = \frac{151.2\times10^3}{98.5} = 1535\,\text{K} \approx 1.5\times10^3\,\text{K}$$

75. **(M) (a)** The oxide with the most positive (least negative) value of $\Delta G°_f$ is the one that most readily decomposes to the free metal and $O_2(g)$, since the decomposition is the reverse of the formation reaction. Thus the oxide that decomposes most readily is $Ag_2O(s)$.

(b) The decomposition reaction is $2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$ For this reaction $K_p = P_{O_2(g)}$. Thus, we need to find the temperature where $K_p = 1.00$.Since $\Delta G° = -RT\ln K_p$ and $\ln(1.00) = 0$, we wish to know the temperature where $\Delta G° = 0$. Note also that the decomposition is the reverse of the formation reaction. Thus, the following values are valid for the decomposition reaction at 298 K.

$\Delta H° = +31.05$ kJ/mol $\qquad \Delta G° = +11.20$ kJ/mol

We use these values to determine the value of $\Delta S°$ for the reaction.

$$\Delta G° = \Delta H° - T\,\Delta S° \quad T\,\Delta S° = \Delta H° - \Delta G° \quad \Delta S° = \frac{\Delta H° - \Delta G°}{T}$$

$$\Delta S° = \frac{31.05\times10^3\text{ J/mol} - 11.20\times10^3\text{ J/mol}}{298\,\text{K}} = +66.6\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Now we determine the value of T where $\Delta G° = 0$.

$$T = \frac{\Delta H° - \Delta G°}{\Delta S°} = \frac{31.05\times10^3\text{ J/mol} - 0.0\text{ J/mol}}{+66.6\,\text{J mol}^{-1}\,\text{K}^{-1}} = 466\,\text{K} = 193\,°\text{C}$$

76. **(M)** At 127 °C = 400 K, the two phases are in equilibrium, meaning that

$$\Delta G°_{rxn} = 0 = \Delta H°_{rxn} - T\Delta S°_{rxn} = [\Delta H°_f\,(\text{yellow}) - \Delta H°_f\,(\text{red})] - T[S°(\text{yellow}) - S°(\text{red})]$$

$$= [-102.9 - (-105.4)]\times10^3\text{ J} - 400\,\text{K}\times[S°(\text{yellow}) - 180\,\text{J mol}^{-1}\,\text{K}^{-1}]$$

$$= 2.5\times10^3\text{ J/mol} - 400\,\text{K}\times S°(\text{yellow}) + 7.20\times10^4\text{ J/mol}$$

$$S°(\text{yellow}) = \frac{(7.20\times10^4 + 2.5\times10^3)\text{ J/mol}}{400\,\text{K}} = 186\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Then we compute the value of the "entropy of formation" of the yellow form at 298 K.

$$\Delta S°_f = S°[HgI_2] - S°[Hg(l)] - S°[I_2(s)] = [186 - 76.02 - 116.1]\ \text{J mol}^{-1}\,\text{K}^{-1} = -6\,\text{J mol}^{-1}\,\text{K}^{-1}$$

Now we can determine the value of the free energy of formation for the yellow form.

$$\Delta G°_f = \Delta H°_f - T\Delta S°_f = -102.9\frac{\text{kJ}}{\text{mol}} - [298\,\text{K}\times(-6\frac{\text{J}}{\text{K mol}})\times\frac{1\text{kJ}}{1000\,\text{J}}] = -101.1\frac{\text{kJ}}{\text{mol}}$$

<u>77</u>. **(M)** First we need a value for the equilibrium constant. 1% conversion means that 0.99 mol $N_2(g)$ are present at equilibrium for every 1.00 mole present initially.

$$K = K_p = \frac{P_{NO(g)}{}^2}{P_{N_2(g)}\,P_{O_2(g)}} = \frac{[n\{NO(g)\}RT/V]^2}{[n\{N_2(g)\}RT/V][n\{O_2(g)\}RT/V]} = \frac{n\{NO(g)\}^2}{n\{N_2(g)\}\ n\{O_2(g)\}}$$

Reaction:	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\,NO(g)$
Initial:	1.00 mol		1.00 mol		0 mol
Changes(1% rxn):	-0.010 mol		-0.010 mol		$+0.020$ mol
Equil:	0.99 mol		0.99 mol		0.020 mol

$$K=\frac{(0.020)^2}{(0.99)(0.99)}=4.1\times10^{-4}$$

The cited reaction is twice the formation reaction of NO(g), and thus

$$\Delta H° = 2\Delta H°_f\,[NO(g)] = 2\times 90.25\,\text{kJ/mol} = 180.50\,\text{kJ/mol}$$

$$\Delta S° = 2\,S°[NO(g)] - S°[N_2(g)] - S°[O_2(g)]$$

$$=2\,(210.7\,\text{J mol}^{-1}\,\text{K})\text{-}191.5\,\text{J mol}^{-1}\,\text{K}^{-1}\text{-}205.0\,\text{J mol}^{-1}\,\text{K}^{-1} = 24.9\,\text{J mol}^{-1}\,\text{K}^{-1}$$

$$\Delta G° = \text{-}RT\ln K = \text{-}8.31447\,\text{JK}^{-1}\text{mol}^{-1}(T)\ln(4.1\times10^{-4}) = 64.85(T)$$

$$\Delta G° = \Delta H°\text{-}T\Delta S° = 64.85(T) = 180.5\,\text{kJ/mol} - (T)24.9\,\text{J mol}^{-1}\,\text{K}^{-1}$$

$$180.5\times 10\,\text{J/mol} = 64.85(T) + (T)24.9\,\text{J mol}^{-1}\,\text{K}^{-1} = 89.75(T) \qquad T = 2.01\times10^3\ \text{K}$$

78. **(E)** $Sr(IO_3)_2(s) \rightleftharpoons Sr^{2+}(aq) + 2\,IO_3^-(aq)$

$\Delta G° = (2\text{ mol}\times(-128.0\text{ kJ/mol}) + (1\text{ mol}\times-500.5\text{ kJ/mol})) - (1\text{ mol}\times-855.1\text{ kJ/mol}) = -0.4\text{ kJ}$

$\Delta G° = -RT\ln K = -8.31447\text{ JK}^{-1}\text{mol}^{-1}(298.15\text{ K})\ln K = -0.4\text{ kJ} = -400\text{ J}$

$\ln K = 0.16$ and $K = 1.\underline{175} = [Sr^{2+}][IO_3^-]^2$ Let x = solubility of $Sr(IO_3)_2$

$[Sr^{2+}][IO_3^-]^2 = 1.\underline{175} = x(2x)^2 = 4x^3$ $x = 0.6\underline{65}$ M for a saturated solution of $Sr(IO_3)_2$.

79. **(M)** P_{H2O} = 75 torr or $0.098\underline{7}$ atm. $K = (P_{H2O})^2 = (0.098\underline{7})^2 = 9.7\underline{4}\times10^{-3}$

$\Delta G° = (2\text{ mol}\times(-228.6\text{ kJ/mol}) + (1\text{ mol})\times-918.1\text{ kJ/mol}) - (1\text{ mol})\times-1400.0\text{ kJ/mol} = 309.0\text{ kJ}$

$\Delta H° = (2\text{ mol}\times(-241.8\text{ kJ/mol}) + (1\text{ mol})\times-1085.8.1\text{ kJ/mol}) - (1\text{ mol})\times-1684.3\text{ kJ/mol} = 114.9\text{ kJ}$

$\Delta S° = (2\text{ mol}\times(188.\text{J/K mol}) + (1\text{ mol}\times146.\text{J/K mol}) + (1\text{ mol})\times221.3.\text{J/K mol} = 302.3\text{ J/K mol}$

$$\Delta G° = \text{-}RT\ln K_{eq} = \text{-}8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}\times T\times\ln(9.74\times10^{-3}) = 38.\underline{5}(T)$$

$$\Delta G° = 38.\underline{5}(T) = \Delta H°\text{-}T\Delta S° = 114{,}900\,\text{J mol}^{-1}\text{-}\ (T)\times302.3\,\text{J K}^{-1}\ \text{mol}^{-1}$$

$$114{,}900 = 340.8\,\text{K}^{-1}(T) \quad \text{Hence: } T = 337\,\text{K} = 64\,°\text{C}$$

80. **(D)** **(a)** $\Delta G° = -RT\ln K$ $\ln K = -\dfrac{\Delta G°}{RT} = -\dfrac{131\times10^3\text{ J/mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}\times298.15\text{ K}} = -52.8$

$$K = e^{-52.8} = 1.2\times10^{-23}\text{ atm}\times\frac{760\text{ mmHg}}{1\text{atm}} = 8.9\times10^{-21}\text{ mmHg}$$

Since the system cannot produce a vacuum lower than 10^{-9} mmHg, this partial pressure of $CO_2(g)$ won't be detected in the system.

(b) Since we have the value of ΔG° for the decomposition reaction at a specified temperature (298.15 K), and we need ΔH° and ΔS° for this same reaction to determine $P\{CO_2(g)\}$ as a function of temperature, obtaining either ΔH° or ΔS° will enable us to determine the other.

(c) $\Delta H^\circ = \Delta H^\circ_f\,[\mathrm{CaO(s)}] + \Delta H^\circ_f\,[\mathrm{CO_2(g)}] - \Delta H^\circ_f\,[\mathrm{CaCO_3(s)}]$

$= -635.1\,\text{kJ/mol} - 393.5\,\text{kJ/mol} - (-1207\,\text{kJ/mol}) = +178\,\text{kJ/mol}$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ \qquad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$\Delta S^\circ = \frac{178\ \text{kJ/mol} - 131\ \text{kJ/mol}}{298.\ \text{K}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = 1.6\times 10^2\ \ \text{J}\ \ \text{mol}^{-1}\ \ \text{K}^{-1}$$

$$K = 1.0\times 10^{-9}\ \ \text{mmHg} \times \frac{1\ \ \text{atm}}{760\ \ \text{mmHg}} = 1.3\times 10^{-12}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = -RT\ln K_{eq} \qquad \Delta H^\circ = T\,\Delta S^\circ - RT\ln K$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - R\ln K} = \frac{178\times 10^3\ \text{J/mol}}{1.6\times 10^2\ \text{J mol}^{-1}\ \text{K}^{-1} - 8.3145\,\text{J mol}^{-1}\ \text{K}^{-1}\ \ln(1.3\times 10^{-12})} = 4.6\times 10^2\ \text{K}$$

<u>81</u>. (D) $\Delta H^\circ = \Delta H^\circ_f\,[\mathrm{PCl_3(g)}] + \Delta H^\circ_f\,[\mathrm{Cl_2(g)}] - \Delta H^\circ_f\,[\mathrm{PCl_5(g)}]$

$= -287.0\ \ \text{kJ/mol} + 0.00\ \ \text{kJ/mol} - (-374.9\ \ \text{kJ/mol}) = 87.9\ \ \text{kJ/mol}$

$\Delta S^\circ = S^\circ[\mathrm{PCl_3(g)}] + S^\circ[\mathrm{Cl_2(g)}] - S^\circ[\mathrm{PCl_5(g)}]$

$= 311.8\ \text{J mol}^{-1}\ \text{K}^{-1} + 223.1\ \text{J mol}^{-1}\ \text{K}^{-1} - 364.6\ \text{J mol}^{-1}\ \text{K}^{-1} = +170.3\ \text{J mol}^{-1}\ \text{K}^{-1}$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = 87.9\times 10^3\ \text{J/mol} - 500\,\text{K}\times 170.3\,\text{J mol}^{-1}\ \text{K}^{-1}$$

$$\Delta G^\circ = 2.8\times 10^3\ \text{J/mol} = -RT\ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} = \frac{-2.8\times 10^3\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\ \text{K}^{-1}\times 500\,\text{K}} = -0.67 \qquad K_p = e^{-0.67} = 0.51$$

$$P_i[\mathrm{PCl_5}] = \frac{nRT}{V} = \frac{0.100\,\text{mol}\times 0.08206\,\text{L atm mol}^{-1}\ \text{K}^{-1}\times 500\,\text{K}}{1.50\,\text{L}} = 2.74\,\text{atm}$$

Reaction:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
Initial:	2.74 atm		0 atm	0 atm
Changes:	$-x$ atm		$+x$ atm	$+x$ atm
Equil:	$(2.74-x)$ atm		x atm	x atm

$$K_p = \frac{P[PCl_3]P[Cl_2]}{P[PCl_5]} = 0.51 = \frac{x \cdot x}{2.74 - x}$$

$$x^2 = 0.51(2.74 - x) = 1.4 - 0.51x \quad x^2 + 0.51x - 1.4 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.51 \pm \sqrt{0.26 + 5.6}}{2} = 0.96\,\text{atm}, -1.47\,\text{atm}$$

$$P_{\text{total}} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = (2.74 - x) + x + x = 2.74 + x = 2.74 + 0.96 = 3.70\,\text{atm}$$

82. **(M)** The value of $\Delta H°$ determined in Exercise 64 is $\Delta H° = +128\,\text{kJ/mol}$. We use any one of the values of $K_p = K_{eq}$ to determine a value of $\Delta G°$. At 30 °C = 303 K,

$$\Delta G° = -RT \ln K_{eq} = -(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})(303\,\text{K})\ln(1.66 \times 10^{-5}) = +2.77 \times 10^4\ \text{J/mol}$$

Now we determine $\Delta S°$. $\Delta G° = \Delta H - T\,\Delta S°$

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} = \frac{128 \times 10^3\ \text{J/mol} - 2.77 \times 10^4\ \text{J/mol}}{303\,\text{K}} = +331\,\text{J mol}^{-1}\ \text{K}^{-1}$$

By using the appropriate $S°$ values in Appendix D, we calculate $\Delta S° = +334\,\text{J mol}^{-1}\,\text{K}^{-1}$.

83. **(M)** In this problem we are asked to estimate the temperature at which the vapor pressure of cyclohexane is 100 mmHg. We begin by using Trouton's rule to determine the value of ΔH_{vap} for cyclohexane. The temperature at which the vapor pressure is 100.00 mmHg can then be determined using Clausius–Clapeyron equation.

Stepwise approach:

Use Trouton's rule to find the value of ΔH_{vap}:

$$\Delta H_{vap} = T_{nbp}\,\Delta S_{vap} = 353.9\,\text{K} \times 87\,\text{J mol}^{-1}\,\text{K}^{-1} = 31 \times 10^3\ \text{J/mol}$$

Next, use Clausius–Clapeyron equation to find the required temperature:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln\frac{100\,\text{mmHg}}{760\,\text{mmHg}}$$

$$= \frac{31 \times 10^3\,\text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}}\left(\frac{1}{353.9\,\text{K}} - \frac{1}{T}\right) = -2.028$$

$$\frac{1}{353.9} - \frac{1}{T} = \frac{-2.028 \times 8.3145}{31 \times 10^3} = -5.4 \times 10^{-4} =$$

$$2.826 \times 10^{-3} - \frac{1}{T} \qquad \frac{1}{T} = 3.37 \times 10^{-3} K^{-1}$$

$$T = 297\,\text{K} = 24\,°\text{C}$$

Conversion pathway approach:

$$\ln\frac{P_2}{P_1}=\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{T_{\text{nbp}}\,\Delta S_{\text{vap}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{R}{T_{\text{nbp}}\,\Delta S_{\text{vap}}}\ln\frac{P_2}{P_1}\Rightarrow\frac{1}{T_2}=\frac{1}{T_1}-\frac{R}{T_{\text{nbp}}\,\Delta S_{\text{vap}}}\ln\frac{P_2}{P_1}$$

$$\frac{1}{T_2}=\frac{1}{353.9\text{K}}-\frac{8.314\text{JK}^{-1}\text{mol}^{-1}}{353.9K\times 87\text{JK}^{-1}\text{mol}^{-1}}\ln\frac{100\text{mmHg}}{760\text{mmHg}}=3.37\times10^{-3}$$

$$T_2=297\text{K}=24^{o}C$$

84. (M)**(a)** $2\text{Ag(s)}+\frac{1}{2}\text{O}_2\text{(g)}\rightarrow\text{Ag}_2\text{O}$

$$\Delta\text{G}^{\text{o}}_{\text{f}}=\Delta\text{G}^{\text{o}}_{\text{f}}(\text{Ag}_2\text{O(s)})\text{-}\{2\Delta\text{G}^{\text{o}}_{\text{f}}(Ag(s))+\frac{1}{2}\Delta\text{G}^{\text{o}}_{\text{f}}(O_2)\}$$

$$\Delta\text{G}^{\text{o}}_{\text{f}}=\text{ -11.2 kJ-}\{2(0)\ +\frac{1}{2}(0)\}=-11.2\ kJ\Rightarrow\text{Ag}_2\text{O is thermodynamically stable at }25^{\text{o}}\text{C}$$

(b) Assuming $\Delta\text{H}^{\text{o}}$, $\Delta\text{S}^{\text{o}}$ are constant from 25-200°C (not so, but a reasonable assumption !)

$$\Delta\text{S}^{\text{o}}=\text{S}^{\text{o}}(\text{Ag}_2\text{O})\text{-}\{2\ \text{S}^{\text{o}}(\text{Ag(s)})+\frac{1}{2}\ \text{S}^{\text{o}}(\text{O}_2)\}=121.3-(2(42.6)+\frac{1}{2}(205.1))=-66.5\text{ J/K}$$

$$\Delta\text{G}^{\text{o}}=-31.0\text{ kJ}-\frac{(473\text{ K})(\text{-}66.5\text{ J/K})}{1000\text{ J/kJ}}=\Delta H^{\text{o}}-T\Delta S^{\text{o}}=+0.45\text{ kJ}$$

$\Rightarrow$ thermodynamically *unstable* at 200°C

85. **(M)** ΔG = 0 since the system is at equilibrium. As well, ΔG° = 0 because this process is under standard conditions. Since ΔG° = ΔH° - TΔS° = 0. = ΔH° = TΔS° =273.15 K×21.99 J K^{-1} mol^{-1} = 6.007 kJ mol^{-1}. Since we are dealing with 2 moles of ice melting, the values of ΔH° and ΔS° are doubled. Hence, ΔH° = 12.01 kJ and ΔS° = 43.98 J K^{-1}.
Note: The densities are not necessary for the calculations required for this question.

86. **(D)** First we determine the value of K_{p} that corresponds to 15% dissociation. We represent the initial pressure of phosgene as x atm.

Reaction:	$\text{COCl}_2\text{(g)}$	$\rightleftharpoons$	CO(g)	+	$\text{Cl}_2\text{(g)}$
Initial:	x atm		0 atm		0 atm
Changes:	$-0.15x$ atm		$+0.15x$ atm		$+0.15x$ atm
Equil:	$0.85x$ atm		$0.15x$ atm		$0.15x$ atm

$$P_{\text{total}} = 0.85\,x\,\text{atm} + 0.15\,x\,\text{atm} + 0.15\,x\,\text{atm} = 1.15\,x\,\text{atm} = 1.00\,\text{atm} \qquad x = \frac{1.00}{1.15} = 0.870\,\text{atm}$$

$$K_{\text{p}} = \frac{P_{\text{CO}}\,P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{(0.15\times 0.870)^2}{0.85\times 0.870} = 0.0230$$

Next we find the value of ΔH° for the decomposition reaction.

$$\ln\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \ln\frac{6.7\times 10^{-9}}{4.44\times 10^{-2}} = -15.71 = \frac{\Delta H^\circ}{R}\left(\frac{1}{668}-\frac{1}{373.0}\right) = \frac{\Delta H^\circ}{R}(-1.18\times 10^{-3})$$

$$\frac{\Delta H^\circ}{R} = \frac{-15.71}{-1.18\times 10^{-3}} = 1.33\times 10^{4},$$

$$\Delta H^\circ = 1.33\times 10^{4}\times 8.3145 = 111\times 10^{3}\ \text{J/mol} = 111\,\text{kJ/mol}$$

And finally we find the temperature at which $K = 0.0230$.

$$\ln\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \ln\frac{0.0230}{0.0444} = \frac{111\times 10^{3}\ \text{J/mol}}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}}\left(\frac{1}{668\,\text{K}}-\frac{1}{T}\right) = -0.658$$

$$\frac{1}{668}-\frac{1}{T} = \frac{-0.658\times 8.3145}{111\times 10^{3}} = -4.93\times 10^{-5} = 1.497\times 10^{-3}-\frac{1}{T} \qquad \frac{1}{T} = 1.546\times 10^{-3}$$

$$T = 647\,\text{K} = 374\,^\circ\text{C}$$

87. **(D)** First we write the solubility reaction for AgBr. Then we calculate values of ΔH° and ΔS° for the reaction: $\text{AgBr(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Br}^-\text{(aq)} \quad K_{\text{eq}} = K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-] = s^2$

$$\Delta H^\circ = \Delta H^\circ_{\text{f}}\,[\text{Ag}^+\text{(aq)}] + \Delta H^\circ_{\text{f}}\,[\text{Br}^-\text{(aq)}] - \Delta H^\circ_{\text{f}}\,[\text{AgBr(s)}]$$

$$= +105.6\,\text{kJ/mol} - 121.6\,\text{kJ/mol} - (-100.4\,\text{kJ/mol}) = +84.4\,\text{kJ/mol}$$

$$\Delta S^\circ = S^\circ[\text{Ag}^+\text{(aq)}] + S^\circ[\text{Br}^-\text{(aq)}] - S^\circ[\text{AgBr(s)}]$$

$$= +72.68\,\text{J mol}^{-1}\,\text{K}^{-1} + 82.4\,\text{J mol}^{-1}\,\text{K}^{-1} - 107.1\,\text{J mol}^{-1}\,\text{K}^{-1} = +48.0\,\text{J mol}^{-1}\,\text{K}^{-1}$$

These values are then used to determine the value of ΔG° for the solubility reaction, and the standard free energy change, in turn, is used to obtain the value of *K*.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 84.4\times 10^{3}\ \text{J mol}^{-1} - (100+273)\,\text{K}\times 48.0\,\text{J mol}^{-1}\,\text{K}^{-1} = 66.5\times 10^{3}\ \text{J/mol}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-66._5\times 10^{3}}{\frac{8.3145\,\text{J}}{\text{mol K}}\times 373\,\text{K}} = -21.4 \qquad K = K_{\text{sp}} = \text{e}^{-21.4} = 5.0\times 10^{-10} = \text{s}^2$$

And now we compute the solubility of AgBr in mg/L.

$$s = \sqrt{5.0\times 10^{-10}}\times\frac{187.77\,\text{g AgBr}}{1\,\text{mol AgBr}}\times\frac{1000\,\text{mg}}{1\,\text{g}} = 4.2\,\text{mg AgBr/L}$$

88. **(M)** $S°_{298.15} = S°_{274.68} + \Delta S_{\text{fusion}} + \Delta S_{\text{heating}}$

$$S°_{298.15} = 67.15 \text{ J K}^{-} \text{ mol}^{-1} + \frac{12{,}660 \text{ J mol}^{-1}}{274.68 \text{ K}} + \int_{274.68}^{298.15} 97.78\frac{\text{J}}{\text{mol K}} + 0.0586\frac{\text{J}}{\text{mol K}^2} \times (T - 274.68)$$

$$S°_{298.15} = 67.15 \text{ J K}^{-1} \text{ mol}^{-1} + 46.09 \text{ J K}^{-1} \text{ mol}^{-1} + 8.07 \text{ J K}^{-1} \text{ mol}^{-1} = 121.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

89. **(M)** $S° = S°_{\text{solid}} + \Delta S_{\text{fusion}} + \Delta S_{\text{heating}} + \Delta S_{\text{vaporization}} + \Delta S_{\text{pressure change}}$

$$S° = 128.82 \text{ J K}^{-1} \text{ mol}^{-1} + \frac{9866 \text{ J mol}^{-1}}{278.68 \text{ K}} + \int_{278.68}^{298.15} \frac{134.0\frac{\text{J}}{\text{mol K}}\, dT}{\text{T}} + \frac{33{,}850 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

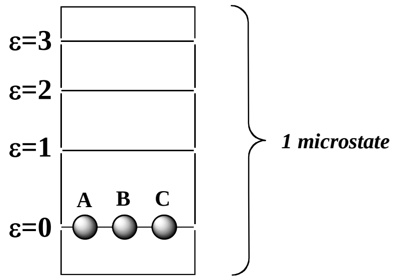
$$+ 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln\left(\frac{95.13 \text{ torr}}{760 \text{ torr}}\right)$$

$$S° = 128.82 \text{ J K}^{-1} \text{ mol}^{-1} + 35.40 \text{ J K}^{-1} \text{ mol}^{-1} + 9.05 \text{ J K}^{-1} \text{ mol}^{-1} + 113.5 \text{ J K}^{-1} \text{ mol}^{-1} + (-17.28 \text{ J K}^{-1} \text{ mol}^{-1})$$

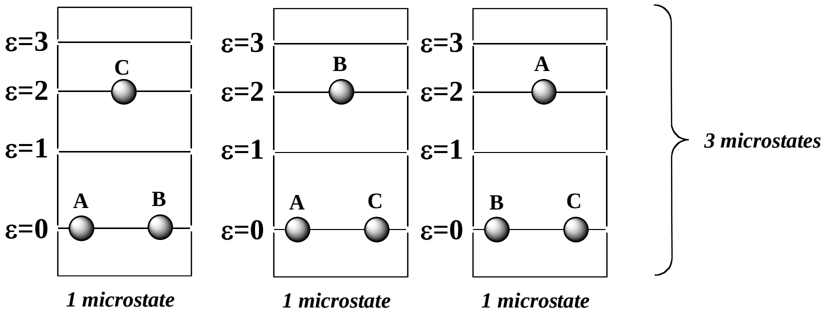
$$S° = 269.53 \text{ J K}^{-1} \text{ mol}^{-1}$$

90. **(D)** Start by labeling the particles A, B and C. Now arrange the particles among the states. One possibility includes A, B, and C occupying one energy state (ε=0,1,2 or 3). This counts as one microstate. Another possibility is two of the particles occupying one energy state with the remaining one being in a different state. This possibility includes a total of three microstates. The final set of combinations is one with each particle being in different energy state. This combination includes a total of six microstates. Therefore, the total number of microstates in the system is 10. See pictorial representation on the following page illustrating the three different cases.

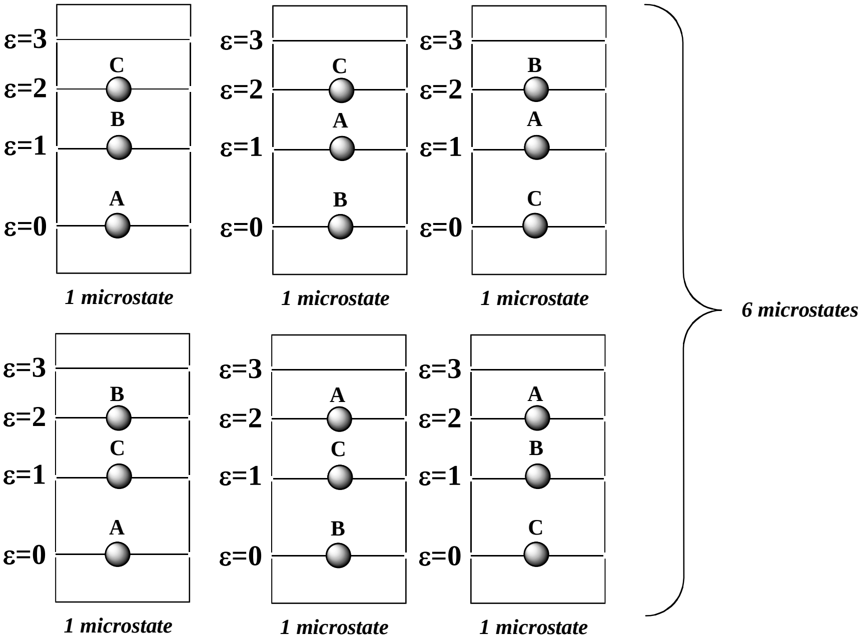
All particles are in a single
energy level (i.e. ε=0)



Two particles are in one energy level (i.e. ε=0) and the remaining
particle is in a different level (i.e. ε=2)



All particles are in different energy levels (i.e. ε=0, 1 and 2)



<u>91.</u> (M) (a) In the solid as the temperature increases, so do the translational, rotational, and vibrational degrees of freedom. In the liquid, most of the vibrational degrees of freedom are saturated and only translational and rotational degrees of freedom can increase. In the gas phase, all degrees of freedom are saturated. **(b)** The increase in translation and rotation on going from solid to liquid is much less than on going from liquid to gas. This is where most of the change in entropy is derived.

92. (D) Because KNO_3 is a strong electrolyte, its solution reaction will be:

$$KNO_3(s) + H_2O \rightleftharpoons K^+(aq) + NO_3^-(aq)$$

This reaction can be considered to be at equilibrium when the solid is in contact with a saturated solution, i.e. the conditions when crystallization begins. The solubility, s, of the salt, in moles per liter, can be calculated from the amount of salt weighted out and the volume of the solution. The equilibrium constant K for the reaction will be:

$$K=[K^+(aq)][NO_3^-(aq)]=(s)(s)=s^2$$

In the case of 25.0 mL solution at 340 K, the equilibrium constant K is:

$$n(KNO_3) = \frac{m}{M} = \frac{20.2\text{g}}{101.103\text{gmol}^{-1}} = 0.200\text{mol} \Rightarrow \text{s}=\frac{n}{V} = \frac{0.200\text{mol}}{0.0250\text{L}} = 8.0\text{molL}^{-1}$$

$$K = s^2 = 8^2 = 64$$

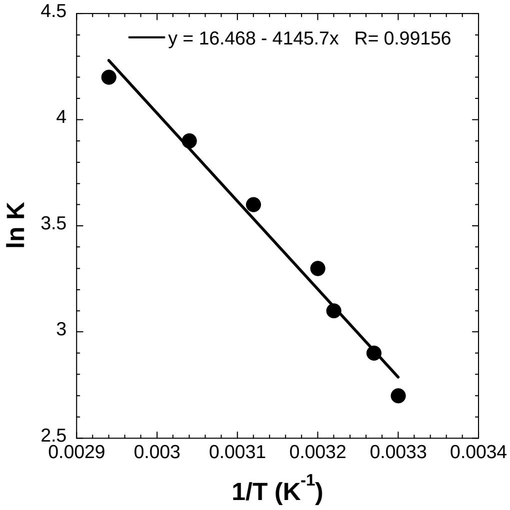
The equilibrium constant K can be used to calculate ΔG for the reaction using ΔG=-RTlnK:

$$\Delta G = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 340\text{K} \times \ln 64 = -12\text{kJmol}^{-1}$$

The values for K and ΔG at all other temperatures are summarized in the table below.

Volume (mL)	T/(K)	1/T (K^{-1})	s ($molL^{-1}$)	K	lnK	ΔG ($kJmol^{-1}$)
25.0	340	0.00294	8.0	64	4.2	-12
29.2	329	0.00304	6.9	48	3.9	-11
33.4	320	0.00312	6.0	36	3.6	-9.6
37.6	313	0.00320	5.3	28	3.3	-8.6
41.8	310	0.00322	4.8	23	3.1	-8.0
46.0	306	0.00327	4.3	18.5	2.9	-7.4
51.0	303	0.00330	3.9	15	2.7	-6.8

The plot of lnK v.s. 1/T provides ΔH (slope=-ΔH/R) and ΔS (y-intercept=ΔS/R) for the reaction:



$$\Delta H = -slope \times R = 4145.7 \times 8.314\text{JK}^{-1}\text{mol}^{-1} = 34.5\text{kJmol}^{-1}$$

$$\Delta S = y-\text{intercept} \times R = 16.468 \times 8.314\text{JK}^{-1}\text{mol}^{-1} = 136.9\text{JK}^{-1}\text{mol}^{-1}$$

ΔH for the crystallization process is -35.4 kJmol^{-1}. It is negative as expected because crystallization is an exothermic process. Furthermore, the positive value for ΔS shows that crystallization is a process that decreases the entropy of a system.

FEATURE PROBLEMS

93. **(M) (a)** The first method involves combining the values of ΔG_f^o . The second uses

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G^o = \Delta G_f^\circ\left[H_2O(g)\right] - \Delta G_f^\circ\left[H_2O(l)\right]$$

$$= -228.572 \text{ kJ/mol} - (-237.129 \text{ kJ/mol}) = +8.557 \text{ kJ/mol}$$

$$\Delta H^o = \Delta H_f^\circ\left[H_2O(g)\right] - \Delta H_f^\circ\left[H_2O(l)\right]$$

$$= -241.818 \text{ kJ/mol} - (-285.830 \text{ kJ/mol}) = +44.012 \text{ kJ/mol}$$

$$\Delta S^o = S^o\left[H_2O(g)\right] - S^o\left[H_2O(l)\right]$$

$$= 188.825 \text{ J mol}^{-1}\text{ K}^{-1} - 69.91 \text{ J mol}^{-1}\text{ K}^{-1} = +118.92 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$= 44.012 \text{ kJ/mol} - 298.15 \text{ K} \times 118.92 \times 10^{-3} \text{ kJ mol}^{-1}\text{ K}^{-1} = +8.556 \text{ kJ/mol}$$

(b) We use the average value: $\Delta G^o = +8.558 \times 10^3$ J/mol $= -RT \ln K$

$$\ln K = -\frac{8558 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1} \times 298.15 \text{ K}} = -3.452; \quad K = e^{-3.452} = 0.0317 \text{ bar}$$

(c) $$P\{H_2O\} = 0.0317 \text{ bar} \times \frac{1 \text{ atm}}{1.01325 \text{ bar}} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 23.8 \text{ mmHg}$$

(d) $$\ln K = -\frac{8590 \text{ J/mol}}{8.3145 \text{ J mol}^{-1}\text{ K}^{-1} \times 298.15 \text{ K}} = -3.465;$$

$$K = e^{-3.465} = 0.0312_7 \text{ atm};$$

$$P\{H_2O\} = 0.0313 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 23.8 \text{ mmHg}$$

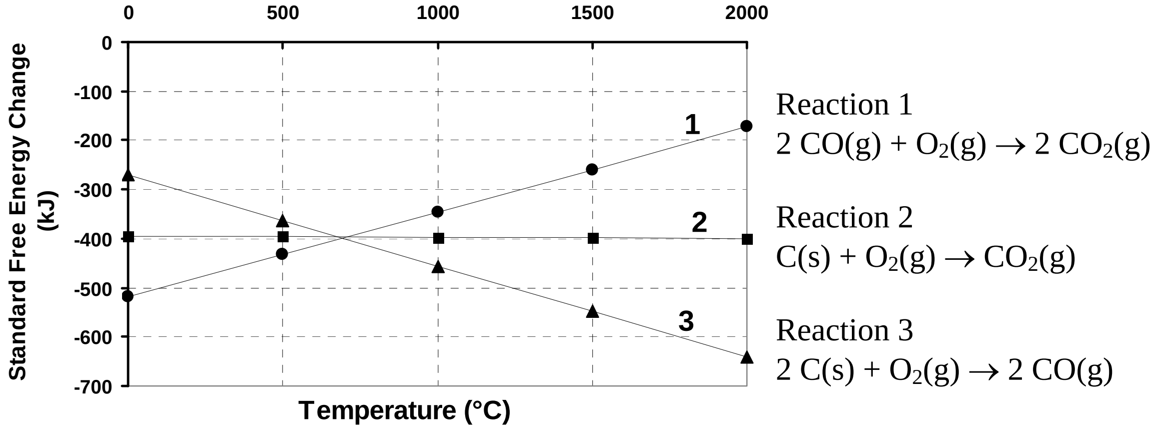
94. **(D) (a)** When we combine two reactions and obtain the overall value of ΔG^o, we subtract the value on the plot of the reaction that becomes a reduction from the value on the plot of the reaction that is an oxidation. Thus, to reduce ZnO with elemental Mg, we subtract the values on the line labeled "$2Zn + O_2 \rightarrow 2ZnO$" from those on the line labeled "$2Mg + O_2 \rightarrow 2MgO$". The result for the overall ΔG^o will always be negative because every point on the "zinc" line is above the corresponding point on the "magnesium" line

(b) In contrast, the "carbon" line is only below the "zinc" line at temperatures above about $1000^\circ C$. Thus, only at these elevated temperatures can ZnO be reduced by carbon.

(c) The decomposition of zinc oxide to its elements is the reverse of the plotted reaction, the value of ΔG° for the decomposition becomes negative, and the reaction becomes spontaneous, where the value of ΔG° for the plotted reaction becomes positive. This occurs above about $1850^{\circ}\mathrm{C}$.

(d) The "carbon" line has a negative slope, indicating that carbon monoxide becomes more stable as temperature rises. The point where CO(g) would become less stable than 2C(s) and O_2(g) looks to be below $-1000^{\circ}\mathrm{C}$ (by extrapolating the line to lower temperatures). Based on this plot, it is not possible to decompose CO(g) to C(s) and $O_2(g)$ in a spontaneous reaction.

(e)



All three lines are straight-line plots of ΔG° vs. T following the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The general equation for a straight line is given below with the slightly modified Gibbs Free-Energy equation as a reference: $\Delta G^\circ = -\Delta S^\circ T + \Delta H^\circ$ (here ΔH° assumed constant)

$y = \mathrm{m}x + \mathrm{b}$ (m = $-\Delta S^\circ$ = slope of the line)

Thus, the slope of each line multiplied by minus one is equal to the ΔS° for the oxide formation reaction. It is hardly surprising, therefore, that the slopes for these lines differ so markedly because these three reactions have quite different ΔS° values (ΔS° for Reaction 1 = -173 J K^{-1}, ΔS° for Reaction 2 = 2.86 J K^{-1}, ΔS° for Reaction 3 = 178.8 J K^{-1})

(f) Since other metal oxides apparently have positive slopes similar to Mg and Zn, we can conclude that in general, the stability of metal oxides <u>decreases</u> as the temperature increases. Put another way, the decomposition of metal oxides to their elements becomes more spontaneous as the temperature is increased. By contrast, the two reactions involving elemental carbon, namely Reaction 2 and Reaction 3, have negative slopes, indicating that the formation of CO_2(g) and CO(g) from graphite becomes more favorable as the temperature rises. This means that the ΔG° for the reduction of metal oxides by carbon becomes more and more negative with increasing temperature. Moreover, there must exist a threshold temperature for each metal oxide above which the reaction with carbon will occur spontaneously. Carbon would appear to be an excellent reducing agent, therefore, because it will reduce virtually any metal oxide to its corresponding metal as long as the temperature chosen for the reaction is higher than the threshold temperature (the threshold temperature is commonly referred to as the transition temperature).

Consider for instance the reaction of MgO(s) with graphite to give $CO_2(g)$ and Mg metal:
$2\,MgO(s) + C(s) \rightarrow 2\,Mg(s) + CO_2(g)$ $\Delta S^\circ_{rxn} = 219.4$ J/K and $\Delta H^\circ_{rxn} = 809.9$ kJ

$$T_{transition} = \frac{\Delta H^o_{rxn}}{\Delta S^o_{rxn}} = \frac{809.9\text{ kJ}}{0.2194\text{ kJ K}^{-1}} = 3691\text{ K} = T_{threshold}$$

Consequently, above 3691 K, carbon will spontaneously reduce MgO to Mg metal.

95. (D) (a) With a 36% efficiency and a condenser temperature (T_l) of 41 °C = 314 K,

$$\text{efficiency} = \frac{T_h - T_l}{T_h} \times 100\% = 36\% \qquad \frac{T_h - 314}{T_h} = 0.36\,;$$

$T_h = (0.36 \times T_h) + 314$ K; $0.64\,T_h = 314$ K; $T_h = 4.9 \times 10^2$ K

(b) The overall efficiency of the power plant is affected by factors other than the thermodynamic efficiency. For example, a portion of the heat of combustion of the fuel is lost to parts of the surroundings other than the steam boiler; there are frictional losses of energy in moving parts in the engine; and so on. To compensate for these losses, the thermodynamic efficiency must be greater than 36%. To obtain this higher thermodynamic efficiency, T_h must be greater than 4.9×10^2 K.

(c) The steam pressure we are seeking is the vapor pressure of water at 4.9×10^2 K. We also know that the vapor pressure of water at 373 K (100 °C) is 1 atm. The enthalpy of vaporization of water at 298 K is $\Delta H^\circ = \Delta H_f^\circ[H_2O(g) - \Delta H_f^\circ[H_2O(l)] = -241.8$ kJ/mol $- (-285.8$ kJ/mol$) = 44.0$ kJ/mol. Although the enthalpy of vaporization is somewhat temperature dependent, we will assume that this value holds from 298 K to 4.9×10^2 K, and make appropriate substitutions into the Clausius-Clapeyron equation.

$$\ln\left(\frac{P_2}{1\text{ atm}}\right) = \frac{44.0\text{ kJ mol}^{-1}}{8.3145\times10^{-3}\text{ kJ mol}^{-1}}\left(\frac{1}{373\text{ K}} - \frac{1}{490\text{ K}}\right) = 5.29\times10^{-3}\left(2.68\times10^{-3} - 2.04\times10^{-3}\right)$$

$$\ln\left(\frac{P_2}{1\text{ atm}}\right) = 3.39\,; \quad \left(\frac{P_2}{1\text{ atm}}\right) = 29.7\,; \quad P_2 \approx 30\text{ atm}$$

The answer cannot be given with greater certainty because of the weakness of the assumption of a constant H°_{vapn}.

(d) It is not possible to devise a heat engine with 100% efficiency or greater. For 100% efficiency, $T_l = 0$ K, which is unattainable. To have an efficiency greater than 100 % would require a *negative* T_l, which is also unattainable.

96. **(D) (a)** Under biological standard conditions:

$ADP^{3-} + HPO_4^{2-} + H^+ \rightarrow ATP^{4-} + H_2O \quad \Delta G^{o'} = 32.4$ kJ/mol

If all of the energy of combustion of 1 mole of glucose is employed in the conversion of ADP to ATP, then the maximum number of moles ATP produced is

$$\text{Maximum number} = \frac{2870\ \text{kJ mol}^{-1}}{32.4\ \text{kJ mol}^{-1}} = 88.6\ \text{moles ATP}$$

(b) In an actual cell the number of ATP moles produced is 38, so that the efficiency is:

$$\text{Efficiency} = \frac{\text{number of ATP's actually produced}}{\text{Maximum number of ATP's that can be produced}} = \frac{38}{88.6} = 0.43$$

Thus, the cell's efficiency is about 43%.

(c) The previously calculated efficiency is based upon the biological standard state. We now calculate the Gibbs energies involved under the actual conditions in the cell. To do this we require the relationship between ΔG and $\Delta G^{\circ'}$ for the two coupled reactions. For the combustion of glucose we have

$$\Delta G = \Delta G^{\circ\prime} + RT\ln\left(\frac{a_{CO_2}^6\, a_{H_2O}^6}{a_{glu}\, a_{O_2}^6}\right)$$

For the conversion of ADP to ATP we have

$$\Delta G = \Delta G^{\circ\prime} + RT\ln\left(\frac{a_{ATP}\, a_{H_2O}}{a_{ADP}\, a_{P_i}\left(\left[H^+\right]/10^{-7}\right)}\right)$$

Using the concentrations and pressures provided we can calculate the Gibbs energy for the combustion of glucose under biological conditions. First, we need to replace the activities by the appropriate effective concentrations. That is,

$$\Delta G = \Delta G^{\circ\prime} + RT\ln\left(\frac{\left(p/p^{o}\right)_{CO_2}^{6}\ a_{H_2O}^6}{\left[\text{glu}\right]/\left[\text{glu}\right]^{o}\left(p/p^{o}\right)_{O_2}^{6}}\right)$$

using $a_{H_2O} \approx 1$ for a dilute solution we obtain

$$\Delta G = \Delta G^{\circ\prime} + RT\ln\left(\frac{\left(0.050\ \text{bar}/1\ \text{bar}\right)^6 \times 1^6}{\left[\text{glu}\right]/1 \times \left(0.132\ \text{bar}/1\ \text{bar}\right)^6}\right)$$

The concentration of glucose is given in mg/mL and this has to be converted to molarity as follows:

$$[\text{glu}] = \frac{1.0\ \text{mg}}{\text{mL}} \times \frac{\text{g}}{1000\ \text{mg}} \times \frac{1000\ \text{mL}}{\text{L}} \times \frac{1}{180.16\ \text{g mol}^{-1}} = 0.00555\ \text{mol L}^{-1},$$

where the molar mass of glucose is 180.16 g mol^{-1}.

Assuming a temperature of 37 °C for a biological system we have, for one mole of glucose:

$$\Delta G = -2870\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\ln\left(\frac{\left(0.050\ \right)^{6}\times1^{6}}{0.00555/1\times\left(0.132\right)^{6}}\right)$$

$$\Delta G = -2870\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\ln\left(\frac{2.954\times10^{-3}}{0.00555}\right)$$

$$\Delta G = -2870\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\ln\left(0.5323\right)$$

$$\Delta G = -2870\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\left(-0.6305\right)$$

$$\Delta G = -2870\times10^{3}\,\mathrm{J} - 1.625\times10^{3}\,\mathrm{J}$$

$$\Delta G = -2872\times10^{3}\,\mathrm{J}$$

In a similar manner we calculate the Gibbs free energy change for the conversion of ADP to ATP:

$$\Delta G = \Delta G^{6} + RT\ln\left(\frac{\left[ATP\right]/1\times1}{\left[ADP\right]/1\times\left[P_i\right]/1\times(\left[H^{+}\right]/10^{-7})}\right)$$

$$\Delta G = 32.4\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\ln\left(\frac{0.0001}{0.0001\times0.0001\times(10^{-7}/10^{-7})}\right)$$

$$\Delta G = 32.4\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\ln\left(10^{4}\right)$$

$$\Delta G = 32.4\times10^{3}\,\mathrm{J} + 8.314\,\mathrm{JK^{-1}}\times310\,\mathrm{K}\times\left(9.2103)\right) = 32.4\times10^{3}\,\mathrm{J} + 23.738\times10^{3}\,\mathrm{J} = 56.2\times10^{3}\,\mathrm{J}$$

(d) The efficiency under biological conditions is

$$\text{Efficiency} = \frac{\text{number of ATP's actually produced}}{\text{Maximum number of ATP's that can be produced}} = \frac{38}{2872/56.2} = 0.744$$

Thus, the cell's efficiency is about 74%.

The theoretical efficiency of the diesel engine is:

$$\text{Efficiency} = \frac{T_{\mathrm{h}} - T_{\mathrm{l}}}{T_{\mathrm{h}}}\times100\% = \frac{1923-873}{1923}\times100\% = 55\%$$

Thus, the diesel's actual efficiency is 0.78 × 55 % = 43 %.
The cell's efficiency is 74% whereas that of the diesel engine is only 43 %. Why is there such a large discrepancy? The diesel engine supplies heat to the surroundings, which is at a lower temperature than the engine. This dissipation of energy raises the temperature of the surroundings and the entropy of the surroundings. A cell operates under isothermal conditions and the energy not utilized goes only towards changing the entropy of the cell's surroundings. The cell is more efficient since it does not heat the surroundings.

97. **(E) (a)** In this case CO can exist in two states, therefore, W=2. There are N of these states in the crystal, and so we have

$S = k\ln 2^N = 1.381\times10^{-23}\text{JK}^{-1}\times 6.022\times10^{23}\text{mol}^{-1}\ln 2 = 5.8\text{JK}^{-1}\text{mol}^{-1}$

(b) For water, W=3/2, which leads to

$S = k\ln(\frac{3}{2})^N = 1.381\times10^{-23}\text{JK}^{-1}\times 6.022\times10^{23}\text{mol}^{-1}\ln 1.5 = 3.4\text{JK}^{-1}\text{mol}^{-1}$

SELF-ASSESSMENT EXERCISES

98. **(E)** **(a)** ΔS_{univ} or total entropy contains contributions from the entropy change of the system (ΔS_{sys}) and the surroundings (ΔS_{surr}). According to the second law of thermodynamics, ΔS_{univ} is always greater then zero.

(b) ΔG_f^o or standard free energy of formation is the free energy change for a reaction in which a substances in its standard state is formed from its elements in their reference forms in their standard states.

(c) For a hypothetical chemical reaction $\text{aA+bB} \rightleftharpoons \text{cC+dD}$, the equilibrium constant K is defined as $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.

99. **(E)** **(a)** Absolute molar entropy is the entropy at zero-point energy (lowest possible energy state) and it is equal to zero.

(b) Coupled reactions are spontaneous reactions (ΔG<0) that are obtained by pairing reactions with positive ΔG with the reactions with negative ΔG.

(c) Trouton's rule states that for many liquids at their normal boiling points, the standard molar entropy of vaporization has a value of approximately 87 $\text{Jmol}^{-1}\text{K}^{-1}$.

(d) Equilibrium constant K for a certain chemical reaction can be evaluated using either ΔG_f^o or ΔH_f^o in conjunction with S^o (which are often tabulated). The relationship used to calculate K is $\Delta G^o = -RT\ln K$.

100. **(E)** **(a)** A spontaneous process is a process that occurs in a system left to itself; once started, no external action form outsize the system is necessary to make the process continue. A nonspontaneous process is a process that will not occur unless some external action is continuously applied.

(b) Second law of thermodynamics states that the entropy of universe is always greater than zero or in other words that all spontaneous processes produce an increase in the entropy of the universe. The third law of thermodynamics states that the entropy of perfect pure crystal at 0K is zero.

(c) ΔG is the Gibbs free energy defined as ΔG=ΔH-TΔS. ΔG^0 is the standard free energy change.

101. **(E)** Second law of thermodynamics states that all spontaneous processes produce an increase in the entropy of the universe. In other words, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$. Therefore, the correct answer is (d).

102. **(E)** The Gibbs free energy is a function of ΔH, ΔS and temperature T. It cannot be used to determine how much heat is absorbed from the surroundings or how much work the system does on the surroundings. Furthermore, it also cannot be used to determine the proportion of the heat evolved in an exothermic reaction that can be converted to various forms of work. Since Gibbs free energy is related to the equilibrium constant of a chemical reaction ($\Delta G = -RT\ln K$) its value can be used to access the net direction in which the reaction occurs to reach equilibrium. Therefore, the correct answer is (c).

103. **(M)** In order to answer this question, we must first determine whether the entropy change for the given reaction is positive or negative. The reaction produces three moles of gas from two moles, therefore there is an increase in randomness of the system, i.e. entropy change for the reaction is positive. Gibbs free energy is a function of enthalpy, entropy and temperature ($\Delta G = \Delta H - T\Delta S$). Since $\Delta H < 0$ and $\Delta S > 0$, this reaction will be spontaneous at any temperature. The correct answer is (a).

104. **(M)** Recall that $\Delta G^o = -RT\ln K$. If $\Delta G^o = 0$, then it follows that $\Delta G^o = -RT\ln K = 0$. Solving for K yields: $\ln K = 0 \Rightarrow K = e^0 = 1$. Therefore, the correct answer is (b).

105. **(E)** In this reaction, the number of moles of reactants equals the number of moles of products. Therefore, K is equal to K_p and K_c. The correct answers are (a) and (d).

106. **(M)** **(a)** The two lines will intersect at the normal melting point of $I_2(s)$ which is 113.6 ^oC. **(b)** ΔG^o for this process must be equal to zero because solid and liquid are at equilibrium and also in their standard states.

107. **(M)** **(a)** No reaction is expected because of the decrease in entropy and the expectation that the reaction is endothermic. As a check with data from Appendix D, ΔG^o=326.4 kJmol^{-1} for the reaction as written-a very large value. **(b)** Based on the increase in entropy, the forward reaction should occur, at least to some extent. For this reaction ΔG^o=75.21 kJmol^{-1}. **(c)** ΔS is probably small, and ΔH is probably also small (one Cl-Cl bond and one Br-Br bonds are broken and two Br-Cl bonds are formed). ΔG^o should be small and the forward reaction should occur to a significant extent. For this reaction ΔG^o=-5.07 kJmol^{-1}.

108. **(M)** **(a)** Entropy change must be accessed for the system and its surroundings (ΔS_{univ}), not just for the system alone. **(b)** Equilibrium constant can be calculated from ΔG^o ($\Delta G^o = -RT\ln K$), and K permits equilibrium calculations for nonstandard conditions.

109. **(D)** **(a)** First we need to determine ΔH^o_{vap} which is simply equal to: $\Delta H^o_{vap} = \Delta H^o_f[(C_5H_{10}(g)] - \Delta H^o_f[(C_5H_{10}(l)] = -77.2\text{kJ/mol} - (-105.9\text{kJ/mol}) = 28.7\text{kJ/mol}$. Now we use Trouton's rule to calculate the boiling point of cyclopentane:

$$\Delta S^o_{vap} = \frac{\Delta H^o_{vap}}{T_{bp}} = 87\text{Jmol}^{-1}\text{K}^{-1} \Rightarrow T_{bp} = \frac{\Delta H^o_{vap}}{87\text{Jmol}^{-1}\text{K}^{-1}} = \frac{28.7 \times 1000\text{Jmol}^{-1}}{87\text{Jmol}^{-1}\text{K}^{-1}} = 330K$$

$$T_{bp} = 330K - 273.15K = 57^oC$$

(b) If we assume that ΔH^o_{vap} and ΔS^o_{vap} are independent of T we can calculate ΔG^o_{vap}:

$$\Delta G^o_{vap,298K} = \Delta H^o_{vap} - T\Delta S^o_{vap} = 28.7\text{kJmol}^{-1} - 298.15K \times \frac{87}{1000}\text{kJK}^{-1}\text{mol}^{-1} = 2.8\text{kJmol}^{-1}$$

(c) Because $\Delta G^o_{vap,298K}$ >0, the vapor pressure is less than 1 atm at 298 K, consistent with T_{bp}=57 °C.

110. **(M)** **(a)** We can use the data from Appendix D to determine the change in enthalpy and entropy for the reaction:

$$\Delta H^o = \Delta H^o_f(N_2O(g)) + 2\Delta H^o_f(H_2O(l)) - \Delta H^o_f(NH_4NO_3(s))$$

$$\Delta H^o = 82.05\text{kJmol}^{-1} + 2 \times (-285.8\text{kJmol}^{-1}) - (-365.6\text{kJmol}^{-1}) = -124\text{kJmol}^{-1}$$

$$\Delta S^o = S^o(N_2O(g)) + 2S^o(H_2O(l)) - S^o(NH_4NO_3(s))$$

$$\Delta S^o = 219.9\text{JK}^{-1}\text{mol}^{-1} + 2 \times 69.91\text{JK}^{-1}\text{mol}^{-1} - 151.1\text{JK}^{-1}\text{mol}^{-1} = 208.6\text{JK}^{-1}\text{mol}^{-1}$$

(b) From the values of ΔH^o and ΔS^o determined in part (a) we can calculate ΔG^o at 298K:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G^o = -124\text{kJmol}^{-1} - 298K \times \frac{208.6\text{kJmol}^{-1}\text{K}^{-1}}{1000} = -186.1\text{kJmol}^{-1}$$

Alternatively, ΔG^o can also be calculated directly using ΔG^o_f values tabulated in Appendix D.

(c) The equilibrium constant for the reaction is calculated using $\Delta G^o = -RT\ln K$:

$$\Delta G^o = -RT\ln K \Rightarrow -186.1 \times 1000\text{Jmol}^{-1} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298K \times \ln K$$

$$-186100\text{Jmol}^{-1} = -2477.6\ln K \Rightarrow \ln K = 75.1 \Rightarrow K = e^{75.1} = 4.1 \times 10^{32}$$

(d) The reaction has $\Delta H^o < 0$ and $\Delta S^o > 0$. Because $\Delta G^o = \Delta H^o - T\Delta S^o$, the reaction will be spontaneous at all temperatures.

111. **(M)** Recall from exercise 104 that $\Delta G^o = 0$ when K=1. Therefore, we are looking for the diagram with smallest change in Gibbs free energy between the products and the reactants. The correct answer is diagram (a). Notice that diagrams (b) and (c) represent chemical reactions with small and large values of equilibrium constants, respectively.

112. **(M)** Carbon dioxide is a gas at room temperature. The melting point of carbon dioxide is expected to be very low. At room temperature and normal atmospheric pressure this process is spontaneous. The entropy of the universe if positive.

CHAPTER 20

ELECTROCHEMISTRY

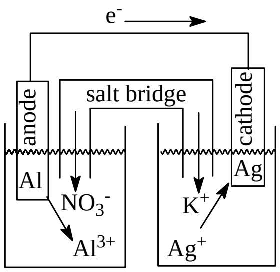
PRACTICE EXAMPLES

1A **(E)** The conventions state that the anode material is written first, and the cathode material is written last.

Anode, oxidation: $\mathrm{Sc(s) \rightarrow Sc^{3+}(aq) + 3e^-}$

Cathode, reduction: $\mathrm{\{Ag^+(aq) + e^- \rightarrow Ag(s)\} \quad \times 3}$

Net reaction $\mathrm{Sc(s) + 3\,Ag^+(aq) \rightarrow Sc^{3+}(aq) + 3\,Ag(s)}$



1B **(E)** Oxidation of Al(s) at the anode: $\mathrm{Al(s) \rightarrow Al^{3+}(aq) + 3e^-}$

Reduction of $\mathrm{Ag^+(aq)}$ at the cathode: $\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$

Overall reaction in cell: $\mathrm{Al(s) + 3\,Ag^+(aq) \rightarrow Al^{3+}(aq) + 3\,Ag(s)}$ Diagram: $\mathrm{Al(s)|Al^{3+}(aq)||Ag^+(aq)|Ag(s)}$

2A **(E)** Anode, oxidation: $\mathrm{Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-}$

Cathode, reduction: $\{Ag^+(aq) + 1e \rightarrow Ag(s)\} \times 2$

Overall reaction in cell: $Sn(s) + 2Ag^+(aq) \rightarrow Sn^{2+}(aq) + 2Ag(s)$

2B **(E)** Anode, oxidation: $\{In(\mathrm{s}) \rightarrow In^{3+}(\mathrm{aq}) + \mathrm{3e^-}\} \times 2$

Cathode, reduction: $\{Cd^{2+}(aq) + 2e \rightarrow Cd(s)\} \times 3$

Overall reaction in cell: $2In(s) + 3Cd^{2+}(aq) \rightarrow 2In^{3+}(aq) + 3Cd(s)$

3A **(M)** We obtain the two balanced half-equations and the half-cell potentials from Table 20-1.

Oxidation: $\mathrm{\{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-\} \quad \times 2}$ $\quad -E^\circ = -0.771\mathrm{V}$

Reduction: $\mathrm{Cl_2(g) + 2e^- \rightarrow 2\,Cl^-(aq)}$ $\quad E^\circ = +1.358\mathrm{V}$

Net: $\mathrm{2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)}$; $\quad E^\circ_{\mathrm{cell}} = +1.358\mathrm{V} - 0.771\mathrm{V} = +0.587\,\mathrm{V}$

3B **(M)** Since we need to refer to Table 20-1, in any event, it is perhaps a bit easier to locate the two balanced half-equations in the table. There is only one half-equation involving both $\mathrm{Fe^{2+}(aq)}$ and $\mathrm{Fe^{3+}(aq)}$ ions. It is reversed and written as an oxidation below. The half-equation involving $\mathrm{MnO_4^-(aq)}$ is also written below. [Actually, we need to know that in acidic solution $\mathrm{Mn^{2+}(aq)}$ is the principal reduction product of $\mathrm{MnO_4^-(aq)}$.]

Oxidation: $\mathrm{\{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-\} \quad \times 5}$ $\quad -E^\circ = -0.771\mathrm{V}$

Reduction: $\mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$ $\quad E^\circ = +1.51\mathrm{V}$

Net: $\mathrm{MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \rightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4H_2O(l)}$

$E^{o}_{cell} = +1.51\,V - 0.771\,V = +0.74\,V$

4A **(M)** We write down the oxidation half-equation following the method of Chapter 5, and obtain the reduction half-equation from Table 20-1, along with the reduction half-cell potential.

$$\text{Oxidation: } \{H_2C_2O_4(aq) \longrightarrow 2\,CO_2\,(aq) + 2\,H^+(aq) + 2\,e^-\} \times 3 \qquad -E^{\circ}\{CO_2/H_2C_2O_4\}$$
$$\text{Reduction: } Cr_2O_7{}^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) \qquad E^{o} = +1.33\,V$$

$$\text{Net: } Cr_2O_7{}^{2-}(aq) + 8\,H^+(aq) + 3\,H_2C_2O_4(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) + 6\,CO_2(g)$$
$$E^{o}_{cell} = +1.81\,V = +1.33\,V - E^{o}\{CO_2/H_2C_2O_4\}; \quad E^{o}\{CO_2/H_2C_2O_4\} = 1.33\,V - 1.81\,V = -0.48\,V$$

4B **(M)** The 2nd half-reaction must have $O_2(g)$ as reactant and $H_2O(l)$ as product.

$$\text{Oxidation: } \{Cr^{2+} + (aq) \longrightarrow Cr^{3+}(aq) + e^-\} \times 4 \qquad -E^{\circ}\{Cr^{3+}/Cr^{2+}\}$$
$$\text{Reduction: } O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E^{o} = +1.229V$$

$$\text{Net: } O_2(g) + 4H^+(aq) + 4\,Cr^{2+}(aq) \rightarrow 2H_2O(l) + 4Cr^{3+}(aq)$$
$$E_{cell}{}^{o} = +1.653V = +1.229V - E^{o}\{Cr^{3+}/Cr^{2+}\}; \quad E^{o}\{Cr^{3+}/Cr^{2+}\} = 1.229V - 1.653V = -0.424V$$

5A **(M)** First we write down the two half-equations, obtain the half-cell potential for each, and then calculate E^{o}_{cell}. From that value, we determine ΔG^{o}

$$\text{Oxidation: } \{Al(s) \rightarrow Al^{3+}(aq) + 3e^-\} \times 2 \qquad -E^{o} = +1.676V$$
$$\text{Reduction: } \{Br_2(l) + 2e^- \rightarrow 2\ Br^-(aq)\} \times 3 \qquad E^{o} = +1.065V$$

$$\text{Net: } 2\,Al(s) + 3\,Br_2(l) \rightarrow 2\,Al^{3+}(aq) + 6\,Br^-(aq) \quad E^{o}_{cell} = 1.676\,V + 1.065\,V = 2.741\,V$$

$$\Delta G^{o} = -nFE^{o}_{cell} = -6\,\text{mol } e^- \times \frac{96,485\ C}{1\,\text{mol } e^-} \times 2.741\,V = -1.587 \times 10^6\,J = -1587\,kJ$$

5B **(M)** First we write down the two half-equations, one of which is the reduction equation from the previous example. The other is the oxidation that occurs in the standard hydrogen electrode.

$$\text{Oxidation: } 2H_2(g) \rightarrow 4H^+(aq) + 4e^-$$
$$\text{Reduction: } O_2(g) + 4\,H^+(aq) + 4e^- \rightarrow 2\,H_2O(l)$$

$$\text{Net: } \qquad 2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \qquad n = 4 \text{ in this reaction.}$$

This net reaction is simply twice the formation reaction for $H_2O(l)$ and, therefore,

$$\Delta G^{o} = 2\Delta G_f{}^{o}\left[H_2O(l)\right] = 2 \times (-237.1\ kJ) = -474.2 \times 10^3\ J = -nFE^{o}_{cell}$$

$$E^{o}_{cell} = \frac{-\Delta G^{o}}{nF} = \frac{-\left(-474.2 \times 10^3\ J\right)}{4\ \text{mol } e^- \times \dfrac{96{,}485\,C}{\text{mol}\,e^-}} = +1.229\,V = E^{o}\text{, as we might expect.}$$

6A **(M)** Cu(s) will displace metal ions of a metal less active than copper. Silver ion is one example.

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $\quad -E^o = -0.340 V$ (from Table 20.1)

Reduction: $\{Ag^+(aq) + e^- \rightarrow Ag(s)\} \times 2$ $\quad E^o = +0.800 V$

Net: $2Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ $\quad E^o_{cell} = -0.340 V + 0.800 V = +0.460 V$

6B **(M)** We determine the value for the hypothetical reaction's cell potential.

Oxidation: $\{Na(s) \rightarrow Na^+(aq) + e^-\} \times 2$ $\quad -E^o = +2.713 V$

Reduction: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $\quad E^o = -2.356 V$

Net: $2Na(s) + Mg^{2+}(aq) \rightarrow 2Na^+(aq) + Mg(s)$ $\quad E^o_{cell} = 2.713 V - 2.356 V = +0.357 V$

The method is not feasible because another reaction occurs that has a more positive cell potential, i.e., Na(s) reacts with water to form $H_2(g)$ and NaOH(aq):

Oxidation: $\{Na(s) \rightarrow Na^+(aq) + e^-\} \times 2$ $\quad -E^o = +2.713 V$

Reduction: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E^o = -0.828 V$

$E^o_{cell} = 2.713 V - 0.828 V = +1.885 V$.

7A **(M)** The oxidation is that of SO_4^{2-} to $S_2O_8^{2-}$, the reduction is that of O_2 to H_2O.

Oxidation: $\{2 SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-\} \times 2$ $\quad -E^o = -2.01 V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $\quad E^o = +1.229 V$

Net: $O_2(g) + 4 H^+(aq) + 2 SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2H_2O(l)$ $\quad E^\circ_{cell} = -0.78 V$

Because the standard cell potential is negative, we conclude that this cell reaction is nonspontaneous under standard conditions. This would not be a feasible method of producing peroxodisulfate ion.

7B **(M) (1)** The oxidation is that of $Sn^{2+}(aq)$ to $Sn^{4+}(aq)$; the reduction is that of O_2 to H_2O.

Oxidation: $\{Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-\} \times 2$ $\quad -E^o = -0.154 V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $\quad E^o = +1.229 V$

Net: $O_2(g) + 4H^+(aq) + 2Sn^{2+}(aq) \rightarrow 2Sn^{4+}(aq) + 2H_2O(l)$ $\quad E^o_{cell} = +1.075 V$

Since the standard cell potential is positive, this cell reaction is spontaneous under standard conditions.

(2) The oxidation is that of Sn(s) to $Sn^{2+}(aq)$; the reduction is still that of O_2 to H_2O.

Oxidation: $\{Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-\} \times 2$ $\quad -E^o = +0.137 V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $\quad E^o = +1.229 V$

Net: $O_2(g) + 4H^+(aq) + 2Sn(s) \rightarrow 2Sn^{2+}(aq) + 2H_2O(l)$

$E^o_{cell} = 0.137 V + 1.229 V = +1.366 V$

The standard cell potential for this reaction is more positive than that for situation (1). Thus, reaction (2) should occur preferentially. Also, if $\mathrm{Sn^{4+}(aq)}$ is formed, it should react with Sn(s) to form $\mathrm{Sn^{2+}(aq)}$.

Oxidation: $\mathrm{Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-}$ $\quad -E^\circ = +0.137\,\mathrm{V}$

Reduction: $\mathrm{Sn^{4+}(aq) + 2\,e^- \rightarrow Sn^{2+}(aq)}$ $\quad E^\circ = +0.154\,\mathrm{V}$

Net: $\mathrm{Sn^{4+}(aq) + Sn(s) \rightarrow 2\,Sn^{2+}(aq)}$ $\quad E^\circ_{\mathrm{cell}} = +0.137\,\mathrm{V} + 0.154\,\mathrm{V} = +0.291\,\mathrm{V}$

8A **(M)** For the reaction $\mathrm{2\,Al(s) + 3Cu^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3Cu(s)}$ we know $n = 6$ and $E^\circ_{\mathrm{cell}} = +2.013\,\mathrm{V}$. We calculate the value of K_{eq}.

$$E^\circ_{\mathrm{cell}} = \frac{0.0257}{n}\ln K_{\mathrm{eq}};\quad \ln K_{\mathrm{eq}} = \frac{nE^\circ_{\mathrm{cell}}}{0.0257} = \frac{6\times(+2.013)}{0.0257} = 470;\qquad K_{\mathrm{eq}} = e^{470} = 10^{204}$$

The huge size of the equilibrium constant indicates that this reaction indeed will go to essentially 100% to completion.

8B **(M)** We first determine the value of E°_{cell} from the half-cell potentials.

Oxidation: $\mathrm{Sn(s) \rightarrow Sn^{2+}(aq) + 2\,e^-}$ $\quad -E^\circ = +0.137\,\mathrm{V}$

Reduction: $\mathrm{Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)}$ $\quad E^\circ = -0.125\,\mathrm{V}$

Net: $\mathrm{Pb^{2+}(aq) + Sn(s) \rightarrow Pb(s) + Sn^{2+}(aq)}$ $\quad E^\circ_{\mathrm{cell}} = +0.137\,\mathrm{V} - 0.125\,\mathrm{V} = +0.012\,\mathrm{V}$

$$E^\circ_{\mathrm{cell}} = \frac{0.0257}{n}\ln K_{\mathrm{eq}}\qquad \ln K_{\mathrm{eq}} = \frac{nE^\circ_{\mathrm{cell}}}{0.0257} = \frac{2\times(+0.012)}{0.0257} = 0.93\qquad K_{\mathrm{eq}} = e^{0.93} = 2.5$$

The equilibrium constant's small size ($0.001 < K < 1000$) indicates that this reaction will not go to completion.

9A **(M)** We first need to determine the standard cell voltage and the cell reaction.

Oxidation: $\mathrm{\{Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-\}}\ \times 2$ $\quad -E^\circ = +1.676\,\mathrm{V}$

Reduction: $\mathrm{\{Sn^{4+}(aq) + 2\ e^- \rightarrow Sn^{2+}(aq)\}}\ \times 3$ $\quad E^\circ = +0.154\,\mathrm{V}$

Net: $\mathrm{2\ Al(s) + 3\ Sn^{4+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Sn^{2+}(aq)}$ $\quad E^\circ_{\mathrm{cell}} = +1.676\,\mathrm{V} + 0.154\,\mathrm{V} = +1.830\,\mathrm{V}$

Note that $n = 6$. We now set up and substitute into the Nernst equation.

$$E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \frac{0.0592}{n}\log\frac{[\mathrm{Al^{3+}}]^2[\mathrm{Sn^{2+}}]^3}{[\mathrm{Sn^{4+}}]^3} = +1.830 - \frac{0.0592}{6}\log\frac{(0.36\,\mathrm{M})^2(0.54\,\mathrm{M})^3}{(0.086\,\mathrm{M})^3}$$

$$= +1.830\,\mathrm{V} - 0.0149\,\mathrm{V} = +1.815\,\mathrm{V}$$

9B **(M)** We first need to determine the standard cell voltage and the cell reaction.

Oxidation: $\mathrm{2\ Cl^-(1.0\ M) \rightarrow Cl_2(1\ atm) + 2e^-}$ $\quad -E^\circ = -1.358\ \mathrm{V}$

Reduction: $\mathrm{PbO_2(s) + 4\,H^+(aq) + 2\,e^- \rightarrow Pb^{2+}(aq) + 2\,H_2O(l)}$ $\quad E^\circ = +1.455\ \mathrm{V}$

Net: $PbO_2(s) + 4H^+(0.10\text{ M}) + 2Cl^-(1.0\text{ M}) \rightarrow Cl_2(1\text{ atm}) + Pb^{2+}(0.050\text{ M}) + 2H_2O(l)$

$E^o_{cell} = -1.358\text{ V} + 1.455\text{ V} = +0.097\text{ V}$ Note that $n = 2$. Substitute values into the Nernst equation.

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log\frac{P\{Cl_2\}[Pb^{2+}]}{[H^+]^4[Cl^-]^2} = +0.097 - \frac{0.0592}{2}\log\frac{(1.0\,\text{atm})(0.050\,\text{M})}{(0.10\,\text{M})^4(1.0\,\text{M})^2}$$

$$= +0.097\text{ V} - 0.080\text{ V} = +0.017\text{ V}$$

10A **(M)** The cell reaction is $2\text{ Fe}^{3+}(0.35\text{ M}) + Cu(s) \rightarrow 2\text{ Fe}^{2+}(0.25\text{ M}) + Cu^{2+}(0.15\text{ M})$ with $n = 2$ and $E^o_{cell} = -0.337\text{ V} + 0.771\text{ V} = 0.434\text{ V}$ Next, substitute this voltage and the concentrations into the Nernst equation.

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log\frac{[Fe^{2+}]^2[Cu^{2+}]}{[Fe^{3+}]^2} = 0.434 - \frac{0.0592}{2}\log\frac{(0.25)^2(0.15)}{(0.35)^2} = 0.434 + 0.033$$

$E_{cell} = +0.467\text{ V}$ Thus the reaction is spontaneous under standard conditions as written.

10B **(M)** The reaction is not spontaneous under standard conditions in either direction when $E_{cell} = 0.000\text{ V}$. We use the standard cell potential from Example 20-10.

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log\frac{[Ag^+]^2}{[Hg^{2+}]}; \quad 0.000\text{ V} = -0.054\text{ V} - \frac{0.0592}{2}\log\frac{[Ag^+]^2}{[Hg^{2+}]}$$

$$\log\frac{[Ag^+]^2}{[Hg^{2+}]} = \frac{-0.054 \times 2}{0.0592} = -1.82; \quad \frac{[Ag^+]^2}{[Hg^{2+}]} = 10^{-1.82} = 0.0150$$

11A **(M)** In this concentration cell $E^o_{cell} = 0.000\text{ V}$ because the same reaction occurs at anode and cathode, only the concentrations of the ions differ. $[Ag^+] = 0.100\text{ M}$ in the cathode compartment. The anode compartment contains a saturated solution of AgCl(aq).

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = s^2; \quad s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\text{ M}$$

Now we apply the Nernst equation. The cell reaction is

$$Ag^+(0.100\,\text{M}) \rightarrow Ag^+(1.3 \times 10^{-5}\,\text{M})$$

$$E_{cell} = 0.000 - \frac{0.0592}{1}\log\frac{1.3 \times 10^{-5}\text{ M}}{0.100\text{ M}} = +0.23\text{V}$$

11B **(D)** Because the electrodes in this cell are identical, the standard electrode potentials are numerically equal and subtracting one from the other leads to the value $E^o_{cell} = 0.000\text{V}$. However, because the ion concentrations differ, there is a potential difference between the

two half cells (non-zero nonstandard voltage for the cell). $\left[\mathrm{Pb}^{2+}\right] = 0.100\ \mathrm{M}$ in the cathode compartment, while the anode compartment contains a saturated solution of PbI_2.
We use the Nernst equation (with $n = 2$) to determine $\left[\mathrm{Pb}^{2+}\right]$ in the saturated solution.

$$E_{\mathrm{cell}} = +0.0567\ \mathrm{V} = 0.000 - \frac{0.0592}{2}\log\frac{x\,\mathrm{M}}{0.100\,\mathrm{M}}; \quad \log\frac{x\,\mathrm{M}}{0.100\,\mathrm{M}} = \frac{2\times 0.0567}{-0.0592} = -1.92$$

$$\frac{x\,\mathrm{M}}{0.100\,\mathrm{M}} = 10^{-1.92} = 0.012; \quad \left[\mathrm{Pb}^{2+}\right]_{\mathrm{anode}} = x\ \mathrm{M} = 0.012\times 0.100\ \mathrm{M} = 0.0012\ \mathrm{M};$$

$$\left[\mathrm{I}^-\right] = 2\times 0.0012\ \mathrm{M} = 0.0024\ \mathrm{M}$$

$K_{\mathrm{sp}} = \left[\mathrm{Pb}^{2+}\right]\left[\mathrm{I}^-\right]^2 = (0.0012)(0.0024)^2 = 6.9\times 10^{-9}$ compared with 7.1×10^{-9} in Appendix D

12A **(M)** From Table 20-1 we choose one oxidations and one reductions reaction so as to get the least negative cell voltage. This will be the most likely pair of ½ -reactions to occur.

Oxidation: $2\mathrm{I}^-(\mathrm{aq}) \rightarrow \mathrm{I}_2(\mathrm{s}) + 2\ \mathrm{e}^-$ $\quad -E^\circ = -0.535\ \mathrm{V}$

$2\,\mathrm{H_2O(l)} \rightarrow \mathrm{O}_2(\mathrm{g}) + 4\,\mathrm{H}^+(\mathrm{aq}) + 4\,\mathrm{e}^-$ $\quad -E^\circ = -1.229\,\mathrm{V}$

Reduction: $\mathrm{K}^+(\mathrm{aq}) + \mathrm{e}^- \rightarrow \mathrm{K}(\mathrm{s})$ $\quad E^\circ = -2.924\ \mathrm{V}$

$2\,\mathrm{H_2O(l)} + 2\,\mathrm{e}^- \rightarrow \mathrm{H}_2(\mathrm{g}) + 2\,\mathrm{OH}^-(\mathrm{aq})$ $\quad E^\circ = -0.828\ \mathrm{V}$

The least negative standard cell potential $(-0.535\,\mathrm{V} - 0.828\,\mathrm{V} = -1.363\,\mathrm{V})$ occurs when $\mathrm{I}_2(\mathrm{s})$ is produced by oxidation at the anode, and $\mathrm{H}_2(\mathrm{g})$ is produced by reduction at the cathode.

12B **(M)** We obtain from Table 20-1 all the possible oxidations and reductions and choose one of each to get the least negative cell voltage. That pair is the most likely pair of half-reactions to occur.

Oxidation: $2\,\mathrm{H_2O(l)} \rightarrow \mathrm{O}_2(\mathrm{g}) + 4\,\mathrm{H}^+(\mathrm{aq}) + 4\mathrm{e}^-$ $\quad -E^\circ = -1.229\mathrm{V}$

$\mathrm{Ag}(\mathrm{s}) \rightarrow \mathrm{Ag}^+(\mathrm{aq}) + \mathrm{e}^-$ $\quad -E^\circ = -0.800\mathrm{V}$

[We cannot further oxidize $\mathrm{NO}_3^-(\mathrm{aq})$ or $\mathrm{Ag}^+(\mathrm{aq})$.]

Reduction: $\mathrm{Ag}^+(\mathrm{aq}) + \mathrm{e}^- \rightarrow \mathrm{Ag}(\mathrm{s})$ $\quad E^\circ = +0.800\mathrm{V}$

$2\,\mathrm{H_2O(l)} + 2\mathrm{e}^- \rightarrow \mathrm{H}_2(\mathrm{g}) + 2\,\mathrm{OH}^-(\mathrm{aq})$ $\quad E^\circ = -0.828\mathrm{V}$

Thus, we expect to form silver metal at the cathode and $\mathrm{Ag}^+(\mathrm{aq})$ at the anode.

13A **(M)** The half-cell equation is $\mathrm{Cu}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \rightarrow \mathrm{Cu}(\mathrm{s})$, indicating that two moles of electrons are required for each mole of copper deposited. Current is measured in amperes, or coulombs per second. We convert the mass of copper to coulombs of electrons needed for the reduction and the time in hours to seconds.

$$\text{Current} = \frac{12.3\ \text{g Cu} \times \dfrac{1\ \text{mol Cu}}{63.55\ \text{g Cu}} \times \dfrac{2\ \text{mol e}^-}{1\ \text{mol Cu}} \times \dfrac{96{,}485\ \text{C}}{1\text{mol e}^-}}{5.50\ \text{h} \times \dfrac{60\ \text{min}}{1\text{h}} \times \dfrac{60\ \text{s}}{1\text{min}}} = \frac{3.735 \times 10^4\ \text{C}}{1.98 \times 10^4\ \text{s}} = 1.89\ \text{amperes}$$

13B **(D)** We first determine the moles of $O_2(g)$ produced with the ideal gas equation.

$$\text{moles}\, O_2(g) = \frac{\left(738\ \text{mm Hg} \times \dfrac{1\ \text{atm}}{760\ \text{mm Hg}}\right) \times 2.62\ \text{L}}{\dfrac{0.08206\ \text{L atm}}{\text{mol K}} \times (26.2 + 273.2)\ \text{K}} = 0.104\ \text{mol}\, O_2$$

Then we determine the time needed to produce this amount of O_2.

$$\text{elapsed time} = 0.104\ \text{mol}\ O_2 \times \frac{4\ \text{mol e}^-}{1\ \text{mol}\ O_2} \times \frac{96{,}485\ \text{C}}{1\text{mol e}^-} \times \frac{1\text{s}}{2.13\text{C}} \times \frac{1\text{h}}{3600\text{s}} = 5.23\text{h}$$

INTEGRATIVE EXAMPLE

14A **(D)** In this problem we are asked to determine E^o for the reduction of $CO_2(g)$ to $C_3H_8(g)$ in an acidic solution. We proceed by first determining ΔG^o for the reaction using tabulated values for ΔG_f^o in Appendix D. Next, E_{cell}^o for the reaction can be determined using $\Delta G^o = -zFE_{cell}^o$. Given reaction can be separated into reduction and oxidation. Since we are in acidic medium, the reduction half-cell potential can be found in Table 20.1. Lastly, the oxidation half-cell potential can be calculated using $E_{cell}^o = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$.

Stepwise approach

First determine ΔG^o for the reaction using tabulated values for ΔG_f^o in Appendix D:

$$\begin{array}{cccccccccc} & C_3H_8(g) & + & 5O_2(g) & \rightarrow & 3CO_2(g) & + & 4H_2O(l) \\ \Delta G_f^o & -23.3\ \text{kJ/mol} & & 0\ \text{kJ/mol} & & -394.4\ \text{kJ/mol} & & -237.1\ \text{kJ/mol} \end{array}$$

$$\Delta G^o = 3 \times \Delta G_f^o(CO_2(g)) + 4 \times \Delta G_f^o(H_2O(l)) - [\Delta G_f^o(C_3H_8(g)) + 5 \times \Delta G_f^o(O_2(g))]$$

$$\Delta G^o = 3 \times (-394.4) + 4 \times (-237.1) - [-23.3 + 5 \times 0]\text{kJ/mol}$$

$$\Delta G^o = -2108\text{kJ/mol}$$

In order to calculate E_{cell}^o for the reaction using $\Delta G^o = -zFE_{cell}^o$, *z* must be first determined. We proceed by separating the given reaction into oxidation and reduction:

Reduction: $5\times\{O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l)\}$ E^o=+1.229 V
Oxidation: $C_3H_8(g) + 6H_2O(l) \rightarrow 3CO_2(g) + 20H^+ + 20e^-$ E^o=xV

Overall: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ E^o=+1.229 V-xV

Since z=20, E_{cell}^o can now be calculated using $\Delta G^o = -zFE_{cell}^o$:

$$\Delta G^o = -zFE^o_{cell}$$

$$-2108 \times 1000\text{J/mol} = -20\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times E^o_{cell}$$

$$E^o_{cell} = \frac{-2108 \times 1000}{-20 \times 96485} V = 1.092 V$$

Finally, E^o(reduction half-cell) can be calculated using

$E^o_{cell} = E^o$(reduction half-cell) – E^o(oxidation half-cell):

1.092 V = 1.229 V – E^o(oxidation half-cell) V

E^o(oxidation half-cell) =1.229 V – 1.092 V = 0.137 V

Therefore, E^o for the reduction of $CO_2(g)$ to $C_3H_8(g)$ in an acidic medium is 0.137 V.

Conversion pathway approach:

Reduction: $5\times\{O_2(g)+4H^+(aq)+4e^- \rightarrow 2H_2O(l)\}$ E^o=+1.229 V

Oxidation: $C_3H_8(g) + 6H_2O(l) \rightarrow 3CO_2(g) + 20H^+ + 20e^-$ E^o=x V

Overall:	$C_3H_8(g)$	+	$5O_2(g)$	$\rightarrow$	$3CO_2(g)$	+	$4H_2O(l)$	E^o=+1.229 V-x V
ΔG^o_f	-23.3 kJ/mol		0 kJ/mol		-394.4 kJ/mol		-237.1 kJ/mol	

$$\Delta G^o = 3\times\Delta G^o_f(CO_2(g)) + 4\times\Delta G^o_f(H_2O(l)) - [\Delta G^o_f(C_3H_8(g)) + 5\times\Delta G^o_f(O_2(g))]$$

$$\Delta G^o = 3\times(-394.4) + 4\times(-237.1) - [-23.3 + 5\times 0]\text{kJ/mol}$$

$$\Delta G^o = -2108\text{kJ/mol}$$

$$\Delta G^o = -zFE^o_{cell}$$

$$-2108 \times 1000\text{J/mol} = -20\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times E^o_{cell}$$

$$E^o_{cell} = \frac{-2108 \times 1000}{-20 \times 96485} V = 1.092 V$$

1.092 V = 1.229 V – E^o(oxidation half-cell) V

E^o(oxidation half-cell) =1.229 V – 1.092 V = 0.137 V

14B **(D)** This is a multi component problem dealing with a flow battery in which oxidation occurs at an aluminum anode and reduction at a carbon-air cathode. Al^{3+} produced at the anode is complexed with OH^- anions from NaOH(aq) to form $[Al(OH)_4]^-$.

Stepwise approach:

Part (a): The flow battery consists of aluminum anode where oxidation occurs and the formed Al^{3+} cations are complexes with OH^- anions to form $[Al(OH)_4]^-$. The plausible half-reaction for the oxidation is:

Oxidation: $Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^- + 3e^-$

The cathode, on the other hand consists of carbon and air. The plausible half-reaction for the reduction involves the conversion of O_2 and water to form OH^- anions (basic medium):

Reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Combining the oxidation and reduction half-reactions we obtain overall reaction for the process:

Oxidation: $\{Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^- + 3e^-\}\times4$

Reduction: $\{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)\} \times 3$

Overall: $4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4[Al(OH)_4]^-(aq)$

Part(b): In order to find E_o for the reduction, use the known value for E^o_{cell} as well as E^o for the reduction half-reaction from Table 20.1:

$$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$$

$$E^o_{cell} = +0.401V - E^o(\text{oxidation half-cell}) = +2.73V$$

$$E^o(\text{oxidation half-cell}) = +0.401V - 2.73V = -2.329V$$

Part (c): From the given value for E^o_{cell} (+2.73V) first calculate ΔG^o using $\Delta G^o = -zFE^o_{cell}$ (notice that z=12 from part (a) above):

$$\Delta G^o = -zFE^o_{cell} = -12\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times 2.73V$$

$$\Delta G^o = -3161\text{kJ/mol}$$

Given the overall reaction (part (a)) and ΔG^o_f for $OH^-(aq)$ anions and $H_2O(l)$, we can calculate the Gibbs energy of formation of the aluminate ion, $[Al(OH)_4]^-$:

Overall reaction:	$4Al(s)$	+	$4OH^-(aq)$	+	$3O_2(g)$	+	$6H_2O(l)$	$\rightarrow$	$4[Al(OH)_4]^-(aq)$
ΔG^o_f	0 kJ/mol		-157 kJ/mol		0 kJ/mol		-237.2 kJ/mol		x

$$\Delta G^o = 4 \times x - [4 \times 0 + 4 \times (-157) + 3 \times 0 + 6 \times (-237.2)\text{kJ/mol} = -3161\text{kJ/mol}$$

$$4x = -3161 - 2051.2 = -5212.2\text{kJ/mol}$$

$$x = -1303\text{kJ/mol}$$

Therefore, $\Delta G^o_f([Al(OH)_4]^-) = -1303\text{kJ/mol}$

Part(d): First calculate the number of moles of electrons:

$$\text{number of mol e}^- = \text{current}(C/s) \times \text{time(s)} \times \frac{1\text{mol e}^-}{96485C}$$

$$\text{number of mol e}^- = 4.00h \times \frac{60\min}{1h} \times \frac{60s}{1\min} \times 10.0\frac{C}{s} \times \frac{1\text{mol e}^-}{96485C}$$

$$\text{number of mol e}^- = 1.49\text{mol e}^-$$

Now, use the oxidation half-reaction to determine the mass of Al(s) consumed:

$$mass(Al) = 1.49\text{mol e}^- \times \frac{1\text{mol Al}}{3\text{mol e}^-} \times \frac{26.98\text{g Al}}{1\text{mol Al}} = 13.4g$$

Conversion pathway approach:

Part (a):

Oxidation: $\{Al(s) + 4OH^-(aq) \rightarrow [Al(OH)_4]^- + 3e^-\} \times 4$

Reduction: $\{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)\} \times 3$

Overall: $4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4[Al(OH)_4]^-(aq)$

Part (b):

$$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$$

$$E^o_{cell} = +0.401V - E^o(\text{oxidation half-cell}) = +2.73V$$

$$E^o(\text{oxidation half-cell}) = +0.401V - 2.73V = -2.329V$$

Part (c):

$$\Delta G^o = -zFE^o_{cell} = -12\text{mol e}^- \times \frac{96485\text{C}}{1\text{mol e}^-} \times 2.73V$$

$$\Delta G^o = -3161\text{kJ/mol}$$

Overall reaction:	$4Al(s)$	+	$4OH^-(aq)$	+	$3O_2(g)$	+	$6H_2O(l) \rightarrow$	$4[Al(OH)_4]^-(aq)$
ΔG^o_f	0 kJ/mol		-157 kJ/mol		0 kJ/mol		-237.2 kJ/mol	x

$$\Delta G^o = 4 \times x - [4 \times 0 + 4 \times (-157) + 3 \times 0 + 6 \times (-237.2)\text{kJ/mol} = -3161\text{kJ/mol}$$

$$4x = -3161 - 2051.2 = -5212.2\text{kJ/mol}$$

$$x = \Delta G^o_f([Al(OH)_4]^-) = -1303\text{kJ/mol}$$

Part (d):

$$\text{number of mol e}^- = \text{current}(C/s) \times \text{time(s)} \times \frac{1\text{mol e}^-}{96485C}$$

$$\text{number of mol e}^- = 4.00h \times \frac{60\,\text{min}}{1h} \times \frac{60s}{1\text{min}} \times 10.0\frac{C}{s} \times \frac{1\text{mol e}^-}{96485C}$$

$$\text{number of mol e}^- = 1.49\text{mol e}^-$$

$$mass(Al) = 1.49\text{mol e}^- \times \frac{1\text{mol Al}}{3\text{mol e}^-} \times \frac{26.98\text{g Al}}{1\text{mol Al}} = 13.4g$$

EXERCISES

Standard Electrode Potential

1. **(E) (a)** If the metal dissolves in HNO_3, it has a reduction potential that is smaller than $E^o\{NO_3^-(aq)/NO(g)\} = 0.956\,V$. If it also does not dissolve in HCl, it has a reduction potential that is larger than $E^o\{H^+(aq)/H_2(g)\} = 0.000\,V$. If it displaces $Ag^+(aq)$ from solution, then it has a reduction potential that is smaller than $E^o\{Ag^+(aq)/Ag(s)\} = 0.800\,V$. But if it does not displace $Cu^{2+}(aq)$ from solution, then its reduction potential is larger than $E^o\{Cu^{2+}(aq)/Cu(s)\} = 0.340\,V$ Thus, $0.340\text{ V} < E^o < 0.800\,V$

(b) If the metal dissolves in HCl, it has a reduction potential that is smaller than $E^o\{H^+(aq)/H_2(g)\} = 0.000\text{ V}$. If it does not displace $Zn^{2+}(aq)$ from solution, its reduction potential is larger than $E^o\{Zn^{2+}(aq)/Zn(s)\} = -0.763\text{ V}$. If it also does not displace $Fe^{2+}(aq)$ from solution, its reduction potential is larger than

$E^\circ\{Fe^{2+}(aq)/Fe(s)\} = -0.440\text{ V}$. $\quad -0.440\text{ V} < E^\circ < 0.000\text{ V}$

2. **(E)** We would place a strip of solid indium metal into each of the metal ion solutions and see if the dissolved metal plates out on the indium strip. Similarly, strips of all the other metals would be immersed in a solution of In^{3+} to see if indium metal plates out. Eventually, we will find one metal whose ions are displaced by indium and another metal that displaces indium from solution, which are adjacent to each other in Table 20-1. The standard electrode potential for the $In/In^{3+}(aq)$ pair will lie between the standard reduction potentials for these two metals. This technique will work only if indium metal does not react with water, that is, if the standard reduction potential of $In^{3+}(aq)/In(s)$ is greater than about -1.8 V. The inaccuracy inherent in this technique is due to overpotentials, which can be as much as 0.200 V. Its imprecision is limited by the closeness of the reduction potentials for the two bracketing metals

3. **(M)** We separate the given equation into its two half-equations. One of them is the reduction of nitrate ion in acidic solution, whose standard half-cell potential we retrieve from Table 20-1 and use to solve the problem.

Oxidation: $\{Pt(s) + 4Cl^-(aq) \longrightarrow [PtCl_4]^{2-}(aq) + 2e^-\} \times 3;\quad -E^\circ\{[PtCl_4]^{2-}(aq)/Pt(s)\}$

Reduction: $\{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)\} \times 2;\quad E^\circ = +0.956\text{ V}$

Net: $3Pt(s) + 2NO_3^-(aq) + 8H^+(aq) + 12Cl^-(aq) \rightarrow 3[PtCl_4]^{2-}(aq) + 2NO(g) + 6H_2O(l)$

$$E^\circ_{cell} = 0.201\text{ V} = +0.956\text{ V} - E^\circ\{[PtCl_4]^{2-}(aq)/Pt(s)\}$$

$$E^\circ\{[PtCl_4]^{2-}(aq)/Pt(s)\} = 0.956\text{ V} - 0.201\text{ V} = +0.755\text{ V}$$

4. **(M)** In this problem, we are dealing with the electrochemical reaction involving the oxidation of Na(in Hg) to $Na^+(aq)$ and the reduction of $Cl_2(s)$ to $Cl^-(aq)$. Given that $E^o_{cell} = 3.20V$, we are asked to find E^o for the reduction of Na^+ to Na(in Hg). We proceed by separating the given equation into its two half-equations. One of them is the reduction of $Cl_2(g)$ to $Cl^-(aq)$ whose standard half-cell potential we obtain from Table 20-1 and use to solve the problem.

Stepwise approach:

Separate the given equation into two half-equations:

Oxidation: $\{Na(in\ Hg) \rightarrow Na^+(aq) + e^-\} \times 2 \qquad -E^\circ\{Na^+(aq)/Na(in\ Hg)\}$

Reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E^\circ = +1.358\text{ V}$

Net: $2Na(in\ Hg) + Cl_2(g) \rightarrow 2Na^+(aq) + 2Cl^-(aq) \qquad E^\circ_{cell} = 3.20\text{ V}$

Use $E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell})$ to solve for $E^o(\text{oxidation half-cell})$:

$$E^\circ_{cell} = 3.20\text{ V} = +1.385\text{ V} - E^\circ\{Na^+(aq)/Na(in\ Hg)\}$$

$$E^\circ\{Na^+(aq)/Na(in\ Hg)\} = 1.358\text{ V} - 3.20\text{ V} = -1.84\text{ V}$$

Conversion pathway approach:

Oxidation: $\{Na(in\ Hg) \rightarrow Na^+(aq) + e^-\} \times 2 \qquad -E^\circ\{Na^+(aq)/Na(in\ Hg)\}$

Reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	$E^\circ = +1.358$ V
Net: $2Na(\text{in Hg}) + Cl_2(g) \rightarrow 2Na^+(aq) + 2Cl^-(aq)$	$E^\circ_{cell} = 3.20$ V

$3.20V = 1.358 - E^o\{Na^+(aq)/Na(\text{in Hg})\}$

$E^o\{Na^+(aq)/Na(\text{in Hg})\} = 1.358V - 3.20V = -1.84V$

5. **(M)** We divide the net cell equation into two half-equations.

Oxidation: $\{Al(s) + 4\ OH^-(aq) \rightarrow [Al(OH)_4]^-(aq) + 3\ e^-\} \times 4$;	$-E^o\{[Al(OH)_4]^-(aq)/Al(s)\}$
Reduction: $\{O_2(g) + 2\ H_2O(l) + 4e^- \rightarrow 4\ OH^-(aq)\}\ \times 3$;	$E^o = +0.401V$
Net: $4Al(s) + 3O_2(g) + 6H_2O(l) + 4OH^-(aq) \rightarrow 4[Al(OH)_4]^-(aq)$	$E_{cell}{}^o = 2.71V$

$E^o_{cell} = 2.71V = +0.401V - E^o\{[Al(OH)_4]^-(aq)/Al(s)\}$

$E^o\{[Al(OH)_4]^-(aq)/Al(s)\} = 0.401V - 2.71V = -2.31V$

6. **(M)** We divide the net cell equation into two half-equations.

Oxidation: $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$	$-E^o\{CO_2(g)/CH_4(g)\}$
Reduction: $\{O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)\}\ \times 2$	$E^o = +1.229V$
Net: $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	$E^o_{cell} = 1.06V$

$E^o_{cell} = 1.06V = +1.229V - E^o\{CO_2(g)/CH_4(g)\}$

$E^o\{CO_2(g)/CH_4(g)\} = 1.229V - 1.06V = +0.17V$

7. **(M) (a)** We need standard reduction potentials for the given half-reactions from Table 10.1:

$Ag^+(aq)+e^- \rightarrow Ag(s)$	E_o=+0.800 V
$Zn^{2+}(aq)+2e^- \rightarrow Zn(s)$	E_o=-0.763 V
$Cu^{2+}(aq)+2e^- \rightarrow Cu(s)$	E_o=+0.340 V
$Al^{3+}(aq)+3e^- \rightarrow Al(s)$	E_o=-1.676 V

Therefore, the largest positive cell potential will be obtained for the reaction involving the oxidation of Al(s) to Al^{3+}(aq) and the reduction of Ag^+(aq) to Ag(s):

$Al(s) + 3Ag^+(aq) \rightarrow 3Ag(s)+Al^{3+}(aq)$ $\quad E^o_{cell} = +1.676V + 0.800V = 2.476V$

Ag is the anode and Al is the cathode.

(b) Reverse to the above, the cell with the smallest positive cell potential will be obtained for the reaction involving the oxidation of Zn(s) to Zn^{2+}(aq) (anode) and the reduction of Cu^{+2}(aq) to Cu(s) (cathode):

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s)+Zn^{2+}(aq)$ $\quad E^o_{cell} = 0.763V + 0.340V = 1.103V$

8. **(M) (a)** The largest positive cell potential will be obtained for the reaction:

$Zn(s) + 4NH_3(aq) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow [Zn(NH_3)_4]^{2+}(aq)+2V^{3+}(aq)+2H_2O(l)$

$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell}) = 0.340V - (-1.015V) = 1.355V$

Zn is the anode and VO^{2+} is the cathode.

(b) Reverse to the above, the cell with the smallest positive cell potential will be obtained for the reaction involving the oxidation of Ti^{2+}(aq) to Ti^{3+}(aq) (anode) and the reduction of Sn^{+2}(aq) to Sn(s) (cathode):

$2Ti^{2+}(aq) + Sn^{2+}(aq) \rightarrow 2Ti^{3+}(aq) + Sn(aq)$

$E^o_{cell} = E^o(\text{reduction half-cell}) - E^o(\text{oxidation half-cell}) = -0.14V - (-0.37V) = 0.23V$

Predicting Oxidation-Reduction Reactions

9. **(E)** **(a)** Ni^{2+}, **(b)** Cd.

10. **(E)** **(a)** potassium, **(b)** barium.

11. **(M) (a)** Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$ $\quad -E^o = +0.137$ V

Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $\quad E^o = -0.125$ V

Net: $Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+}(aq) + Pb(s)$ $\quad E^o_{cell} = +0.012$ V Spontaneous

(b) Oxidation: $2I^-(aq) \rightarrow I_2(s) + 2e^-$ $\quad -E^o = -0.535$ V

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E^o = +0.340$ V

Net: $2I^-(aq) + Cu^{2+}(aq) \rightarrow Cu(s) + I_2(s)$ $\quad E^o_{cell} = -0.195$ V Nonspontaneous

(c) Oxidation: $\{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-\} \times 3$ $\quad -E^o = -1.229$ V

Reduction: $\{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)\} \times 4$ $\quad E^o = +0.956$ V

Net: $4NO_3^-(aq) + 4H^+(aq) \rightarrow 3O_2(g) + 4NO(g) + 2H_2O(l)$ $\quad E^o_{cell} = -0.273$ V
Nonspontaneous

(d) Oxidation: $Cl^-(aq) + 2OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l) + 2e^-$ $\quad -E^o = -0.890$ V

Reduction: $O_3(g) + H_2O(l) + 2e^- \rightarrow O_2(g) + 2OH^-(aq)$ $\quad E^o = +1.246$ V

Net: $Cl^-(aq) + O_3(g) \rightarrow OCl^-(aq) + O_2(g)$ (basic solution) $\quad E^o_{cell} = +0.356$ V
Spontaneous

12. **(M)** It is more difficult to oxidize Hg(l) to Hg_2^{2+} $(-0.797\,V)$ than it is to reduce H^+ to H_2 (0.000 V); Hg(l) will not dissolve in 1 M HCl. The standard reduction of nitrate ion to NO(g) in acidic solution is strongly spontaneous in acidic media ($+0.956$ V). This can help overcome the reluctance of Hg to be oxidized. Hg(l) will react with and dissolve in the $HNO_3(aq)$.

13. **(M) (a)** Oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $\quad -E^o = +2.356$ V

Reduction: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $\quad E^o = -0.125$ V

Net: $Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$ $\quad E^o_{cell} = +2.231$ V

This reaction occurs to a significant extent.

(b) Oxidation: $\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-}$ $\qquad -E^{\mathrm{o}} = +0.137\,\mathrm{V}$

Reduction: $2\,\mathrm{H^+(aq)} \rightarrow \mathrm{H_2(g)}$ $\qquad E^{\mathrm{o}} = 0.000\,\mathrm{V}$

Net: $\mathrm{Sn(s)} + 2\,\mathrm{H^+(aq)} \rightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}$ $\qquad E^{\mathrm{o}}_{\mathrm{cell}} = +0.137\,\mathrm{V}$

This reaction will occur to a significant extent.

(c) Oxidation: $\mathrm{Sn^{2+}(aq)} \rightarrow \mathrm{Sn^{4+}(aq)} + 2\,\mathrm{e^-}$ $\qquad -E^{\mathrm{o}} = -0.154\,\mathrm{V}$

Reduction: $\mathrm{SO_4{}^{2-}(aq)} + 4\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{SO_2(g)} + 2\mathrm{H_2O(l)}$ $\qquad E^{\mathrm{o}} = +0.17\,\mathrm{V}$

Net: $\mathrm{Sn^{2+}(aq)} + \mathrm{SO_4{}^{2-}(aq)} + 4\,\mathrm{H^+(aq)} \rightarrow \mathrm{Sn^{4+}(aq)} + \mathrm{SO_2(g)} + 2\mathrm{H_2O(l)}$ $\qquad E^{\mathrm{o}}_{\mathrm{cell}} = +\,0.02\,\mathrm{V}$

This reaction will occur, but not to a large extent.

(d) Oxidation: $\{\mathrm{H_2O_2(aq)} \rightarrow \mathrm{O_2(g)} + 2\,\mathrm{H^+(aq)} + 2\mathrm{e^-}\} \ \times 5$ $\qquad -E^{\mathrm{o}} = -0.695\,\mathrm{V}$

Reduction: $\{\mathrm{MnO_4{}^-(aq)} + 8\mathrm{H^+(aq)} + 5\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}(aq)} + 4\mathrm{H_2O(l)}\} \ \times 2$ $\qquad E^{\mathrm{o}} = +1.51\,\mathrm{V}$

Net: $5\mathrm{H_2O_2(aq)} + 2\mathrm{MnO_4{}^-(aq)} + 6\mathrm{H^+(aq)} \rightarrow 5\mathrm{O_2(g)} + 2\mathrm{Mn^{2+}(aq)} + 8\mathrm{H_2O(l)}$ $\qquad E^{\mathrm{o}}_{\mathrm{cell}} = +0.82\,\mathrm{V}$

This reaction will occur to a significant extent.

(e) Oxidation: $2\,\mathrm{Br^-(aq)} \rightarrow \mathrm{Br_2(aq)} + 2\,\mathrm{e^-}$ $\qquad -E^{\mathrm{o}} = -1.065\,\mathrm{V}$

Reduction: $\mathrm{I_2(s)} + 2\mathrm{e^-} \rightarrow 2\,\mathrm{I^-(aq)}$ $\qquad E^{\mathrm{o}} = +0.535\,\mathrm{V}$

Net: $2\,\mathrm{Br^-(aq)} + \mathrm{I_2(s)} \rightarrow \mathrm{Br_2(aq)} + 2\,\mathrm{I^-(aq)}$ $\qquad E^{\mathrm{o}}_{\mathrm{cell}} = -0.530\,\mathrm{V}$

This reaction will not occur to a significant extent.

14. **(M)** In this problem we are asked to determine whether the electrochemical reaction between Co(s) and $\mathrm{Ni^{2+}(aq)}$ to yield $\mathrm{Co^{2+}(aq)}$ + Ni(s) will proceed to completion based on the known E^{o}_{cell} value. This question can be answered by simply determining the equilibrium constant.

Stepwise approach

First comment on the value of E^{o}_{cell}:

The relatively small positive value of $E^{\mathrm{o}}_{\mathrm{cell}}$ for the reaction indicates that the reaction will proceed in the forward direction, but will stop short of completion. A much larger positive value of $E^{\mathrm{o}}_{\mathrm{cell}}$ would be necessary before we would conclude that the reaction goes to completion.

Calculate the equilibrium constant for the reaction using $E^{\mathrm{o}}_{\mathrm{cell}} = \dfrac{0.0257}{n} \ln K_{\mathrm{eq}}$:

$$E^{\mathrm{o}}_{\mathrm{cell}} = \frac{0.0257}{n} \ln K_{\mathrm{eq}} \qquad \ln K_{\mathrm{eq}} = \frac{n \times E^{\mathrm{o}}_{\mathrm{cell}}}{0.0257} = \frac{2 \times 0.02}{0.0257} = 2$$

$$K_{\mathrm{eq}} = \mathrm{e}^2 = 7$$

Comment on the value of K_{eq}:

K_{eq} is small. A value of 1000 or more is needed before we can describe the reaction as one that goes to completion.

Conversion pathway approach:

$$E^{\circ}_{\text{cell}} = \frac{0.0257}{n}\ln K_{\text{eq}}$$

$$\ln K_{\text{eq}} = \frac{n\times E^{\circ}_{\text{cell}}}{0.0257}$$

$$K_{eq} = e^{\frac{n\times E^{\circ}_{\text{cell}}}{0.0257}} = e^{\frac{2\times 0.02}{0.0257}} = 7$$

K_{eq} is too small. The reaction does not go to completion.

15. **(M)** If E°_{cell} is positive, the reaction will occur. For the reduction of $Cr_2O_7^{2-}$ to $Cr^{3+}(aq)$:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\circ} = +1.33\,V$$

If the oxidation has $-E^{\circ}$ smaller (more negative) than $-1.33\,V$, the oxidation will not occur.

(a) $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^- \qquad -E^{\circ} = -0.154\,V$

Hence, $Sn^{2+}(aq)$ can be oxidized to $Sn^{4+}(aq)$ by $Cr_2O_7^{2-}(aq)$.

(b) $I_2(s) + 6H_2O(l) \rightarrow 2IO_3^-(aq) + 12H^+(aq) + 10e^- \qquad -E^{\circ} = -1.20\,V$

$I_2(s)$ can be oxidized to $IO_3^-(aq)$ by $Cr_2O_7^{2-}(aq)$.

(c) $Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^- \qquad -E^{\circ} = -1.51\,V$

$Mn^{2+}(aq)$ cannot be oxidized to $MnO_4^-(aq)$ by $Cr_2O_7^{2-}(aq)$.

16. **(M)** In order to reduce Eu^{3+} to Eu^{2+}, a stronger reducing agent than Eu^{2+} is required. From the list given, Al(s) and $H_2C_2O_4(aq)$ are stronger reducing agents. This is determined by looking at the reduction potentials (-1.676 V for Al^{3+}/Al(s) and -0.49 V for CO_2, $H^+/H_2C_2O_4(aq)$), are more negative than -0.43 V). Co(s), H_2O_2 and Ag(s) are not strong enough reducing agents for this process. A quick look at their reduction potentials shows that they all have more positive reduction potentials than that for Eu^{3+} to Eu^{2+} (-0.277 V for Co^{2+}/Co(s), +0.695 V for O_2, $H^+/H_2O_2(aq)$ and +0.800 V for Ag^+/Ag(s).

17. **(M) (a)** Oxidation: $\{Ag(s) \rightarrow Ag^+(aq) + e^-\} \times 3 \qquad -E^{\circ} = -0.800\,V$

Reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l) \qquad E^{\circ} = +0.956\,V$

Net: $3Ag(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow 3Ag^+(aq) + NO(g) + 2H_2O(l) \qquad E^{\circ}_{\text{cell}} = +0.156\,V$

Ag(s) reacts with $HNO_3(aq)$ to form a solution of $AgNO_3(aq)$.

(b) Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad -E^{\circ} = +0.763\,V$

Reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^{\circ} = 0.000\,V$

Net: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E^{\circ}_{\text{cell}} = +0.763\,V$

Zn(s) reacts with HI(aq) to form a solution of $ZnI_2(aq)$.

(c) Oxidation: $\mathrm{Au(s) \rightarrow Au^{3+}(aq) + 3e^-}$ $-E^\circ = -1.52\,\mathrm{V}$
Reduction: $\mathrm{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)}$ $E^\circ = +0.956\,\mathrm{V}$

Net: $\mathrm{Au(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow Au^{3+}(aq) + NO(g) + 2\ H_2O(l)}$; $E^\circ_{\mathrm{cell}} = -0.56\,\mathrm{V}$
Au(s) does not react with 1.00 M $\mathrm{HNO_3(aq)}$.

18. **(M)** In each case, we determine whether E^o_{cell} is greater than zero; if so, the reaction will occur.

(a) Oxidation: $\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-}$ $-E^\circ = 0.440\,\mathrm{V}$
Reduction: $\mathrm{Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)}$ $E^\circ = -0.763\,\mathrm{V}$

Net: $\mathrm{Fe(s) + Zn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Zn(s)}$ $E^\circ_{\mathrm{cell}} = -0.323\,\mathrm{V}$
The reaction is not spontaneous under standard conditions as written

(b) Oxidation: $\mathrm{\{2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-\}} \times 5$ $-E^\circ = -1.358\,\mathrm{V}$
Reduction: $\mathrm{\{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)\}} \times 2$; $E^\circ = 1.51\,\mathrm{V}$

Net: $\mathrm{10Cl^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)}$
$E^\circ_{\mathrm{cell}} = +0.15\,\mathrm{V}$. The reaction is spontaneous under standard conditions as written.

(c) Oxidation: $\mathrm{\{Ag(s) \rightarrow Ag^+(aq) + e^-\}} \times 2$ $-E^\circ = -0.800\,\mathrm{V}$
Reduction: $\mathrm{2H^+(aq) + 2e^- \rightarrow H_2(g)}$ $E^\circ = +0.000\,\mathrm{V}$

Net: $\mathrm{2Ag(s) + 2H^+(aq) \rightarrow 2Ag^+(aq) + H_2(g)}$ $E^\circ_{\mathrm{cell}} = -0.800\,\mathrm{V}$
The reaction is not spontaneous under standard conditions as written.

(d) Oxidation: $\mathrm{\{2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-\}} \times 2$ $-E^\circ = -1.358\,\mathrm{V}$
Reduction: $\mathrm{O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)}$ $E^\circ = +1.229\,\mathrm{V}$

Net: $\mathrm{4Cl^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(l)}$ $E^\circ_{\mathrm{cell}} = -0.129\,\mathrm{V}$
The reaction is not spontaneous under standard conditions as written.

Galvanic Cells

19. **(M) (a)** Oxidation: $\mathrm{\{Al(s) \rightarrow Al^{3+}(aq) + 3e^-\}} \times 2$ $-E^\circ = +1.676\ \mathrm{V}$
Reduction: $\mathrm{\{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)\}} \times 3$ $E^\circ = -0.137\ \mathrm{V}$

Net: $\mathrm{2\ Al(s) + 3\ Sn^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Sn(s)}$ $E^\circ_{\mathrm{cell}} = +1.539\ \mathrm{V}$

(b) Oxidation: $\mathrm{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-}$ $-E^\circ = -0.771\ \mathrm{V}$
Reduction: $\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$ $E^\circ = +0.800\ \mathrm{V}$

Net: $\mathrm{Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)}$ $E^\circ_{\mathrm{cell}} = +0.029\ \mathrm{V}$

(c) Oxidation: $\mathrm{\{Cr(s) \rightarrow Cr^{2+}(aq) + 2e^-\}} \times 3$ $-E^\circ = +0.90\,\mathrm{V}$

Reduction: $\{Au^{3+}(aq)+3e^{-} \rightarrow Au(s)\} \times 2$ $\quad E^{o} = 1.52V$

Net: $3Cr(s)+2Au^{3+}(aq) \rightarrow 3Cr^{2+}(aq)+2Au(s)$ $\quad E^{o}_{cell} = 2.42V$

(d) Oxidation: $2H_2O(l) \rightarrow O_2(g)+4H^{+}(aq)+4e^{-}$ $\quad -E^{o} = -1.229V$

Reduction: $O_2(g)+2H_2O(l)+4e^{-} \rightarrow 4OH^{-}(aq)$ $\quad E^{o} = +0.401V$

Net: $H_2O(l) \rightarrow H^{+}(aq)+OH^{-}(aq)$ $\quad E^{o}_{cell} = -0.828V$

20. **(M)** In this problem we are asked to write the half-reactions, balanced chemical equation and determine E^{o}_{cell} for a series of electrochemical cells.

(a) *Stepwise approach*

First write the oxidation and reduction half-reactions and find E_o values from Appendix D:

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq)+2e^{-}$ $\quad -E^{o} = -0.340$ V

Reduction: $Cu^{+}(aq)+e^{-} \rightarrow Cu(s)$ $\quad E^{o} = +0.520$ V

In order to obtain balanced net equation, the reduction half-reaction needs to be multiplied by 2:

$2Cu^{+}(aq)+2e^{-} \rightarrow 2Cu(s)$

Add the two half-reactions to obtain the net reaction:

$Cu(s) \rightarrow Cu^{2+}(aq)+2e^{-}$

$2Cu^{+}(aq)+2e^{-} \rightarrow 2Cu(s)$

Net: $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq)+Cu(s)$

Determine E^{o}_{cell}:

E^{o}_{cell} =-0.340V+0.520V= +0.18 V

Conversion pathway approach:

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq)+2e^{-}$ $\quad -E^{o} = -0.340$ V

Reduction: $\{Cu^{+}(aq)+e^{-} \rightarrow Cu(s)\} \times 2$ $\quad E^{o} = +0.520$ V

Net: $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq)+Cu(s)$ $\quad E^{o}_{cell} = +0.18V$

Follow the same methodology for parts (b), (c), and (d).

(b) Oxidation: $Ag(s)+I^{-}(aq) \rightarrow AgI(s)+e^{-}$ $\quad -E^{o} = +0.152$ V

Reduction: $AgCl(s)+e^{-} \rightarrow Ag(s)+Cl^{-}(aq)$ $\quad E^{o} = +0.2223$ V

Net: $AgCl(s)+I^{-}(aq) \rightarrow AgI(s)+Cl^{-}(aq)$ $\quad E^{o}_{cell} = +0.3743$ V

(c) Oxidation: $\{Ce^{3+}(aq) \rightarrow Ce^{4+}(aq)+e^{-}\} \times 2$ $\quad -E^{o} = -1.76V$

Reduction: $I_2(s)+2e^{-} \rightarrow 2I^{-}(aq)$ $\quad E^{o} = +0.535$ V

Net: $2Ce^{3+}(aq)+I_2(s) \rightarrow 2Ce^{4+}(aq)+2I^{-}(aq)$ $\quad E^{o}_{cell} = -1.225$ V

(d) Oxidation: $\{U(s) \rightarrow U^{3+}(aq)+3e^-\} \times 2$ $-E^o = +1.66V$

Reduction: $\{V^{2+}(aq)+2e^- \rightarrow V(s)\} \times 3$ $E^o = -1.13V$

Net: $2U(s)+3V^{2+}(aq) \rightarrow 2U^{3+}(aq)+3V(s)$ $E^o_{cell} = +0.53$ V

21. **(M)** In each case, we determine whether E^o_{cell} is greater than zero; if so, the reaction will occur.

(a) Oxidation: $H_2(g) \rightarrow 2H^+ + 2e^-(aq)$ $-E^o = 0.000$ V

Reduction: $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ $E^o = 2.866$ V

Net: $H_2(g) + F_2(g) \rightarrow 2H^+(aq) + 2F^-(aq)$ $E^o_{cell} = +2.866$ V

The reaction is spontaneous under standard conditions as written

(b) Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $-E^o = -0.340$ V

Reduction: $Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$; $E^o = -2.92$ V

Net: $Cu(s) + Ba^{2+}(aq) \rightarrow Cu^{2+}(aq) + Ba(s)$ $E^o_{cell} = -3.26$ V .

The reaction is not spontaneous under standard conditions as written.

(c) Oxidation: $\{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-\} \times 2$ $-E^o = -0.771$ V

Reduction: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^o = -0.440$ V

Net: $3Fe^{2+}(aq) \rightarrow Fe(s) + 2Fe^{3+}(aq)$ $E^o_{cell} = -1.211$ V

The reaction is not spontaneous as written.

(d) Oxidation: $2Hg(l) + 2Cl^- \rightarrow Hg_2Cl_2(s) + 2e^-$ $-E^o = -(0.2676)$ V

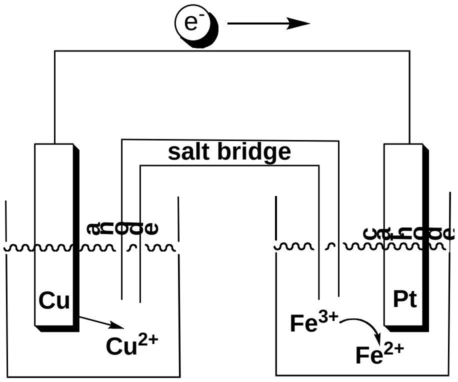
Reduction: $2HgCl_2(aq) + 2e^- \rightarrow Hg_2Cl_2(s) + 2Cl^-(aq)$ $E^o = +0.63$V

Net: $2Hg(l) + 2HgCl_2(aq) \rightarrow 2Hg_2Cl_2(s)$ $E^o_{cell} = +0.36$ V

(divide by 2 to get $Hg(l) + HgCl_2(aq) \rightarrow Hg_2Cl_2(s)$)

The reaction is spontaneous under standard conditions as written.

22. (M) (a)

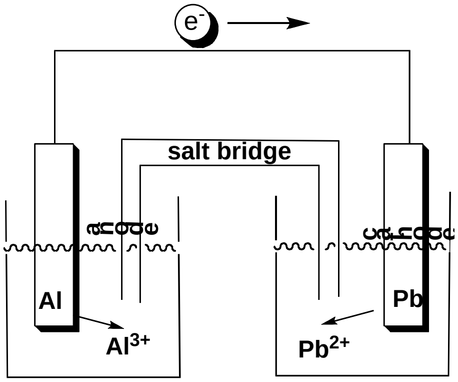


Anode, oxidation: $\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-}$ $\qquad -E^{\circ} = -0.340\,\mathrm{V}$

Cathode, reduction: $\{\mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)}\} \times 2\,;\ E^{\circ} = +0.771\,\mathrm{V}$

Net: $\mathrm{Cu(s) + 2\,Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2\,Fe^{2+}(aq)}$ $\qquad E^{\circ}_{\mathrm{cell}} = +0.431\,\mathrm{V}$

(b)

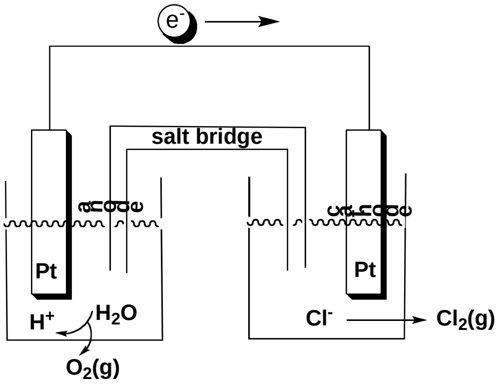


Anode, oxidation: $\{\mathrm{Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-}\} \times 2$ $\qquad -E^{\circ} = +1.676\,\mathrm{V}$

Cathode, reduction: $\{\mathrm{Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)}\} \times 3\,;$ $\qquad E^{\circ} = -0.125\ \mathrm{V}$

Net: $\mathrm{2Al(s) + 3Pb^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Pb(s)}$ $\qquad E^{\circ}_{\mathrm{cell}} = +1.551\ \mathrm{V}$

(c)

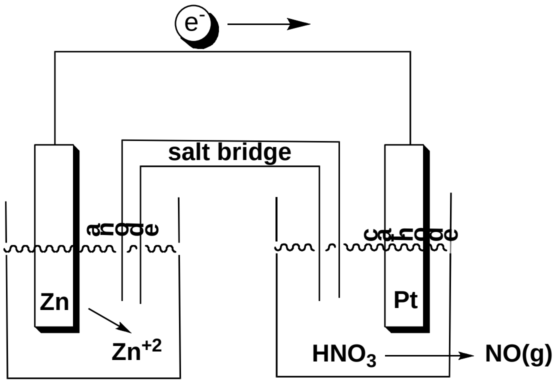


Anode, oxidation: $\mathrm{2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-}$ $\qquad -E^{\circ} = -1.229\,\mathrm{V}$

Cathode, reduction: $\{\mathrm{Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)}\} \times 2$ $\quad E^{\circ} = +1.358\,\mathrm{V}$

Net: $2\,H_2O(l) + 2\,Cl_2(g) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,Cl^-(aq) \quad E^o_{cell} = +0.129\,V$

(d)



Anode, oxidation: $\{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-\} \quad \times 3 \qquad -E^o = +0.763\,V$

Cathode, reduction: $\{NO_3^-(aq) + 4\,H^+(aq) + 3e^- \rightarrow NO(g) + 2\,H_2O(l)\} \times 2; \quad E^o = +0.956\ V$

Net: $3Zn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Zn^{2+}(aq) + 2NO(g) + 4H_2O(l) \quad E^o_{cell} = +1.719\,V$

23. **(M)** In each case, we determine whether E^o_{cell} is greater than zero; if so, the reaction will occur.

(a) Oxidation: $Ag(s) \rightarrow Ag^+(aq) + e^- \qquad -E^o = -0.800\,V$

Reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^o = +0.771\ V$

Net: $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq) \qquad E^o_{cell} = -0.029\,V$

The reaction is not spontaneous under standard conditions as written.

(b) Oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \qquad -E^o = +0.137\,V$

Reduction: $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{+2}(aq) \qquad E^o = +0.154\ V$

Net: $Sn(s) + Sn^{4+}(aq) \rightarrow 2Sn^{2+}(aq) \qquad E^o_{cell} = +0.291\,V$

The reaction is spontaneous under standard conditions as written.

(c) Oxidation: $2Br^-(aq) \rightarrow Br_2(l) + 2e^- \qquad -E^o = -1.065\,V$

Reduction: $2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^+(aq) \qquad E^o = +0.630\ V$

Net: $2Br^-(aq) + 2Hg^{2+}(aq) \rightarrow Br_2(l) + Hg_2^+ \qquad E^o_{cell} = -0.435\,V$

The reaction is not spontaneous under standard conditions as written.

(d) Oxidation: $\{NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)\} \times 2 \qquad -E^o = -2.326\,V$

Reduction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^o = +1.563\,V$

Net: $2NO_3^-(aq) + 4H^+(aq) + Zn(s) \rightarrow 2NO_2(g) + 2H_2O(l) + Zn^{2+}(aq) \qquad E^o_{cell} = -0.435\,V$

The reaction is not spontaneous under standard conditions as written.

24. **(M) (a)** $\mathrm{Fe(s)|Fe^{2+}(aq)||Cl^{-}(aq)Cl_2(g)|Pt(s)}$

Oxidation:	$\mathrm{Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^{-}}$	$-E^{o} = +0.440\,\mathrm{V}$
Reduction:	$\mathrm{Cl_2(g) + 2\,e^{-} \rightarrow 2Cl^{-}(aq)}$	$E^{o} = +1.358\,\mathrm{V}$
Net:	$\mathrm{Fe(s) + Cl_2(g) \rightarrow Fe^{2+}(aq) + 2Cl^{-}(aq)}$	$E^{o}_{\mathrm{cell}} = +1.798\ \mathrm{V}$

(b) $\mathrm{Zn(s)|Zn^{2+}(aq)||Ag^{+}(aq)|Ag(s)}$

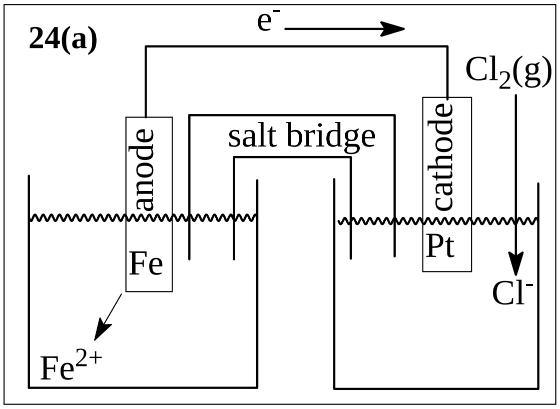
Oxidation:	$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-}}$	$-E^{o} = +0.763\,\mathrm{V}$
Reduction:	$\mathrm{\{Ag^{+}(aq) + e^{-} \rightarrow Ag(s)\}} \quad \times 2$	$E^{o} = +0.800\,\mathrm{V}$
Net:	$\mathrm{Zn(s) + 2\,Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)}$	$E^{o}_{\mathrm{cell}} = +1.563\,\mathrm{V}$

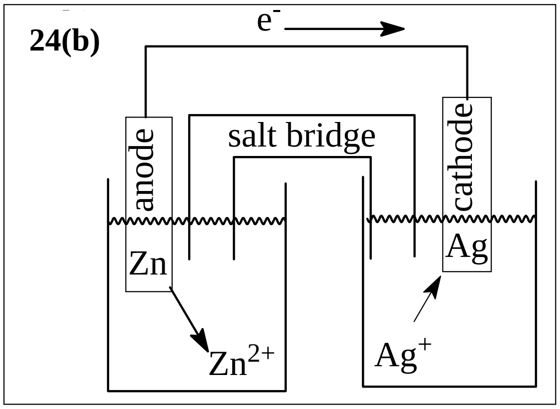
(c) $\mathrm{Pt(s)|Cu^{+}(aq),Cu^{2+}(aq)||Cu^{+}(aq)|Cu(s)}$

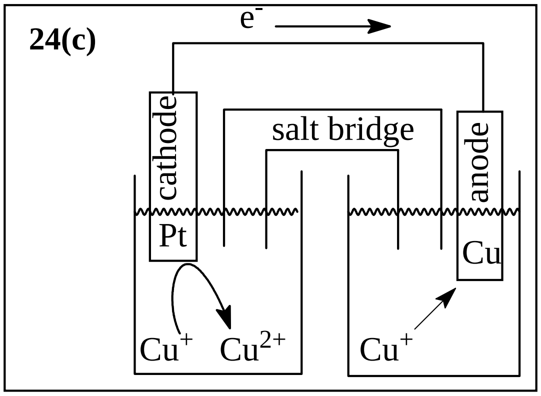
Oxidation:	$\mathrm{Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + e^{-}}$	$-E^{o} = -0.159\,\mathrm{V}$
Reduction:	$\mathrm{Cu^{+}(aq) + e^{-} \rightarrow Cu(s)}$	$E^{o} = +0.520\,\mathrm{V}$
Net:	$\mathrm{2\,Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)}$	$E^{o}_{\mathrm{cell}} = +0.361\,\mathrm{V}$

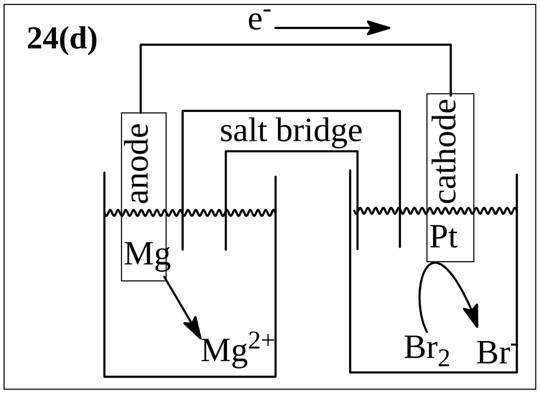
(d) $\mathrm{Mg(s)|Mg^{2+}(aq)||Br^{-}(aq)Br_2(l)|Pt(s)}$

Oxidation:	$\mathrm{Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^{-}}$	$-E^{o} = +2.356\,\mathrm{V}$
Reduction:	$\mathrm{Br_2(l) + 2\,e^{-} \rightarrow 2\,Br^{-}(aq)}$	$E^{o} = +1.065\,\mathrm{V}$
Net:	$\mathrm{Mg(s) + Br_2(l) \rightarrow Mg^{2+}(aq) + 2\,Br^{-}(aq)}$	$E^{o}_{\mathrm{cell}} = +3.421\,\mathrm{V}$









ΔG^{o}, E^{o}_{cell}, and K

25. **(M) (a)** Oxidation: $\{Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}\} \times 2$ $\quad -E^{o} = +1.676\,V$

Reduction: $\{Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)\} \times 3$ $\quad E^{o} = +0.337\,V$

Net: $2\,Al(s) + 3\,Cu^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Cu(s)$ $\quad E^{o}_{cell} = +2.013\,V$

$$\Delta G^{o} = -nFE^{o}_{cell} = -(6\text{ mol e}^{-})(96,485\text{ C/mol e}^{-})(2.013\,V)$$

$$\Delta G^{o} = -1.165\times10^{6}\text{ J} = -1.165\times10^{3}\text{ kJ}$$

(b) Oxidation: $\{2\,I^{-}(aq) \rightarrow I_2(s) + 2\,e^{-}\} \times 2$ $\quad -E^{o} = -0.535\text{ V}$

Reduction: $O_2(g) + 4\,H^{+}(aq) + 4\,e^{-} \rightarrow 2\,H_2O(l)$ $\quad E^{o} = +1.229\text{ V}$

Net: $4\,I^{-}(aq) + O_2(g) + 4\,H^{+}(aq) \rightarrow 2\,I_2(s) + 2\,H_2O(l)$ $\quad E^{o}_{cell} = +0.694\text{ V}$

$$\Delta G^{o} = -nFE^{o}_{cell} = -(4\text{ mol e}^{-})(96,485\text{ C/mol e}^{-})(0.694\text{ V}) = -2.68\times10^{5}\text{ J} = -268\text{ kJ}$$

(c) Oxidation: $\{Ag(s) \rightarrow Ag^{+}(aq) + e^{-}\} \times 6$ $\quad -E^{o} = -0.800\text{ V}$

Reduction: $Cr_2O_7{}^{2-}(aq) + 14\,H^{+}(aq) + 6\,e^{-} \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$ $\quad E^{o} = +1.33\,V$

Net: $6\,Ag(s) + Cr_2O_7{}^{2-}(aq) + 14\,H^{+}(aq) \rightarrow 6\,Ag^{+}(aq) + 2\,Cr^{3+}(aq) + 7\,H_2O(l)$

$$E^{o}_{cell} = -0.800\,V + 1.33\,V = +0.53\,V$$

$$\Delta G^{o} = -nFE^{o}_{cell} = -(6\text{mol e}^{-})(96{,}485\text{C/mol e}^{-})(0.53\,V) = -3.1\times10^{5}\text{ J} = -3.1\times10^{2}\text{ kJ}$$

26. **(M)** In this problem we need to write the equilibrium constant expression for a set of redox reactions and determine the value of K at 25 °C. We proceed by calculating E^{o}_{cell} from standard electrode reduction potentials (Table 20.1). Then we use the expression $\Delta G^{o} = -nFE^{o}_{cell} = -RT\ln K$ to calculate K.

(a)

Stepwise approach:

Determine E^{o}_{cell} from standard electrode reduction potentials (Table 20.1):

Oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$ $\quad -E^{o} = 0.257\text{ V}$

Reduction: $\{V^{3+}(aq) + e^{-} \rightarrow V^{2+}(aq)\} \times 2$ $\quad E^{o} = -0.255\text{ V}$

Net: $Ni(s) + 2V^{3+}(aq) \rightarrow Ni^{2+}(aq) + 2V^{2+}(aq)$ $\quad E^{o}_{cell} = 0.003\,V$

Use the expression $\Delta G^{o} = -nFE^{o}_{cell} = -RT\ln K$ to calculate K:

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -RT\ln K;$$

$$\Delta G^{o} = -2 mol e^{-} \times 96485\frac{C}{mol} \times 0.003V = -578.9J$$

$$\Delta G^{o} = -RT\ln K \Rightarrow -578.9J = -8.314JK^{-1}mol^{-1} \times 298.15K\ln K$$

$$\ln K = 0.233 \Rightarrow K = e^{0.233} = 1.26$$

$$K = 1.26 = \frac{\left[\text{Ni}^{2+}\right]\left[\text{V}^{2+}\right]^{2}}{\left[\text{V}^{3+}\right]^{2}}$$

Conversion pathway approach:

Determine E^{o}_{cell} from standard electrode reduction potentials (Table 20.1):

Oxidation: $\text{Ni(s)} \rightarrow \text{Ni}^{2+}\text{(aq)+2e}^{-}$ $\quad -E^{\circ} = 0.257\text{ V}$

Reduction: $\{\text{V}^{3+}\text{(aq)+e}^{-} \rightarrow \text{V}^{2+}\text{(aq)}\} \times 2$ $\quad E^{\circ} = -0.255\text{ V}$

Net: $\text{Ni(s)+2V}^{3+}\text{(aq)} \rightarrow \text{Ni}^{2+}\text{(aq)+2V}^{2+}\text{(aq)}$ $\quad E^{\circ}_{\text{cell}}\text{=0.003V}$

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -RT\ln K \Rightarrow \ln K_{eq} = \frac{nFE^{o}_{cell}}{RT} = \frac{n \times 96485Cmol^{-1}}{8.314JK^{-1}mol^{-1} \times 298.15K}E^{o}_{cell}$$

$$\ln K_{\text{eq}} = \frac{n}{0.0257}E^{\circ}_{\text{cell}} = \frac{2\text{ mol e}^{-} \times 0.003V}{0.0257} = 0.233$$

$$K_{\text{eq}} = e^{0.233} = 1.26 = \frac{\left[\text{Ni}^{2+}\right]\left[\text{V}^{2+}\right]^{2}}{\left[\text{V}^{3+}\right]^{2}}$$

Similar methodology can be used for parts (b) and (c)

(b) Oxidation: $2\text{Cl}^{-}\left(\text{aq}\right) \rightarrow \text{Cl}_2\left(\text{g}\right) + 2\text{ e}^{-}$ $\quad -E^{\circ} = -1.358\text{ V}$

Reduction: $\text{MnO}_2\left(\text{s}\right) + 4\text{H}^{+}\left(\text{aq}\right) + 2\text{e}^{-} \rightarrow \text{Mn}^{2+}\left(\text{aq}\right) + 2\text{H}_2\text{O(l)}$ $\quad E^{\circ} = +1.23\text{V}$

Net: $2\text{ Cl}^{-}\left(\text{aq}\right) + \text{MnO}_2\left(\text{s}\right) + 4\text{ H}^{+}\left(\text{aq}\right) \rightarrow \text{Mn}^{2+}\left(\text{aq}\right) + \text{Cl}_2\left(\text{g}\right) + 2\text{ H}_2\text{O(l)}$ $\quad E^{\circ}_{\text{cell}} = -0.13\text{V}$

$$\ln K_{\text{eq}} = \frac{2\text{ mol e}^{-} \times \left(-0.13\text{ V}\right)}{0.0257} = -10._{1};\quad K_{\text{eq}} = \text{e}^{-10.1} = 4 \times 10^{-5} = \frac{\left[\text{Mn}^{2+}\right]P\{\text{Cl}_2\left(\text{g}\right)\}}{\left[\text{Cl}^{-}\right]^{2}\left[\text{H}^{+}\right]^{4}}$$

(c) Oxidation: $4\text{ OH}^{-}\left(\text{aq}\right) \rightarrow \text{O}_2\left(\text{g}\right) + 2\text{H}_2\text{O(l)} + 4\text{ e}^{-}$ $\quad -E^{\circ} = -0.401\text{ V}$

Reduction: $\{\text{OCl}^{-}\text{(aq)+H}_2\text{O(l)+2e}^{-} \rightarrow \text{Cl}^{-}\text{(aq)+2OH}^{-}\} \times 2$ $\quad E^{\circ} = +0.890\text{ V}$

Net: $2\text{OCI}^{-}\text{(aq)} \longrightarrow 2\text{CI}^{-}\text{(aq)} + \text{O}_2\text{(g)}$ $\quad E^{\circ}_{\text{cell}} = +0.489\text{ V}$

$$\ln K_{\text{eq}} = \frac{4\text{ mol e}^{-}(0.489\text{ V})}{0.0257} = 76.1 \qquad K_{\text{eq}} = \text{e}^{76.1} = 1 \times 10^{33} = \frac{\left[\text{Cl}^{-}\right]^{2}\text{P}\left\{\text{O}_2\text{(g)}\right\}}{\left[\text{OCl}^{-}\right]^{2}}$$

27. **(M)** First calculate E^{o}_{cell} from standard electrode reduction potentials (Table 20.1). Then use $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -RT\ln K$ to determine ΔG^{o} and K.

(a)

$$\text{Oxidation: } \{Ce^{3+}(aq) \rightarrow Ce^{4+}(aq) + e^-\} \times 5 \qquad -E^o = -1.61\text{ V}$$

$$\text{Reduction: } \mathrm{MnO_4^-(aq)+8H^+(aq)+5e^- \rightarrow Mn^{2+}(aq)+4H_2O(l)} \qquad E^o = +1.51\text{V}$$

$$\text{Net: } \mathrm{MnO_4^-(aq)+8H^+(aq)+5Ce^{3+}(aq) \rightarrow Mn^{2+}(aq)+4H_2O(l)+5Ce^{4+}(aq)} \quad E^o_{cell} = -0.100V$$

(b)

$$\Delta G^o = -nFE^o_{\text{cell}} = -RT\ln K;$$

$$\Delta G^o = -5 \times 96485\frac{\text{C}}{\text{mol}} \times (-0.100V) = 48.24\text{kJmol}^{-1}$$

(c)

$$\Delta G^o = -RT\ln K \Rightarrow 48.24 \times 1000\text{Jmol}^{-1} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K}\ln K$$

$$\ln K = -19.46 \Rightarrow K = e^{-19.46} = 3.5 \times 10^{-9}$$

(d) Since K is very small the reaction will not go to completion.

28. **(M)** First calculate E^o_{cell} from standard electrode reduction potentials (Table 20.1). Then use $\Delta G^o = -nFE^o_{\text{cell}} = -RT\ln K$ to determine ΔG^o and K.

(a)

$$\text{Oxidation: } \mathrm{Pb^{2+}(aq) \rightarrow Pb^{4+}(aq)+2e^-} \qquad E_o = -0.180V$$

$$\text{Reduction: } \mathrm{Sn^{4+}(aq)+2e^- \rightarrow Sn^{2+}(aq)} \qquad E_o = +0.154V$$

$$\text{Net: } \mathrm{Pb^{2+}(aq)+Sn^{4+}(aq) \rightarrow Pb^{4+}(aq)+Sn^{2+}(aq)} \qquad E^o_{cell} = -0.026V$$

(b) $$\Delta G^o = -nFE^o_{\text{cell}} = -RT\ln K \Rightarrow \quad \Delta G^o = -2 \times 96485\frac{\text{C}}{\text{mol}} \times (-0.026) = 5017\text{Jmol}^{-1}$$

(c)

$$\Delta G^o = -RT\ln K \Rightarrow 5017\text{Jmol}^{-1} = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K}\ln K$$

$$\ln K = -2.02 \Rightarrow K = e^{-2.02} = 0.132$$

(d) The value of K is small and the reaction does not go to completion.

29. **(M) (a)** A negative value of E^o_{cell} (-0.0050 V) indicates that $\Delta G^o = -nFE^o_{\text{cell}}$ is positive which in turn indicates that K_{eq} is less than one $\left(K_{\text{eq}} < 1.00\right)$; $\Delta G^o = -RT\ln K_{\text{eq}}$.

$$K_{\text{eq}} = \frac{\left[\text{Cu}^{2+}\right]^2\left[\text{Sn}^{2+}\right]}{\left[\text{Cu}^{+}\right]^2\left[\text{Sn}^{4+}\right]}$$

Thus, when all concentrations are the same, the ion product, *Q*, equals 1.00. From the negative standard cell potential, it is clear that K_{eq} must be (slightly) less than one. Therefore, all the concentrations cannot be 0.500 M at the same time.

(b) In order to establish equilibrium, that is, to have the ion product become less than 1.00, and equal the equilibrium constant, the concentrations of the products must decrease and those of the reactants must increase. A net reaction to the left (towards the reactants) will occur.

30. **(D) (a)** First we must calculate the value of the equilibrium constant from the standard cell potential.

$$E^{\circ}_{\text{cell}} = \frac{0.0257}{n}\ln K_{\text{eq}};\ \ln K_{\text{eq}} = \frac{nE^{\circ}_{\text{cell}}}{0.0257} = \frac{2\text{ mol e}^- \times (-0.017)\text{ V}}{0.0257} = -1.32$$

$$K_{\text{eq}} = e^{-1.32} = 0.266$$

To determine if the described solution is possible, we compare

K_{eq} with Q. Now $K_{\text{eq}} = \dfrac{\left[\text{BrO}_3^-\right]\left[\text{Ce}^{4+}\right]^2}{\left[\text{H}^+\right]^2\left[\text{BrO}_4^-\right]\left[\text{Ce}^{3+}\right]^2}$. Thus, when

$\left[\text{BrO}_4^-\right] = \left[\text{Ce}^{4+}\right] = 0.675\text{ M}$, $\left[\text{BrO}_3^-\right] = \left[\text{Ce}^{3+}\right] = 0.600\text{ M}$ and pH=1 ($\left[\text{H}^+\right]$=0.1M

the ion product, $Q = \dfrac{0.600 \times 0.675^2}{0.1^2 \times 0.675 \times 0.600^2} = 112.5 > 0.266 = K_{\text{eq}}$. Therefore, the described situation can occur

(b) In order to establish equilibrium, that is, to have the ion product (112.5) become equal to 0.266, the equilibrium constant, the concentrations of the reactants must increase and those of the products must decrease. Thus, a net reaction to the left (formation of reactants) will occur.

31. **(M)** Cell reaction: $\text{Zn(s)} + \text{Ag}_2\text{O(s)} \rightarrow \text{ZnO(s)} + 2\text{Ag(s)}$. We assume that the cell operates at 298 K.

$$\begin{aligned}\Delta G^{\circ} &= \Delta G^{\circ}_f\left[\text{ZnO(s)}\right] + 2\Delta G^{\circ}_f\left[\text{Ag(s)}\right] - \Delta G^{\circ}_f\left[\text{Zn(s)}\right] - \Delta G^{\circ}_f\left[\text{Ag}_2\text{O(s)}\right]\\ &= -318.3\text{ kJ/mol} + 2(0.00\text{ kJ/mol}) - 0.00\text{ kJ/mol} - (-11.20\text{ kJ/mol})\\ &= -307.1\text{ kJ/mol} = -nFE^{\circ}_{\text{cell}}\end{aligned}$$

$$E^{\circ}_{\text{cell}} = -\frac{\Delta G^{\circ}}{nF} = -\frac{-307.1\times10^3\text{ J/mol}}{2\text{ mol e}^-/\text{mol rxn} \times 96{,}485\text{ C/mol e}^-} = 1.591\text{ V}$$

32. **(M)** From equation (20.15) we know $n = 12$ and the overall cell reaction. First we must compute value of ΔG°.

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -12\text{ mol e}^- \times \frac{96485\text{ C}}{1\text{ mol e}^-} \times 2.71\text{ V} = -3.14\times10^6\text{ J} = -3.14\times10^3\text{ kJ}$$

Then we will use this value, the balanced equation and values of $\Delta G_f{}^{\circ}$ to calculate $\Delta G^{\circ}_f\left[\text{Al(OH)}_4\right]^-$.

$$4\text{ Al(s)} + 3\text{O}_2\text{(g)} + 6\text{H}_2\text{O(l)} + 4\text{OH}^-\text{(aq)} \rightarrow 4\left[\text{Al(OH)}_4\right]^-\text{(aq)}$$

$$\Delta G^{\circ} = 4\Delta G^{\circ}_f\left[\text{Al(OH)}_4\right]^- - 4\Delta G^{\circ}_f[\text{Al(s)}] - 3\Delta G^{\circ}_f[\text{O}_2\text{(g)}] - 6\Delta G^{\circ}_f[\text{H}_2\text{O(l)}] - 4\Delta G^{\circ}_f[\text{OH}^-\text{(aq)}]$$

$$-3.14\times10^{3}\text{ kJ} = 4\Delta G_f^{o}\left[\text{Al}\left(\text{OH}\right)_4\right]^{-} - 4\times0.00\text{ kJ} - 3\times0.00\text{ kJ} - 6\times\left(-237.1\text{ kJ}\right) - 4\times\left(-157.2\right)$$

$$= 4\Delta G_f^{o}\left[\text{Al}\left(\text{OH}\right)_4\right]^{-} + 2051.4\text{ kJ}$$

$$\Delta G_f^{o}\left[\text{Al}\left(\text{OH}\right)_4\right]^{-} = \left(-3.14\times10^{3}\text{ kJ} - 2051.4\text{ kJ}\right)\div4 = -1.30\times10^{3}\text{ kJ/mol}$$

33. **(D)** From the data provided we can construct the following Latimer diagram.

$$\begin{tikzcd} IrO_2 \arrow[r, "0.223\text{ V}"] & Ir^{3+} \arrow[r, "1.156\text{ V}"] & Ir & \text{(Acidic conditions)} \\ \text{(IV)} & \text{(III)} & \text{(0)} & \end{tikzcd}$$

Latimer diagrams are used to calculate the standard potentials of non-adjacent half-cell couples. Our objective in this question is to calculate the voltage differential between IrO_2 and iridium metal (Ir), which are separated in the diagram by Ir^{3+}. The process basically involves adding two half-reactions to obtain a third half-reaction. The potentials for the two half-reactions cannot, however, simply be added to get the target half-cell voltage because the electrons are not cancelled in the process of adding the two half-reactions. Instead, to find $E°_{1/2\text{ cell}}$ for the target half-reaction, we must use free energy changes, which are additive. To begin, we will balance the relevant half-reactions in acidic solution:

$$4\text{ H}^{+}(aq) + IrO_2(s) + e^{-} \rightarrow Ir^{3+}(aq) + 2\text{ H}_2O(l) \qquad E°_{1/2red(a)} = 0.223\text{ V}$$
$$Ir^{3+}(aq) + 3\text{ e}^{-} \rightarrow Ir(s) \qquad E°_{1/2red(b)} = 1.156\text{V}$$

$$4\text{ H}^{+}(aq) + IrO_2(s) + 4e^{-} \rightarrow 2\text{ H}_2O(l) + Ir(s) \qquad E°_{1/2red(c)} = ?$$

$E°_{1/2red(c)} \neq E°_{1/2red(a)} + E°_{1/2red(b)}$ but $\Delta G°_{(a)} + \Delta G°_{(b)} = \Delta G°_{(c)}$ and $\Delta G° = -nFE°$

$-4F(E°_{1/2red(c)}) = -1F(E°_{1/2red(a)}) + -3F(E°_{1/2red(b)})$

$-4F(E°_{1/2red(c)}) = -1F(0.223) + -3F(1.156)$

$$E°_{1/2red(c)} = \frac{-1F(0.223) + -3F(1.156)}{-4F} = \frac{-1(0.223) + -3(1.156)}{-4} = 0.923\text{ V}$$

In other words, $E°_{(c)}$ is the weighted average of $E°_{(a)}$ and $E°_{(b)}$

34. **(D)** This question will be answered in a manner similar to that used to solve 31. Let's get underway by writing down the appropriate Latimer diagram:

$$\begin{tikzcd} H_2MoO_4 \arrow[r, "0.646\text{ V}"] & MoO_2 \arrow[r, "?\text{ V}"] & Mo^{3+} & \text{(Acidic conditions)} \\ \text{(VI)} \arrow[rr, bend right, "0.428\text{ V}"'] & \text{(IV)} & \text{(III)} & \end{tikzcd}$$

This time we want to calculate the standard voltage change for the 1 e^{-} reduction of MoO_2 to Mo^{3+}. Once again, we must balance the half-cell reactions in acidic solution:

$$H_2MoO_4(aq) + 2\text{ e}^{-} + 2\text{ H}^{+}(aq) \rightarrow MoO_2(s) + 2\text{ H}_2O(l) \qquad E°_{1/2red(a)} = 0.646\text{ V}$$
$$MoO_2(s) + 4\text{ H}^{+}(aq) + 1\text{ e}^{-} \rightarrow Mo^{3+}(aq) + 2\text{ H}_2O(l) \qquad E°_{1/2red(b)} = ?\text{ V}$$

$$H_2MoO_4(aq) + 3\text{ e}^{-} + 6\text{ H}^{+}(aq) \rightarrow Mo^{3+}(aq) + 4\text{ H}_2O(l) \qquad E°_{1/2red(c)} = 0.428\text{ V}$$

So, $-3F(E°_{1/2red(c)}) = -2F(E°_{1/2red(a)}) + -1F(E°_{1/2red(b)})$

$-3F(0.428\text{ V}) = -2F(0.646) + -1F(E°_{1/2red(b)})$

$-1FE°_{1/2red(b)} = -3F(0.428\text{ V}) + 2F(0.646)$

$$E°_{1/2\text{red(c)}} = \frac{-3F(0.428\text{ V}) + 2F(0.646)}{-1F} = 1.284\text{ V} - 1.292\text{ V} = -0.008\text{ V}$$

Concentration Dependence of E_{cell}—the Nernst Equation

35. **(M)** In this problem we are asked to determine the concentration of [Ag^+] ions in electrochemical cell that is not under standard conditions. We proceed by first determining E^o_{cell}. Using the Nerst equation and the known value of E, we can then calculate the concentration of [Ag^+].

Stepwise approach:

First, determine E^o_{cell}:

$$\begin{array}{ll} \text{Oxidation: } \mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\,e^- & -E^o = +0.763\text{ V} \\ \text{Reduction: } \{\mathrm{Ag^+(aq)} + e^- \rightarrow \mathrm{Ag(s)}\} \times 2 & E^o = +0.800\text{ V} \\ \hline \text{Net: } \mathrm{Zn(s)} + 2\,\mathrm{Ag^+(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{Ag(s)} & E^o_{\text{cell}} = +1.563\text{ V} \end{array}$$

Use the Nerst equation and the known value of E to solve for $[Ag]^+$:

$$E = E^o_{\text{cell}} - \frac{0.0592}{n}\log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} = +1.563\text{ V} - \frac{0.0592}{2}\log\frac{1.00}{x^2} = +1.250\text{ V}$$

$$\log\frac{1.00\text{ M}}{x^2} = \frac{-2\times(1.250-1.563)}{0.0592} = 10.6\,; \quad x = \sqrt{2.\underline{5}\times10^{-11}} = 5\times10^{-6}\text{ M}$$

Therefore, [Ag^+] = 5×10^{-6} M

Conversion pathway approach:

$$\begin{array}{ll} \text{Oxidation: } \mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\,e^- & -E^o = +0.763\text{ V} \\ \text{Reduction: } \{\mathrm{Ag^+(aq)} + e^- \rightarrow \mathrm{Ag(s)}\} \times 2 & E^o = +0.800\text{ V} \\ \hline \text{Net: } \mathrm{Zn(s)} + 2\,\mathrm{Ag^+(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{Ag(s)} & E^o_{\text{cell}} = +1.563\text{ V} \end{array}$$

$$E = E^o_{\text{cell}} - \frac{0.0592}{n}\log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} \Rightarrow \log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Ag^+}]^2} = -\frac{n}{0.0592}(E - E^o_{cell})$$

$$[\mathrm{Ag^+}]^2 = \frac{[\mathrm{Zn^{2+}}]}{10^{-\frac{n}{0.0592}(E-E^o_{cell})}} \Rightarrow [\mathrm{Ag^+}] = \sqrt{\frac{[\mathrm{Zn^{2+}}]}{10^{-\frac{n}{0.0592}(E-E^o_{cell})}}}$$

$$[\mathrm{Ag^+}] = \sqrt{\frac{1.00}{10^{-\frac{2}{0.0592}(1.250-1.563)}}} = 5\times10^{-6}$$

36. **(M)** In each case, we employ the equation $E_{\text{cell}} = 0.0592\text{ pH}$.

(a) $E_{\text{cell}} = 0.0592\text{ pH} = 0.0592\times5.25 = 0.311\text{ V}$

(b) $\text{pH} = -\log(0.0103) = 1.987 \quad E_{\text{cell}} = 0.0592\text{ pH} = 0.0592\times1.987 = 0.118\text{ V}$

(c) $$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8\times10^{-5} = \frac{x^2}{0.158-x} \approx \frac{x^2}{0.158}$$

$$x = \sqrt{0.158\times1.8\times10^{-5}} = 1.7\times10^{-3}\ \text{M}$$

$$\text{pH} = -\log(1.7\times10^{-3}) = 2.77$$

$$E_{\text{cell}} = 0.0592\ \text{pH} = 0.0592\times2.77 = 0.164\ \text{V}$$

37. **(M)** We first calculate $E^{\text{o}}_{\text{cell}}$ for each reaction and then use the Nernst equation to calculate E_{cell}.

(a) Oxidation: $\{\text{Al(s)} \rightarrow \text{Al}^{3+}(0.18\ \text{M}) + 3\ e^-\}\ \times2$ $\qquad -E^{\text{o}} = +1.676\ \text{V}$

Reduction: $\{\text{Fe}^{2+}(0.85\,\text{M}) + 2\,e^- \rightarrow \text{Fe(s)}\}\ \times3$ $\qquad E^{\text{o}} = -0.440\ \text{V}$

Net: $2\,\text{Al(s)} + 3\,\text{Fe}^{2+}(0.85\ \text{M}) \rightarrow 2\,\text{Al}^{3+}(0.18\ \text{M}) + 3\text{Fe(s)}$ $\qquad E^{\text{o}}_{\text{cell}} = +1.236\ \text{V}$

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{n}\log\frac{[\text{Al}^{3+}]^2}{[\text{Fe}^{2+}]^3} = 1.236\ \text{V} - \frac{0.0592}{6}\log\frac{(0.18)^2}{(0.85)^3} = 1.249\ \text{V}$$

(b) Oxidation: $\{\text{Ag(s)} \rightarrow \text{Ag}^+(0.34\,\text{M}) + e^-\}\ \times2$ $\qquad -E^{\text{o}} = -0.800\ \text{V}$

Reduction: $\text{Cl}_2(0.55\ \text{atm}) + 2\ e^- \rightarrow 2\ \text{Cl}^-(0.098\ \text{M})$ $\qquad E^{\text{o}} = +1.358\ \text{V}$

Net: $\text{Cl}_2(0.55\,\text{atm}) + 2\ \text{Ag(s)} \rightarrow 2\ \text{Cl}^-(0.098\,\text{M}) + 2\,\text{Ag}^+(0.34\,\text{M})$; $E^{\text{o}}_{\text{cell}} = +0.558\ \text{V}$

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} = \frac{0.0592}{n}\log\frac{[\text{Cl}^-]^2[\text{Ag}^+]^2}{P\{\text{Cl}_2(\text{g})\}} = +0.558 - \frac{0.0592}{2}\log\frac{(0.34)^2(0.098)^2}{0.55} = +0.638\ \text{V}$$

38. **(M) (a)** Oxidation: $\text{Mn(s)} \rightarrow \text{Mn}^{2+}(0.40\,\text{M}) + 2\,e^-$ $\qquad -E^{\text{o}} = +1.18\ \text{V}$

Reduction: $\{\text{Cr}^{3+}(0.35\,\text{M}) + 1e^- \rightarrow \text{Cr}^{2+}(0.25\ \text{M})\}\ \times2$ $\qquad E^{\text{o}} = -0.424\ \text{V}$

Net: $2\,\text{Cr}^{3+}(0.35\,\text{M}) + \text{Mn(s)} \rightarrow 2\,\text{Cr}^{2+}(0.25\,\text{M}) + \text{Mn}^{2+}(0.40\,\text{M})$ $\qquad E^{\text{o}}_{\text{cell}} = +0.76\ \text{V}$

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{n}\log\frac{[\text{Cr}^{2+}]^2[\text{Mn}^{2+}]}{[\text{Cr}^{3+}]^2} = +0.76\ \text{V} - \frac{0.0592}{2}\log\frac{(0.25)^2(0.40)}{(0.35)^2} = +0.78\ \text{V}$$

(b) Oxidation: $\{\text{Mg(s)} \rightarrow \text{Mg}^{2+}(0.016\text{M}) + 2e^-\}\ \times3$ $\qquad -E^{\text{o}} = +2.356\ \text{V}$

Reduction: $\{[\text{Al(OH)}_4]^-(0.25\text{M}) + 3\ e^- \rightarrow 4\text{OH}^-(0.042\ \text{M}) + \text{Al(s)}\}\times 2$; $E^{\text{o}} = -2.310\ \text{V}$

Net: $3\ \text{Mg(s)} + 2[\text{Al(OH)}_4]^-(0.25\text{M}) \rightarrow 3\text{Mg}^{2+}(0.016\ \text{M}) + 8\text{OH}^-(0.042\text{M}) + 2\text{Al(s)}$;

$E^{\text{o}}_{\text{cell}} = +0.046\ \text{V}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{6}\log\frac{\left[\text{Mg}^{2+}\right]^3\left[\text{OH}^-\right]^8}{\left[\left[\text{Al}(\text{OH})_4\right]^-\right]^2} = +0.046 - \frac{0.0592}{6}\log\frac{(0.016)^3(0.042)^8}{(0.25)^2}$$
$$= 0.046\text{ V} + 0.150\text{ V} = 0.196\text{ V}$$

39. **(M)** All these observations can be understood in terms of the procedure we use to balance half-equations: the ion—electron method.

(a) The reactions for which *E* depends on pH are those that contain either $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ in the balanced half-equation. These reactions involve oxoacids and oxoanions whose central atom changes oxidation state.

(b) $\text{H}^+(\text{aq})$will inevitably be on the left side of the reduction of an oxoanion because reduction is accompanied by not only a decrease in oxidation state, but also by the loss of oxygen atoms, as in $\text{ClO}_3{}^- \rightarrow \text{ClO}_2{}^-$, $\text{SO}_4{}^{2-} \rightarrow \text{SO}_2$, and $\text{NO}_3{}^- \rightarrow \text{NO}$. These oxygen atoms appear on the right-hand side as H_2O molecules. The hydrogens that are added to the right-hand side with the water molecules are then balanced with $\text{H}^+(\text{aq})$ on the left-hand side.

(c) If a half-reaction with $\text{H}^+(\text{aq})$ ions present is transferred to basic solution, it may be re-balanced by adding to each side $\text{OH}^-(\text{aq})$ ions equal in number to the $\text{H}^+(\text{aq})$ originally present. This results in $\text{H}_2\text{O(l)}$ on the side that had $\text{H}^+(\text{aq})$ ions (the left side in this case) and $\text{OH}^-(\text{aq})$ ions on the other side (the right side.)

40. **(M)** Oxidation: $2\,\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\,\text{e}^-$ $\quad -E^{\circ} = -1.358\text{ V}$

Reduction: $\text{PbO}_2(\text{s}) + 4\,\text{H}^+(\text{aq}) + 2\,\text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\,\text{H}_2\text{O(l)}$ $\quad E^{\circ} = +1.455\text{ V}$

Net: $\text{PbO}_2(\text{s}) + 4\,\text{H}^+(\text{aq}) + 2\,\text{Cl}^-(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\,\text{H}_2\text{O(l)} + \text{Cl}_2(\text{g})$; $\quad E^{\circ}_{\text{cell}} = +0.097\text{ V}$

We derive an expression for E_{cell} that depends on just the changing $\left[\text{H}^+\right]$.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{P\{\text{Cl}_2\}[\text{Pb}^{2+}]}{[\text{H}^+]^4[\text{Cl}^-]^2} = +0.097 - 0.0296\log\frac{(1.00\text{ atm})(1.00\text{ M})}{[\text{H}^+]^4(1.00)^2}$$
$$= +0.097 + 4\times 0.0296\log[\text{H}^+] = +0.097 + 0.118\log[\text{H}^+] = +0.097 - 0.118\text{ pH}$$

(a) $E_{\text{cell}} = +0.097 + 0.118\ \log(6.0) = +0.189\text{ V}$

$\therefore$ Forward reaction is spontaneous under standard conditions

(b) $E_{\text{cell}} = +0.097 + 0.118\ \log(1.2) = +0.106\text{ V}$

$\therefore$ Forward reaction is spontaneous under standard conditions

(c) $E_{\text{cell}} = +0.097 - 0.118 \times 4.25 = -0.405$ V

$\therefore$ Forward reaction is nonspontaneous under standard conditions

The reaction is spontaneous in strongly acidic solutions (very low pH), but is nonspontaneous under standard conditions in basic, neutral, and weakly acidic solutions.

41. **(M)** Oxidation: $\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$ $\quad -E^{\circ} = +0.763\,\mathrm{V}$

Reduction: $\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$ $\quad E^{\circ} = +0.337\,\mathrm{V}$

Net: $\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)}$ $\quad E^{\circ}_{\text{cell}} = +1.100\,\mathrm{V}$

(a) We set $E = 0.000\,\mathrm{V}$, $\left[\mathrm{Zn^{2+}}\right] = 1.00\,\mathrm{M}$, and solve for $\left[\mathrm{Cu^{2+}}\right]$ in the Nernst equation.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{\left[\mathrm{Zn^{2+}}\right]}{\left[\mathrm{Cu^{2+}}\right]}; \quad 0.000 = 1.100 - 0.0296\ \log\frac{1.0\,\mathrm{M}}{\left[\mathrm{Cu^{2+}}\right]}$$

$$\log\frac{1.0\,\mathrm{M}}{\left[\mathrm{Cu^{2+}}\right]} = \frac{0.000 - 1.100}{-0.0296} = 37.2; \quad \left[\mathrm{Cu^{2+}}\right] = 10^{-37.2} = 6 \times 10^{-38}\ \mathrm{M}$$

(b) If we work the problem the other way, by assuming initial concentrations of $\left[\mathrm{Cu^{2+}}\right]_{\textit{initial}} = 1.0\,\mathrm{M}$ and $\left[\mathrm{Zn^{2+}}\right]_{\textit{initial}} = 0.0\,\mathrm{M}$, we obtain $\left[\mathrm{Cu^{2+}}\right]_{\textit{final}} = 6 \times 10^{-38}\,\mathrm{M}$ and $\left[\mathrm{Zn^{2+}}\right]_{\textit{final}} = 1.0\,\mathrm{M}$. Thus, we would conclude that this reaction goes to completion.

42. **(M)** Oxidation: $\mathrm{Sn(s) \rightarrow Sn^{2+}(aq) + 2\,e^-}$ $\quad -E^{\circ} = +0.137$ V

Reduction: $\mathrm{Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)}$ $\quad E^{\circ} = -0.125$ V

Net: $\mathrm{Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+}(aq) + Pb(s)}$ $\quad E^{\circ}_{\text{cell}} = +0.012\,\mathrm{V}$

Now we wish to find out if $\mathrm{Pb^{2+}(aq)}$ will be completely displaced, that is, will $\left[\mathrm{Pb^{2+}}\right]$ reach 0.0010 M, if $\left[\mathrm{Sn^{2+}}\right]$ is fixed at 1.00 M? We use the Nernst equation to determine if the cell voltage still is positive under these conditions.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{\left[\mathrm{Sn^{2+}}\right]}{\left[\mathrm{Pb^{2+}}\right]} = +0.012 - \frac{0.0592}{2}\log\frac{1.00}{0.0010} = +0.012 - 0.089 = -0.077\ \mathrm{V}$$

The negative cell potential tells us that this reaction will not go to completion under the conditions stated. The reaction stops being spontaneous when $E_{\text{cell}} = 0$. We can work this the another way as well: assume that $\left[\mathrm{Pb^{2+}}\right] = (1.0 - x)\,\mathrm{M}$ and calculate $\left[\mathrm{Sn^{2+}}\right] = x$ M at equilibrium, that is, where $E_{\text{cell}} = 0$.

$$E_{\text{cell}} = 0.00 = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{\left[\mathrm{Sn^{2+}}\right]}{\left[\mathrm{Pb^{2+}}\right]} = +0.012 - \frac{0.0592}{2}\log\frac{x}{1.0 - x}$$

$$\log\frac{x}{1.0-x}=\frac{2\times 0.012}{0.0592}=0.41 \quad x=10^{0.41}(1.0-x)=2.6-2.6x \quad x=\frac{2.6}{3.6}=0.72\text{ M}$$

We would expect the final $\left[\text{Sn}^{2+}\right]$ to equal 1.0 M (or at least 0.999 M) if the reaction went to completion. Instead it equals 0.72 M and consequently, the reaction fails to go to completion.

<u>43.</u> **(M) (a)** The two half-equations and the cell equation are given below. $E^\circ_{\text{cell}} = 0.000\text{ V}$

Oxidation: $H_2(g)\rightarrow 2\,H^+(0.65\text{ M KOH})+2\,e^-$

Reduction: $2\,H^+(1.0\text{ M})+2\,e^-\rightarrow H_2(g)$

Net: $2\,H^+(1.0\text{ M})\rightarrow 2\,H^+(0.65\text{ M KOH})$

$$\left[H^+\right]_{\text{base}}=\frac{K_w}{\left[OH^-\right]}=\frac{1.00\times10^{-14}\text{ M}^2}{0.65\text{ M}}=1.5\times10^{-14}\text{ M}$$

$$E_{\text{cell}}=E^\circ_{\text{cell}}-\frac{0.0592}{2}\log\frac{\left[H^+\right]^2_{\text{base}}}{\left[H^+\right]^2_{\text{acid}}}=0.000-\frac{0.0592}{2}\log\frac{\left(1.5\times10^{-14}\right)^2}{(1.0)^2}=+0.818\text{ V}$$

(b) For the reduction of $H_2O(l)$ to $H_2(g)$ in basic solution, $2\,H_2O(l)+2\,e^-\rightarrow 2\,H_2(g)+2\,OH^-(aq)$, $E^\circ=-0.828\text{ V}$. This reduction is the reverse of the reaction that occurs in the anode of the cell described, with one small difference: in the standard half-cell, [OH$^-$] = 1.00 M, while in the anode half-cell in the case at hand, [OH$^-$] = 0.65 M. Or, viewed in another way, in 1.00 M KOH, [H$^+$] is smaller still than in 0.65 M KOH. The forward reaction (dilution of H^+) should be even more spontaneous, (i.e. a more positive voltage will be created), with 1.00 M KOH than with 0.65 M KOH. We expect that E°_{cell} (1.000 M NaOH) should be a little larger than E_{cell} (0.65 M NaOH), which, is in fact, the case.

44. **(M) (a)** Because $NH_3(aq)$ is a weaker base than KOH(aq), [OH$^-$] will be smaller than in the previous problem. Therefore the [H$^+$] will be higher. Its logarithm will be less negative, and the cell voltage will be less positive. Or, viewed as in Exercise 41(b), the difference in [H$^+$] between 1.0 M H$^+$ and 0.65 M KOH is greater than the difference in [H$^+$] between 1.0 M H$^+$ and 0.65 M NH$_3$. The forward reaction is "less spontaneous" and E_{cell} is less positive.

(b)

Reaction:	$NH_3(aq)+H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)+$	$OH^-(aq)$
Initial:	0.65 M		0 M	$\approx 0\text{ M}$
Changes:	$-x\text{ M}$		$+x\text{ M}$	$+x\text{ M}$
Equil:	$(0.65-x)\text{ M}$		$x\text{ M}$	$x\text{ M}$

$$K_b=\frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]}=1.8\times10^{-5}=\frac{x\cdot x}{0.65-x}\approx\frac{x^2}{0.65}$$

$$x=\left[OH^-\right]=\sqrt{0.65\times1.8\times10^{-5}}=3.4\times10^{-3}\text{ M};\qquad [H_3O^+]=\frac{1.00\times10^{-14}}{3.4\times10^{-3}}=2.9\times10^{-12}\text{ M}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{H}^+]^2_{\text{base}}}{[\text{H}^+]^2_{\text{acid}}} = 0.000 - \frac{0.0592}{2}\ \log\frac{(2.9\times10^{-12})^2}{(1.0)^2} = +0.683\text{ V}$$

45. **(M)** First we need to find $\left[\text{Ag}^+\right]$ in a saturated solution of Ag_2CrO_4.

$$K_{\text{sp}} = \left[\text{Ag}^+\right]^2\left[\text{CrO}_4^{2-}\right] = (2s)^2(s) = 4s^3 = 1.1\times10^{-12} \quad s = \sqrt[3]{\frac{1.1\times10^{-12}}{4}} = 6.5\times10^{-5}\text{ M}$$

The cell diagrammed is a concentration cell, for which $E^{\circ}_{\text{cell}} = 0.000\,\text{V}$, $n = 1$,

$\left[\text{Ag}^+\right]_{\text{anode}} = 2s = 1.3\times10^{-4}\,\text{M}$

Cell reaction: $\text{Ag(s)} + \text{Ag}^+(0.125\text{ M}) \rightarrow \text{Ag(s)} + \text{Ag}^+(1.3\times10^{-4}\,\text{M})$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\ \log\frac{1.3\times10^{-4}\,\text{M}}{0.125\text{ M}} = 0.000 + 0.177\text{ V} = 0.177\text{ V}$$

46. **(M)** First we need to determine $\left[\text{Ag}^+\right]$ in the saturated solution of Ag_3PO_4.

The cell diagrammed is a concentration cell, for which $E^{\circ}_{\text{cell}} = 0.000\text{V}, n = 1$.

Cell reaction: $\text{Ag(s)} + \text{Ag}^+(0.140\text{ M}) \rightarrow \text{Ag(s)} + \text{Ag}^+(x\text{ M})$

$$E_{\text{cell}} = 0.180\text{V} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\log\frac{x\text{ M}}{0.140\text{ M}}; \quad \log\frac{x\text{ M}}{0.140\,\text{M}} = \frac{0.180}{-0.0592} = -3.04$$

$$x\text{M} = 0.140\text{ M}\times10^{-3.04} = 0.140\text{ M}\times9.1\times10^{-4} = 1.3\times10^{-4}\text{ M} = \left[\text{Ag}^+\right]_{\text{anode}}$$

$$K_{\text{sp}} = \left[\text{Ag}^+\right]^3\left[\text{PO}_4^{3-}\right] = (3s)^3(s) = \left(1.3\times10^{-4}\right)^3\left(1.3\times10^{-4}\div3\right) = 9.5\times10^{-17}$$

47. **(D)** **(a)** Oxidation: $\text{Sn(s)} \rightarrow \text{Sn}^{2+}(0.075\text{ M}) + 2\text{ e}^-$ $\qquad -E^{\circ} = +0.137\text{ V}$

Reduction: $\text{Pb}^{2+}(0.600\text{ M}) + 2\text{ e}^- \rightarrow \text{Pb(s)}$ $\qquad E^{\circ} = -0.125\text{ V}$

Net: $\text{Sn(s)} + \text{Pb}^{2+}(0.600\,\text{M}) \rightarrow \text{Pb(s)} + \text{Sn}^{2+}(0.075\text{ M}); E^{\circ}_{\text{cell}} = +0.012\,\text{V}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\ \log\frac{\left[\text{Sn}^{2+}\right]}{\left[\text{Pb}^{2+}\right]} = 0.012 - 0.0296\ \log\frac{0.075}{0.600} = 0.012 + 0.027 = 0.039\text{ V}$$

(b) As the reaction proceeds, [Sn^{2+}] increases while [Pb^{2+}] decreases. These changes cause the driving force behind the reaction to steadily decrease with the passage of time. This decline in driving force is manifested as a decrease in E_{cell} with time.

(c) When $\left[\text{Pb}^{2+}\right] = 0.500\,\text{M} = 0.600\,\text{M} - 0.100\,\text{M}$, $\left[\text{Sn}^{2+}\right] = 0.075\,\text{M} + 0.100\text{ M}$, because the stoichiometry of the reaction is 1:1 for Sn^{2+} and Pb^{2+}.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{\left[\text{Sn}^{2+}\right]}{\left[\text{Pb}^{2+}\right]} = 0.012 - 0.0296\log\frac{0.175}{0.500} = 0.012 + 0.013 = 0.025\text{ V}$$

(d)

Reaction:	Sn(s) +	$Pb^{2+}(aq)$	$\rightarrow$	$Pb(s)$	+	$Sn^{2+}(aq)$
Initial:	—	0.600 M		—		0.075 M
Changes:	—	$-x$ M		—		$+x$ M
Final:	—	$(0.600-x)$ M		—		$(0.075+x)$ M

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2}\log\frac{[Sn^{2+}]}{[Pb^{2+}]} = 0.020 = 0.012 - 0.0296\log\frac{0.075+x}{0.600-x}$$

$$\log\frac{0.075+x}{0.600-x} = \frac{E_{\text{cell}}-0.012}{-0.0296} = \frac{0.020-0.012}{-0.0296} = -0.27;\quad \frac{0.075+x}{0.600-x} = 10^{-0.27} = 0.54$$

$$0.075 + x = 0.54(0.600-x) = 0.324 - 0.54x;\quad x = \frac{0.324-0.075}{1.54} = 0.162\ \text{M}$$

$$[Sn^{2+}] = 0.075 + 0.162 = 0.237\ \text{M}$$

(e) Here we use the expression developed in part (d).

$$\log\frac{0.075+x}{0.600-x} = \frac{E_{\text{cell}}-0.012}{-0.0296} = \frac{0.000-0.012}{-0.0296} = +0.41$$

$$\frac{0.075+x}{0.600-x} = 10^{+0.41} = 2.6;\quad 0.075 + x = 2.6(0.600-x) = 1.6 - 2.6x$$

$$x = \frac{1.6-0.075}{3.6} = 0.42\ \text{M}$$

$$[Sn^{2+}] = 0.075 + 0.42 = 0.50\ \text{M};\qquad [Pb^{2+}] = 0.600 - 0.42 = 0.18\ \text{M}$$

48. (D) (a)

Oxidation: $Ag(s) \rightarrow Ag^{+}(0.015\ \text{M}) + e^{-}$ $\qquad -E^{\circ} = -0.800\ \text{V}$

Reduction: $Fe^{3+}(0.055\ \text{M}) + e^{-} \rightarrow Fe^{2+}(0.045\ \text{M})$ $\qquad E^{\circ} = +0.771\ \text{V}$

Net: $Ag(s) + Fe^{3+}(0.055\ \text{M}) \rightarrow Ag^{+}(0.015\ \text{M}) + Fe^{2+}(0.045\ \text{M})$ $\qquad E^{\circ}_{\text{cell}} = -0.029\ \text{V}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[Ag^{+}][Fe^{2+}]}{[Fe^{3+}]} = -0.029 - 0.0592\log\frac{0.015\times 0.045}{0.055}$$

$$= -0.029\ \text{V} + 0.113\ \text{V} = +0.084\ \text{V}$$

(b) As the reaction proceeds, $[Ag^{+}]$ and $[Fe^{2+}]$ will increase, while $[Fe^{3+}]$ decrease. These changes cause the driving force behind the reaction to steadily decrease with the passage of time. This decline in driving force is manifested as a decrease in E_{cell} with time.

(c) When $[Ag^{+}] = 0.020\,\text{M} = 0.015\,\text{M} + 0.005\,\text{M}$, $[Fe^{2+}] = 0.045\,\text{M} + 0.005\,\text{M} = 0.050\,\text{M}$ and $[Fe^{3+}] = 0.055\ \text{M} - 0.005\,\text{M} = 0.500\,\text{M}$, because, by the stoichiometry of the reaction, a mole of Fe^{2+} is produced and a mole of Fe^{3+} is consumed for every mole of Ag^{+} produced.

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[\text{Ag}^+][\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = -0.029 - 0.0592\log\frac{0.020\times 0.050}{0.050}$$

$$= -0.029\ \text{V} + 0.101\ \text{V} = +0.072\ \text{V}$$

(d) Reaction: $\text{Ag(s)} + \text{Fe}^{3+}(0.055\,\text{M}) \rightleftharpoons \text{Ag}^+(0.015\ \text{M}) + \text{Fe}^{2+}(0.045\ \text{M})$

Reaction:	$\text{Ag(s)} +$ $\text{Fe}^{3+}(0.055\,\text{M})$	$\rightleftharpoons$	$\text{Ag}^+(0.015\ \text{M}) +$	$\text{Fe}^{2+}(0.045\ \text{M})$
Initial:	0.055 M		0.015 M	0.045 M
Changes:	$-x$ M		$+x$ M	$+x$ M
Final:	$(0.055-x)$ M		$(0.015+x)$ M	$(0.045+x)$ M

$$E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{0.0592}{1}\log\frac{[\text{Ag}^+][\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = -0.029 - 0.0592\ \log\frac{(0.015+x)(0.045+x)}{(0.055-x)}$$

$$\log\frac{(0.015+x)(0.045+x)}{(0.055-x)} = \frac{E_{\text{cell}}+0.029}{-0.0592} = \frac{0.010+0.029}{-0.0592} = -0.66$$

$$\frac{(0.015+x)(0.045+x)}{(0.055-x)} = 10^{-0.66} = 0.22$$

$$0.00068 + 0.060x + x^2 = 0.22(0.055-x) = 0.012 - 0.22x \qquad x^2 + 0.28x - 0.011 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.28\pm\sqrt{(0.28)^2+4\times 0.011}}{2} = 0.035\ \text{M}$$

$[\text{Ag}^+] = 0.015\ \text{M} + 0.035\ \text{M} = 0.050\ \text{M}$

$[\text{Fe}^{2+}] = 0.045\ \text{M} + 0.035\ \text{M} = 0.080\ \text{M}$

$[\text{Fe}^{3+}] = 0.055\ \text{M} - 0.035\ \text{M} = 0.020\ \text{M}$

(e) We use the expression that was developed in part (d).

$$\log\frac{(0.015+x)(0.045+x)}{(0.055-x)} = \frac{E_{\text{cell}}+0.029}{-0.0592} = \frac{0.000+0.029}{-0.0592} = -0.49$$

$$\frac{(0.015+x)(0.045+x)}{(0.055-x)} = 10^{-0.49} = 0.32$$

$$0.00068 + 0.060x + x^2 = 0.32(0.055-x) = 0.018 - 0.32x \qquad x^2 + 0.38x - 0.017 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.38\pm\sqrt{(0.38)^2+4\times 0.017}}{2} = 0.040\,\text{M}$$

$[\text{Ag}^+] = 0.015\ \text{M} + 0.040\ \text{M} = 0.055\ \text{M}$

$[\text{Fe}^{2+}] = 0.045\ \text{M} + 0.040\ \text{M} = 0.085\ \text{M}$

$[\text{Fe}^{3+}] = 0.055\ \text{M} - 0.040\ \text{M} = 0.015\ \text{M}$

49. **(M)** First we will need to come up with a balanced equation for the overall redox reaction. Clearly, the reaction must involve the oxidation of Cl^{-}(aq) and the reduction of $Cr_2O_7^{2-}$(aq):

$14\ H^{+}(aq) + Cr_2O_7^{2-}(aq) + 6\ e^{-} \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ $\quad E°_{1/2red} = 1.33$ V
$\{Cl^{-}(aq) \rightarrow 1/2\ Cl_2(g) + 1\ e^{-}\} \times 6$ $\quad E°_{1/2ox} = -1.358$ V

$14\ H^{+}(aq) + Cr_2O_7^{2-}(aq) + 6\ Cl^{-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ Cl_2(g)$ $E°_{cell} = -0.03$ V

A negative cell potential means, the oxidation of Cl^{-}(aq) to Cl_2(g) by $Cr_2O_7^{2-}$(aq) at standard conditions will not occur spontaneously. We could obtain some Cl_2(g) from this reaction by driving it to the product side with an external voltage. In other words, the reverse reaction is the spontaneous reaction at standard conditions and if we want to produce some Cl_2(g) from the system, we must push the non-spontaneous reaction in its forward direction with an external voltage, (i.e., a DC power source). Since $E°_{cell}$ is only slightly negative, we could also drive the reaction by removing products as they are formed and replenishing reactants as they are consumed.

50. **(D)** We proceed by first deriving a balanced equation for the reaction occurring in the cell:

Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$

Reduction: $\{Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)\} \times 2$

Net: $Fe(s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$

(a) ΔG^{o} and the equilibrium constant K_{eq} can be calculated using

$$\Delta G^{o} = -nFE^{o}_{cell} = -RT\ln K_{eq}:$$

$$\Delta G^{o} = -nFE^{o}_{cell} = -2 \times 96485\text{Cmol}^{-1} \times 1.21\text{V} = -233.5\text{kJmol}^{-1}$$

$$\Delta G^{o} = -RT\ln K = -8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K} \times \ln K = -233.5 \times 1000\text{Jmol}^{-1}$$

$$\ln K = 94.2 \Rightarrow K = e^{94.2} = 8.1 \times 10^{40}$$

(b) Before calculating voltage using the Nernst equation, we need to re-write the net reaction to take into account concentration gradient for Fe^{2+}(aq):

Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq, 1.0 \times 10^{-3}M) + 2e^{-}$

Reduction: $\{Fe^{3+}(aq, 1.0 \times 10^{-3}M) + e^{-} \rightarrow Fe^{2+}(aq, 0.10M)\} \times 2$

Net: $Fe(s) + 2Fe^{3+}(aq, 1.0 \times 10^{-3}) \rightarrow Fe^{2+}(aq, 1.0 \times 10^{-3}M) + 2Fe^{2+}(aq, 0.10M)$

Therefore,

$$Q = \frac{1.0 \times 10^{-3} \times (0.10)^{2}}{(1.0 \times 10^{-3})^{2}} = 10$$

Now, we can apply the Nerst equation to calculate the voltage:

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n}\log\left(Q\right) = 1.21\text{ V} - \frac{0.0592}{2}\log 10 = 1.18\text{ V}$$

(c) From parts (a) and (b) we can conclude that the reaction between Fe(s) and Fe^{3+}(aq) is spontaneous. The reverse reaction (i.e. disproportionation of Fe^{2+}(aq)) must therefore be nonspontaneous.

Batteries and Fuel Cells

51. **(M)** *Stepwise approach:*

(a) The cell diagram begins with the anode and ends with the cathode.

Cell diagram: $\mathrm{Cr(s)|Cr^{2+}(aq),Cr^{3+}(aq)||Fe^{2+}(aq),Fe^{3+}(aq)|Fe(s)}$

(b)

$$\text{Oxidation: } \mathrm{Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^-} \qquad -E^{\mathrm{o}} = +0.424\,\mathrm{V}$$

$$\text{Reduction: } \mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)} \qquad E^{\mathrm{o}} = +0.771\,\mathrm{V}$$

$$\text{Net: } \mathrm{Cr^{2+}(aq) + Fe^{3+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{2+}(aq)} \qquad E^{\mathrm{o}}_{\mathrm{cell}} = +1.195\,\mathrm{V}$$

Conversion pathway approach:

$\mathrm{Cr(s)|Cr^{2+}(aq),Cr^{3+}(aq)||Fe^{2+}(aq),Fe^{3+}(aq)|Fe(s)}$

$-E^{\mathrm{o}} = +0.424\,\mathrm{V} \qquad E^{\mathrm{o}} = +0.771\,\mathrm{V}$

$E^{\mathrm{o}}_{\mathrm{cell}} = +0.424V + 0.771V = +1.195V$

52. **(M) (a)**

$$\text{Oxidation: } \mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-} \qquad -E^{\mathrm{o}} = +0.763\,\mathrm{V}$$

$$\text{Reduction: } \mathrm{2MnO_2(s) + H_2O(l) + 2\,e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)}$$

$$\text{Acid-base: } \mathrm{\{NH_4{}^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)\}} \qquad \times 2$$

$$\text{Complex: } \mathrm{Zn^{2+}(aq) + 2NH_3(aq) + 2Cl^-(aq) \rightarrow \left[Zn(NH_3)_2\right]Cl_2(s)}$$

$$\text{Net: } \mathrm{Zn(s) + 2\,MnO_2(s) + 2\,NH_4{}^+(aq) + 2\,Cl^-(aq) \rightarrow Mn_2O_3(s) + H_2O(l) + [Zn(NH_3)_2]Cl_2(s)}$$

(b) $\Delta G^{\mathrm{o}} = -nFE^{\mathrm{o}}_{\mathrm{cell}} = -(2\ \mathrm{mol\ e^-})(96485\ \mathrm{C/mol\ e^-})(1.55\ \mathrm{V}) = -2.99\times10^5\,\mathrm{J/mol}$

This is the standard free energy change for the entire reaction, which is composed of the four reactions in part (a). We can determine the values of ΔG^{o} for the acid-base and complex formation reactions by employing the appropriate data from Appendix D and $\mathrm{p}K_f = -4.81$ (the negative log of the K_{f} for $[\mathrm{Zn(NH_3)_2}]^{2+}$).

$$\Delta G^{\mathrm{o}}_{\mathrm{a-b}} = -RT\ln K_{\mathrm{b}}{}^2 = -(8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}})(298.15\ \mathrm{K})\ln\left(1.8\times10^{-5}\right)^2 = 5.417\times10^4\ \mathrm{J/mol}$$

$$\Delta G^{\mathrm{o}}_{\mathrm{cmplx}} = -RT\ln K_f = -(8.3145\,\mathrm{J\ mol^{-1}\ K^{-}})(298.15\ \mathrm{K})\ln\left(10^{4.81}\right) = -2.746\times10^4\ \mathrm{J/mol}$$

Then $\Delta G^{\mathrm{o}}_{\mathrm{total}} = \Delta G^{o}_{\mathrm{redox}} + \Delta G^{o}_{\mathrm{a-b}} + \Delta G^{\mathrm{o}}_{\mathrm{cmplx}} \qquad \Delta G^{o}_{\mathrm{redox}} = \Delta G^{\mathrm{o}}_{\mathrm{total}} - \Delta G^{o}_{\mathrm{a-b}} - \Delta G^{\mathrm{o}}_{\mathrm{cmplx}}$

$$= -2.99\times10^5\ \mathrm{J/mol} - 5.417\times10^4 + 2.746\times10^4\ \mathrm{J/mol} = -3.26\times10^5\ \mathrm{J/mol}$$

Thus, the voltage of the redox reactions alone is

$$E^{\mathrm{o}} = \frac{-3.26\times10^5\,\mathrm{J}}{-2\mathrm{mol\ e^-}\times 96485\ \mathrm{C/mol\ e^-}} = 1.69\ \mathrm{V} \qquad 1.69\mathrm{V} = +0.763\mathrm{V} + E^{\mathrm{o}}\left\{\mathrm{MnO_2/Mn_2O_3}\right\}$$

$$E^{\mathrm{o}}\left\{\mathrm{MnO_2/Mn_2O_3}\right\} = 1.69\mathrm{V} - 0.763\mathrm{V} = +0.93\mathrm{V}$$

The electrode potentials were calculated by using equilibrium constants from Appendix D. These calculations do not take into account the cell's own internal resistance to the flow of electrons, which makes the actual voltage developed by the electrodes less than the theoretical values derived from equilibrium constants. Also because the solid species (other than Zn) do not appear as compact rods, but rather are dispersed in a paste, and since very little water is present in the cell, the activities for the various species involved in the electrochemical reactions will deviate markedly from unity. As a result, the equilibrium constants for the reactions taking place in the cell will be substantially different from those provided in Appendix D, which apply only to dilute solutions and reactions involving solid reactants and products that posses small surface areas. The actual electrode voltages, therefore, will end up being different from those calculated here.

53. **(M) (a)** Cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

$$\Delta G_{rxn}{}^{o} = 2\Delta G_{f}{}^{o}\left[H_2O(l)\right] = 2(-237.1 \text{ kJ/mol}) = -474.2 \text{ kJ/mol}$$

$$E_{\text{cell}}{}^{o} = -\frac{\Delta G^{o}}{nF} = -\frac{-474.2\times10^{3} \text{ J/mol}}{4 \text{ mol e}^{-}\times 96485 \text{ C/mol e}^{-}} = 1.229 \text{ V}$$

(b) Anode, oxidation: $\{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}\} \quad \times 2$ $\qquad -E^{o} = +0.763\text{V}$

Cathode, reduction: $O_2(g) + 4\ H^{+}(aq) + 4e^{-} \rightarrow 2H_2O(l)$ $\qquad E^{o} = +1.229\text{ V}$

Net: $2\,Zn(s) + O_2(g) + 4H^{+}(aq) \rightarrow 2\,Zn^{2+}(aq) + 2\,H_2O(l)$ $\qquad E^{o}_{\text{cell}} = +1.992\text{V}$

(c) Anode, oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$ $\qquad -E^{o} = +2.356\text{V}$

Cathode, reduction: $I_2(s) + 2e^{-} \rightarrow 2\ I^{-}(aq)$ $\qquad E^{o} = +0.535\text{V}$

Net: $Mg(s) + I_2(s) \rightarrow Mg^{2+}(aq) + 2\ I^{-}(aq)$ $\qquad E^{o}_{\text{cell}} = +2.891\text{V}$

54. **(M) (a)** Oxidation: $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2\ e^{-}$

Precipitation: $Zn^{2+}(aq) + 2\ OH^{-}(aq) \rightleftharpoons Zn(OH)_2(s)$

Reduction: $2\ MnO_2(s) + H_2)(l) + 2\ e^{-} \rightleftharpoons Mn_2O_3(s) + 2\ OH^{-}(aq)$

Net : $Zn(s) + 2\ MnO_2(s) + H_2O(l) + 2\ OH^{-}(aq) \rightleftharpoons Mn_2O_3(s) + Zn(OH)_2(s)$

(b) In 50, we determined that the standard voltage for the reduction reaction is +0.93 V (n = 2 e^{-}). To convert this voltage to an equilibrium constant (at 25 °C) use:

$$\log K_{\text{red}} = \frac{nE^{o}}{0.0592} = \frac{2(0.93)}{0.0592} = 31.\underline{4}; \qquad K_{\text{red}} = 10^{31.42} = 3\times10^{31}$$

and for $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2\ e^{-}$ ($E°$ = 0.763 V and n = 2 e^{-})

$$\log K_{\text{ox}} = \frac{nE^{o}}{0.0592} = \frac{2(0.763)}{0.0592} = 25.\underline{8}; \qquad K_{\text{ox}} = 10^{25.78} = 6\times10^{25}$$

$$\Delta G^{\circ}_{\text{total}} = \Delta G^{\circ}_{\text{precipitation}} + \Delta G^{\circ}_{\text{oxidation}} + \Delta G^{\circ}_{\text{reduction}}$$

$$\Delta G^{\circ}_{\text{total}} = -RT \ln\frac{1}{K_{\text{sp, Zn(OH)}_2}} + (-RT \ln K_{\text{ox}}) + (-RT \ln K_{\text{red}})$$

$$\Delta G^\circ_{\text{total}} = -RT\,(\ln\frac{1}{K_{\text{sp, Zn(OH)}_2}} + \ln K_{\text{ox}} + \ln K_{\text{red}})$$

$$\Delta G^\circ_{\text{total}} = -0.0083145\,\frac{\text{kJ}}{\text{K mol}}\,(298\text{ K})\,(\ln\frac{1}{1.2\times10^{-17}} + \ln(6.0\times10^{25}) + \ln(2.6\times10^{31}))$$

$$\Delta G^\circ_{\text{total}} = -423\text{ kJ} = -nFE^\circ_{\text{total}}$$

$$\text{Hence, } E^\circ_{\text{total}} = E^\circ_{\text{cell}} = \frac{-423\times10^3\text{ J}}{-(2\text{ mol})(96485\text{ C mol}^{-1})} = 2.19\text{ V}$$

<u>55.</u> **(M)** Aluminum-Air Battery: $2\text{ Al(s)} + 3/2\text{ O}_2\text{(g)} \rightarrow \text{Al}_2\text{O}_3\text{(s)}$
Zinc-Air Battery: $\text{Zn(s)} + ½\text{ O}_2\text{(g)} \rightarrow \text{ZnO(s)}$
Iron-Air Battery $\text{Fe(s)} + ½\text{ O}_2\text{(g)} \rightarrow \text{FeO(s)}$
Calculate the quantity of charge transferred when 1.00 g of metal is consumed in each cell.

Aluminum-Air Cell:

$$1.00\text{ g Al(s)}\times\frac{1\text{ mol Al(s)}}{26.98\text{ g Al(s)}}\times\frac{3\text{ mol e}^-}{1\text{ mol Al(s)}}\times\frac{96,485\text{C}}{1\text{ mol e}^-}=1.07\times10^4\text{ C}$$

Zinc-Air Cell:

$$1.00\text{ g Zn(s)}\times\frac{1\text{ mol Zn(s)}}{65.39\text{ g Zn(s)}}\times\frac{2\text{ mol e}^-}{1\text{ mol Zn(s)}}\times\frac{96,485\text{ C}}{1\text{ mol e}^-}=2.95\times10^3\text{ C}$$

Iron-Air Cell:

$$1.00\text{ g Fe(s)}\times\frac{1\text{ mol Fe(s)}}{55.847\text{ g Fe(s)}}\times\frac{2\text{ mol e}^-}{1\text{ mol Fe(s)}}\times\frac{96,485\text{ C}}{1\text{ mol e}^-}=3.46\times10^3\text{ C}$$

As expected, aluminum has the greatest quantity of charge transferred per unit mass (1.00 g) of metal oxidized. This is because aluminum has the smallest molar mass and forms the most highly charged cation (3+ for aluminum vs 2+ for Zn and Fe).

56. **(M) (a)** A voltaic cell with a voltage of 0.1000 V would be possible by using two half-cells whose standard reduction potentials differ by approximately 0.10 V, such as the following pair.

Oxidation: $2\text{ Cr}^{3+}(\text{aq})+7\text{ H}_2\text{O(l)}\rightarrow\text{Cr}_2\text{O}_7^{2-}(\text{aq})+14\text{ H}^+(\text{aq})+6\text{ e}^-$ $-E^\circ = -1.33\text{ V}$

Reduction: $\{\text{PbO}_2(\text{s})+4\text{ H}^+(\text{aq})+2\text{e}^-\rightarrow\text{Pb}^{2+}(\text{aq})+2\text{ H}_2\text{O(l)}\}\ \times3$ $E^\circ = +1.455\text{ V}$

Net: $2\text{Cr}^{3+}(\text{aq})+3\text{PbO}_2(\text{s})+\text{H}_2\text{O(l)}\rightarrow\text{Cr}_2\text{O}_7^{2-}(\text{aq})+3\text{Pb}^{2+}(\text{aq})+2\text{H}^+(\text{aq})$ $E^\circ_{\text{cell}}=0.12\underline{5}\text{ V}$

The voltage can be adjusted to 0.1000 V by a suitable alteration of the concentrations. $\left[\text{Pb}^{2+}\right]$ or $\left[\text{H}^+\right]$ could be increased or $\left[\text{Cr}^{3+}\right]$ could be decreased, or any combination of the three of these.

(b) To produce a cell with a voltage of 2.500 V requires that one start with two half-cells whose reduction potentials differ by about that much. An interesting pair follows.

Oxidation: $\text{Al}(\text{s})\rightarrow\text{Al}^{3+}(\text{aq})+3\text{e}^-$ $-E^\circ = +1.676\text{ V}$

Reduction: $\{Ag^{+}(aq) + e^{-} \rightarrow Ag(s)\} \times 3$ $\qquad E^{o} = +0.800\,V$

Net: $Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$ $\qquad E^{o}_{cell} = +2.476\ V$

Again, the desired voltage can be obtained by adjusting the concentrations. In this case increasing $\left[Ag^{+}\right]$ and/or decreasing $\left[Al^{3+}\right]$ would do the trick.

(c) Since no known pair of half-cells has a potential difference larger than about 6 volts, we conclude that producing a single cell with a potential of 10.00 V is currently impossible. It is possible, however, to join several cells together into a battery that delivers a voltage of 10.00 V. For instance, four of the cells from part (b) would deliver ~10.0 V at the instant of hook-up.

57. **(M)** Oxidation (anode): $Li(s) \rightarrow Li^{+}(aq)+e^{-}$ $\qquad -E^{o} = +3.040V$

Reduction (cathode): $MnO_2(s)+2H_2O(l)+e^{-} \rightarrow Mn(OH)_3(s)+OH^{-}(aq)$ $\qquad E^{o} = -0.20V$

Net: $MnO_2(s)+2H_2O(l)+Li(s) \rightarrow Mn(OH)_3(s)+OH^{-}(aq)+Li^{+}(aq)$ $\qquad E^{o}_{cell} = 2.84V$

Cell diagram: $Li(s), Li^{+}(aq)|KOH(satd)|MnO_2(s), Mn(OH)_3(s)|$

58. **(M)** **(a)** Oxidation (anode): $Zn(s) \rightarrow Zn^{+2}(aq)+2e^{-}$ $\qquad -E^{o} = +0.763V$

Reduction (cathode): $Br_2(l)+2e^{-} \rightarrow 2Br^{-}(aq)$ $\qquad E^{o} = +1.065V$

Net: $Zn(s)+Br_2(l) \rightarrow Zn^{2+}(aq)+2Br^{-}(aq)$ $\qquad E^{o}_{cell} = 1.828V$

(b) Oxidation (anode): $\{Li(s) \rightarrow Li^{+}(aq)+e^{-}\} \times 2$ $\qquad -E^{o} = +3.040V$

Reduction (cathode): $F_2(g)+2e^{-} \rightarrow 2F^{-}(aq)$ $\qquad E^{o} = +2.866V$

Net: $2Li(s)+F_2(g) \rightarrow 2Li^{+}(aq)+2F^{-}(aq)$ $\qquad E^{o}_{cell} = 4.868V$

Electrochemical Mechanism of Corrosion

59. **(M) (a)** Because copper is a less active metal than is iron (i.e. a weaker reducing agent), this situation would be similar to that of an iron or steel can plated with a tin coating that has been scratched. Oxidation of iron metal to Fe^{2+}(aq) should be enhanced in the body of the nail (blue precipitate), and hydroxide ion should be produced in the vicinity of the copper wire (pink color), which serves as the cathode.

(b) Because a scratch tears the iron and exposes “fresh” metal, it is more susceptible to corrosion. We expect blue precipitate in the vicinity of the scratch.

(c) Zinc should protect the iron nail from corrosion. There should be almost no blue precipitate; the zinc corrodes instead. The pink color of OH^{-} should continue to form.

60. **(M)** The oxidation process involved at the anode reaction, is the formation of Fe^{2+}(aq). This occurs far below the water line. The reduction process involved at the cathode, is the formation of $OH^{-}(aq)$ from O_2(g). It is logical that this reaction would occur at or near the water line close to the atmosphere (which contains O_2). This reduction reaction requires O_2(g) from the atmosphere and H_2O(l) from the water. The oxidation reaction, on the other hand simply requires iron from the pipe together with an aqueous solution into which the $Fe^{2+}(aq)$ can disperse and not build up to such a high concentration that corrosion is inhibited.

Anode, oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Cathode, reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

61. **(M)**During the process of corrosion, the metal that corrodes loses electrons. Thus, the metal in these instances behaves as an anode and, hence, can be viewed as bearing a latent negative polarity. One way in which we could retard oxidation of the metal would be to convert it into a cathode. Once transformed into a cathode, the metal would develop a positive charge and no longer release electrons (or oxidize). This change in polarity can be accomplished by hooking up the metal to an inert electrode in the ground and then applying a voltage across the two metals in such a way that the inert electrode becomes the anode and the metal that needs protecting becomes the cathode. This way, any oxidation that occurs will take place at the negatively charged inert electrode rather than the positively charged metal electrode.

62. **(M)** As soon as the iron and copper came into direct contact, an electrochemical cell was created, in which the more powerfully reducing metal (Fe) was oxidized. In this way, the iron behaved as a sacrificial anode, protecting the copper from corrosion. The two half-reactions and the net cell reaction are shown below:

Anode (oxidation)	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$	$-E° = 0.440$ V
Cathode (reduction)	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E° = 0.337$ V
Net:	$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$	$E°_{cell} = 0.777$ V

Note that because of the presence of iron and its electrical contact with the copper, any copper that does corrode is reduced back to the metal.

Electrolysis Reactions

63. **(M)** Here we start by calculating the total amount of charge passed and the number of moles of electrons transferred.

$$\text{mol e}^- = 75 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.15 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} = 0.10 \text{ mol e}^-$$

(a) $$\text{mass Zn} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Zn}^{2+}}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Zn}}{1 \text{ mol Zn}^{2+}} \times \frac{65.39 \text{ g Zn}}{1 \text{ mol Zn}} = 3.3 \text{ g Zn}$$

(b) $$\text{mass Al} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Al}^{3+}}{3 \text{ mol e}^-} \times \frac{1 \text{ mol Al}}{1 \text{ mol Al}^{3+}} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 0.90 \text{ g Al}$$

(c) $$\text{mass Ag} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Ag}^{+}}{1 \text{ mol e}^-} \times \frac{1 \text{ mol Ag}}{1 \text{ mol Ag}^{+}} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 11 \text{ g Ag}$$

(d) $\text{mass Ni} = 0.10 \text{ mol e}^- \times \frac{1 \text{ mol Ni}^{2+}}{2 \text{ mol e}^-} \times \frac{1 \text{ mol Ni}}{1 \text{ mol Ni}^{2+}} \times \frac{58.69 \text{ g Ni}}{1 \text{ mol Ni}} = 2.9 \text{ g Ni}$

64. **(M)** We proceed by first writing down the net electrochemical reaction. The number of moles of hydrogen produced in the reaction can be calculated from the reaction stoichiometry. Lastly, the volume of hydrogen can be determined using ideal gas law.

Stepwise approach:

The two half reactions follow: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ and $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$

Thus, two moles of electrons are needed to produce each mole of Cu(s) and two moles of electrons are needed to produce each mole of $H_2(g)$. With this information, we can compute the moles of $H_2(g)$ that will be produced.

$$\text{mol } H_2(g) = 3.28 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{1 \text{ mol } H_2(g)}{2 \text{ mol e}^-} = 0.0516 \text{ mol } H_2(g)$$

Then we use the ideal gas equation to find the volume of $H_2(g)$.

$$\text{Volume of } H_2(g) = \frac{0.0516 \text{ mol } H_2 \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times (273.2 + 28.2)\text{ K}}{763 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 1.27 \text{ L}$$

This answer assumes the $H_2(g)$ is not collected over water, and that the H_2(g) formed is the only gas present in the container (i.e. no water vapor present)

Conversion pathway approach:

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ and $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$

$$\text{mol } H_2(g) = 3.28 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \times \frac{1 \text{ mol } H_2(g)}{2 \text{ mol e}^-} = 0.0516 \text{ mol } H_2(g)$$

$$V(H_2(g)) = \frac{0.0516 \text{ mol } H_2 \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times (273.2 + 28.2)\text{K}}{763 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 1.27 \text{ L}$$

65. **(M)** Here we must determine the standard cell voltage of each chemical reaction. Those chemical reactions that have a negative voltage are the ones that require electrolysis.

(a) Oxidation: $2\,H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4\,e^-$ $\qquad -E^o = -1.229$ V

Reduction: $\{2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)\} \times 2$ $\qquad E^o = 0.000$ V

Net: $2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g)$ $\qquad E^o_{cell} = -1.229$ V

This reaction requires electrolysis, with an applied voltage greater than +1.229V.

(b) Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$ $\qquad -E^o = +0.763$ V

Reduction: $Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$ $\qquad E^o = -0.440$ V

Net: $Zn(s) + Fe^{2+}(aq) \rightarrow Fe(s) + Zn^{2+}(aq)$ $E^{o}_{cell} = +0.323\,V$

This is a spontaneous reaction under standard conditions.

(c) Oxidation: $\{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}\} \times 2$ $-E^{o} = -0.771\,V$

Reduction: $I_2(s) + 2e^{-} \rightarrow 2I^{-}(aq)$ $E^{o} = +0.535\,V$

Net: $2Fe^{2+}(aq) + I_2(s) \rightarrow 2Fe^{3+}(aq) + 2I^{-}(aq)$ $E^{o}_{cell} = -0.236\,V$

This reaction requires electrolysis, with an applied voltage greater than $+0.236\,V$.

(d) Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $-E^{o} = -0.337\,V$

Reduction: $\{Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)\} \times 2$ $E^{o} = +0.154\,V$

Net: $Cu(s) + Sn^{4+}(aq) \rightarrow Cu^{2+}(aq) + Sn^{2+}(aq)$ $E^{o}_{cell} = -0.183\,V$

This reaction requires electrolysis, with an applied voltage greater than $+0.183\,V$.

66. **(M) (a)** Because oxidation occurs at the anode, we know that the product cannot be H_2 (H_2 is produced from the reduction of H_2O), SO_2, (which is a reduction product of SO_4^{2-}), or SO_3 (which is produced from SO_4^{2-} without a change of oxidation state; it is the dehydration product of H_2SO_4). It is, in fact O_2 that forms at the anode. The oxidation of water at the anode produces the $O_2(g)$.

(b) Reduction should occur at the cathode. The possible species that can be reduced are H_2O to $H_2(g)$, $K^{+}(aq)$ to $K(s)$, and $SO_4^{2-}(aq)$ to perhaps $SO_2(g)$. Because potassium is a highly active metal, it will not be produced in aqueous solution. In order for $SO_4^{2-}(aq)$ to be reduced, it would have to migrate to the negatively charged cathode, which is not very probable since like charges repel each other. Thus, $H_2(g)$ is produced at the cathode.

(c) At the anode: $2H_2O(l) \rightarrow 4H^{+}(aq) + O_2(g) + 4e^{-}$ $-E^{o} = -1.229\,V$

At the cathode: $\{2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)\} \times 2$ $E^{o} = 0.000\,V$

Net cell reaction: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ $E^{o}_{cell} = -1.229\,V$

A voltage greater than 1.229 V is required. Because of the high overpotential required for the formation of gases, we expect that a higher voltage will be necessary.

67. **(M) (a)** The two gases that are produced are $H_2(g)$ and $O_2(g)$.

(b) At the anode: $2\,H_2O(l) \rightarrow 4\,H^{+}(aq) + O_2(g) + 4e^{-}$ $-E^{o} = -1.229\,V$

At the cathode: $\{2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)\} \times 2$ $E^{o} = 0.000\,V$

Net cell reaction: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ $E^{o}_{cell} = -1.229\,V$

68. **(M)** The electrolysis of $Na_2SO_4(aq)$ produces molecular oxygen at the anode. $-E^{o}\{O_2(g)/H_2O\} = -1.229\ V$. The other possible product is $S_2O_8^{2-}(aq)$. It is however, unlikely to form because it has a considerably less favorable half-cell potential.

$-E^{\circ}\left\{\mathrm{S_2O_8}^{2-}(\mathrm{aq})/\mathrm{SO_4}^{2-}(\mathrm{aq})\right\} = -2.01\ \mathrm{V}$.

$\mathrm{H_2(g)}$ is formed at the cathode.

$$\text{mol } \mathrm{O_2} = 3.75\,\mathrm{h} \times \frac{3600\,\mathrm{s}}{1\,\mathrm{h}} \times \frac{2.83\,\mathrm{C}}{1\,\mathrm{s}} \times \frac{1\ \mathrm{mol\ e^-}}{96485\ \mathrm{C}} \times \frac{1\,\mathrm{mol\ O_2}}{4\,\mathrm{mol\ e^-}} = 0.0990\ \mathrm{mol\ O_2}$$

The vapor pressure of water at $25^{\circ}\mathrm{C}$, from Table 12-2, is 23.8 mmHg.

$$V = \frac{nRT}{P} = \frac{0.0990\ \mathrm{mol} \times 0.08206\ \mathrm{L\,atm\ mol^{-1}\ K^{-1}} \times 298\ \mathrm{K}}{(742 - 23.8)\ \mathrm{mmHg} \times \dfrac{1\ \mathrm{atm}}{760\ \mathrm{mmHg}}} = 2.56\ \mathrm{L\ O_2(g)}$$

<u>69.</u> **(M) (a)** $\mathrm{Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)}$

$$\text{mass of Zn} = 42.5\ \mathrm{min} \times \frac{60\ \mathrm{s}}{1\ \mathrm{min}} \times \frac{1.87\ \mathrm{C}}{1\ \mathrm{s}} \times \frac{1\ \mathrm{mol\ e^-}}{96,485\ \mathrm{C}} \times \frac{1\ \mathrm{mol\ Zn}}{2\ \mathrm{mol\ e^-}} \times \frac{65.39\,\mathrm{g\ Zn}}{1\ \mathrm{mol\ Zn}} = 1.62\ \mathrm{g\ Zn}$$

(b) $\mathrm{2I^-(aq) \rightarrow I_2(s) + 2e^-}$

$$\text{time needed} = 2.79\,\mathrm{g\,I_2} \times \frac{1\,\mathrm{mol\,I_2}}{253.8\,\mathrm{g\,I_2}} \times \frac{2\ \mathrm{mol\ e^-}}{1\,\mathrm{mol\,I_2}} \times \frac{96,485\ \mathrm{C}}{1\ \mathrm{mol\ e^-}} \times \frac{1\ \mathrm{s}}{1.75\,\mathrm{C}} \times \frac{1\ \mathrm{min}}{60\ \mathrm{s}} = 20.2\ \mathrm{min}$$

70. **(M) (a)** $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$

$$\text{mmol } \mathrm{Cu^{2+}} \text{consumed} = 282\ \mathrm{s} \times \frac{2.68\ \mathrm{C}}{1\ \mathrm{s}} \times \frac{1\ \mathrm{mol\ e^-}}{96,485\ \mathrm{C}} \times \frac{1\ \mathrm{mol\ Cu^{2+}}}{2\ \mathrm{mol\ e^-}} \times \frac{1000\,\mathrm{mmol}}{1\,\mathrm{mol}}$$

$$= 3.92\ \mathrm{mmol\ Cu^{2+}}$$

$$\text{decrease in } \left[\mathrm{Cu^{2+}}\right] = \frac{3.92\ \mathrm{mmol\ Cu^{2+}}}{425\ \mathrm{mL}} = 0.00922\,\mathrm{M}$$

$$\text{final } \left[\mathrm{Cu^{2+}}\right] = 0.366\ \mathrm{M} - 0.00922\,\mathrm{M} = 0.357\,\mathrm{M}$$

(b) $\text{mmol } \mathrm{Ag^+} \text{consumed} = 255\ \mathrm{mL}\left(0.196\ \mathrm{M} - 0.175\ \mathrm{M}\right) = 5.3\underline{6}\ \mathrm{mmol\ Ag^+}$

$$\text{time needed} = 5.36\ \mathrm{mmol\ Ag^+} \times \frac{1\ \mathrm{mol\ Ag^+}}{1000\ \mathrm{mmol\ Ag^+}} \times \frac{1\ \mathrm{mol\ e^-}}{1\ \mathrm{mol\ Ag^+}} \times \frac{96485\mathrm{C}}{1\ \mathrm{mol\ e^-}} \times \frac{1\ \mathrm{s}}{1.84\ \mathrm{C}}$$

$$= 28\underline{1}\ \mathrm{s} \approx 2.8 \times 10^2\ \mathrm{s}$$

<u>71.</u> **(M) (a)** $\text{charge} = 1.206\ \mathrm{g\ Ag} \times \dfrac{1\ \mathrm{mol\ Ag}}{107.87\ \mathrm{g\ Ag}} \times \dfrac{1\ \mathrm{mol\ e^-}}{1\ \mathrm{mol\ Ag}} \times \dfrac{96{,}485\ \mathrm{C}}{1\ \mathrm{mol\ e^-}} = 1079\ \mathrm{C}$

(b) $\text{current} = \dfrac{1079\ \mathrm{C}}{1412\ \mathrm{s}} = 0.7642\ \mathrm{A}$

72. **(D) (a)** Anode, oxidation: $2H_2O(l) \rightarrow 4H^+(aq) + 4e^- + O_2(g)$ $\quad -E^o = -1.229V$

Cathode, reduction: $\{Ag^+(aq) + e^- \rightarrow Ag(s)\} \quad \times 4$ $\quad E^o = +0.800\,V$

Net: $2H_2O(l) + 4Ag^+(aq) \rightarrow 4H^+(aq) + O_2(g) + 4Ag(s)$ $\quad E^o_{cell} = -0.429\,V$

(b) $$\text{charge} = (25.8639 - 25.0782)\text{ g Ag} \times \frac{1\text{ mol Ag}}{107.87\text{ g Ag}} \times \frac{1\text{ mol e}^-}{1\text{ mol Ag}} \times \frac{96,485\text{ C}}{1\text{ mol e}^-} = 702.8\,C$$

$$\text{current} = \frac{702.8\,C}{2.00\text{ h}} \times \frac{1h}{3600\text{ s}} = 0.0976\,A$$

(c) The gas is molecular oxygen.

$$V = \frac{nRT}{P} = \frac{\left(702.8\text{ C} \times \frac{1\text{ mol e}^-}{96485\text{ C}} \times \frac{1\text{mol }O_2}{4\text{mol e}^-}\right) 0.08206 \frac{\text{L atm}}{\text{mol K}} (23+273)\text{ K}}{755\text{ mmHg} \times \frac{1\text{ atm}}{760\text{ mmHg}}}$$

$$= 0.0445\text{ L }O_2 \times \frac{1000\text{ mL}}{1\text{ L}} = 44.5\text{ mL of }O_2$$

73. **(D)** **(a)** The electrochemical reaction is:

Anode (oxidation): $\{Ag(s) \rightarrow Ag^+(aq) + e^-(aq)\} \times 2$ $\quad -E^o = -0.800V$

Cathode (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E_o = +0.340V$

Net: $2Ag(s) + Cu^{2+}(aq) \rightarrow Cu(s) + 2Ag^+(aq)$ $\quad E^o_{cell} = -0.46V$

Therefore, copper should plate out first.

(b) $$\text{current} = \frac{\text{charge}}{2.50\text{hmin}} \times \frac{1h}{3600\text{ s}} = 0.75A \Rightarrow \text{charge} = 6750C$$

$$\text{mass} = 6750\text{ C} \times \frac{1\text{ mole}^-}{96485\text{ C}} \times \frac{1\text{mol Cu}}{2\text{ mol e}^-} \times \frac{63.546\text{ g Cu}}{1\text{ mol Cu}} = 2.22\text{ g Cu}$$

(c) The total mass of the metal is 3.50 g out of which 2.22g is copper. Therefore, the mass of silver in the sample is 3.50g-2.22g=1.28g or (1.28/3.50)x100=37%.

74. **(D)** First, calculate the number of moles of electrons involved in the electrolysis:

$$1.20C/s \times 32.0\text{ min} \times \frac{60\text{ sec}}{1\text{min}} \times \frac{1\text{mole e}^-}{96485C} = 0.0239\text{mol e}^-$$

From the known mass of platinum, determine the number of moles:

$$2.12\text{gPt} \times \frac{1\text{mol Pt}}{195.078\text{gPt}} = 0.0109\text{molPt}$$

Determine the number of electrons transferred:

$$\frac{0.0239\text{ mol e}^-}{0.0109\text{ mol Pt}} = 2.19$$

Therefore, 2.19 is shared between Pt^{2+} and Pt^{x+}. Since we know the mole ratio between Pt^{2+} and Pt^{x+}, we can calculate x:
2.19=0.90×(+2) + 0.10× (x).
$2.19 = 1.80 + 0.10 \times x \Rightarrow x \approx 4$
(a) The oxidation state of the contaminant is +4.

INTEGRATIVE AND ADVANCED EXERCISES

75. **(M)** Oxidation: $V^{3+} + H_2O \longrightarrow VO^{2+} + 2\,H^+ + e^-$ $\qquad -E^\circ_a$

Reduction: $\underline{Ag^+ + e^- \longrightarrow Ag(s) \qquad\qquad E^\circ = +0.800\text{ V}}$

Net: $V^{3+} + H_2O + Ag^+ \longrightarrow VO^{2+} + 2\,H^+ + Ag(s) \qquad E^\circ_{cell} = 0.439\text{ V}$

$0.439\text{ V} = -E^\circ_a + 0.800\text{ V} \qquad E^\circ_a = 0.800\text{ V} - 0.439\text{ V} = 0.361\text{ V}$

Oxidation: $V^{2+} \longrightarrow V^{3+} + e^- \qquad -E^\circ_b$

Reduction: $\underline{VO^{2+} + 2\,H^+ + e^- \longrightarrow V^{3+} + H_2O \qquad E^\circ = +0.361\text{ V}}$

Net: $V^{2+} + VO^{2+} + 2\,H^+ \longrightarrow 2\,V^{3+} + H_2O \qquad E^\circ_{cell} = +0.616\text{ V}$

$0.616\text{ V} = -E^\circ_b + 0.361\text{ V} \quad E^\circ_b = 0.361\text{ V} - 0.616\text{ V} = -0.255\text{ V}$

Thus, for the cited reaction: $V^{3+} + e^- \longrightarrow V^{2+} \qquad E^\circ = -0.255\text{ V}$

76. **(M)**The cell reaction for discharging a lead storage battery is equation (20.24).

$Pb(s) + PbO_2(s) + 2\,H^+(aq) + 2\,HSO_4{}^-(aq) \longrightarrow PbSO_4(s) + 2\,H_2O(l)$

The half-reactions with which this equation was derived indicates that two moles of electrons are transferred for every two moles of sulfate ion consumed. We first compute the amount of H_2SO_4 initially present and then the amount of H_2SO_4 consumed.

$$\text{initial amount } H_2SO_4 = 1.50\text{ L} \times \frac{5.00\text{ mol } H_2SO_4}{1\text{ L soln}} = 7.50\text{ mol } H_2SO_4$$

$$\text{amount } H_2SO_4 \text{ consumed} = 6.0\text{ h} \times \frac{3600\text{ s}}{1\text{ h}} \times \frac{2.50\text{ C}}{1\text{ s}} \times \frac{1\text{ mol e}^-}{96485\text{ C}} \times \frac{2\text{ mol } SO_4{}^{2-}}{2\text{ mol e}^-} \times \frac{1\text{ mol } H_2SO_4}{1\text{ mol } SO_4{}^{2-}}$$

$$= 0.56\text{ mol } H_2SO_4$$

$$\text{final}\,[H_2SO_4] = \frac{7.50\text{ mol} - 0.56\text{ mol}}{1.50\text{ L}} = 4.63\text{ M}$$

77. **(M)** The cell reaction is $2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,OH^-(aq) + H_2(g) + Cl_2(g)$

We first determine the charge transferred per 1000 kg Cl_2.

$$\text{charge} = 1000\text{ kg } Cl_2 \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{1\text{ mol } Cl_2}{70.90\text{ g } Cl_2} \times \frac{2\text{ mol e}^-}{1\text{ mol } \quad Cl_2} \times \frac{96,485\text{ C}}{1\text{ mol e}^-} = 2.72 \times 10^9\text{ C}$$

(a) $\text{energy} = 3.45\ \text{V} \times 2.72 \times 10^{9}\ \text{C} \times \dfrac{1\ \text{J}}{1\ \text{V}\cdot\text{C}} \times \dfrac{1\ \text{kJ}}{1000\ \text{J}} = 9.38 \times 10^{6}\ \text{kJ}$

(b) $\text{energy} = 9.38 \times 10^{9}\ \text{J} \times \dfrac{1\ \text{W}\cdot\text{s}}{1\ \text{J}} \times \dfrac{1\ \text{h}}{3600\ \text{s}} \times \dfrac{1\ \text{kWh}}{1000\ \text{W}\cdot\text{h}} = 2.61 \times 10^{3}\ \text{kWh}$

78. **(D)** We determine the equilibrium constant for the reaction.

$$\begin{array}{lll}
\text{Oxidation:} & \text{Fe(s)} \longrightarrow \text{Fe}^{2+}\text{(aq)} + 2\text{e}^{-} & -E° = +0.440\ \text{V} \\
\text{Reduction:} & \{\text{Cr}^{3+}\text{(aq)} + \text{e}^{-} \longrightarrow \text{Cr}^{2+}\text{(aq)}\} \times 2 & E° = -0.424\ \text{V} \\
\hline
\text{Net:} & \text{Fe(s)} + 2\ \text{Cr}^{3+}\text{(aq)} \longrightarrow \text{Fe}^{2+}\text{(aq)} + 2\ \text{Cr}^{2+}\text{(aq)} & \text{E}^{\circ}_{\text{cell}} = +0.016\ \text{V}
\end{array}$$

$$\Delta G^{o} = -nFE^{o}_{cell} = -RT \ln K \Rightarrow \ln K = \frac{nFE^{o}_{cell}}{RT}$$

$$\ln\ K = \frac{2\ \text{mol e}^{-} \times 96485\ \text{Coul/mol e}^{-} \times 0.016\ \text{V}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}} = 1.2 \qquad K = \text{e}^{1..2} = 3.3$$

Reaction:	Fe(s) +	$2\ \text{Cr}^{3+}\text{(aq)} \rightleftharpoons$	$\text{Fe}^{2+}\text{(aq)}$ +	$2\text{Cr}^{2+}\text{(aq)}$
Initial :		1.00 M	0 M	0 M
Changes :		$-2x$ M	$+x$ M	$+2x$ M
Equil:		$(1.00 - 2x)$M	x M	$2x$ M

$$K = \frac{[\text{Fe}^{2+}][\text{Cr}^{2+}]^{2}}{[\text{Cr}^{3+}]^{2}} = 3.3 = \frac{x\ (2x)^{2}}{(1.00 - 2x)^{2}}$$

Let us simply substitute values of x into this cubic equation to find a solution. Notice that x cannot be larger than 0.50, (values > 0.5 will result in a negative value for the denominator.

$x = 0.40 \quad K = \dfrac{0.40\,(0.80)^{2}}{(1.00 - 0.80)^{2}} = 6.4 > 3.3 \qquad x = 0.35 \quad K = \dfrac{0.35\,(0.70)^{2}}{(1.00 - 0.70)^{2}} = 1.9 > 3.3$

$x = 0.37 \quad K = \dfrac{0.37\,(0.74)^{2}}{(1.00 - 0.74)^{2}} = 3.0 < 3.3 \qquad x = 0.38 \quad K = \dfrac{0.38\,(0.76)^{2}}{(1.00 - 0.76)^{2}} = 3.8 > 3.3$

Thus, we conclude that $x = 0.37$ M = $[\text{Fe}^{2+}]$.

79. **(D)** First we calculate the standard cell potential.

$$\begin{array}{lll}
\text{Oxidation:} & \text{Fe}^{2+}\text{(aq)} \longrightarrow \text{Fe}^{3+}\text{(aq)} + \text{e}^{-} & -E^{o} = -0.771\ \text{V} \\
\text{Reduction:} & \text{Ag}^{+}\text{(aq)} + \text{e}^{-} \longrightarrow \text{Ag(s)} & E^{o} = +0.800\ \text{V} \\
\hline
\text{Net:} & \text{Fe}^{2+}\text{(aq)} + \text{Ag}^{+}\text{(aq)} \longrightarrow \text{Fe}^{3+}\text{(aq)} + \text{Ag(s)} & E^{o}_{\text{cell}} = 0.029\ \text{V}
\end{array}$$

Next, we use the given concentrations to calculate the cell voltage with the Nernst equation.

$$E_{\text{cell}} = E^{o}_{\text{cell}} - \frac{0.0592}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = 0.029 - 0.0592 \log \frac{0.0050}{0.0050 \times 2.0} = 0.029 + 0.018 = 0.047\ \text{V}$$

The reaction will continue to move in the forward direction until concentrations of reactants decrease and those of products increase a bit more. At equilibrium, $E_{\text{cell}} = 0$, and we have the following.

$$E^{\circ}_{\text{cell}} = \frac{0.0592}{1}\log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = 0.029 \qquad \log\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = \frac{0.029}{0.0592} = 0.49$$

Reaction:	$\text{Fe}^{2+}(\text{aq})$	+	$\text{Ag}^{+}(\text{aq})$	$\rightleftharpoons$	$\text{Fe}^{3+}(\text{aq})$	+	Ag(s)
Initial:	0.0050 M		2.0 M		0.0050 M		–
Changes:	$-x$ M		$-x$ M		$+x$ M		–
Equil:	$(0.0050 - x)$ M		$(2.0 - x)$ M		$(0.0050 + x)$ M		–

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^{+}]} = 10^{0.49} = 3.1 = \frac{0.0050 + x}{(0.0050 - x)(2.0 - x)} \approx \frac{0.0050 + x}{2.0(0.0050 - x)}$$

$$6.2(0.0050 - x) = 0.0050 + x = 0.031 - 6.2\,x \qquad 7.2\,x = 0.026 \qquad x = \frac{0.026}{7.2} = 0.0036\text{ M}$$

Note that the assumption that $x << 2.0$ is valid. $[\text{Fe}^{2+}]$ = 0.0050 M – 0.0036 M = 0.0014 M

80. **(D)** We first note that we are dealing with a concentration cell, one in which the standard oxidation reaction is the reverse of the standard reduction reaction, and consequently its standard cell potential is precisely zero volts. For this cell, the Nernst equation permits us to determine the ratio of the two silver ion concentrations.

$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592}{1}\log\frac{[\text{Ag}^{+}(\text{satd AgI})]}{[\text{Ag}^{+}(\text{satd AgCl, } x\text{ M Cl}^{-})]} = 0.0860\text{ V}$$

$$\log\frac{[\text{Ag}^{+}(\text{satd AgI})]}{[\text{Ag}^{+}(\text{satd AgCl, } x\text{ M Cl}^{-})]} = \frac{-0.0860}{0.0592} = -1.45 \qquad \frac{[\text{Ag}^{+}(\text{satd AgI})]}{[\text{Ag}^{+}(\text{satd AgCl, } x\text{ M Cl}^{-})]} = 10^{-1.45} = 0.035$$

We can determine the numerator concentration from the solubility product expression for AgI(s)

$$K_{\text{sp}} = [\text{Ag}^{+}][\text{I}^{-}] = 8.5\times10^{-17} = s^{2} \qquad s = \sqrt{8.5\times10^{-17}} = 9.2\times10^{-9}\text{ M}$$

This permits the determination of the concentration in the denominator.

$$[\text{Ag}^{+}(\text{satd AgCl}, x\text{ M Cl}^{-})] = \frac{9.2\times10^{-9}}{0.035} = 2.6\times10^{-7}\text{ M}$$

We now can determine the value of *x*. Note: Cl^{-} arises from two sources, one being the dissolved AgCl.

$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Cl}^{-}] = 1.8\times10^{-10} = (2.6\times10^{-7})(2.6\times10^{-7} + x) = 6.8\times10^{-14} + 2.6\times10^{-7}\,x$$

$$x = \frac{1.8\times10^{-10} - 6.8\times10^{-14}}{2.6\times10^{-7}} = 6.9\times10^{-4}\text{ M} = [\text{Cl}^{-}]$$

81. **(M)** The Faraday constant can be evaluated by measuring the electric charge needed to produce a certain quantity of chemical change. For instance, let's imagine that an electric circuit contains the half-reaction $\text{Cu}^{2+}(\text{aq}) + 2\text{ e}^{-} \rightleftharpoons \text{Cu(s)}$. The electrode on which the solid copper plates out is weighed before and after the passage of electric current. The mass gain is the mass of copper reduced, which then is converted into the moles of copper reduced. The number of moles of electrons involved in the reduction then is computed from the stoichiometry for the reduction half-reaction. In addition, the amperage is measured during the reduction, and the time is recorded. For simplicity, we assume the amperage is constant. Then the total charge (in coulombs) equals the current (in amperes, that is, coulombs per second) multiplied by the time (in seconds). The ratio of the total charge (in coulombs) required by the reduction divided by the amount (in moles) of electrons is the Faraday constant. To determine the Avogadro constant, one uses the charge of the electron, 1.602×10^{-19} C and the Faraday constant in the following calculation.

$$N_A = \frac{96{,}485\,\text{C}}{1\,\text{mol electrons}} \times \frac{1\,\text{electron}}{1.602 \times 10^{-19}\,\text{C}} = 6.023 \times 10^{23}\,\frac{\text{electrons}}{\text{mole}}$$

82. **(M)** In this problem we are asked to determine ΔG_f^o for N_2H_4(aq) using the electrochemical data for hydrazine fuel cell. We first determine the value of ΔG° for the cell reaction, a reaction in which $n = 4$. ΔG_f^o can then be determined using data in Appendix D.

Stewise approach:

Calculate ΔG° for the cell reaction (n=4):

$$\Delta G^\circ = -n\,FE^o_{cell} - 4\ \text{mol e}^- \times \frac{96{,}485\ \text{C}}{1\ \text{mol e}^-} \times 1.559\ \text{V} = -6.017 \times 10^5\ \text{J} = -601.7\ \text{kJ}$$

Using the data in Appendix D, determine ΔG_f^o for hydrazine (N_2H_4):

$$\text{-601.7 kJ} = \Delta G_f^o[N_2(g)] + 2\,\Delta G_f^o[H_2O(l)] - \Delta G_f^o[N_2H_4(aq)] - \Delta G_f^o[O_2(g)]$$

$$= 0.00\ \text{kJ} + 2 \times (-237.2\ \text{kJ}) - \Delta G_f^o[N_2H_4(aq)] - 0.00\ \text{kJ}$$

$$\Delta G_f^o[N_2H_4(aq)] = 2 \times (-237.2\ \text{kJ}) + 601.7\ \text{kJ} = +127.3\ \text{kJ}$$

Conversion pathway approach:

$$\Delta G^\circ = -n\,FE^o_{cell} - 4\ \text{mol e}^- \times \frac{96{,}485\ \text{C}}{1\ \text{mol e}^-} \times 1.559\ \text{V} = -6.017 \times 10^5\ \text{J} = -601.7\ \text{kJ}$$

$$\text{-601.7 kJ} = \Delta G_f^o[N_2(g)] + 2\,\Delta G_f^o[H_2O(l)] - \Delta G_f^o[N_2H_4(aq)] - \Delta G_f^o[O_2(g)]$$

$$= 0.00\ \text{kJ} + 2 \times (-237.2\ \text{kJ}) - \Delta G_f^o[N_2H_4(aq)] - 0.00\ \text{kJ}$$

$$\Delta G_f^o[N_2H_4(aq)] = 2 \times (-237.2\ \text{kJ}) + 601.7\ \text{kJ} = +127.3\ \text{kJ}$$

83. **(M)** In general, we shall assume that both ions are present initially at concentrations of 1.00 M. Then we shall compute the concentration of the more easily reduced ion when its reduction potential has reached the point at which the other cation starts being reduced by electrolysis. In performing this calculation we use the Nernst equation, but modified for use with a half-reaction. We find that, in general, the greater the difference in *E*° values for two reduction half-reactions, the more effective the separation.

(a) In this case, no calculation is necessary. If the electrolysis takes place in aqueous solution, H_2(g) rather than K(s) will be produced at the cathode. Cu^{2+} can be separated from K^+ by electrolysis.

(b) $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)\ E^\circ = +0.340\ \text{V} \qquad Ag^+(aq) + e^- \rightarrow Ag(s) \quad E^\circ = +0.800\ \text{V}$

Ag^+ will be reduced first. Now we ask what $[Ag^+]$ will be when $E = +0.337$ V.

$$0.337\ \text{V} = 0.800\ \text{V} - \frac{0.0592}{1}\log\frac{1}{[Ag^+]} \qquad \log\frac{1}{[Ag^+]} = \frac{0.800 - 0.340}{0.0592} = +7.77$$

$[Ag^+] = 1.7 \times 10^{-8}$ M. Separation of the two cations is essentially complete.

(c) $Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)\; E^o = -0.125$ V $\qquad Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s) \qquad E^o = -0.137$ V

Pb^{2+} will be reduced first. We now ask what $[Pb^{2+}]$ will be when $E° = -0.137$ V.

$$-0.137\text{ V} = -0.125\text{ V} - \frac{0.0592}{2}\log\frac{1}{[Pb^{2+}]} \qquad \log\frac{1}{[Pb^{2+}]} = \frac{2(0.137-0.125)}{0.0592} = 0.41$$

$[Pb^{2+}] = 10^{-0.41} = 0.39$ M Separation of Pb^{2+} from Sn^{2+} is not complete.

84. **(D)** The efficiency value for a fuel cell will be greater than 1.00 for any exothermic reaction ($\Delta H^o < 0$) that has $\Delta G°$ that is more negative than its ΔH^o value. Since $\Delta G^o = \Delta H^o - T\,\Delta S^o$, this means that the value of ΔS^o must be positive. Moreover, for this to be the case, Δn_{gas} is usually greater than zero. Let us consider the situation that might lead to this type of reaction. The combustion of carbon-hydrogen-oxygen compounds leads to the formation of $H_2O(l)$ and $CO_2(g)$. Since most of the oxygen in these compounds comes from $O_2(g)$ (some is present in the C-H-O compound), there is a balance in the number of moles of gas produced—$CO_2(g)$—and those consumed—$O_2(g)$—which is offset in a negative direction by the $H_2O(l)$ produced. Thus, the combustion of these types of compounds will only have a positive value of Δn_{gas} if the number of oxygens in the formula of the compound is more than twice the number of hydrogens. By comparison, the decomposition of NOCl(g), an oxychloride of nitrogen, does produce more moles of gas than it consumes. Let us investigate this decomposition reaction.

$$NOCl(g) \longrightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}Cl_2(g)$$

$$\Delta H^o = \tfrac{1}{2}\Delta H^o_f\,[N_2(g)] + \tfrac{1}{2}\Delta H^o_f\,[O_2(g)] + \tfrac{1}{2}\Delta H^o_f\,[Cl_2(g)] - \Delta H^o_f\,[NOCl(g)]$$

$$= 0.500\,(0.00\text{ kJ/mol} + 0.00\text{ kJ/mol} + 0.00\text{ kJ/mol}) - 51.71\text{ kJ/mol} = -51.71\text{ kJ/mol}$$

$$\Delta G^o = \tfrac{1}{2}\Delta G^o_f\,[N_2(g)] + \tfrac{1}{2}\Delta G^o_f\,[O_2(g)] + \tfrac{1}{2}\Delta G^o_f\,[Cl_2(g)] - \Delta G^o_f\,[NOCl(g)]$$

$$= 0.500\,(0.00\text{ kJ/mol} + 0.00\text{ kJ/mol} + 0.00\text{ kJ/mol}) - 66.08\text{ kJ/mol} = -66.08\text{ kJ/mol}$$

$$\varepsilon = \frac{\Delta G^o}{\Delta H^o} = \frac{-66.08\text{ kJ/mol}}{-51.71\text{ kJ/mol}} = 1.278$$

Yet another simple reaction that meets the requirement that $\Delta G^o < \Delta H^o$ is the combustion of graphite: $C(graphite) + O_2(g) \longrightarrow CO_2(g)$ We see from Appendix D that $\Delta G^o_f[CO_2(g)] = -394.4$ kJ/mol is more negative than $\Delta H^o_f[CO_2(g)] = -393.5$ kJ/mol. (This reaction is accompanied by an increase in entropy; ΔS =213.7-5.74-205.1 =2.86 J/K, ε = 1.002.) $\Delta G^o < \Delta H^o$ is true of the reaction in which CO(g) is formed from the elements. From Appendix D, $\Delta H^o_f\{CO(g)\} = -110.5$ kJ/mol, and $\Delta G^o_f\{CO(g)\} = -137.2$ kJ/mol, producing ε = (–137.2/–110.5) = 1.242.

Note that any reaction that has ε > 1.00 will be spontaneous under standard conditions at all temperatures. (There, of course, is another category, namely, an endothermic reaction that has $\Delta S^o < 0$. This type of reaction is nonspontaneous under standard conditions at all temperatures. As such it consumes energy while it is running, which is clearly not a desirable result for a fuel cell.)

85. **(M)** We first write the two half-equations and then calculate a value of ΔG^o from thermochemical data. This value then is used to determine the standard cell potential.

Oxidation: $CH_3CH_2OH(g) + 3\ H_2O(l) \longrightarrow 2\ CO_2(g) + 12\ H^+(aq) + 12\ e^-$

Reduction: $\{O_2(g) + 4\ H^+(aq) + 4e^- \longrightarrow 2\ H_2O(l)\} \times 3$

Overall: $CH_3CH_2OH(g)\ + 3\ O_2(g) \longrightarrow 3\ H_2O(l) + 2\ CO_2(g)$

Thus, $n = 12$

(a) $\Delta G^o = 2\Delta G_f^o[CO_2(g)] + 3\Delta G_f^o[H_2O(l)] - \Delta G_f^o[CH_3CH_2OH(g)] - 3\Delta G_f^o[O_2(g)]$

$= 2(-394.4\text{ kJ/mol}) + 3(-237.1\text{ kJ/mol}) - (-168.5\text{ kJ/mol}) - 3(0.00\text{ kJ/mol}) = -1331.6\text{ kJ/mol}$

$$E^\circ_{cell} = -\frac{\Delta G^\circ}{n\ F} = -\frac{-1331.6 \times 10^3\ \text{J/mol}}{12\ \text{mol e}^- \times 96,485\ \text{C/mol e}^-} = +1.1501\ \text{V}$$

(b) $E^\circ_{cell} = E^\circ[O_2(g)/H_2O] - E^\circ[CO_2(g)/CH_3CH_2OH(g)] = 1.1501\ V$

$= 1.229\ V - E^\circ[CO_2(g)/CH_3CH_2OH(g)]$

$E^\circ[CO_2(g)/CH_3CH_2OH(g)] = 1.229 - 1.1501 = +0.079\ V$

86. **(M)** First we determine the change in the amount of H^+ in each compartment.

Oxidation: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$ Reduction: $2\ H^+(aq)\ + 2\ e^- \rightarrow H_2(g)$

$$\Delta\ \text{amount}\ H^+ = 212\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{1.25\ \text{C}}{1\ \text{s}} \times \frac{1\ \text{mol e}^-}{96,485\ \text{C}} \times \frac{1\ \text{mol H}^+}{1\ \text{mol e}^-} = 0.165\ \text{mol H}^+$$

Before electrolysis, there is 0.500 mol $H_2PO_4^-$ and 0.500 mol HPO_4^{2-} in each compartment. The electrolysis adds 0.165 mol H^+ to the anode compartment, which has the effect of transforming 0.165 mol HPO_4^{2-} into 0.165 mol $H_2PO_4^-$, giving a total of 0.335 mol HPO_4^{2-} (0.500 mol – 0.165 mol) and 0.665 mol $H_2PO_4^-$ (0.500 mol + 0.165 mol). We can use the Henderson-Hasselbalch equation to determine the pH of the solution in the anode compartment.

$$\text{pH} = \text{p}K_{a_2} + \log\frac{[HPO_4^{\ 2-}]}{[H_2PO_4]} = 7.20 + \log\frac{0.335\ \text{mol}\ HPO_4^{\ 2-}/0.500\ \text{L}}{0.665\ \text{mol}\ H_2PO_4^{\ -}/0.500\ \text{L}} = 6.90$$

Again we use the Henderson-Hasselbalch equation in the cathode compartment. After electrolysis there is 0.665 mol HPO_4^{2-} and 0.335 mol $H_2PO_4^-$. Again we use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_{a_2} + \log\frac{[HPO_4^{\ 2-}]}{[H_2PO_4^{\ -}]} = 7.20 + \log\frac{0.665\ \text{mol}\ HPO_4^{\ 2-}/0.500\ \text{L}}{0.335\ \text{mol}\ H_2PO_4^{\ -}/0.500\ \text{L}} = 7.50$$

87. **(M)** We first determine the change in the amount of M^{2+} ion in each compartment.

$$\Delta M^{2+} = 10.00\text{h} \times \frac{3600\ \text{s}}{1\ \text{h}} \times \frac{0.500\ \text{C}}{1\ \text{s}} \times \frac{1\text{mol e}^-}{96485\ \text{C}} \times \frac{1\text{mol M}^{2+}}{2\text{mol e}^-} = 0.0933\ \text{mol M}^{2+}$$

This change in amount is the increase in the amount of Cu^{2+} and the decrease in the amount of Zn^{2+}. We can also calculate the change in each of the concentrations.

$$\Delta[\mathrm{Cu}^{2+}]=\frac{+0.0933\ \mathrm{mol\ Cu}^{2+}}{0.1000\ \mathrm{L}}=+0.933\ \mathrm{M}\qquad \Delta[\mathrm{Zn}^{2+}]=\frac{-0.0933\ \mathrm{mol\ Zn}^{2+}}{0.1000\ \mathrm{L}}=-0.933\ \mathrm{M}$$

Then the concentrations of the two ions are determined.

$$[\mathrm{Cu}^{2+}]=1.000\ \mathrm{M}+0.933\ \mathrm{M}=1.933\ \mathrm{M}\qquad [\mathrm{Zn}^{2+}]=1.000\ \mathrm{M}-0.933\ \mathrm{M}=0.067\ \mathrm{M}$$

Now we run the cell as a voltaic cell, first determining the value of $E_{\text{cell}}°$.

$$\begin{array}{lllr}
\text{Oxidation}: & \mathrm{Zn(s)} \longrightarrow \mathrm{Zn}^{2+}\mathrm{(aq)} + 2\ \mathrm{e}^- & -E° = +0.763\ \mathrm{V} \\
\text{Reduction}: & \mathrm{Cu}^{2+}\mathrm{(aq)} + 2\ \mathrm{e}^-\quad \mathrm{Cu(s)} & E° = +0.340\ \mathrm{V} \\
\hline
\text{Net}: & \mathrm{Zn(s)} + \mathrm{Cu}^{2+}\mathrm{(aq)} \longrightarrow \mathrm{Cu(s)} & E^{\circ}_{\text{cell}} = +1.103\ \mathrm{V}
\end{array}$$

Then we use the Nernst equation to determine the voltage of this cell.

$$E_{\text{cell}}=E^{\circ}_{\text{cell}}-\frac{0.0592}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}=1.103-\frac{0.0592}{2}\log\frac{0.067\ \mathrm{M}}{1.933\ \mathrm{M}}=1.103+0.043=1.146\ \mathrm{V}$$

88. (M)(a)

$$\begin{array}{llr}
\text{Anode: } \mathrm{Zn(s)} \longrightarrow \mathrm{Zn}^{2+}\mathrm{(aq)} + 2\mathrm{e}^- & & -E° = +0.763\ \mathrm{V} \\
\text{Cathode: } \{\mathrm{AgCl(s)} + \mathrm{e}^-\mathrm{(aq)} \longrightarrow \mathrm{Ag(s)} + \mathrm{Cl}^-\mathrm{(1\ M)}\} & \times\ 2 & E°=+0.2223\ \mathrm{V} \\
\hline
\text{Net: } \mathrm{Zn(s)} + 2\mathrm{AgCl(s)} \longrightarrow \mathrm{Zn}^{2+}\mathrm{(aq)} + 2\mathrm{Ag(s)} + 2\mathrm{Cl}^-\mathrm{(1\ M)} & & E^{\circ}_{\text{cell}} = +0.985\ \mathrm{V}
\end{array}$$

(b) The major reason why this electrode is easier to use than the standard hydrogen electrode is that it does not involve a gas. Thus there are not the practical difficulties involved in handling gases. Another reason is that it yields a higher value of E°_{cell}, thus, this is a more spontaneous system.

(c)

$$\begin{array}{lll}
\text{Oxidation:} & \mathrm{Ag(s)} \longrightarrow \mathrm{Ag}^+\mathrm{(aq)} + \mathrm{e}^- & -E^{\mathrm{o}} = -0.800\ \mathrm{V} \\
\text{Reduction:} & \mathrm{AgCl(s)} + \mathrm{e}^- \longrightarrow \mathrm{Ag(s)} + \mathrm{Cl}^-\mathrm{(aq)} & E = +0.2223\ \mathrm{V} \\
\hline
\text{Net:} & \mathrm{AgCl(s)} \longrightarrow \mathrm{Ag}^+\mathrm{(aq)} + \mathrm{Cl}^-\mathrm{(aq)} & E^{\mathrm{o}}_{\text{cell}} = -0.578\ \mathrm{V}
\end{array}$$

The net reaction is the solubility reaction, for which the equilibrium constant is K_{sp}.

$$\Delta G° = -nFE° = -RT\ \ln K_{\text{sp}}$$

$$\ln K_{\text{sp}}=\frac{nFE°}{RT}=\frac{1\ \mathrm{mol\ e}^-\times\dfrac{96485\ \mathrm{C}}{1\ \mathrm{mol\ e}^-}\times(-0.578\ \mathrm{V})\times\dfrac{1\ \mathrm{J}}{1\ \mathrm{V.C}}}{8.3145\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}\times 298.15\ \mathrm{K}}=-22.5$$

$$K_{\text{sp}}=\mathrm{e}^{-22.5}=1.7\times 10^{-10}$$

This value is in good agreement with the value of 1.8×10^{-10} given in Table 18-1.

89. (D) (a)

$$\begin{array}{ll}
\mathrm{Ag(s)} \rightarrow \mathrm{Ag}^+\mathrm{(aq)} + \mathrm{e}^- & -E° = -0.800\ \mathrm{V} \\
\underline{\mathrm{AgCl(s)} + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} + \mathrm{Cl}^-\mathrm{(aq)}} & \underline{E° = 0.2223\ \mathrm{V}} \\
\mathrm{AgCl(s)} \rightarrow \mathrm{Ag}^+\mathrm{(aq)} + \mathrm{Cl}^-\mathrm{(aq)} & E°_{\text{cell}} = -0.577\underline{7}\ \mathrm{V}
\end{array}$$

$$\mathrm{E}_{\text{cell}}=\mathrm{E}_{\text{cell}}-\frac{0.0592}{1}\left(\log\frac{[\mathrm{Ag}^+][\mathrm{Cl}^-]}{1}\right)=-0.577\underline{7}\ \mathrm{V}-\frac{0.0592}{1}\log\left(\frac{[1.00][1.00\times10^{-3}]}{1}\right)=-0.400\ \mathrm{V}$$

(b) 10.00 mL of 0.0100 M $\mathrm{CrO_4}^{2-}$ + 100.0 mL of 1.00×10^{-3} M Ag^+ (V_{total} = 110.0 mL)

Concentration of CrO_4^{2-}after dilution: 0.0100 M×10.00 mL /110.00 mL = 0.000909 M
Concentration of Ag^+ after dilution: 0.00100 M×100.0 mL /110.00 mL = 0.000909 M

$Ag_2CrO_4(s) \xrightleftharpoons{K_{sp}=1.1\times10^{-12}}$	$2Ag^+(aq)$ +	$CrO_4^{2-}(aq)$
Initial	0.000909 M	0.000909 M
Change(100% rxn)	-0.000909 M	-0.000455 M
New initial	0 M	0.000455 M
Change	$+2x$	$+x$
Equilibrium	$2x$	$0.000455\ M + x \approx 0.000455\ M$

$1.1 \times 10^{-12} = (2x)^2(0.000454)$
$x = 0.0000246$ M Note: 5.4% of 0.000455 M (assumption may be considered valid)
(Answer would be $x = 0.0000253$ using method of successive approx.)
$[Ag^+] = 2x = 0.0000492$ M (0.0000506 M using method of successive approx.)

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{1}\log[Ag^+][Cl^-] = -0.577\underline{7} - \frac{0.0592}{1}\log[1.00M][4.92\times10^{-4}M]$$

$= -0.323$ V (-0.306 V for method of successive approximations)

(c) 10.00 mL 0.0100 M NH_3 + 10.00 mL 0.0100 M CrO_4^{2-} + 100.0 mL 1.00×10^{-3} M Ag^+ (V_{total} = 120.0 mL)
Concentration of NH_3 after dilution: 10.0 M×10.00 mL /120.00 mL = 0.833 M
Concentration of CrO_4^{2-}after dilution: 0.0100 M×10.00 mL /110.00 mL = 0.000833 M
Concentration of Ag^+ after dilution: 0.00100 M×100.0 mL /110.00 mL = 0.000833 M

In order to determine the equilibrium concentration of free $Ag^+(aq)$, we first consider complexation of $Ag^+(aq)$ by $NH_3(aq)$ and then check to see if precipitation occurs.

	$Ag^+(aq)$ +	$2NH_3(aq) \xrightleftharpoons{K_f=1.6\times10^7}$	$Ag(NH_3)_2^+(aq)$
Initial	0.000833 M	0.833 M	0 M
Change(100% rxn)	-0.000833 M	-0.00167 M	+0.000833 M
New initial	0 M	0.831 M	0.000833 M
Change	$+x$	$+2x$	$-x$
Equilibrium	x	$(0.831+2x)$ M	$(0.000833 - x)$ M
Equilibrium ($x \approx 0$)	x	0.831 M	0.000833 M

$1.6 \times 10^7 = 0.000833 / x(0.831)^2$ $x = 7.5\underline{4}\times10^{-11}\ M = [Ag^+]$
Note: The assumption is valid
Now we look to see if a precipitate forms: $Q_{sp} = (7.5\underline{4}\times10^{-11})^2(0.000833) = 4.7\times10^{-24}$
Since $Q_{sp} < K_{sp}$ (1.1×10^{-12}), no precipitate forms and $[Ag^+] = 7.5\underline{4}\times10^{-11}$ M

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{1}\log[Ag^+][Cl^-] = -0.577\underline{7}\ V - \frac{0.0592}{1}\log[1.00M][7.5\underline{4}\times10^{-11}M]$$

$$E_{\text{cell}} = 0.021\underline{5}\,V$$

90. **(M)** We assume that the $Pb^{2+}(aq)$ is “ignored” by the silver electrode, that is, the silver electrode detects only silver ion in solution.

$$\text{Oxidation}: \text{H}_2(\text{g}) \longrightarrow 2\ \text{H}^+(\text{aq}) + 2\ \text{e}^- \qquad -E° = 0.000\ \text{V}$$

$$\text{Reduction}: \{\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)}\} \times 2 \qquad E° = \ 0.800\ \text{V}$$

$$\text{Net}: \quad \text{H}_2(\text{g}) + 2\ \text{Ag}^+ \longrightarrow 2\ \text{H}^+(\text{aq}) + 2\ \text{Ag(s)} \quad E°_{\text{cell}} = 0.800\ \text{V}$$

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{H}^+]^2}{[\text{Ag}^+]^2} \qquad 0.503\ \text{V} = 0.800\ \text{V} - \frac{0.0592}{2}\log\frac{1.00^2}{[\text{Ag}^+]^2}$$

$$\log\frac{1.00^2}{[\text{Ag}^+]^2} = \frac{2(0.800 - 0.503)}{0.0592} = 10.0 \qquad \frac{1.00^2}{[\text{Ag}^+]^2} = 10^{+10.0} = 1.0 \times 10^{10}$$

$$[\text{Ag}^+]^2 = 1.0 \times 10^{-10}\text{M}^2 \Rightarrow [\text{Ag}^+] = 1.0 \times 10^{-5}$$

$$\text{mass Ag} = 0.500\ \text{L} \times \frac{1.0 \times 10^{-5}\ \text{mol Ag}^+}{1\ \text{L soln}} \times \frac{1\ \text{mol Ag}}{1\ \text{mol Ag}^+} \times \frac{107.87\ \text{g Ag}}{1\ \text{mol Ag}} = 5.4 \times 10^{-4}\ \text{g Ag}$$

$$\%\ \text{Ag} = \frac{5.4 \times 10^{-4}\ \text{g Ag}}{1.050\ \text{g sample}} \times 100\ \% = 0.051\%\ \text{Ag (by mass)}$$

91. **(M)** 250.0 mL of 0.1000 M $CuSO_4$ = 0.02500 moles Cu^{2+} initially.

$$\text{moles of Cu}^{2+}\text{ plated out} = \frac{3.512\,\text{C}}{\text{s}} \times 1368\ \text{s} \times \frac{1\ \text{mol e}^-}{96{,}485\ \text{C}} \times \frac{1\ \text{mol Cu}^{2+}}{2\ \text{mole}^-} = 0.02490\,\text{mol Cu}^{2+}$$

moles of Cu^{2+} in solution = 0.02500 mol – 0.02490 mol = 0.00010 mol Cu^{2+}

$[Cu^{2+}]$ = 0.00010 mol Cu^{2+}/0.250 L = 4.0 × 10^{-4} M

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \xrightleftharpoons{K_f = 1.1\times10^{13}}$	$Cu(NH_3)_4{}^{2+}(aq)$
Initial	0.00040 M	0.10 M	0 M
Change(100% rxn)	-0.00040M	maintained	+0.00040 M
New initial	0 M	0.10 M	0.00040 M
Change	+x	maintained	-x
Equilibrium	x	0.10 M	$(0.00040 - x)$ M ≈ 0.00040 M

$$\text{K}_\text{f} = \frac{[\text{Cu(NH}_3)_4{}^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{0.00040}{[\text{Cu}^{2+}](0.10)^4} = 1.1\times10^{13} \qquad [\text{Cu}^{2+}] = 3.6\times10^{-13}\,M$$

Hence, the assumption is valid. The concentration of $Cu(NH_3)_4{}^{2+}$(aq) = 0.00040 M which is 40 times greater than the 1 × 10^{-5} detection limit. Thus, the blue color should appear.

<u>92</u>. **(M)** First we determine the molar solubility of AgBr in 1 M NH_3 .

*S*um	$AgBr(s) + 2NH_3(aq) \rightleftharpoons$	$Ag(NH_3)^{2+}(aq) +$	$Br^-(aq)$	$K = K_{sp} \times K_f = 8.0\times10^{-6}$
Initial	1.00 M	0 M	0 M	
*E*quil.	1.00-2s	s	s	{s ⇒ AgBr molar solubility}

$$\text{K} = \frac{[\text{Ag(NH}_3)_2{}^+][\text{Br}^-]}{[\text{NH}_3(\text{aq})]} = \frac{s^2}{(1-2s)^2} = 8.0\times10^{-6} \qquad s = 2.8\underline{1}\times10^{-3}\ \text{M (also [Br}^-])$$

$$\text{So }[\text{Ag}^+] = \frac{\text{K}_{\text{sp}}}{[\text{Br}^-]} = \frac{5.0\times10^{-13}}{2.8\underline{1}\times10^{-3}} = 1.8\times10^{-10}\,M$$

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+ + Br^-} \qquad \mathrm{K_{sp} = 5.0\times10^{-13}}$$

$$\underline{\mathrm{Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2{}^+}} \qquad \mathrm{K_f = 1.6\times10^{7}}$$

$$\text{(sum)}\ \mathrm{AgBr(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+ + Br^-} \qquad \mathrm{K = K_{sp} \times K_f = 8.0\times10^{-6}}$$

Now, let's construct the cell, guessing that the standard hydrogen electrode is the anode.

$$\text{Oxidation:}\quad H_2(\mathrm{g}) \longrightarrow 2\ \mathrm{H^+} + \ 2\ \mathrm{e^-} \qquad E^\circ = -0.000\ \mathrm{V}$$

$$\text{Reduction:}\quad \underline{\{\mathrm{A}g^+(\mathrm{aq}) + \ \mathrm{e^-} \longrightarrow \mathrm{A}g(\mathrm{s})\ \} \ \times\ 2 \qquad E^\circ = +0.800\ \mathrm{V}}$$

$$\text{Net:}\quad 2\ \mathrm{Ag^+(aq) + H_2(g)} \longrightarrow 2\ \mathrm{Ag(s)}\ + 2\ \mathrm{H^+(aq)} \qquad E^\circ_{\mathrm{cell}} = +0.800\mathrm{V}$$

From the Nernst equation:

$$\mathrm{E}\ =\ \mathrm{E^o} - \frac{0.0592}{\mathrm{n}}\log_{10} Q = \mathrm{E^o} - \frac{0.0592}{\mathrm{n}}\log\frac{[H^+]^2}{[Ag^+]^2} = 0.800\ \mathrm{V} - \frac{0.0592}{2}\log_{10}\frac{1^2}{(1.7\underline{8}\times10^{-10})^2}$$

and E = 0.22$\underline{3}$ V. Since the voltage is positive, our guess is correct and the standard hydrogen electrode is the anode (oxidizing ele*ctrode*).

93. **(M) (a)** Anode: $2\mathrm{H_2O(l)} \rightarrow 4\ \mathrm{e^-} + 4\ \mathrm{H^+(aq)} + \mathrm{O_2(g)}$

Cathode: $\underline{2\ \mathrm{H_2O(l)} + 2\ \mathrm{e^-} \rightarrow 2\ \mathrm{OH^-(aq)} + \mathrm{H_2(g)}}$

Overall: $2\ \mathrm{H_2O(l)} + \cancel{4\ \mathrm{H_2O(l)}} \rightarrow \cancel{4\ \mathrm{H^+(aq)}} + \cancel{4\ \mathrm{OH^-(aq)}} + 2\ \mathrm{H_2(g)} + \mathrm{O_2(g)}$

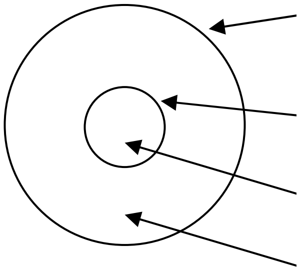
$2\ \mathrm{H_2O(l)} \rightarrow 2\ \mathrm{H_2(g)} + \mathrm{O_2(g)}$

(b) 21.5 mA = 0.0215 A or 0.0215 C $\mathrm{s^{-1}}$ for 683 s

$$\text{mol } \mathrm{H_2SO_4}\ = \frac{0.0215\ \mathrm{C}}{\mathrm{s}} \times 683\mathrm{s} \times \frac{1\ \mathrm{mol\ e^-}}{96485\mathrm{C}} \times \frac{1\ \mathrm{mol\ H^+}}{1\ \mathrm{mol\ e^-}} \times \frac{1\ \mathrm{mol\ H_2SO_4}}{2\ \mathrm{mol\ H^+}} = 7.61\times10^{-5}\ \mathrm{mol\ H_2SO_4}$$

7.61×10^{-5} mol $\mathrm{H_2SO_4}$ in 10.00 mL. Hence $[\mathrm{H_2SO_4}] = 7.61\times10^{-5}$ mol / 0.01000 L = 7.61×10^{-3}M

94. **(D)** First we need to find the total surface area



Outer circumference = 2πr = 2π(2.50 cm) = 15.7 cm
Surface area = circumference × thickness = 15.7 cm × 0.50 cm = 7.8$\underline{5}$ $\mathrm{cm^2}$

Inner circumference = 2πr = 2π(1.00 cm) = 6.28 cm
Surface area = circumference × thickness = 6.28 cm × 0.50 cm = 3.1$\underline{4}$ $\mathrm{cm^2}$

Area of small circle = $\pi r^2 = \pi(1.00\ \mathrm{cm})^2 = 3.14\ \mathrm{cm^2}$

Area of large circle = $\pi r^2 = \pi(2.50\ \mathrm{cm})^2 = 19.6\ \mathrm{cm^2}$

Total area = $7.85\ \mathrm{cm^2} + 3.14\ \mathrm{cm^2} + 2\times(19.6\ \mathrm{cm^2}) - 2\times(3.1\underline{4}\ \mathrm{cm^2}) = 43.9\underline{1}\ \mathrm{cm^2}$

Volume of metal needed = surface area × thickness of plating = $43.9\underline{1}\ \mathrm{cm^2} \times 0.0050\ \mathrm{cm} = 0.22\ \mathrm{cm^3}$

$$\text{Charge required} = 0.22\ \mathrm{cm^3} \times \frac{8.90\ \mathrm{g}}{\mathrm{cm^3}} \times \frac{1\ \mathrm{mol\ Ni}}{58.693\ \mathrm{g\ Ni}} \times \frac{2\ \mathrm{mol\ e^-}}{1\ \mathrm{mol\ Ni}} \times \frac{96485\ \mathrm{C}}{1\ \mathrm{mol\ e^-}} = 6437.5\ \mathrm{C}$$

Time = charge/time = 6437.5 C / 1.50 C/s = 4291.7 s or 71.5 min

95. (M) The overall reaction for the electrolytic cell is:

$$\text{Cu(s)+Zn}^{2+}\text{(aq)} \to \text{Cu}^{2+}\text{(aq)+Zn(s)} \qquad E^o_{cell} = -1.103\text{V}$$

Next, we calculate the number of moles of Zn^{2+}(aq) plated out and number of moles of Cu^{2+}(aq) formed:

$$n(\text{Cu}^{2+}) = = \frac{0.500\text{C}}{\text{s}} \times 10\text{ h} \times \frac{60\,\text{min}}{1\text{h}} \times \frac{60\,\text{s}}{1\text{min}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Cu}^{2+}}{2\text{ mol e}^-} = 0.0935\,\text{mol Cu}^{2+}$$

$$n(\text{Zn}^{2+}) = n(\text{Cu}^{2+})\text{=0.0935mol}$$

Initially, solution contained $1.00\text{molL}^{-1} \times 0.100\text{L=0.100 mol Zn}^{2+}$(aq). Therefore, at the end of electrolysis we are left with:

$$\text{n(Zn}^{2+})_{\text{LEFT}}\text{=(0.100-0.0935)mol=}6.5\times10^{-3}\text{mol} \Rightarrow [\text{Zn}^{2+}]\text{=}\frac{6.5\times10^{-3}\text{mol}}{0.1\text{L}}\text{=}6.5\times10^{-2}\text{M}$$

$$\text{n(Cu}^{2+})_{\text{FORMED}}\text{=0.0935mol} \Rightarrow [\text{Cu}^{2+}]\text{=}\frac{0.0935\text{mol}}{0.1\text{L}}\text{=0.936M}$$

The new potential after the cell was switched to a voltaic one can be calculated using Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.103 - \frac{0.0592}{2}\log\frac{6.5\times10^{-3}\text{ M}}{0.935\text{ M}} = 1.103 + 0.064 = 1.167\text{ V}$$

96. (M) (a) The metal has to have a reduction potential more negative than -0.691 V, so that its oxidation can reverse the tarnishing reaction's -0.691 V reduction potential. Aluminum is a good candidate, because it is inexpensive, readily available, will not react with water and has an E^o of -1.676 V. Zinc is also a possibility with an E^o of -0.763 V, but we don't choose it because there may be an overpotential associated with the tarnishing reaction.

(b) Oxidation: $\{\text{Al(s)} \longrightarrow \text{Al}^{3+}\text{(aq)} + 3\text{ e}^-\} \times 2$

Reduction: $\{\text{Ag}_2\text{S(s)} + 2\text{ e}^- \longrightarrow \text{Ag(s)} + \text{S}^{2-}\text{(aq)}\} \times 3$

Net: $2\text{ Al(s)} + 3\text{ Ag}_2\text{S(s)} \longrightarrow 6\text{Ag(s)} + 2\text{ Al}^{3+}\text{(aq)} + 3\text{ S}^{2-}\text{(aq)}$

(c) The dissolved $NaHCO_3$(s) serves as an electrolyte. It would also enhance the electrical contact between the two objects.

(d) There are several chemicals involved: Al, H_2O, and $NaHCO_3$. Although the aluminum plate will be consumed very slowly because silver tarnish is very thin, it will, nonetheless, eventually erode away. We should be able to detect loss of mass after many uses.

97. (M) (a) Overall: $C_3H_8(g) + 5\ O_2(g) \to 3\ CO_2(g) + 4\ H_2O(l)$

Anode: $6\ H_2O(l) + C_3H_8(g) \to 3\ CO_2(g) + 20\ H^+(g) + 20\ e^-$

Cathode: $20\ e^- + 20\ H^+(g) + 5\ O_2(g) \to 10\ H_2O(l)$

ΔG°_{rxn} = 3(-394.4 kJ/mol) + 4(-237.1 kJ/mol) – 1(-23.3 kJ/mol) = -2108.3 kJ/mol

$\Delta G°_{rxn}$ = -2108.3 kJ/mol = -2,108,300 J/mol
$\Delta G°_{rxn} = -nFE°_{cell}$ = -20 mol e^- × (96485 C/mol e^-) × $E°_{cell}$
$E°_{cell}$ = +1.0926 V

$20\ e^- + 20\ H^+(g) + 5\ O_2(g) \rightarrow 10\ H_2O(l)$ $E°_{cathode}$ = +1.229 V

Hence $E°_{cell} = E°_{cathode} - E°_{anode}$ +1.0926 V = +1.229 V – $E°_{anode}$

$E°_{anode}$ = +0.136 V (reduction potential for $3\ CO_2(g) + 20\ H^+(g) + 20\ e^- \rightarrow 6\ H_2O(l) + C_3H_8(g)$)

(b) Use thermodynamic tables for $3\ CO_2(g) + 20\ H^+(g) + 20\ e^- \rightarrow 6\ H_2O(l) + C_3H_8(g)$

$\Delta G°_{rxn}$ = 6(-237.1 kJ/mol) + 1(-23.3 kJ/mol) – [(-394.4 kJ/mol) + 20(0kJ/mol)]= -262.7 kJ/mol

$\Delta G°_{red}$ = -262.7 kJ/mol = -262,700 J/mol = $-nFE°_{red}$ = -20 mol e^-×(96,485 C/mol e^-)×$E°_{red}$

$E°_{red}$ = 0.136 V (Same value, as found in (a))

98. (D) (a) Equation 20.15 ($\Delta G^o = -zFE^o_{cell}$) gives the relationship between the standard Gibbs energy of a reaction and the standard cell potential. Gibbs free energy also varies with temperature ($\Delta G^o = \Delta H^o - T\Delta S^o$). If we assume that ΔH^o and ΔS^o do not vary significantly over a small temperature range, we can derive an equation for the temperature variation of E^o_{cell}:

$$\Delta G^o = \Delta H^o - T\Delta S^o = zFE^o_{cell} \Rightarrow E^o_{cell} = \frac{\Delta H^o - T\Delta S^o}{zF}$$

Considering two different temperatures one can write:

$$E^o_{cell}(T_1) = \frac{\Delta H^o - T_1\Delta S^o}{zF} \text{ and } E^o_{cell}(T_2) = \frac{\Delta H^o - T_2\Delta S^o}{zF}$$

$$E^o_{cell}(T_1) - E^o_{cell}(T_2) = \frac{\Delta H^o - T_1\Delta S^o}{zF} - \frac{\Delta H^o - T_2\Delta S^o}{zF}$$

$$E^o_{cell}(T_1) - E^o_{cell}(T_2) = \frac{-T_1\Delta S^o + T_2\Delta S^o}{zF} = \frac{\Delta S^o}{zF}\left(T_2 - T_1\right)$$

(b) Using this equation, we can now calculate the cell potential of a Daniel cell at 50 °C:

$$E^o_{cell}(25^oC) - E^o_{cell}(50^oC) = \frac{-10.4\,JK^{-1}mol^{-1}}{2 \times 96485Cmol^{-1}}\left(50-25\right)K = -0.00135$$

$$E^o_{cell}(50^oC) = 1.103V + 0.00135 = 1.104V$$

99. (D) Recall that under non-standard conditions $\Delta G = \Delta G^o + RT\ln K$. Substituting $\Delta G^o = \Delta H^o - T\Delta S^o$ and $\Delta G = -zFE_{cell}$ one obtains:

$$-zFE_{cell} = \Delta H^o - T\Delta S^o + RT\ln Q$$

For two different temperatures (T_1 and T_2) we can write:

$$-zFE_{cell}(T_1) = \Delta H^o - T_1\Delta S^o + RT_1 \ln Q$$
$$-zFE_{cell}(T_2) = \Delta H^o - T_2\Delta S^o + RT_2 \ln Q$$
$$-E_{cell}(T_1) + E_{cell}(T_2) = \frac{\Delta H^o - T_1\Delta S^o + RT_1 \ln Q - \Delta H^o + T_2\Delta S^o - RT_2 \ln Q}{zF}$$
$$-E_{cell}(T_1) + E_{cell}(T_2) = \frac{-T_1\Delta S^o + RT_1 \ln Q + T_2\Delta S^o - RT_2 \ln Q}{zF}$$
$$E_{cell}(T_1) - E_{cell}(T_2) = \frac{T_1\Delta S^o - RT_1 \ln Q}{zF} - \frac{T_2\Delta S^o + RT_2 \ln Q}{zF}$$
$$E_{cell}(T_1) - E_{cell}(T_2) = T_1\left(\frac{\Delta S^o - R\ln Q}{zF}\right) - T_2\left(\frac{\Delta S^o - R\ln Q}{zF}\right)$$
$$E_{cell}(T_1) - E_{cell}(T_2) = (T_1 - T_2)\left(\frac{\Delta S^o - R\ln Q}{zF}\right)$$

The value of Q at 25 ^{o}C can be calculated from E^o_{cell} and E_{cell}. First calculate E^o_{cell}:

Oxidation: $\mathrm{Cu(s) \rightarrow Cu^{2+}(aq)+2e^-}$ $-E_o = -0.340V$

Reduction: $\mathrm{2Fe^{3+}(aq)+2e^- \rightarrow 2Fe^{2+}(aq)}$ $-E_o = +0.771V$

Overall: $\mathrm{Cu(s)+2Fe^{3+} \rightarrow Cu^{2+}(aq)+2Fe^{2+}}$ $E^o_{cell} = 0.431V$

$$0.370 = 0.431 - \frac{0.0592}{2}\log Q \Rightarrow 0.296\log Q = 0.431 - 0.370 = 0.061$$
$$\log Q = 0.206 \Rightarrow Q = 10^{0.206} = 1.61$$

Now, use the above derived equation and solve for ΔS^o:

$$0.394 - 0.370 = (50 - 25)\left(\frac{\Delta S^o - 8.314 \times \ln 1.61}{2 \times 96485}\right)$$
$$0.024 = 25 \times (\frac{\Delta S^o - 3.96}{192970}) \Rightarrow \Delta S^o - 3.96 = 185.3 \Rightarrow \Delta S^o = 189.2\mathrm{JK^{-1}}$$

Since $\Delta G^o = \Delta H^o - T\Delta S^o = -zFE^o_{cell}$ we can calculate ΔG^o, K (at 25 ^{o}C) and ΔH^o:

$$\Delta G^o = -zFE^o_{cell} = -2 \times 96485 \times 0.431 = -83.2\mathrm{kJ}$$
$$\Delta G^o = -RT\ln K \Rightarrow -83.2 \times 1000 = -8.314 \times 298.15 \times \ln K$$
$$\ln K = 33.56 \Rightarrow K = e^{33.56} = 3.77 \times 10^{14}$$
$$\mathrm{-83.2kJ{=}\Delta H^o} - 298.15 \times \frac{189.2}{1000}\mathrm{kJ} \Rightarrow \Delta H^o = -83.2 + 56.4 = -26.8\mathrm{kJ}$$

Since we have ΔH^o and ΔS^o we can calculate the value of the equilibrium constant at 50 ^{o}C:

$$\Delta G^o = \Delta H^o - T\Delta S^o = -26.8\mathrm{kJ} - (273.15 + 50)\mathrm{K} \times \frac{189.2}{1000}\mathrm{kJK^{-1}} = -87.9\mathrm{kJ}$$
$$-87.9 \times 1000\mathrm{J} = -8.314\mathrm{JK^{-1}mol^{-1}} \times (273.15 + 50)\mathrm{K} \times \ln K$$
$$\ln K = 32.7 \Rightarrow K = e^{32.7} = 1.59 \times 10^{14}$$

Choose the values for the concentrations of Fe^{2+}, Cu^{2+} and Fe^{3+} that will give the value of the above calculated Q. For example:

$$Q=\frac{\left[Fe^{2+}\right]^2\left[Cu^{2+}\right]}{\left[Fe^{3+}\right]^2}=1.61$$

$$\frac{0.1^2\times 1.61}{0.1^2}=1.61$$

Determine the equilibrium concentrations at 50 °C. Notice that since Q<K, a net change occurs from left to right (the direction of the forward reaction):

$$Cu(s)+2Fe^{3+}\rightarrow Cu^{2+}(aq)+2Fe^{2+}$$

Initial:	0.1	1.61	0.1
Change:	0.1-x	1.61+x	0.1+x

$$K=\frac{\left[Fe^{2+}\right]_{eq}^2\left[Cu^{2+}\right]_{eq}}{\left[Fe^{3+}\right]_{eq}^2}=1.59\times 10^{14}=\frac{(0.1+x)^2\times(1.61+x)}{(0.1-x)^2}$$

Obviously, the reaction is almost completely shifted towards products. First assume that the reaction goes to completion, and then let the equilibrium be shifted towards reactants:

$$Cu(s)+2Fe^{3+}\rightarrow Cu^{2+}(aq)+2Fe^{2+}$$

Initial:	0.1	1.61	0.1
Final	0	1.71	0.2
Equilibrium	0+x	1.71-x	0.2-x

$$K=\frac{\left[Fe^{2+}\right]_{eq}^2\left[Cu^{2+}\right]_{eq}}{\left[Fe^{3+}\right]_{eq}^2}=1.59\times 10^{14}=\frac{(0.2-x)^2\times(1.71-x)}{(x)^2}\approx\frac{0.2^2\times 1.71}{x^2}$$

$$x^2\approx\frac{0.2^2\times 1.71}{1.59\times 10^{14}}\approx 4.3\times 10^{-16}$$

$$x\approx 2.1\times 10^{-8}\,M$$

Therefore, $[Cu^{2+}]\approx 1.7M$, $[Fe^{2+}]\approx 0.2M$ and $[Fe^{3+}]\approx 2.1x10^{-8}M$

100. **(D)** This problem can be solved by utilizing the relationship between ΔG^o and E^o_{cell} (ΔG^o=-zFE^o_{cell}):

Consider a hypothetical set of the following reactions:

$$A+ne^-\rightarrow A^{n-}\quad E_1^o \text{ and } \Delta G_1^o$$

$$B+me^-\rightarrow B^{m-}\quad E_2^o \text{ and } \Delta G_2^o$$

Overall: $A+B+ne^-+me^-\rightarrow A^{n-}+B^{m-}\quad E^o_{rxn}=?$ and $\Delta G^o_{rxn}=\Delta G_1^o+\Delta G_2^o$

$$\Delta G^o_{rxn}=\Delta G_1^o+\Delta G_2^o=-nFE_1^o-mFE_2^o$$

$$-(n+m)FE^o_{rxn}=-nFE_1^o-mFE_2^o$$

$$(n+m)FE^o_{rxn}=nFE_1^o+mFE_2^o\Rightarrow E^o_{rxn}=\frac{nFE_1^o+mFE_2^o}{n+m}$$

Therefore, for n-sets of half-reactions:

$$E^o = \frac{\sum n_i E_i^o}{\sum n_i}$$

The E_o for the given half-reaction can be determined by combining four half-reactions:

$$\mathrm{H_6IO_6 + H^+ + 2e^- \rightarrow IO_3^- + 3H_2O} \Rightarrow \quad \mathrm{E}_o = 1.60V$$

$$\mathrm{IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O} \Rightarrow \quad \mathrm{E}_o = 1.19V$$

$$\mathrm{I_2 + 2H_2O \rightarrow 2HIO + 2H^+ + 2e^-} \Rightarrow \mathrm{E}_o = -1.45V$$

$$2I^- \rightarrow I_2 + 2e^- \Rightarrow \mathrm{E}_o = -0.535V$$

Overall :

$$\mathrm{H_6IO_6 + H^+ + 2e^- + IO_3^- + 6H^+ + 5e^- + I_2 + 2H_2O} + 2I^- \rightarrow \mathrm{IO_3^- + 3H_2O + \frac{1}{2}I_2 + 3H_2O + 2HIO + 2H^+ + 2e^-} + I_2 + 2e^-$$

$$\mathrm{H_6IO_6 + 5H^+ + 2I^- + 3e^- \rightarrow \frac{1}{2}I_2 + 4H_2O + 2HIO}$$

$$\mathrm{E}^o = \frac{1.60 \times 3 + 1.19 \times 5 - 1.45 \times 2 - 0.535 \times 2}{2 + 5 - 2 - 2} = 2.26V$$

FEATURE PROBLEMS

101. (D) (a) Anode: $\mathrm{H_2(g, 1\ atm) \rightarrow 2H^+(1\,M) + 2e^-}$ $\quad -E^\circ = -0.0000\,\mathrm{V}$

Cathode: $\{\mathrm{Ag^+}(x\ \mathrm{M}) + \mathrm{e^-} \rightarrow \mathrm{Ag(s)}\} \times 2$ $\quad E^\circ = 0.800\,\mathrm{V}$

Net: $\mathrm{H_2(g, 1atm) + 2Ag^+(aq) \rightarrow 2H^+(1\,M) + 2Ag(s)}$ $\quad E^\circ_{\mathrm{cell}} = 0.800$

(b) Since the voltage in the anode half-cell remains constant, we use the Nernst equation to calculate the half-cell voltage in the cathode half-cell, with two moles of electrons. This is then added to $-E$ for the anode half-cell. Because $-E^\circ = 0.000$ for the anode half cell, $E_{\mathrm{cell}} = E_{\mathrm{cathode}}$

$$E = E^\circ - \frac{0.0592}{2}\log\frac{1}{\left[\mathrm{Ag^+}\right]^2} = 0.800 + 0.0592\ \log\left[\mathrm{Ag^+}\right] = 0.800 + 0.0592 \log x$$

(c) **(i)** Initially $\left[\mathrm{Ag^+}\right] = 0.0100$; $\quad E = 0.800 + 0.0592\ \log\ 0.0100 = 0.682\ \mathrm{V} = E_{\mathrm{cell}}$

Note that 50.0 mL of titrant is required for the titration, since both $\mathrm{AgNO_3}$ and KI have the same concentrations and they react in equimolar ratios.

(ii) After 20.0 mL of titrant is added, the total volume of solution is 70.0 mL and the unreacted $\mathrm{Ag^+}$ is that in the untitrated 30.0 mL of $0.0100\ \mathrm{M\ AgNO_3(aq)}$.

$$\left[\mathrm{Ag}^+\right] = \frac{30.0\ \mathrm{mL} \times 0.0100\ \mathrm{M\ Ag}^+}{70.0\ \mathrm{mL}} = 0.00429\mathrm{M}$$

$$E = 0.800 + 0.0592 \log\left(0.00429\right) = 0.660\ \mathrm{V} = E_{\mathrm{cell}}$$

(iii) After 49.0 mL of titrant is added, the total volume of solution is 99.0 mL and the unreacted Ag^+ is that in the untitrated 1.0 mL of $0.0100\ \mathrm{M\ AgNO_3(aq)}$.

$$\left[\mathrm{Ag}^+\right] = \frac{1.0\ \mathrm{mL} \times 0.0100\ \mathrm{M\ Ag}^+}{99.0\ \mathrm{mL}} = 0.00010\ \mathrm{M}$$

$$E = 0.800 + 0.0592 \log\left(0.00010\right) = 0.563\ \mathrm{V} = E_{\mathrm{cell}}$$

(iv) At the equivalence point, we have a saturated solution of AgI, for which

$$\left[\mathrm{Ag}^+\right] = \sqrt{K_{\mathrm{sp}}(\mathrm{AgI})} = \sqrt{8.5\times10^{-17}} = 9.2\times10^{-9}$$

$$E = 0.800 + 0.0592 \log\left(9.2\times10^{-9}\right) = 0.324\ \mathrm{V} = E_{\mathrm{cell}}\ .$$

After the equivalence point, the $\left[\mathrm{Ag}^+\right]$ is determined by the $\left[\mathrm{I}^-\right]$ resulting from the excess KI(aq).

(v) When 51.0 mL of titrant is added, the total volume of solution is 101.0 mL and the excess I^- is that in 1.0 mL of 0.0100 M KI(aq).

$$\left[\mathrm{I}^-\right] = \frac{1.0\ \mathrm{mL} \times 0.0100\ \mathrm{M\ I}^-}{101.0\ \mathrm{mL}} = 9.9 \times 10^{-5}\ \mathrm{M} \qquad \left[\mathrm{Ag}^+\right] = \frac{K_{sp}}{\left[\mathrm{I}^-\right]} = \frac{8.5 \times 10^{-17}}{0.000099} = 8.6 \times 10^{-13}\ \mathrm{M}$$

$$E = 0.800 + 0.0592\ \log\left(8.6\times10^{-13}\right) = 0.086\ \mathrm{V} = E_{\mathrm{cell}}$$

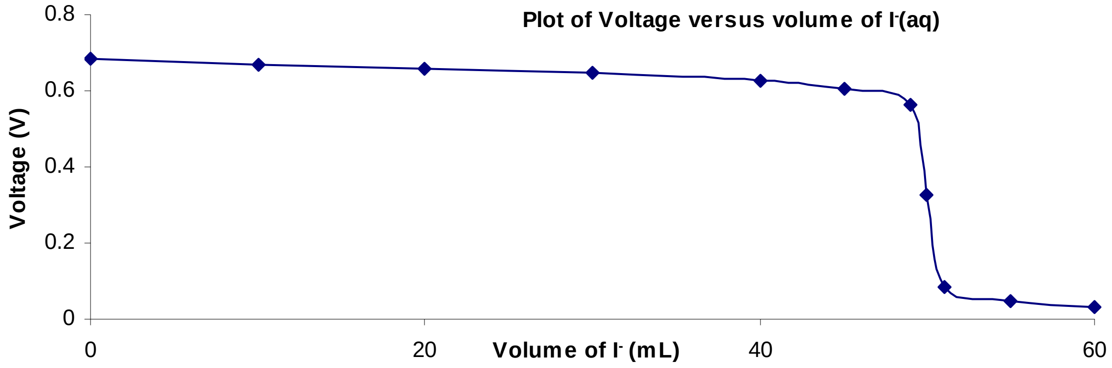
(vi) When 60.0 mL of titrant is added, the total volume of solution is 110.0 mL and the excess I^- is that in 10.0 mL of 0.0100 M KI(aq).

$$\left[\mathrm{I}^-\right] = \frac{10.0\ \mathrm{mL} \times 0.0100\ \mathrm{M\ I}^-}{110.0\ \mathrm{mL}} = 0.00091\ \mathrm{M}$$

$$\left[\mathrm{Ag}^+\right] = \frac{\mathrm{K_{sp}}}{\left[\mathrm{I}^-\right]} = \frac{8.5\times10^{-17}}{0.00091} = 9.3\times10^{-14}\ \mathrm{M}$$

$$E = 0.800 + 0.0592\ \log\left(9.3 \times 10^{-14}\right) = 0.029\ \mathrm{V} = E_{\mathrm{cell}}$$

(d) The titration curve is presented below.



102. **(D) (a)** **(1)** anode: $\mathrm{Na(s) \rightarrow Na^+(in\ ethylamine) + e^-}$

cathode: $\mathrm{Na^+(in\ ethylamine) \rightarrow Na(amalgam,\ 0.206\ \%)}$

Net: $\mathrm{Na(s) \rightarrow Na(amalgam,\ 0.206\%)}$

(2) anode: $\mathrm{2Na(amalgam,\ 0.206\%) \rightarrow 2Na^+(1\ M) + 2e^-}$

cathode: $\mathrm{2H^+(aq,1M) + 2e^- \rightarrow H_2(g,1\ atm)}$

Net: $\mathrm{2Na\ (amalgam,\ 0.206\ \%) + 2H^+(aq,1M) \rightarrow 2\ Na^+(1\ M) + H_2(g,1\ atm)}$

(b) **(1)** $\Delta G = -1\text{ mol e}^- \times \dfrac{96,485\text{ C}}{1\text{mol e}^-} \times 0.8453\text{ V} = -8.156\times10^4\text{ J}$ or -81.56 kJ

(2) $\Delta G = -2\text{ mol e}^- \times \dfrac{96,485\text{C}}{1\text{ mol e}^-} \times 1.8673\text{ V} = -36.033\times10^4\text{ J}$ or -360.33 kJ

(c) **(1)** $\mathrm{2Na(s) \rightarrow 2Na(amalgam,\ 0.206\%)}$ $\Delta G_1 = -2\times8.156\times10^4$ J

(2) $\mathrm{2Na\ (amalg,\ 0.206\%) + 2H^+(aq,1M) \rightarrow 2\,Na^+(1M) + H_2(g,\ 1\ atm)}$

$\Delta G_2 = -36.033\times10^4$ J

Overall: $\mathrm{2Na(s) + 2H^+(aq) \rightarrow 2\,Na^+(1M) + H_2(g,\ 1\ atm)}$

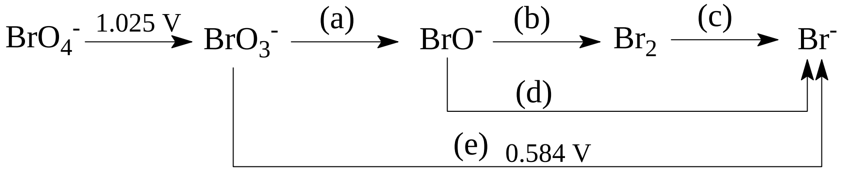
$\Delta G = \Delta G_1 + \Delta G_2 = -16.312\times10^4\text{J} - 36.033\times10^4\text{J} = -52.345\times10^4\text{J}$ or -523.45 kJ

Since standard conditions are implied in the overall reaction, $\Delta G = \Delta G^\circ$.

(d) $$E_{cell}^\circ = -\frac{-52.345\times10^4\text{ J}}{2\text{ mol e}^- \times \dfrac{96,485\text{ C}}{1\text{ mol e}^-} \times \dfrac{1\text{ J}}{1\text{ V}\cdot\text{C}}} = E^\circ\{\mathrm{H^+(1\ M)/H_2(1\ atm)}\} - E^\circ\{\mathrm{Na^+(1\ M)/Na(s)}\}$$

$E^\circ\{\mathrm{Na^+(1\ M)/Na(s)}\} = -2.713\text{V}$. This is precisely the same as the value in Appendix D.

103. **(D)** The question marks in the original Latimer diagram have been replaced with letters in the diagram below to make the solution easier to follow:



By referring to Appendix D and by employing the correct procedure for adding together half-reactions of the same type we obtain:

(c) $\mathrm{Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)}$ $\quad E_c{}^\circ = 1.065\,\mathrm{V}$ (Appendix D)

(d) $\mathrm{BrO^-(aq) + H_2O(l) + 2\,e^- \rightarrow Br^-(aq) + 2\,OH^-(aq)}$ $\quad E_d{}^\circ = 0.766\,\mathrm{V}$ (Appendix D)

(b) $\mathrm{2\,BrO^-(aq) + 2\,H_2O(l) + 2\,e^- \rightarrow Br_2(l) + 4\,OH^-(aq)}$ $\quad E_b{}^\circ = 0.455\,\mathrm{V}$ (Appendix D)

(a) $\mathrm{\{BrO_3{}^-(aq) + 2\,H_2O(l) + 4\,e^- \rightarrow BrO^-(aq) + 4\,OH^-(aq)\}} \quad \times 2$ $\quad E_a{}^\circ = ?$

(b) $\mathrm{2\,BrO^-(aq) + 2\,H_2O(l) + 2\,e^- \rightarrow Br_2(l) + 4\,OH^-(aq)}$ $\quad E_b{}^\circ = 0.455\,\mathrm{V}$

(c) $\mathrm{Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)}$ $\quad E_c{}^\circ = 1.065\,\mathrm{V}$

(e) $\mathrm{2\,BrO_3{}^-(aq) + 6\,H_2O(l) + 12\,e^- \rightarrow 12\,OH^-(aq) + 2\,Br^-(aq)}$ $\quad E_e{}^\circ = 0.584\,\mathrm{V}$

$$\Delta G^\circ_{Total} = \Delta G^\circ_{(a)} + \Delta G^\circ_{(b)} + \Delta G^\circ_{(c)}$$

$$-12F\left(E^\circ_e\right) = -8F\left(E^\circ_a\right) + \text{-}2F\left(E^\circ_b\right) + \text{-}2F\left(E^\circ_c\right)$$

$$-12F\left(0.584\,\mathrm{V}\right) = -8F\left(E^\circ_a\right) + \text{-}2F\left(0.455\,\mathrm{V}\right) + \text{-}2F\left(1.065\,\mathrm{V}\right)$$

$$E^\circ_a = \frac{-12F\left(0.584\,\mathrm{V}\right) + 2F\left(0.455\,\mathrm{V}\right) + 2F\left(1.065\,\mathrm{V}\right)}{-8F} = 0.496\ \mathrm{V}$$

104. **(D) (a)** The capacitance of the cell membrane is given by the following equation,

$$C = \frac{\varepsilon_0 \varepsilon A}{l}$$

where $\varepsilon_0\varepsilon = 3 \times 8.854 \times 10^{-12}\ \mathrm{C^2\ N^{-1}\ m^{-2}}$;
$A = 1 \times 10^{-6}\ \mathrm{cm^2}$; and $l = 1 \times 10^{-6}$ cm.
Together with the factors necessary to convert from cm to m and from cm^2 to m^2, these data yield

$$C = \frac{(3)\left(8.854\times10^{-12}\,\dfrac{\mathrm{C^2}}{\mathrm{N^1\ m^2}}\right)(1\times10^{-6}\ \mathrm{cm^2})\left(\dfrac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)^2}{(1\times10^{-6}\mathrm{cm})\left(\dfrac{1\ \mathrm{m}}{100\ \mathrm{cm}}\right)} = 2.66 \times 10^{-13}\ \frac{\mathrm{C^2}}{\mathrm{N\,m}}$$

$$C = \left(2.66\times10^{-13}\,\frac{\mathrm{C^2}}{\mathrm{N\,m}}\right)\left(\frac{1\mathrm{F}}{1\dfrac{\mathrm{C^2}}{\mathrm{N\,m}}}\right) = 2.66\times10^{-13}\ \mathrm{F}$$

(b) Since the capacitance *C* is the charge in coulombs per volt, the charge on the membrane, *Q*, is given by the product of the capacitance and the potential across the cell membrane.

$$Q = 2.66 \times 10^{-13}\ \frac{\text{C}}{\text{V}} \times 0.085\text{ V} = 2.26 \times 10^{-14}\text{ C}$$

(c) The number of K^+ ions required to produce this charge is

$$\frac{Q}{\text{e}} = \frac{2.26\times10^{-14}\text{ C}}{1.602\times10^{-19}\text{ C/ion}} = 1.41\times10^{5}\text{ K}^+\text{ ions}$$

(d) The number of K^+ ions in a typical cell is

$$\left(6.022\times10^{23}\,\frac{\text{ions}}{\text{mol}}\right)\left(155\times10^{-3}\,\frac{\text{mol}}{\text{L}}\right)\left(\frac{1\text{L}}{1000\text{ cm}^3}\right)(1\times10^{-8}\text{ cm}^3) = 9.3\times10^{11}\text{ ions}$$

(e) The fraction of the ions involved in establishing the charge on the cell membrane is

$$\frac{1.4\times10^{5}\text{ ions}}{9.3\times10^{11}\text{ ions}} = 1.5\times10^{-7}\ (\sim 0.000015\ \%)$$

Thus, the concentration of K^+ ions in the cell remains constant at 155 mM.

105. **(M)** Reactions with a positive cell potential are reactions for which $\Delta G^o < 0$, or reactions for which K>1. ΔS^o, ΔH^o and ΔU^o cannot be used alone to determine whether a particular electrochemical reaction will have a positive or negative value.

106. **(M)** The half-reactions for the first cell are:

Anode (oxidation): $\text{X(s)} \rightarrow \text{X}^+\text{(aq)+e}^-$ $\quad -E^o_{X^+/X}$

Cathode (reduction): $2\text{H}^+\text{(aq)+2e}^- \rightarrow \text{H}_2\text{(g)}$ $\quad E^o = 0V$

Since the electrons are flowing from metal X to the standard hydrogen electrode, $E^o_{X^+/X} < 0V$.

The half-reactions for the second cell are:

Anode (oxidation): $\text{X(s)} \rightarrow \text{X}^+\text{(aq)+e}^-$ $\quad -E^o_{X^+/X}$

Cathode (reduction): $\text{Y}^{2+}\text{+2e}^- \rightarrow \text{Y(s)}$ $\quad E^o_{Y^{2+}/Y}$

Since the electrons are flowing from metal X to metal Y, $-E^o_{X^+/X} + E^o_{Y^{2+}/Y} > 0$.

From the first cell we know that $E^o_{X^+/X} < 0V$. Therefore, $E^o_{X^+/X} > E^o_{Y^{2+}/Y}$.

107. **(M)** The standard reduction potential of the Fe^{2+}(aq)/Fe(s) couple can be determined from:

$\text{Fe}^{2+}\text{(aq)} \rightarrow \text{Fe}^{3+}\text{(aq)+e}^- E_o = -0.771V$

$\text{Fe}^{3+}\text{(aq)+3e}^- \rightarrow \text{Fe(s)} \quad \text{E}_o = -0.04V$

Overall:

$\text{Fe}^{2+}\text{(aq)+2e}^- \rightarrow \text{Fe(s)}$

We proceed similarly to the solution for 100:

$$E^o = \frac{\sum n_i E_i^o}{\sum n_i} = \frac{-0.771 \times (1) - 0.04 \times 3}{3-1} = -0.445V$$

SELF-ASSESSMENT EXERCISES

108. **(E)** **(a)** A standard electrode potential E^o measures the tendency for a reduction process to occur at an electrode.

(b) F is the Faraday constant, or the electric charge per mole of electrons (96485 C/mol).

(c) The anode is the electrode at which oxidation occurs.

(d) The cathode is the electrode at which reduction occurs.

109. **(E)** **(a)** A salt bridge is a devise used to connect the oxidation and reduction half-cells of a galvanic (voltaic) cell.

(b) The standard hydrogen electrode (abbreviated SHE), also called normal hydrogen electrode (NHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. By definition electrode potential for SHE is 0.

(c) Cathodic protection is a technique commonly used to control the corrosion of a metal surface by making it work as a cathode of an electrochemical cell. This is achieved by placing in contact with the metal to be protected another more easily corroded metal to act as the anode of the electrochemical cell.

(d) A fuel cell is an electrochemical cell that produces electricity from fuels. The essential process in a fuel cell is fuel+oxygen$\rightarrow$oxidation products.

110. **(E)** **(a)** An overall cell reaction is a combination of oxidation and reduction half-reactions.

(b) In a galvanic (voltaic) cell, chemical change is used to produce electricity. In an electrolytic cell, electricity is used to produce a nonspontaneous rection.

(c) In a primary cell, the cell reaction is not reversible. In a secondary cell, the cell reaction can be reversed by passing electricity through the cell (charging).

(d) E_{cell}^o refers to the standard cell potential (the ionic species are present in aqueous solution at unit activity (approximately 1M), and gases are at 1 bar pressure (approximately 1 atm).

111. **(M)** **(a)** False. The cathode is the positive electrode in a voltaic cell and negative in electrolytic cell.

(b) False. The function of the salt bridge is to permit the migration of the ions not electrons.

(c) True. The anode is the negative electrode in a voltaic cell.

(d) True.

(e) True. Reduction always occurs at the cathode of an electrochemical cell. Because of the removal of electrons by the reduction half-reaction, the cathode of a voltaic cell is positive. Because of the electrons forced onto it, the cathode of an electrolytic cell is negative. For both types, the cathode is the electrode at which electrons enter the cell.

(f) False. Reversing the direction of the electron flow changes the voltaic cell into an electrolytic cell.
(g) True. The cell reaction is an oxidation-reduction reaction.

112. **(M)** The correct answer is (b), $Hg^{2+}(aq)$ is more readily reduced than $H^{+}(aq)$.

113. **(M)** Under non-standard conditions, apply the Nernst equation to calculate E_{cell}:

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{z}\log Q$$

$$E_{cell} = 0.66 - \frac{0.0592}{2}\log\frac{0.10}{0.01} = 0.63V$$

The correct answer is (d).

114. **(E)** **(c)** The displacement of Ni(s) from the solution will proceed to a considerable extent, but the reaction will not go to completion.

115. **(E)** The gas evolved at the anode when K_2SO_4(aq) is electrolyzed between Pt electrodes is most likely oxygen.

116. **(M)** The electrochemical reaction in the cell is:

Anode (oxidation): $\{Al(s) \rightarrow Al^{3+}(aq)+3e^{-}\} \times 2$

Cathode (reduction): $\{H_2(g)+2e^{-} \rightarrow 2H^{+}(aq)\} \times 3$

Overall: $2Al(s)+3H_2(g) \rightarrow 2Al^{3+}(aq)+6H^{+}(aq)$

$$4.5\text{g Al} \times \frac{1\text{mol Al}}{26.98\text{g Al}} \times \frac{3\text{ mol H}_2}{2\text{ mol Al}} = 0.250\text{mol H}_2$$

$$0.250\text{ mol H}_2 \times \frac{22.4\text{L H}_2}{1\text{mol H}_2} = 5.6\text{L H}_2$$

117. **(E)** The correct answer is (a) ΔG.

118. **(M)** Anode (oxidation): $\{Zn(s) \rightarrow Zn^{2+}(aq)+2e^{-}\} \times 3$ $\quad -E^{o} = 0.763V$

Cathode (reduction): $\{NO_3^{-}(aq)+4H^{+}(aq)+3e^{-} \rightarrow NO(g)+2H_2O(l)\} \times 2$ $\quad E^{o} = +0.956V$

Overall: $3Zn(s)+2NO_3^{-}(aq)+8H^{+}(aq) \rightarrow 3Zn^{2+}(aq)+2NO(g)+4H_2O(l)$ $\quad E^{o}_{cell} = 1.719V$

Cell diagram: $Zn(s)|Zn^{2+}(1M)||H^{+}(1M),NO_3^{-}(1M)|NO(g,1atm)|Pt(s)$

119. **(M)** Apply the Nernst equation:

$$E_{cell} = E^o_{cell} - \frac{0.0592}{z}\log Q$$

$$0.108 = 0 - \frac{0.0592}{2}\log x^2 \Rightarrow \log x^2 = -3.65$$

$$x^2 = 10^{-3.65} \Rightarrow x = 0.0150M$$

$$pH = -\log(0.0150) = 1.82$$

<u>120.</u> **(M)** **(a)** Since we are given E^o_{cell}, we can calculate K for the given reaction:

$$E^o_{cell} = \frac{RT}{nF}\ln K$$

$$-0.0050V = \frac{8.314JK^{-1}mol^{-1} \times 298K}{2 \times 96485Cmol^{-1}}\ln K \Rightarrow \ln K = -0.389$$

$K = e^{-0.389} = 0.68$

Since for the given conditions Q=1, the system is not at equilibrium.

(b) Because Q>K, a net reaction occurs to the left.

<u>121.</u> **(M)** **(a)** $\text{Fe(s)+Cu}^{2+}\text{(1M)} \rightarrow \text{Fe}^{2+}\text{(1M)+Cu(s)}$, $E^o_{cell} = -0.780V$, electron flow from B to A

(b) $\text{Sn}^{2+}\text{(1M)+2Ag}^{+}\text{(1M)} \rightarrow \text{Sn}^{4+}\text{(aq)+2Ag(s)}$, $E^o_{cell} = +0.646V$, electron flow from A to B.

(c) $\text{Zn(s)+Fe}^{2+}\text{(0.0010M)} \rightarrow \text{Zn}^{2+}\text{(0.10M)+Fe(s)}$, $E^o_{cell} = +0.264V$,electron flow from A to B.

<u>122.</u> **(M)** **(a)** Cl_2(g) at anode and Cu(s) at cathode.

(b) O_2(g) at anode and H_2(g) and OH^-(aq) at cathode.

(c) Cl_2(g) at anode and Ba(l) at cathode.

(d) O_2(g) at anode and H_2(g) and OH^-(aq) at cathode.

CHAPTER 24

COMPLEX IONS AND COORDINATION COMPOUNDS

PRACTICE EXAMPLES

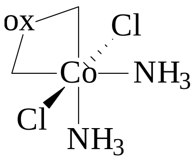
1A **(E)** There are two different kinds of ligands in this complex ion, I^- and CN^-. Both are monodentate ligands, that is, they each form only one bond to the central atom. Since there are five ligands in total for the complex ion, the coordination number is 5: $\text{C.N.} = 5$. Each CN^- ligand has a charge of -1, as does the I^- ligand. Thus, the O.S. must be such that: $\text{O.S.} + \left[(4+1)\times(-1)\right] = -3 = \text{O.S.} - 5$. Therefore, $\text{O.S.} = +2$.

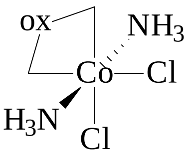
1B **(E)** The ligands are all CN^-. Fe^{3+} is the central metal ion. The complex ion is $\left[Fe(CN)_6\right]^{3-}$.

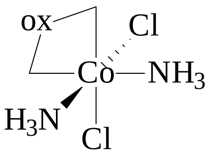
2A **(E)** There are six "Cl^-" ligands (chloride), each with a charge of 1−. The platinum metal center has an oxidation state of $+4$. Thus, the complex ion is $\left[PtCl_6\right]^{2-}$, and we need two K^+ to balance charge: $K_2\left[PtCl_6\right]$.

2B **(E)** The "SCN^-" ligand is the thiocyanato group, with a charge of 1−, bonding to the central metal ion through the sulfur atom. The "NH_3" ligand is ammonia, a neutral ligand. There are five (penta) ammine ligands bonded to the metal. The oxidation state of the cobalt atom is $+3$. The complex ion is not negatively charged, so its name does not end with "-ate". The name of the compound is pentaamminethiocyanato-*S*-cobalt(III) chloride.

3A **(M)** The oxalato ligand must occupy two *cis*- positions. Either the two NH_3 or the two Cl^- ligands can be coplanar with the oxalate ligand, leaving the other two ligands axial. The other isomer has one NH_3 and one Cl^- ligand coplanar with the oxalate ligand. The structures are sketched below.

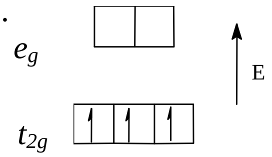






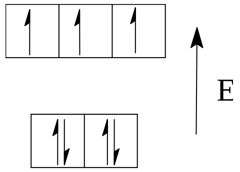
3B **(M)** We start out with the two pyridines, C_5H_5N, located *cis* to each other. With this assignment imposed, we can have the two Cl^- ligands *trans* and the two CO ligands *cis*, the two CO ligands *trans* and the two Cl^- ligands *cis*, or both the Cl^- ligands and the two CO ligands *cis*. If we now place the two pyridines *trans*, we can have either both other pairs *trans*, or both other pairs *cis*. There are five geometric isomers. They follow, in the order described.

4A **(M)** The F^- ligand is a weak field ligand. $[MnF_6]^{2-}$ is an octahedral complex. Mn^{4+} has three 3*d* electrons. The ligand field splitting diagram for $[MnF_6]^{2-}$ is sketched below. There are three unpaired electrons.

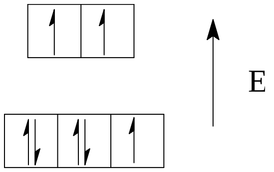


4B **(M)** Co^{2+} has seven 3*d* electrons. Cl^- is a weak field ligand. H_2O is a moderate field ligand. There are three unpaired electrons in each case. The number of unpaired electrons has no dependence on geometry for either metal ion complex.

$[CoCl_4]^{2-}$



$[Co(H_2O)_6]^{2+}$



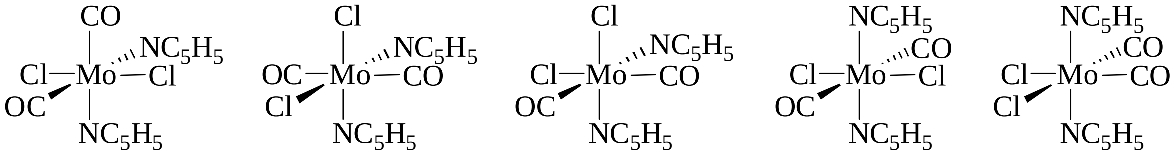
5A **(M)** CN^- is a strong field ligand. Co^{2+} has seven 3*d* electrons. In the absence of a crystal field, all five *d* orbitals have the same energy. Three of the seven *d* electrons in this case will be unpaired. We need an orbital splitting diagram in which there are three orbitals of the same energy at higher energy. This is the case with a tetrahedral orbital diagram.

↑↓ ↑↓ ↑ ↑ ↑	t_{2g} ↑ ↑ ↑	e_g ↑ —
In absence of a crystal field	e_g ↑↓ ↑↓	t_{2g} ↑↓ ↑↓ ↑↓
	Tetrahedral geometry	Octahedral geometry

Thus, $[Co(CN)_4]^{2-}$ must be tetrahedral (3 unpaired electrons) and not octahedral (1 unpaired electron) because the magnetic behavior of a tetrahedral arrangement would agree with the experimental observations (3 unpaired electrons).

5B **(M)** NH_3 is a strong field ligand. Cu^{2+} has nine 3*d* electrons. There is only one way to arrange nine electrons in five *d*-orbitals and that is to have four fully occupied orbitals (two electrons in each orbital), and one half-filled orbital. Thus, the complex ion must be paramagnetic to the extent of one unpaired electron, regardless of the geometry the ligands adopt around the central metal ion.

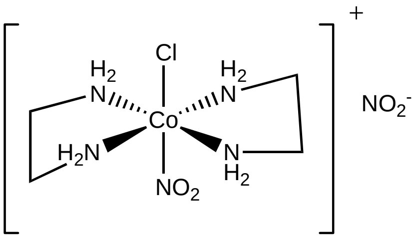
6A **(M)** We are certain that $[Co(H_2O)_6]^{2+}$ is octahedral with a moderate field ligand. Tetrahedral $[CoCl_4]^{2-}$ has a weak field ligand. The relative values of ligand field splitting for the same ligand are $\Delta_t = 0.44\,\Delta_o$. Thus, $[Co(H_2O)_6]^{2+}$ absorbs light of higher energy, blue or green light, leaving a light pink as the complementary color we observe. $\left[\text{CoCl}_4\right]^{2-}$ absorbs lower energy red light, leaving blue light to pass through and be seen.



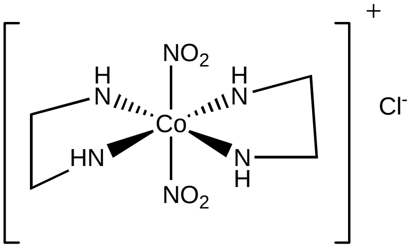
6B **(M)** In order, the two complex ions are $\left[\text{Fe}\left(\text{H}_2\text{O}\right)_6\right]^{2+}$ and $\left[\text{Fe}\left(\text{CN}\right)_6\right]^{4-}$. We know that CN^- is a strong field ligand; it should give rise to a large value of Δ_o and absorb light of the shorter wavelength. We would expect the cyano complex to absorb blue or violet light and thus $\text{K}_4\left[\text{Fe}\left(\text{CN}\right)_6\right]\cdot 3\ \text{H}_2\text{O}$ should appear yellow. The compound $\left[\text{Fe}\left(\text{H}_2\text{O}\right)_6\right]\left(\text{NO}_3\right)_2$, contains the weak field ligand H_2O and thus should be green. (The weak field would result in the absorption of light of long wavelength (namely, red light), which would leave green as the color we observe.)

INTEGRATIVE EXAMPLE

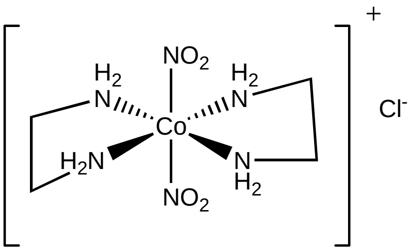
A **(M) (a)** There is no reaction with $AgNO_3$ or en, so the compound must be *trans*-chlorobis(ethylenediamine)nitrito-*N*-cobalt(III) nitrite



(b) If the compound reacts with $AgNO_3$, but not with en, it must be *trans*-bis(ethylenediamine)dinitrito-*N*-cobalt(III) chloride.



(c) If it reacts with $AgNO_3$ and en and is optically active, it must be *cis*-bis(ethylenediamine)dinitrito-*N*-cobalt(III) chloride.



B **(D)** We first need to compute the empirical formula of the complex compound:

$$46.2\text{ g Pt}\times\frac{1\text{ mol Pt}}{195.1\text{ g Pt}}=0.236\text{ mol Pt}\Rightarrow\frac{0.236}{0.236}=1\text{ mol Pt}$$

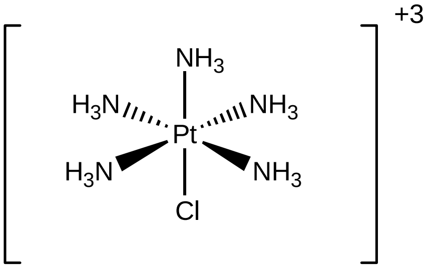
$$33.6\text{ g Cl}\times\frac{1\text{ mol Cl}}{35.5\text{ g Cl}}=0.946\text{ mol Cl}\Rightarrow\frac{0.946}{0.236}=4\text{ mol Pt}$$

$$16.6\text{ g N}\times\frac{1\text{ mol N}}{14.01\text{ g N}}=1.18\text{ mol N}\Rightarrow\frac{1.18}{0.236}=5\text{ mol N}$$

$$3.6\text{ g Pt}\times\frac{1\text{ mol H}}{1\text{ g H}}=3.6\text{ mol H}\Rightarrow\frac{3.6}{0.236}=15\text{ mol H}$$

The nitrogen ligand is NH_3, apparently, so the empirical formula is $Pt(NH_3)_5Cl_4$.

The effective molality of the solution is $m=\frac{\Delta T}{K_{fp}}=\frac{0.74^{o}C}{1.86^{o}C/m}=0.4m$. The effective molality is 4 times the stated molality, so we have 4 particles produced per mole of Pt complex, and therefore 3 ionizable chloride ions. We can write this in the following way: $[Pt(NH_3)_5Cl][Cl]3$. Only one form of the cation (with charge 3+) shown below will exist.



EXERCISES

Nomenclature

1. **(E) (a)** $\left[CrCl_4(NH_3)_2\right]^-$ diamminetetrachlorochromate(III) ion

(b) $\left[Fe(CN)_6\right]^{3-}$ hexacyanoferrate(III) ion

(c) $\left[Cr(en)_3\right]_2\left[Ni(CN)_4\right]_3$. tris(ethylenediamine)chromium(III) tetracyanonickelate(II) ion

2. **(E) (a)** $\left[Co(NH_3)_6\right]^{2+}$ The coordination number of Co is 6; there are six monodentate NH_3 ligands attached to Co. Since the NH_3 ligand is neutral, the oxidation state of cobalt is $+2$, the same as the charge for the complex ion; hexaamminecobalt(II) ion.

(b) $[\mathrm{AlF_6}]^{3-}$ The coordination number of Al is 6; $\mathrm{F^-}$ is monodentate. Each $\mathrm{F^-}$ has a $1-$ charge; thus the oxidation state of Al is $+3$; hexafluoroaluminate(III) ion.

(c) $[\mathrm{Cu(CN)_4}]^{2-}$ The coordination number of Cu is 4; $\mathrm{CN^-}$ is monodentate. $\mathrm{CN^-}$ has a $1-$ charge; thus the oxidation state of Cu is $+2$; tetracyanocuprate(II) ion

(d) $[\mathrm{CrBr_2(NH_3)_4}]^{+}$ The coordination number of Cr is 6; $\mathrm{NH_3}$ and $\mathrm{Br^-}$ are monodentate. $\mathrm{NH_3}$ has no charge; $\mathrm{Br^-}$ has a $1-$ charge. The oxidation state of chromium is $+3$; tetraamminedibromochromium(III) ion

(e) $[\mathrm{Co(ox)_3}]^{4-}$ The coordination number of Co is 6; oxalate is bidentate. $\mathrm{C_2O_4^{2-}}$ (ox) has a $2-$ charge; thus the oxidation state of cobalt is $+2$; trioxalatocobaltate(II) ion.

(f) $[\mathrm{Ag(S_2O_3)_2}]^{3-}$ The coordination number of Ag is 2; $\mathrm{S_2O_3}^{2-}$ is monodentate. $\mathrm{S_2O_3}^{2-}$ has a $2-$ charge; thus the oxidation state of silver is $+1$; dithiosulfatoargentate(I) ion. (Although +1 is by far the most common oxidation state for silver in its compounds, stable silver(III) complexes are known. Thus, strictly speaking, silver is not a non-variable metal, and hence when naming silver compounds, the oxidation state(s) for the silver atom(s) should be specified).

3. **(M) (a)** $[\mathrm{Co(OH)(H_2O)_4(NH_3)}]^{2+}$ amminetetraaquahydroxocobalt(III) ion

(b) $[\mathrm{Co(ONO)_3(NH_3)_3}]$ triamminetrinitrito-*O*-cobalt(III)

(c) $[\mathrm{Pt(H_2O)_4}][\mathrm{PtCl_6}]$ tetraaquaplatinum(II) hexachloroplatinate(IV)

(d) $[\mathrm{Fe(ox)_2(H_2O)_2}]^{-}$ diaquadioxalatoferrate(III) ion

(e) $\mathrm{Ag_2[HgI_4]}$ silver(I) tetraiodomercurate(II)

4. **(M) (a)** $\mathrm{K_3[Fe(CN)_6]}$ potassium hexacyanoferrate(III)

(b) $[\mathrm{Cu(en)_2}]^{2+}$ bis(ethylenediamine)copper(II) ion

(c) $[\mathrm{Al(OH)(H_2O)_5}]\ \mathrm{Cl_2}$ pentaaquahydroxoaluminum(III) chloride

(d) $[\mathrm{CrCl(en)_2\,NH_3}]\ \mathrm{SO_4}$ amminechlorobis(ethylenediammine)chromium(III) sulfate

(e) $[\mathrm{Fe(en)_3}]_4[\mathrm{Fe(CN)_6}]_3$ tris(ethylenediamine)iron(III) hexacyanoferrate(II)

Bonding and Structure in Complex Ions

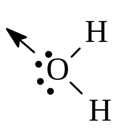
5. **(E)** The Lewis structures are grouped together at the end.

(a) H_2O has $1 \times 2 + 6 = 8$ valence electrons, or 4 pairs.

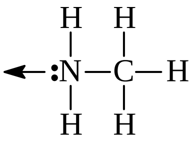
(b) CH_3NH_2 has $4 + 3 \times 1 + 5 + 2 \times 1 = 14$ valence electrons, or 7 pairs.

(c) ONO^- has $2 \times 6 + 5 + 1 = 18$ valence electrons, or 9 pairs. The structure has a 1− formal charge on the oxygen that is singly bonded to N.

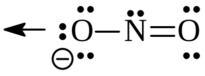
(d) SCN^- has $6 + 4 + 5 + 1 = 16$ valence electrons, or 8 pairs. This structure, appropriately, gives a 1− formal charge to N.



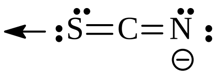
(a)



(b)



(c)



(d)

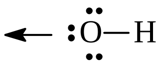
6. **(M)** The Lewis structures are grouped together at the end.

(a) OH^- has $6 + 1 + 1 = 8$ valence electrons, or 4 pairs.

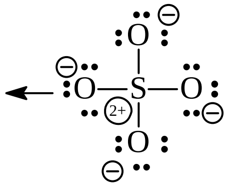
(b) SO_4^{2-} has $6 + 6 \times 4 + 2 = 32$ valence electrons, or 16 pairs.

(c) $C_2O_4^{2-}$ has $2 \times 4 + 6 \times 4 + 2 = 34$ valence electrons, or 17 pairs.

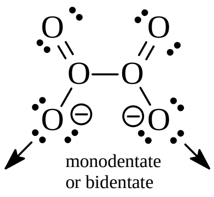
(d) SCN^- has $6 + 4 + 5 + 1 = 16$ valence electrons, or 8 pairs. This structure, appropriately, gives a 1− formal charge to N.



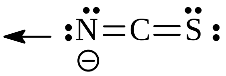
(a)



(b)



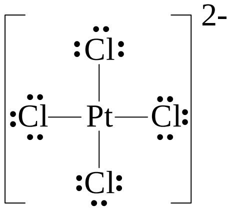
(c)



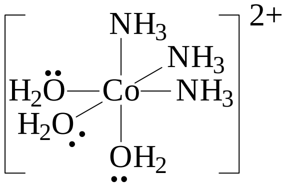
(d)

7. **(M)** We assume that $\left[PtCl_4\right]^{2-}$ is square planar by analogy with $\left[PtCl_2\left(NH_3\right)_2\right]$ in Figure 24-5. The other two complex ions are octahedral.

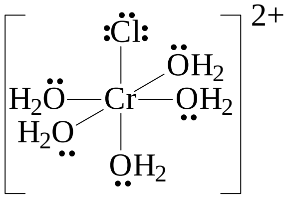
(a)



(b)

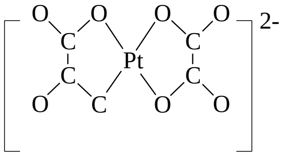


(c)

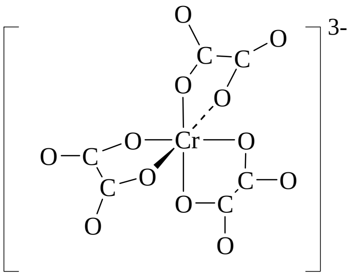


8. **(M)** The structures for $\left[\mathrm{Pt}(\mathrm{ox})_2\right]^{2-}$ and $\left[\mathrm{Cr}(\mathrm{ox})_3\right]^{3-}$ are drawn below. The structure of $\left[\mathrm{Fe}(\mathrm{EDTA})\right]^{2-}$ is the same as the generic structure for $\left[\mathrm{M}(\mathrm{EDTA})\right]^{2-}$ drawn in Figure 24-23, with $\mathrm{M}^{n+} = \mathrm{Fe}^{2+}$.

(a)

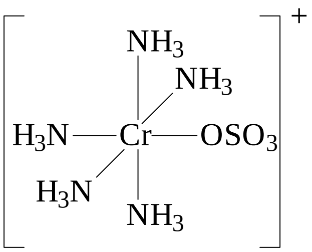


(b)



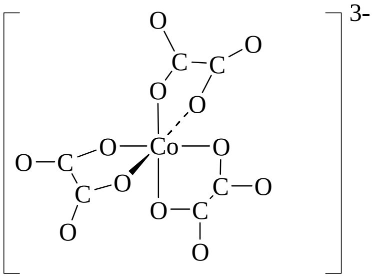
(c) See Figure 24-23.

9. **(M) (a)**



pentaamminesulfateochromium(III)

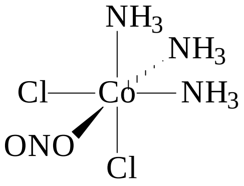
(b)



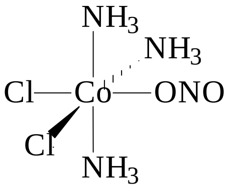
trioxalatocobaltate(III)

(c)

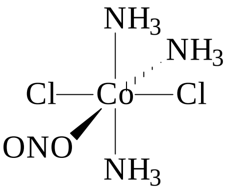
fac-triamminedichloronitro-O-cobalt(III)



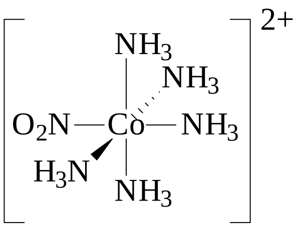
mer-triammine-*cis*-dichloronitro-O-cobalt(III)

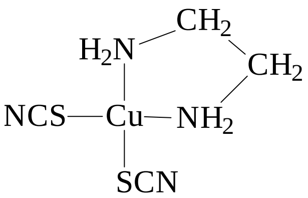


mer-triammine-*trans*-dichloronitro-O-cobalt(III)

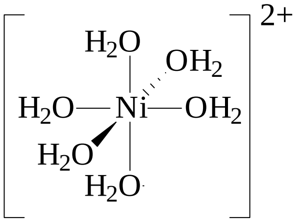


10. **(M) (a)** pentaamminenitroto-N-cobalt(III) ion **(b)** ethylenediaminedithiocyanato-S-copper(II)





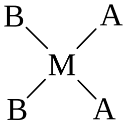
(c) hexaaquanickel(II) ion



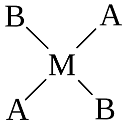
Isomerism

11. **(E) (a)** *cis-trans* isomerism cannot occur with tetrahedral structures because all of the ligands are separated by the same angular distance from each other. One ligand cannot be on the other side of the central atom from another.

(b) Square planar structures can show *cis-trans* isomerism. Examples are drawn following, with the *cis*-isomer drawn on the left, and the *trans*-isomer drawn on the right.



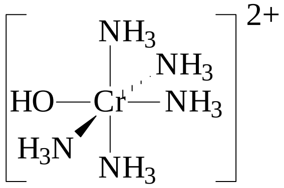
cis-isomer



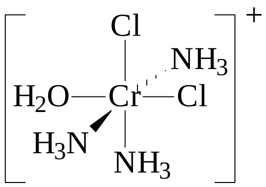
trans-isomer

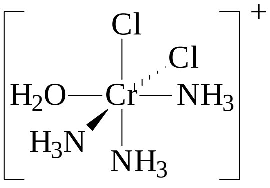
(c) Linear structures do not display *cis-trans* isomerism; there is only one way to bond the two ligands to the central atom.

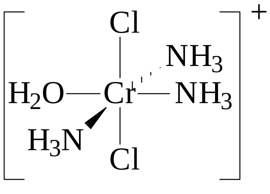
12. **(M) (a)** $\left[\text{CrOH}\left(\text{NH}_3\right)_5\right]^{2+}$ has one isomer.



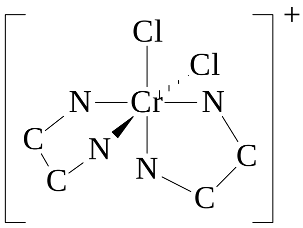
(b) $\left[\text{CrCl}_2\left(\text{H}_2\text{O}\right)\left(\text{NH}_3\right)_3\right]^{+}$ has three isomers.

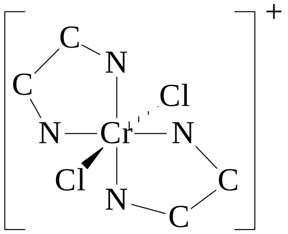




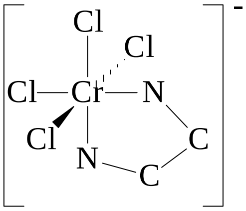


(c) $\left[\text{CrCl}_2\left(\text{en}\right)_2\right]^{+}$ has two geometric isomers, *cis*- and *trans*-.

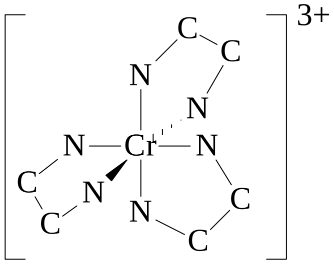




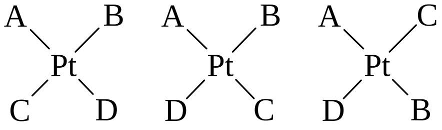
(d) $\left[\mathrm{CrCl_4(en)}\right]^-$ has only one isomer since the ethylenediamine (en) ligand cannot bond *trans* to the central metal atom.

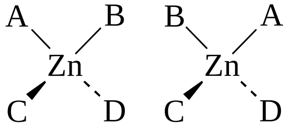


(e) $\left[\mathrm{Cr(en)_3}\right]^{3+}$ has only one geometric isomer; it has two optical isomers.



13. **(M) (a)** There are three different square planar isomers, with D, C, and B, respectively, trans to the A ligand. They are drawn below.



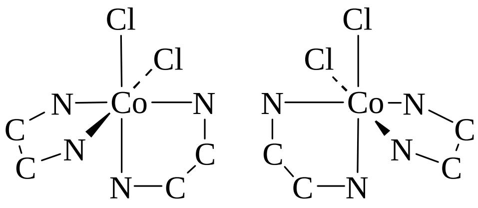


(b) Tetrahedral $\left[\mathrm{ZnABCD}\right]^{2+}$ does display optical isomerism. The two optical isomers are drawn above.

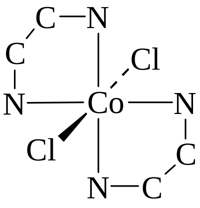
14. **(M)** There are a total of four coordination isomers. They are listed below. We assume that the oxidation state of each central metal ion is $+3$.

$\left[\mathrm{Co(en)_3}\right]\left[\mathrm{Cr(ox)_3}\right]$	tris(ethylenediamine)cobalt(III) trioxalatochromate(III)
$\left[\mathrm{Co(ox)(en)_2}\right]\left[\mathrm{Cr(ox)_2(en)}\right]$	bis(ethylenediamine)oxalatocobalt(III) (ethylenediamine)dioxalatochromate(III)
$\left[\mathrm{Cr(ox)(en)_2}\right]\left[\mathrm{Co(ox)_2(en)}\right]$	bis(ethylenediamine)oxalatochromium(III) (ethylenediamine)dioxalatocobaltate(III)
$\left[\mathrm{Cr(en)_3}\right]\left[\mathrm{Co(ox)_3}\right]$	tris(ethylenediamine)chromium(III) trioxalatocobaltate(III)

15. **(M)** The *cis*-dichlorobis(ethylenediamine)cobalt(III) ion is optically active. The two optical isomers are drawn below. The *trans*-isomer is not optically active: the ion and its mirror image are superimposable.



cis-isomers



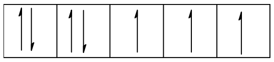
trans-isomer

16. **(M)** Complex ions (a) and (b) are identical; complex ions (a) and (d) are geometric isomers; complex ions (b) and (d) are geometric isomers; complex ion (c) is distinctly different from the other three complex ions (it has a different chemical formula).

Crystal Field Theory

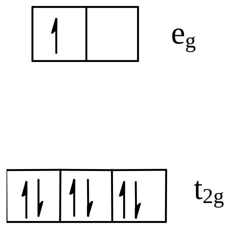
17. **(E)** In crystal field theory, the five *d* orbitals of a central transition metal ion are split into two (or more) groups of different energies. The energy spacing between these groups often corresponds to the energy of a photon of visible light. Thus, the transition-metal complex will absorb light with energy corresponding to this spacing. If white light is incident on the complex ion, the light remaining after absorption will be missing some of its components. Thus, light of certain wavelengths (corresponding to the energies absorbed) will no longer be present in the formerly white light. The resulting light is colored. For example, if blue light is absorbed from white light, the remaining light will be yellow in color.

18. **(E)** The difference in color is due to the difference in the value of Δ, which is the ligand field splitting energy. When the value of Δ is large, short wavelength light, which has a blue color, is absorbed, and the substance or its solution appears yellow. On the other hand, when the value of Δ is small, light of long wavelength, which has a red or yellow color, is absorbed, and the substance or its solution appears blue. The cyano ligand is a strong field ligand, producing a large value of Δ, and thus yellow complexes. On the other hand, the aqua ligands are weak field ligands, which produce a small value of Δ, and hence blue complexes.

19. **(M)** We begin with the 7 electron *d*-orbital diagram for Co^{2+} [Ar] 

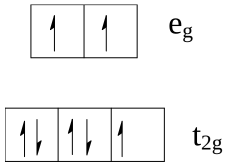
The strong field and weak field diagrams for octahedral complexes follow, along with the number of unpaired electrons in each case.

Strong Field



(1 unpaired electron)

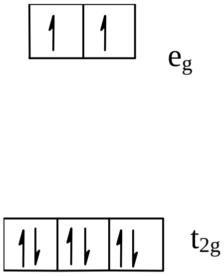
Weak Field



(3 unpaired electrons)

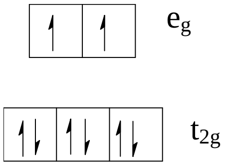
20. **(M)** We begin with the 8 electron *d*-orbital diagram for $\mathrm{Ni^{2+}}\ [\mathrm{Ar}]\ \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$
The strong field and weak field diagrams for octahedral complexes follow, along with the number of unpaired electrons in each case.

Strong Field



(2 unpaired electrons)

Weak Field



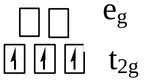
(2 unpaired electrons)

The number of unpaired electrons is the same in both cases.

21. **(M) (a)** Both of the central atoms have the same oxidation state, +3. We give the electron configuration of the central atom to the left, then the completed crystal field diagram in the center, and finally the number of unpaired electrons. The chloro ligand is a weak field ligand in the spectrochemical series.

$\mathrm{Mo^{3+}}$ $[\mathrm{Kr}]\,4d^3$
$[\mathrm{Kr}]_{4d}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}$

weak field

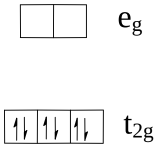


3 unpaired electrons; paramagnetic

The ethylenediamine ligand is a strong field ligand in the spectrochemical series.

$\mathrm{Co^{3+}}$ $[\mathrm{Ar}]\,3d^6$
$[\mathrm{Ar}]\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

strong field

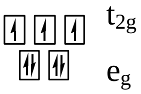


no unpaired electrons; diamagnetic

(b) In $[\mathrm{CoCl_4}]^{2-}$ the oxidation state of cobalt is 2+. Chloro is a weak field ligand. The electron configuration of $\mathrm{Co^{2+}}$ is $[\mathrm{Ar}]\,3d^7$ or $[\mathrm{Ar}]\ \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

The tetrahedral ligand field diagram is shown on the right.

weak field



3 unpaired electrons

22. **(M) (a)** In $[\mathrm{Cu(py)_4}]^{2+}$ the oxidation state of copper is +2. Pyridine is a strong field ligand. The electron configuration of $\mathrm{Cu^{2+}}$ is $[\mathrm{Ar}]\,3d^9$ or $[\mathrm{Ar}]\ \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

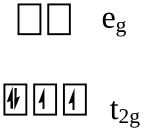
There is no possible way that an odd number of electrons can be paired up, without at least one electron being unpaired. $[\mathrm{Cu(py)_4}]^{2+}$ is paramagnetic.

(b) In $[\mathrm{Mn(CN)_6}]^{3-}$ the oxidation state of manganese is $+3$. Cyano is a strong field ligand. The electron configuration of $\mathrm{Mn^{3+}}$ is $[\mathrm{Ar}]\,3d^4$ or $[\mathrm{Ar}]$ ↑ ↑ ↑ ↑ ☐

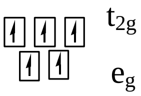
The ligand field diagram follows, on the left-hand side. In $[\mathrm{FeCl_4}]^-$ the oxidation state of iron is $+3$. Chloro is a weak field ligand. The electron configuration of $\mathrm{Fe^{3+}}$ is $[\mathrm{Ar}]\,3d^5$ or [Ar] ↑ ↑ ↑ ↑ ↑

The ligand field diagram follows, below.

strong field



weak field



2 unpaired electrons

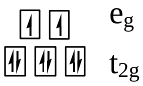
5 unpaired electrons

There are more unpaired electrons in $[\mathrm{FeCl_4}]^-$ than in $[\mathrm{Mn(CN)_6}]^{3-}$.

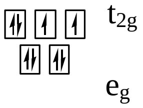
23. **(M)** The electron configuration of $\mathrm{Ni^{2+}}$ is $[\mathrm{Ar}]\,3d^8$ or $[\mathrm{Ar}]$ ⇅ ⇅ ⇅ ↑ ↑

Ammonia is a strong field ligand. The ligand field diagrams follow, octahedral at left, tetrahedral in the center and square planar at right.

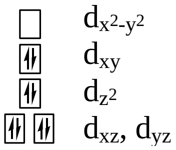
Octahedral



Tetrahedral



Square Planar



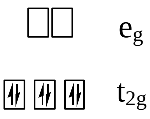
Since the octahedral and tetrahedral configurations have the same number of unpaired electrons (that is, 2 unpaired electrons), we cannot use magnetic behavior to determine whether the ammine complex of nickel(II) is octahedral or tetrahedral. But we can determine if the complex is square planar, since the square planar complex is diamagnetic with zero unpaired electrons.

24. **(M)** The difference is due to the fact that $[\mathrm{Fe(CN_6)}]^{4-}$ is a strong field complex ion, while $[\mathrm{Fe(H_2O)_6}]^{2+}$ is a weak field complex ion. The electron configurations for an iron atom and an iron(II) ion, and the ligand field diagrams for the two complex ions follow.

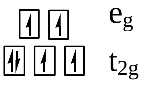
iron atom [Ar] $3d$ ⇅ ↑ ↑ ↑ ↑ $4s$ ⇅

iron(II) ion [Ar] $3d$ ⇅ ↑ ↑ ↑ ↑ $4s$ ☐

$[\mathrm{Fe(CN)_6}]^{4-}$



$[\mathrm{Fe(H_2O)_6}]^{2+}$



Complex-Ion Equilibria

25. **(E) (a)** $\mathrm{Zn(OH)_2(s) + 4\ NH_3(aq) \rightleftharpoons [Zn(NH_3)_4]^{2+}(aq) + 2\ OH^-(aq)}$

(b) $\mathrm{Cu^{2+}(aq) + 2\ OH^-(aq) \rightleftharpoons Cu(OH)_2(s)}$

The blue color is most likely due to the presence of some unreacted $\mathrm{[Cu(H_2O)_4]^{2+}}$ (pale blue)

$$\mathrm{Cu(OH)_2(s) + 4\ NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq,\ dark\ blue) + 2\ OH^-(aq)}$$

$$\mathrm{[Cu(NH_3)_4]^{2+}(aq) + 4\ H_3O^+(aq) \rightleftharpoons [Cu(H_2O)_4]^{2+}(aq) + 4\ NH_4^+(aq)}$$

26. **(M) (a)** $\mathrm{CuCl_2(s) + 2\ Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq,\ yellow)}$

$$\mathrm{2[CuCl_4]^{2-}(aq) + 4H_2O(l)}$$

$$\upharpoonleft\downharpoonright$$

$$\mathrm{[CuCl_4]^{2-}(aq,\ yellow) + [Cu(H_2O)_4]^{2+}(aq,\ pale\ blue) + 4\ Cl^-(aq)}$$

or

$$\mathrm{2[Cu(H_2O)_2Cl_2](aq,\ green) + 4\ Cl^-(aq)}$$

Either $\mathrm{[CuCl_4]^{2-}(aq) + 4\ H_2O(l) \rightleftharpoons [Cu(H_2O)_4]^{2+}(aq) + 4\ Cl^-(aq)}$

Or $\mathrm{[Cu(H_2O)_2Cl_2](aq) + 2H_2O(l) \rightleftharpoons [Cu(H_2O)_4]^{2+}(aq) + 2\ Cl^-(aq)}$

(b) The blue solution is that of $\mathrm{[Cr(H_2O)_6]^{2+}}$. This is quickly oxidized to $\mathrm{Cr^{3+}}$ by $\mathrm{O_2(g)}$ from the atmosphere. The green color is due to $\mathrm{[CrCl_2(H_2O)_4]^{3+}}$.

$$\mathrm{4\ [Cr(H_2O)_6]^{2+}(aq,\ blue) + 4\ H^+(aq) + 8\ Cl^-(aq) + O_2(g)}$$

$$\downarrow$$

$$\mathrm{4\ [CrCl_2(H_2O)_4]^+(aq,\ green) + 10\ H_2O(l)}$$

Over a period of time, we might expect volatile HCl(g) to escape, leading to the formation of complex ions with more $\mathrm{H_2O}$ and less $\mathrm{Cl^-}$.

$$\mathrm{H^+(aq) + Cl^-(aq) \rightleftharpoons HCl(g)}$$

$$\mathrm{[CrCl_2(H_2O)_4]^+(aq,\ green) + H_2O(l) \rightleftharpoons [CrCl(H_2O)_5]^{2+}(aq,\ blue\text{-}green) + Cl^-(aq)}$$

$$\left[\text{CrCl}\left(\text{H}_2\text{O}\right)_5\right]^{2+}\left(\text{aq, blue-green}\right)+\text{H}_2\text{O(l)}\rightleftharpoons\left[\text{Cr}\left(\text{H}_2\text{O}\right)_6\right]^{3+}\left(\text{aq, blue}\right)+\text{Cl}^-\left(\text{aq}\right)$$

Actually, to ensure that these final two reactions actually do occur in a timely fashion, it would be helpful to dilute the solution with water after the chromium metal has dissolved.

27. **(M)** $\left[\text{Co}\left(\text{en}\right)_3\right]^{3+}$ should have the largest overall K_f value. We expect a complex ion with polydentate ligands to have a larger value for its formation constant than complexes that contain only monodentate ligands. This phenomenon is known as the chelate effect. Once one end of a polydentate ligand becomes attached to the central metal, the attachment of the remaining electron pairs is relatively easy because they already are close to the central metal (and do not have to migrate in from a distant point in the solution).

28. **(M) (a)** $\left[\text{Zn}\left(\text{NH}_3\right)_4\right]^{2+}$

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 = 3.9\times10^2\times2.1\times10^2\times1.0\times10^2\times50. = 4.1\times10^8.$$

(b) $\left[\text{Ni}\left(\text{H}_2\text{O}\right)_2\left(\text{NH}_3\right)_4\right]^{2+}$

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 = 6.3\times10^2\times1.7\times10^2\times54\times15 = 8.7\times10^7$$

29. **(M)** First: $\left[\text{Fe}\left(\text{H}_2\text{O}\right)_6\right]^{3+}\left(\text{aq}\right)+\text{en}\left(\text{aq}\right)\rightleftharpoons\left[\text{Fe}\left(\text{H}_2\text{O}\right)_4\left(\text{en}\right)\right]^{3+}\left(\text{aq}\right)+2\text{H}_2\text{O(l)}$
$K_1 = 10^{4.34}$

Second: $\left[\text{Fe}\left(\text{H}_2\text{O}\right)_4\left(\text{en}\right)\right]^{3+}\left(\text{aq}\right)+\text{en}\left(\text{aq}\right)\rightleftharpoons\left[\text{Fe}\left(\text{H}_2\text{O}\right)_2\left(\text{en}\right)_2\right]^{3+}\left(\text{aq}\right)+2\text{H}_2\text{O(l)}$ $K_2 = 10^{3.31}$

Third: $\left[\text{Fe}\left(\text{H}_2\text{O}\right)_2\left(\text{en}\right)_2\right]^{3+}\left(\text{aq}\right)+\text{en}\left(\text{aq}\right)\rightleftharpoons\left[\text{Fe}\left(\text{en}\right)_3\right]^{3+}\left(\text{aq}\right)+2\text{H}_2\text{O(l)}$ $K_3 = 10^{2.05}$

Net: $\left[\text{Fe}\left(\text{H}_2\text{O}\right)_6\right]^{3+}\left(\text{aq}\right)+3\text{ en}\left(\text{aq}\right)\rightleftharpoons\left[\text{Fe}\left(\text{en}\right)_3\right]^{3+}\left(\text{aq}\right)+6\text{H}_2\text{O(l)}$
$K_f = K_1 \times K_2 \times K_3$
$\log K_\text{f} = 4.34 + 3.31 + 2.05 = 9.70$ $\quad K_\text{f} = 10^{9.70} = 5.0\times10^9 = \beta_3$

30. **(E)** Since the overall formation constant is the product of the individual stepwise formation constants, the logarithm of the overall formation constant is the sum of the logarithms of the stepwise formation constants.

$$\log K_\text{f} = \log K_1 + \log K_2 + \log K_3 + \log K_4 = 2.80 + 1.60 + 0.49 + 0.73 = 5.62$$

$$K_\text{f} = 10^{5.62} = 4.2\times10^5$$

31. **(M) (a)** Aluminum(III) forms a stable (and soluble) hydroxo complex but not a stable ammine complex.

$$\left[\mathrm{Al}\left(\mathrm{H_2O}\right)_3\left(\mathrm{OH}\right)_3\right](\mathrm{s}) + \mathrm{OH^-}(\mathrm{aq}) \rightleftharpoons \left[\mathrm{Al}\left(\mathrm{H_2O}\right)_2\left(\mathrm{OH}\right)_4\right]^-(\mathrm{aq}) + \mathrm{H_2O(l)}$$

(b) Although zinc(II) forms a soluble stable ammine complex ion, its formation constant is not sufficiently large to dissolve highly insoluble ZnS. However, it is sufficiently large to dissolve the moderately insoluble $\mathrm{ZnCO_3}$. Said another way, ZnS does not produce sufficient $\left[\mathrm{Zn^{2+}}\right]$ to permit the complex ion to form.

$$\mathrm{ZnCO_3}(\mathrm{s}) + 4\ \mathrm{NH_3}(\mathrm{aq}) \rightleftharpoons \left[\mathrm{Zn}\left(\mathrm{NH_3}\right)_4\right]^{2+}(\mathrm{aq}) + \mathrm{CO_3{}^{2-}}(\mathrm{aq})$$

(c) Chloride ion forms a stable complex ion with silver(I) ion, that dissolves the AgCl(s) that formed when $\left[\mathrm{Cl^-}\right]$ is low.

$$\mathrm{AgCl}(\mathrm{s}) \rightleftharpoons \mathrm{Ag^+}(\mathrm{aq}) + \mathrm{Cl^-}(\mathrm{aq}) \quad \text{and} \quad \mathrm{Ag^+}(\mathrm{aq}) + 2\ \mathrm{Cl^-}(\mathrm{aq}) \rightleftharpoons \left[\mathrm{AgCl_2}\right]^-(\mathrm{aq})$$

$$\text{Overall:}\quad \mathrm{AgCl}(\mathrm{s}) + \mathrm{Cl^-}(\mathrm{aq}) \rightleftharpoons \left[\mathrm{AgCl_2}\right]^-(\mathrm{aq})$$

32. **(M) (a)** Because of the large value of the formation constant for the complex ion, $\left[\mathrm{Co}\left(\mathrm{NH_3}\right)_6\right]^{3+}(\mathrm{aq})$, the concentration of free $\mathrm{Co^{3+}}(\mathrm{aq})$ is too small to enable it to oxidize water to $\mathrm{O_2}(\mathrm{g})$. Since there is not a complex ion present, except, of course, $\left[\mathrm{Co}\left(\mathrm{H_2O}\right)_6\right]^{3+}(\mathrm{aq})$, when $\mathrm{CoCl_3}$ is dissolved in water, the $\left[\mathrm{Co^{3+}}\right]$ is sufficiently high for the oxidation-reduction reaction to be spontaneous.

$$4\ \mathrm{Co^{3+}}(\mathrm{aq}) + 2\ \mathrm{H_2O(l)} \rightarrow 4\ \mathrm{Co^{2+}}(\mathrm{aq}) + 4\ \mathrm{H^+}(\mathrm{aq}) + \mathrm{O_2}(\mathrm{g})$$

(b) Although AgI(s) is often described as insoluble, there is actually a small concentration of $\mathrm{Ag^+}(\mathrm{aq})$ present because of the solubility equilibrium:

$$2\ \mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{I^-(aq)}$$

These silver ions react with thiosulfate ion to form the stable dithiosulfatoargentate(I) complex ion:

$$\mathrm{Ag^+}(\mathrm{aq}) + 2\mathrm{S_2O_3{}^{2-}}(\mathrm{aq}) \rightleftharpoons \left[\mathrm{Ag}\left(\mathrm{S_2O_3}\right)_2\right]^-(\mathrm{aq})$$

Acid-Base Properties

33. **(E)** $\left[\mathrm{Al(H_2O)_6}\right]^{3+}(\mathrm{aq})$ is capable of releasing H^+:

$$\left[\mathrm{Al(H_2O)_6}\right]^{3+}(\mathrm{aq}) + \mathrm{H_2O(l)} \rightleftharpoons \left[\mathrm{AlOH(H_2O)_5}\right]^{2+}(\mathrm{aq}) + \mathrm{H_3O^+}(\mathrm{aq})$$

The value of its ionization constant ($pK_a = 5.01$) approximates that of acetic acid.

34. **(M) (a)** $\left[\mathrm{CrOH(H_2O)_5}\right]^{2+}(\mathrm{aq}) + \mathrm{OH^-}(\mathrm{aq}) \rightarrow \left[\mathrm{Cr(OH)_2(H_2O)_4}\right]^{+}(\mathrm{aq}) + \mathrm{H_2O(l)}$

(b) $\left[\mathrm{CrOH(H_2O)_5}\right]^{2+}(\mathrm{aq}) + \mathrm{H_3O^+}(\mathrm{aq}) \rightarrow \left[\mathrm{Cr(H_2O)_6}\right]^{3+}(\mathrm{aq}) + \mathrm{H_2O(l)}$

Applications

35. **(M) (a)** Solubility: $\mathrm{AgBr(s)} \xrightleftharpoons{K_{sp}=5.0\times10^{-13}} \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)}$

Cplx. Ion Formation: $\mathrm{Ag^+(aq)} + 2\mathrm{S_2O_3}^{2-}(\mathrm{aq}) \xrightleftharpoons{K_f=1.7\times10^{13}} \left[\mathrm{Ag(S_2O_3)_2}\right]^{3-}(\mathrm{aq})$

Net: $\mathrm{AgBr(s)} + 2\mathrm{S_2O_3}^{2-}(\mathrm{aq}) \rightleftharpoons \left[\mathrm{Ag(S_2O_3)_2}\right]^{3-}(\mathrm{aq}) + \mathrm{Br^-(aq)}$ $\quad K_{\mathrm{overall}} = K_{\mathrm{sp}} \times K_{\mathrm{f}}$

$K_{\mathrm{overall}} = 5.0\times10^{-13} \times 1.7\times10^{13} = 8.5$

With a reasonably high $\left[\mathrm{S_2O_3}^{2-}\right]$, this reaction will go essentially to completion.

(b) $\mathrm{NH_3(aq)}$ cannot be used in the fixing of photographic film because of the relatively small value of K_f for $\left[\mathrm{Ag(NH_3)_2}\right]^{+}(\mathrm{aq})$, $K_f = 1.6\times10^7$. This would produce a value of $K = 8.0\times10^{-6}$ in the expression above, which is nowhere large enough to drive the reaction to completion.

36. **(M)** Oxidation: $\left\{\left[\mathrm{Co(NH_3)_6}\right]^{2+}(\mathrm{aq}) \rightarrow \left[\mathrm{Co(NH_3)_6}\right]^{3+}(\mathrm{aq}) + e^-\right\}\times 2 \quad -E° = -0.10\mathrm{V}.$

Reduction: $\left\{\mathrm{H_2O_2(aq)} + 2e^- \rightarrow 2\mathrm{OH^-(aq)}\right\} \quad E° = 0.88\mathrm{V}$

Net: $\mathrm{H_2O_2(aq)} + 2\left[\mathrm{Co(NH_3)_6}\right]^{2+}(\mathrm{aq}) \rightarrow 2\left[\mathrm{Co(NH_3)_6}\right]^{3+}(\mathrm{aq}) + 2\mathrm{OH^-(aq)}$

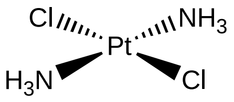
$E^{\circ}_{\mathrm{cell}} = +0.88\ \mathrm{V} + -0.10\ \mathrm{V} = +0.78\ \mathrm{V}.$

The positive value of the standard cell potential indicates that this is a spontaneous reaction.

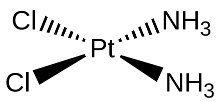
37. **(M)** To make the *cis* isomer, we must use ligands that show a strong tendency for directing incoming ligands to positions that are *trans* to themselves. I^- has a stronger tendency than does Cl^- or NH_3 for directing incoming ligands to the *trans* positions, and so it is beneficial to convert $K_2[PtCl_4]$ to $K_2[PtI_4]$ before replacing ligands around Pt with NH_3 molecules.

38. **(M)** Transplatin is more reactive and is involved in more side reactions before it reaches its target inside of cancer cells. Thus, although it is more reactive, it is less effective at killing cancer cells.

trans-$Pt(NH_3)_2Cl_2$



cis-$Pt(NH_3)_2Cl_2$



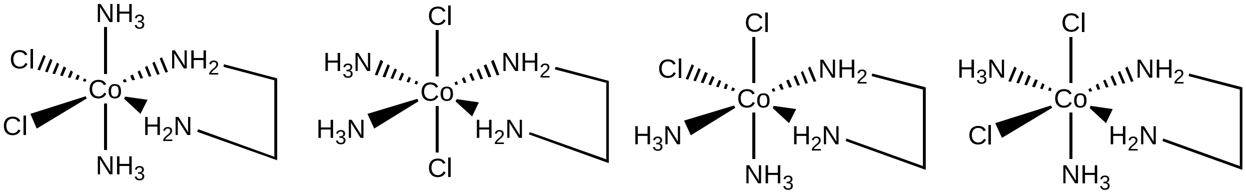
INTEGRATIVE AND ADVANCED EXERCISES

39. **(M)**

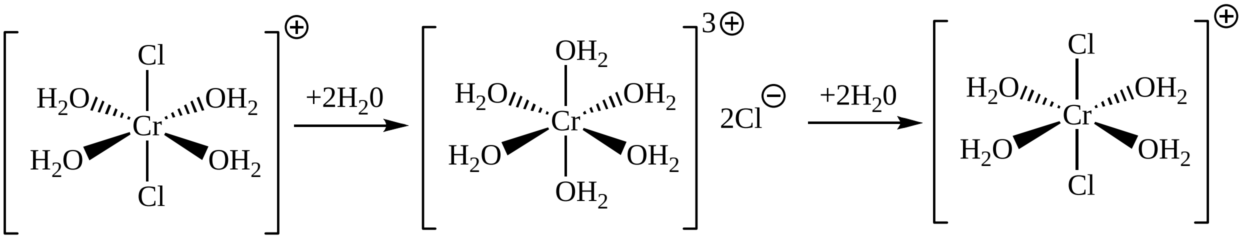
(a)	cupric tetraammine ion	tetraamminecopper(II) ion	$[Cu(NH_3)_4]^{2+}$
(b)	dichlorotetraamminecobaltic chloride	tetraamminedichlorocobalt(III) chloride	$[CoCl_2(NH_3)_4]Cl$
(c)	platinic(IV) hexachloride ion	hexachloroplatinate(IV) ion	$[PtCl_6]^{2-}$
(d)	disodium copper tetrachloride	sodium tetrachlorocuprate(II)	$Na_2[CuCl_4]$
(e)	dipotassium antimony(III) pentachloride	potassium pentachloroantimonate(III)	$K_2[SbCl_5]$

40. **(E)**$[Pt(NH_3)_4][PtCl_4]$ tetraammineplatinum(II) tetrachloroplatinate(II)

41. **(M)** The four possible isomers for $[CoCl_2(en)(NH_3)_2]^+$ are sketched below:



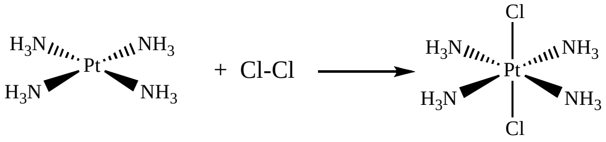
42. **(M)**The color of the green solid, as well as that of the green solution, is produced by the complex ion $[CrCl_2(H_2O)_4]^+$. Over time in solution, the chloro ligands are replaced by aqua ligands, producing violet $[Cr(H_2O)_6]^{3+}$(aq). When the water is evaporated, the original complex is re-formed as the concentration of chloro ligand, $[Cl^-]$, gets higher and the chloro ligands replace the aqua ligands.



43. **(M)**The chloro ligand, being lower in the spectrochemical series than the ethylenediamine ligand, is less strongly bonded to the central atom than is the ethylenediamine ligand. Therefore, of the two types of ligands, we expect the chloro ligand to be replaced more readily. In the *cis* isomer, the two chloro ligands are 90° from each other. This is the angular spacing that can be readily spanned by the oxalato ligand, thus we expect reaction with the cis isomer to occur rapidly. On the other hand, in the *trans* isomer, the two chloro ligands are located 180° from each other. After the chloro ligands are removed, at least one end of one ethylenediamine ligand would have to be relocated to allow the oxalato ligand to bond as a bidentate ligand. Consequently, replacement of the two chloro ligands by the oxalato ligand should be much slower for the *trans* isomer than for the *cis* isomer.

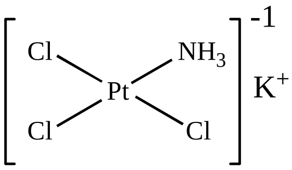
44. **(M)** $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$

$$\underline{[Pt(NH_3)_4]^{2+} \rightarrow [Pt(NH_3)_4]^{4+} + 2\,e^-}$$
$$Cl_2 + [Pt(NH_3)_4]^{2+} \rightarrow [Pt(Cl_2NH_3)_4]^{2+}$$

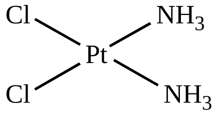


45. **(M)** The successive acid ionizations of a complex ion such as $[Fe(OH)_6]^{3+}$ are more nearly equal in magnitude than those of an uncharged polyprotic acid such as H_3PO_4 principally because the complex ion has a positive charge. The second proton is leaving a species which has one fewer positive charge but which is nonetheless positively charged. Since positive charges repel each other, successive ionizations should not show a great decrease in the magnitude of their ionization constants. In the case of polyprotic acids, on the other hand, successive protons are leaving a species whose negative charge is increasingly greater with each step. Since unlike charges attract each other, it becomes increasingly difficult to remove successive protons.

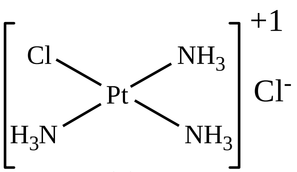
46. (M)



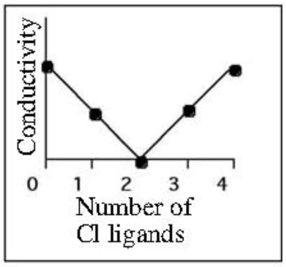
(a)

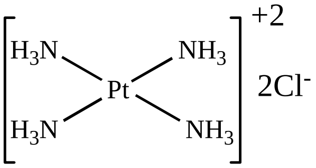


(b)

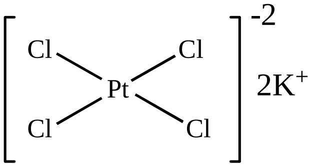


(c)





(d)



(e)

47. **(M) (a)**

$$\begin{array}{lllll}
Fe(H_2O)_6^{3+}(aq) & + \quad H_2O(l) & \xrightleftharpoons{K = 9.0 \times 10^{-4}} & Fe(H_2O)_5OH^{2+}(aq) & + \quad H_3O^+ \\
\text{Initial} \quad 0.100\text{ M} & \quad - & & 0\text{ M} & \approx\ 0\text{ M} \\
\text{Equil.} \quad (0.100 - x)\text{ M} & \quad - & & x & x
\end{array}$$

{where x is the molar quantity of $Fe(H_2O)_6^{3+}(aq)$ hydrolyzed}

$$K = \frac{[[Fe(H_2O)_5OH]^{2+}]\,[H_3O^+]}{[[Fe(H_2O)_6]^{3+}]} = \frac{x^2}{0.100\text{-}x} = 9.0 \times 10^{-4}$$

Solving, we find $x = 9.5 \times 10^{-3}$M, which is the $[H_3O^+]$ so:

$pH = -\log(9.5 \times 10^{-3}) = 2.02$

(b)

	$[Fe(H_2O)_6]^{3+}(aq)$ + $H_2O(l)$	$\xrightleftharpoons{K\,=\,9.0\,\times\,10^{-4}}$	$[Fe(H_2O)_5OH]^{2+}(aq)$	$+\,H_3O^+$
initial	0.100 M –		0 M	0.100 M
equil.	$(0.100-x)$ M –		x M	$(0.100+x)$ M

{where x is $[[Fe(H_2O)_6]^{3+}]$ reacting}

$$K=\frac{[[Fe(H_2O)_5OH]^{2+}]\,[H_3O^+]}{[[Fe(H_2O)_6]^{3+}]}=\frac{x\,(0.100+x)}{(0.100\text{-}x)}=9.0\times 10^{-4}$$

Solving, we find $x=9.0\times10^{-4}$ M, which is the $[[Fe(H_2O)_5OH]^{2+}]$

(c) We simply substitute $[[Fe(H_2O)_5OH]^{2+}]=1.0\times10^{-6}$ M into the K_a expression with $[Fe(H_2O)_6]^{3+}=0.100$ M and determine the concentration of H_3O^+

$$[H_3O^+]=\frac{K_a[[Fe(H_2O)_6]^{3+}]}{[[Fe(H_2O)_5OH]^{2+}]}=\frac{9.0\times10^{-4}(0.100\text{ M})}{[1.0\times10^{-6}\text{M}]}=90.\text{ M}$$

To maintain the concentration at this level requires an impossibly high concentration of H_3O^+

48. (D) Let us first determine the concentration of the uncomplexed (free) Pb^{2+}(aq). Because of the large value of the formation constant, we assume that most of the lead(II) ion is present as the EDTA complex ion ($[Pb(EDTA)]^{2-}$). Once equilibrium is established, we can see if there is sufficient lead(II) ion present in solution to precipitate with the sulfide ion. Note: the concentration of EDTA remains constant at 0.20 M)

Reaction:	$Pb^{2+}(aq)$ +	$EDTA^{4-}(aq)$	$\xrightleftharpoons{2\times10^{18}}$	$[Pb(EDTA)]^{2-}(aq)$
Initial:	0 M	0.20 M		0.010 M
Change:	+x M	constant		-x M
Equilibrium:	x M	0.20 M		(0.010-x) M ≈ 0.010 M

$$K_f=\frac{[Pb(EDTA)^{2-}]}{[Pb^{2+}][EDTA^{4-}]}=2\times10^{18}=\frac{0.010}{0.20(x)}\qquad x=2.\underline{5}\times10^{-20}\text{ M}=[Pb^{2+}]$$

Now determine the $[S^{2-}]$ required to precipitate PbS from this solution. $K_{sp}=[Pb^{2+}][S^{2-}]=8\times10^{-28}$

$[S^{2-}]=\dfrac{8\times10^{-28}}{(5\times10^{-20})}=2.\underline{5}\times10^{-8}$ M Recall (i) that a saturated H_2S solution is ~0.10 M H_2S

and (ii) That the $[S^{2-}]=K_{a2}=1\times10^{-14}$

$Q_{sp}=[Pb^{2+}][S^{2-}]=2.\underline{5}\times10^{-20}\times1\times10^{-14}=2.\underline{5}\times10^{-34}$ $\qquad K_{sp}=8\times10^{-28}$

$Q_{sp}<<K_{sp}$ Hence, PbS(s) will not precipitate from this solution.

49. (M) The formation of $[Cu(NH_3)_4]^{2+}$(aq) from $[Cu(H_2O)_4]^{2+}$(aq) has $K_1=1.9\times10^4$, $K_2=3.9\times10^3$, $K_3=1.0\times10^3$, and $K_4=1.5\times10^2$. Since these equilibrium constants are all considerably larger than 1.00, one expects that the reactions they represent, yielding ultimately the ion $[Cu(NH_3)_4]^{2+}$(aq), will go essentially to completion. However, if the concentration of NH_3 were limited to less than the stoichiometric amount, that is, to less than 4 mol NH_3 per mol of

Cu^{2+}(aq), one would expect that the ammine-aqua complex ions would be present in significantly higher concentrations than the $[Cu(NH_3)_4]^{2+}$(aq) ions.

50. **(D)** For $[Ca(EDTA)]^{2-}$, $K_f = 4 \times 10^{10}$ and for $[Mg(EDTA)]^{2-}$, $K_f = 4 \times 10^{8}$. In Table 18-1, the least soluble calcium compound is $CaCO_3$, $K_{sp} = 2.8 \times 10^{-9}$, and the least soluble magnesium compound is $Mg_3(PO_4)_2$, $K_{sp} = 1 \times 10^{-25}$. We can determine the equilibrium constants for adding carbonate ion to $[Ca(EDTA)]^{2-}$(aq) and for adding phosphate ion to $[Mg(EDTA)]^{2-}$(aq) as follows:

$$\text{Instability:}\quad [Ca(EDTA)]^{2-}(aq) \rightleftharpoons Ca^{2+}(aq) + EDTA^{4-}(aq) \qquad K_i = 1/4 \times 10^{10}$$

$$\text{Precipitation:}\quad \underline{Ca^{2+}(aq) + CO_3^{2-}(aq) + \rightleftharpoons CaCO_3(s) \qquad K_{ppt} = 1/2.8 \times 10^{-9}}$$

$$\text{Net:}\quad [Ca(EDTA)]^{2-} + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) + EDTA^{4-}(aq) \quad K = K_i \times K_{ppt}$$

$$K = \frac{1}{(4 \times 10^{10})(2.8 \times 10^{-9})} = 9 \times 10^{-3}$$

The small value of the equilibrium constant indicates that this reaction does not proceed very far toward products.

$$\text{Instability:}\quad \{[Mg(EDTA)]^{2-}(aq) \rightleftharpoons Mg^{2+}(aq) + EDTA^{4-}(aq)\} \times 3 \qquad K_i^3 = 1/(4 \times 10^8)^3$$

$$\text{Precipitation:}\quad \underline{3\,Mg^{2+}(aq) + 2\,PO_4^{3-}(aq) \rightleftharpoons Mg_3(PO_4)_2(s) \qquad K_{ppt} = 1/1 \times 10^{-25}}$$

$$\text{Net :}\quad 3\,[Mg(EDTA)]^{2-} + 2\,PO_4^{3-}(aq) \rightleftharpoons Mg_3(PO_4)_2(s) + 3\,EDTA^{4-}(aq) \qquad K = K_i^3 \times K_{ppt}$$

$$K = \frac{1}{(4 \times 10^8)^3(1 \times 10^{-25})} = 0.1_6$$

This is not such a small value, but again we do not expect the formation of much product, particularly if the $[EDTA^{4-}]$ is kept high. We can approximate what the concentration of precipitating anion must be in each case, assuming that the concentration of complex ion is 0.10 M and that of $[EDTA^{4-}]$ also is 0.10 M.

$$\text{Reaction:}\quad [Ca(EDTA)]^{2-} + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s) + EDTA^{4-}(aq)$$

$$K = \frac{[EDTA^{4-}]}{[[Ca(EDTA)]^{2-}][CO_3^{2-}]} = 9 \times 10^{-3} = \frac{0.10\text{ M}}{0.10\text{ M}\,[CO_3^{2-}]} \qquad [CO_3^{2-}] = 1 \times 10^{2}\text{ M}$$

This is an impossibly high $[CO_3^{2-}]$.

$$\text{Reaction:}\quad 3[Mg(EDTA)]^{2-} + 2\,PO_4^{3-}(aq) \rightleftharpoons Mg_3(PO_4)_2(s) + 3\,EDTA^{4-}(aq)$$

$$K = \frac{[EDTA^{4-}]^3}{[[Mg(EDTA)]^{2-}]^3[PO_4^{3-}]^2} = 0.1_6 = \frac{(0.10\text{ M})^3}{(0.10\text{ M})^3\,[PO_4^{3-}]^2} \qquad [PO_4^{3-}] = 2._5\text{ M}$$

Although this $[PO_4^{3-}]$ is not impossibly high, it is unlikely that it will occur without the deliberate addition of phosphate ion to the water. *Alternatively*, we can substitute $[[M(EDTA)]^{2-}] = 0.10$ M and $[EDTA^{4-}] = 0.10$ M into the formation constant expression: $K_f = \dfrac{[[M(EDTA)]^{2-}]}{[M^{2+}][EDTA^{4-}]}$

This substitution gives $[\mathrm{M}^{2+}] = \dfrac{1}{K_\mathrm{f}}$, hence, $[\mathrm{Ca}^{2+}] = 2.5 \times 10^{-11}$ M and $[\mathrm{Mg}^{2+}] = 2.5 \times 10^{-9}$ M,

which are concentrations that do not normally lead to the formation of precipitates unless the concentrations of anions are substantial. Specifically, the required anion concentrations are $[\mathrm{CO_3}^{2-}] = 1.1 \times 10^2$ M for $CaCO_3$, and $[\mathrm{PO_4}^{3-}] = 2.5$ M, just as computed above.

51. **(M)** If a 99% conversion to the chloro complex is achieved, which is the percent conversion necessary to produce a yellow color, $[[\mathrm{CuCl_4}]^{2-}] = 0.99 \times 0.10\ \mathrm{M} = 0.099$ M, and $[[\mathrm{Cu(H_2O)_4}]^{2+}] = 0.01 \times 0.10\ \mathrm{M} = 0.0010$ M. We substitute these values into the formation constant expression and solve for $[\mathrm{Cl}^-]$.

$$K_\mathrm{f} = \frac{[[\mathrm{CuCl_4}]^{2-}]}{[[\mathrm{Cu(H_2O)_4}]^{2+}][\mathrm{Cl}^-]^4} = 4.2 \times 10^5 = \frac{0.099\ \mathrm{M}}{0.0010\ \mathrm{M}\,[\mathrm{Cl}^-]^4}$$

$$[\mathrm{Cl}^-] = \sqrt[4]{\frac{0.099}{0.0010 \times 4.2 \times 10^5}} = 0.12\ \mathrm{M}$$

This is the final concentration of free chloride ion in the solution. If we wish to account for all chloride ion that has been added, we must include the chloride ion present in the complex ion.

total $[\mathrm{Cl}^-] = 0.12$ M free Cl^- + (4 × 0.099 M) bound Cl^- = 0.52 M

52. **(M)(a)** Oxidation: $2\mathrm{H_2O(l)} \longrightarrow \mathrm{O_2(g)} + 4\ \mathrm{H^+(aq)} + 4\ \mathrm{e^-}$ $\qquad -E° = -1.229$ V

Reduction: $\{\mathrm{Co^{3+}((aq)} + \mathrm{e^-} \longrightarrow \mathrm{Co^{2+}(aq)}\} \times$ $\qquad E° = +1.82$ V

Net: $4\ \mathrm{Co^{3+}(aq)} + 2\ \mathrm{H_2O(l)} \longrightarrow 4\ \mathrm{Co^{2+}(aq)} + 4\ \mathrm{H^+(aq)} + \mathrm{O_2(g)}$ $\qquad E°_\mathrm{cell} = +0.59$ V

(b) Reaction: $\mathrm{Co^{3+}(aq)} + 6\ \mathrm{NH_3(aq)} \rightleftharpoons [\mathrm{Co(NH_3)_6}]^{3+}\mathrm{(aq)}$

Initial:	1.0 M	0.10 M	0 M
Changes:	$-x$M	constant	$+x$M
Equil:	$(1.0 - x)$M	0.10 M	xM

$$K_\mathrm{f} = \frac{[[\mathrm{Co(NH_3)_6}]^{3+}]}{[\mathrm{Co^{3+}}][\mathrm{NH_3}]^6} = 4.5 \times 10^{33} = \frac{x}{(1.0 - x)(0.10)^6} \qquad \frac{x}{1.0 - x} = 4.5 \times 10^{27}$$

Thus $[[\mathrm{Co(NH_3)_6}]^{3+}] = 1.0$ M because K is so large, and

$$[\mathrm{Co^{3+}}] = \frac{1}{4.5 \times 10^{27}} = 2.2 \times 10^{-28}\ \mathrm{M}$$

(c) The equilibrium and equilibrium constant for the reaction of NH_3 with water follows.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = 1.8\times10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[OH^-]^2}{0.10} \qquad [OH^-] = \sqrt{0.10(1.8\times10^{-5})} = 0.0013\text{ M}$$

In determining the $[OH^-]$, we have noted that $[NH_4^+] = [OH^-]$ by stoichiometry, and also that $[NH_3] = 0.10$ M, as we assumed above. $[H_3O^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.0\times10^{-14}}{0.0013} = 7.7\times10^{-12}\text{ M}$

We use the Nernst equation to determine the potential of reaction (24.12) at the conditions described.

$$E = E^\circ_{cell} - \frac{0.0592}{4}\log\frac{[Co^{2+}]^4\,[H^+]^4\,P[O_2]}{[Co^{3+}]^4}$$

$$E = +0.59 - \frac{0.0592}{4}\log\frac{(1\times10^{-4})^4\,(7.7\times10^{-12})^4\,0.2}{(2.2\times10^{-28})^4} = +0.59\text{ V} - 0.732\text{ V} = -0.142\text{ V}$$

The negative cell potential indicates that the reaction indeed does not occur.

53. **(M)** We use the Nernst equation to determine the value of $[Cu^{2+}]$. The cell reaction follows.

$$Cu(s) + 2\,H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g) \qquad E^\circ_{cell} = -0.337\text{ V}$$

$$E = E^\circ - \frac{0.0592}{2}\log\frac{[Cu^{2+}]}{[H^+]^2} = 0.08\text{ V} = -0.337 - \frac{0.0592}{2}\log\frac{[Cu^{2+}]}{(1.00)^2}$$

$$\log[Cu^{2+}] = \frac{2(-0.337-0.08)}{0.0592} = -14.1 \qquad [Cu^{2+}] = 8\times10^{-15}\text{ M}$$

Now we determine the value of K_f.

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{1.00}{8\times10^{-15}(1.00)^4} = 1\times10^{14}$$

This compares favorably with the value of $K_f = 1.1\times10^{13}$ given in Table 18-2, especially considering the imprecision with which the data are known. ($E_{cell} = 0.08$ V is known to but one significant figure.)

54. **(M)** We first determine [Ag$^+$] in the cyanide solution.

$$K_f = \frac{[[\mathrm{Ag(CN)_2}]^-]}{[\mathrm{Ag^+}][\mathrm{CN^-}]^2} = 5.6\times10^{18} = \frac{0.10}{[\mathrm{Ag^+}](0.10.)^2}$$

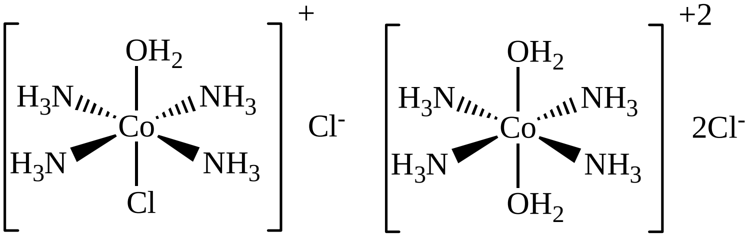
$$[\mathrm{Ag^+}] = \frac{0.10}{5.6\times10^{18}\,(0.10)^2} = 1.8\times10^{-18}$$

The cell reaction is as follows. It has $E^\circ_{\text{cell}} = 0.000\text{ V}$; the same reaction occurs at both anode and cathode and thus the Nernstian voltage is influenced only by the Ag$^+$ concentration.

$$\mathrm{Ag^+}\,(0.10\,\mathrm{M}) \longrightarrow \mathrm{Ag^+}\ (0.10\,\mathrm{M}\,[\mathrm{Ag(CN)_2}]^-,\ 0.10\,\mathrm{M\,KCN})$$

$$E = E^\circ - \frac{0.0592}{1}\log\frac{[\mathrm{Ag^+}]_{\mathrm{CN}}}{[\mathrm{Ag^+}]} = 0.000 - 0.0592\ \log\frac{1.8\times10^{-18}}{0.10} = +\,0.99\ \mathrm{V}$$

55. **(M)**



A 0.10 mol/L solution of these compounds would result in ion concentration of 0.20 mol/L for [Co Cl ($H_2O(NH_3)_4$)]Cl•H_2O or 0.30 mol/L for [Co(H_2O)$_2$ (NH_3)$_4$]Cl_2.

Observed freezing point depression = -0.56 °C.

$\Delta T = -K_f\times m\times i = -0.56\text{ deg} = -1.86\text{ mol kg}^{-1}\text{ deg}(0.10\text{ mol/L})\times i$

Hence, i = 3.0 mol/kg or 3.0 mol/L. This suggests that the compound is [Co(H_2O)$_2$ (NH_3)$_4$]Cl_2.

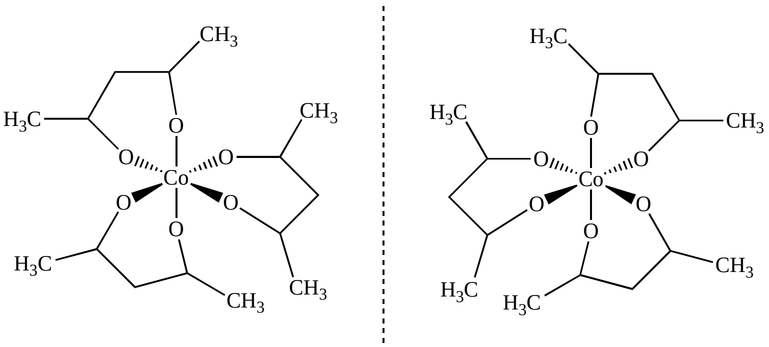
56. **(M)** $Sc(H_2O)_6^{3+}$ and $Zn(H_2O)_4^{2+}$ have outer energy shells with 18 electrons, and thus they do not have any electronic transitions in the energy range corresponding to visible light. $Fe(H_2O)_6^{3+}$ has 17 electrons (not 18) in its outer shell; thus, it does have electronic transitions in the energy range corresponding to visible light.

57. **(M)** The Cr^{3+} ion would have 3 unpaired electrons, each residing in a 3*d* orbital and would be sp^3d^2 hybridized. The hybrid orbitals would be hybrids of 4*s*, 4*p*, and 3*d* (or 4*d*) orbitals. Each Cr–NH_3 coordinate covalent bond is a σ bond formed when a lone pair in an sp^3 orbital on N is directed toward an empty sp^3d^2 orbital on Cr^{3+}. The number of unpaired electrons predicted by valence bond theory would be the same as the number of unpaired electrons predicted by crystal field theory.

58. **(M)** Since these reactions involve Ni^{2+} binding to six identical nitrogen donor atoms, we can assume the ΔH for each reaction is approximately the same. A large formation constant indicates a more negative free energy. This indicates that the entropy term for these reactions is different. The large increase in entropy for each step, can be explained by the chelate effect. The same number of water molecules are displaced by fewer ligands, which is directly related to entropy change.

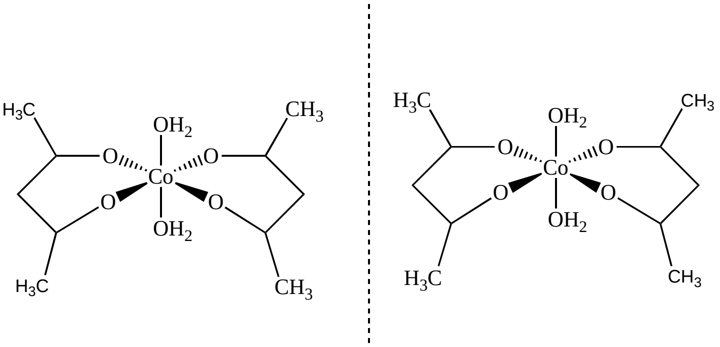
59. (M)

$Co(acac)_3$



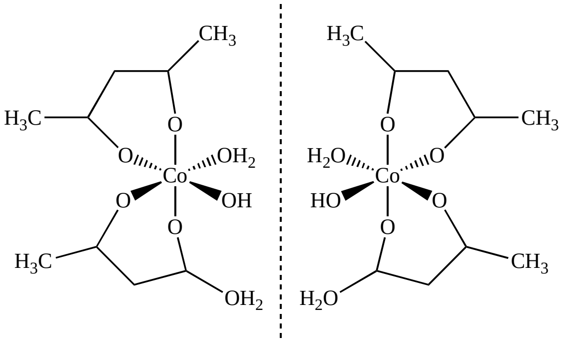
This compound has a non-superimposable mirror image (therefore it is optically active). These are enantiomers. One enantiomer rotates plane polarized light clockwise, while the other rotates plane polarized light counter-clockwise. Polarimetry can be used to determine which isomer rotates plane polarized light in a particular direction.

***trans*-$[Co(acac)_2(H_2O)_2]Cl_2$**



This compound has a superimposable mirror image (therefore it is optically inactive). These are the same compound. This compound will not rotate plane polarized light (net rotation = 0).

***cis*-$[Co(acac)_2(H_2O)_2]Cl_2$**



This compound has a non-superimposable mirror image (therefore it is optically active). These are enantiomers. One enantiomer rotates plane polarized light clockwise, while the other rotates plane polarized light counter-clockwise. By using a polarimeter, we can determine which isomer rotates plane polarized light in a particular direction.

60. (D) $[Co(H_2O)_6]^{3+}(aq) + e^- \rightarrow [Co(H_2O)_6]^{2+}(aq)$

$\log K = nE°/0.0592 = (1)(1.82)/0.0592 = 30.74$ $K = 10^{30.74}$

$$\begin{array}{llll}
[Co(en)_3]^{3+}(aq) + 6\ H_2O(l) & \rightarrow & [Co(H_2O)_6]^{3+}(aq) + 3\ en & K = 1/10^{47.30} \\
[Co(H_2O)_6]^{2+}(aq) + 3\ en & \rightarrow & [Co(en)_3]^{2+}(aq) + 6\ H_2O(l) & K = 10^{12.18} \\
[Co(H_2O)_6]^{3+}(aq) + e^- & \rightarrow & [Co(H_2O)_6]^{2+}(aq) & K = 10^{30.74} \\
\hline
[Co(en)_3]^{3+}(aq) + e^- & \rightarrow & [Co(en)_3]^{2+}(aq) & K_{overall} = ?
\end{array}$$

$K_{\text{overall}} = 1/10^{47.30} \times 10^{12.18} \times 10^{30.74} = 10^{-4.38} = 0.000041\underline{7}$

$E° = (0.0592/n)\log K = (0.0592/1)\log(0.000041\underline{7}) = -0.26\text{ V}$

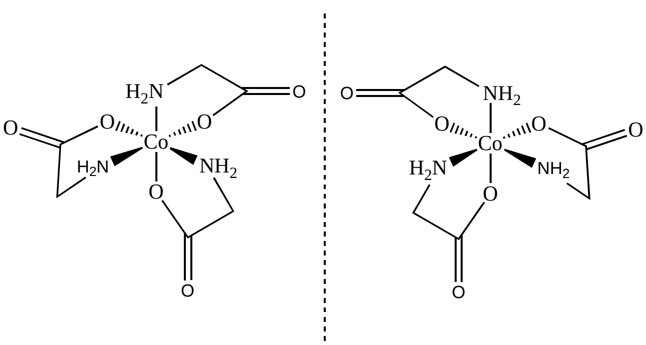
$4\,Co^{3+}(aq) + 4\,e^- \rightarrow 4\,Co^{2+}(aq) \qquad E°_{\text{cathode}} = 1.82\text{ V}$
$\underline{2\,H_2O(l) \rightarrow 4\,H^+(aq) + O_2(g) + 4\,e^- \quad E°_{\text{anode}} = 1.23\text{ V}}$
$4\,Co^{3+}(aq) + 2\,H_2O(l) \rightarrow 4\,H^+(aq) + O_2(g) + 4\,Co^{2+}(aq)$

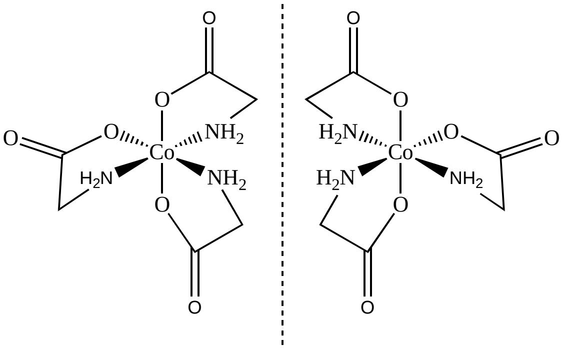
$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} = 1.82\text{V} - 1.23\text{ V} = +0.59\text{ V}$ (Spontaneous)

$4\,[Co(en)_3]^{3+}(aq) + 4\,e^- \rightarrow 4\,[Co(en)_3]^{2+}(aq) \qquad E°_{\text{cathode}} = -0.26\text{ V}$
$\underline{2\,H_2O(l) \rightarrow 4\,H^+(aq) + O_2(g) + 4\,e^- \qquad E°_{\text{anode}} = 1.23\text{ V}}$
$4\,[Co(en)_3]^{3+}(aq) + 2\,H_2O(l) \rightarrow 4\,H^+(aq) + O_2(g) + 4\,[Co(en)_3]^{2+}(aq)$

$E°_{\text{cell}} = E°_{\text{cathode}} - E° = -0.26\text{ V} - 1.23\text{ V} = -1.49\text{ V}$ (non-spontaneous)

61. **(M)** There are two sets of isomers for Co(gly)$_3$. Each set comprises two enantiomers (non-superimposable mirror images). One rotates plane polarized light clockwise (+), the other counter-clockwise (–). Experiments are needed to determine which enantiomer is (+) and which is (–).

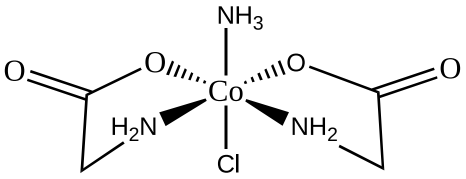


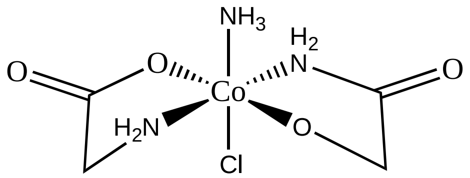


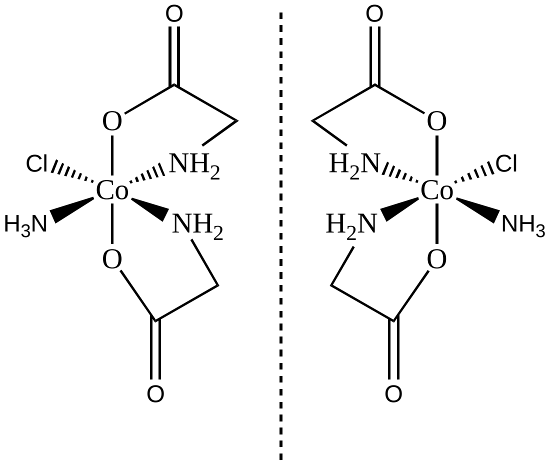
(+)-*fac*-tris(glycinato)cobalt(III) (+)-*mer*-tris(glycinato)cobalt(III)

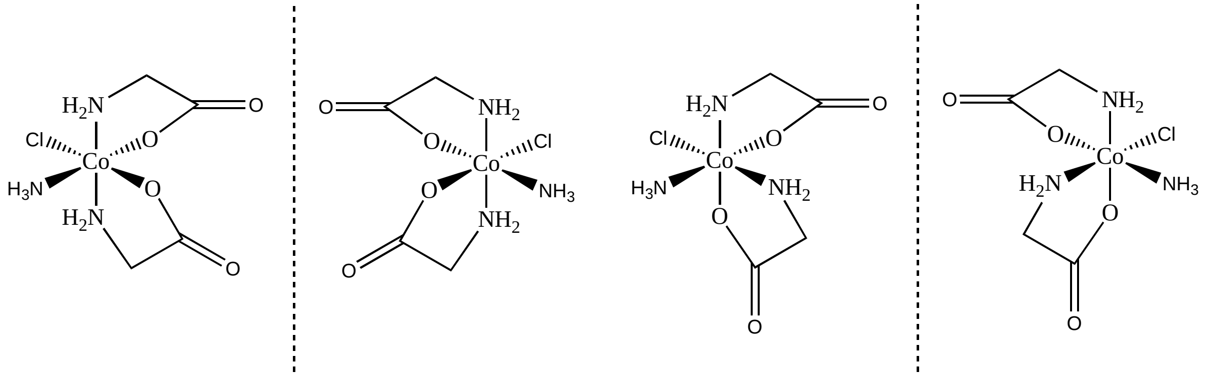
(–)-*fac*-tris(glycinato)cobalt(III) (–)-*mer*-tris(glycinato)cobalt(III)

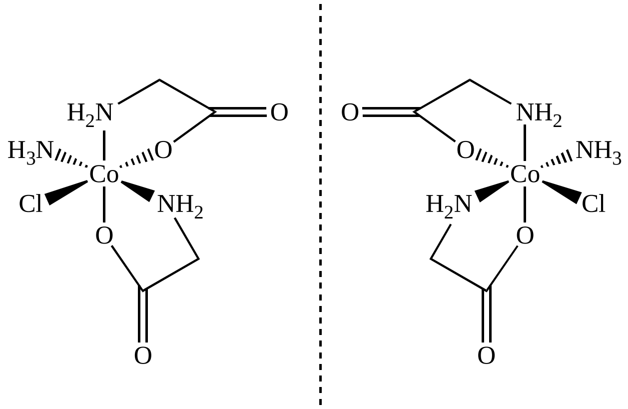
[Co(gly)$_2$Cl(NH$_3$)] has 10 possible isomer, four pairs of enantiomers and two achiral isomers.











62. **(M)** The coordination compound is face-centered cubic, K^+ occupies tetrahedral holes, while $PtCl_6^{2-}$ occupies octahedral holes.

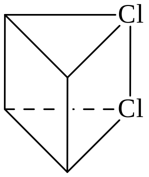
63. **(M)**

# NH_3	0	1	2	3
Formula:	$K_2[PtCl_6]$	$K[PtCl_5(NH_3)]$	$PtCl_4(NH_3)_2$	$[PtCl_3(NH_3)_3]Cl$
Total # ions (per formula unit)	3	2	0	2

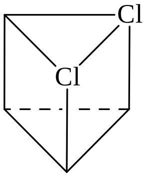
# NH_3	4	5	6
Formula:	$[PtCl_2(NH_3)_4]Cl_2$	$[PtCl(NH_3)_5]Cl_3$	$[Pt(NH_3)_6]Cl_4$
Total # ions (per formula unit)	3	4	5

FEATURE PROBLEMS

64. (M)(a) A trigonal prismatic structure predicts three geometric isomers for $[CoCl_2(NH_3)_4]^+$, which is one more than the actual number of geometric isomers found for this complex ion. All three geometric isomers arising from a trigonal prism are shown below.



(i)



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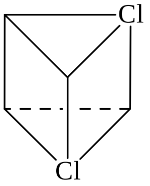
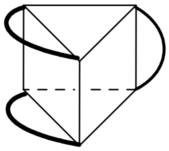


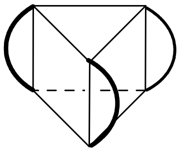
(iii)

The fact that the trigonal prismatic structure does not afford the correct number of isomers is a clear indication that the ion actually adopts some other structural form (i.e., the theoretical model is contradicted by the experimental result). We know now of course, that this ion has an octahedral structure and as a result, it can exist only in *cis* and *trans* configurations.

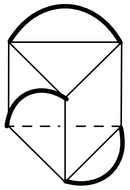
(b) All attempts to produce optical isomers of $[Co(en)_3]^{3+}$ based upon a trigonal prismatic structure are shown below. The ethylenediamine ligand appears as an arc in diagrams below:



(i)



(ii)

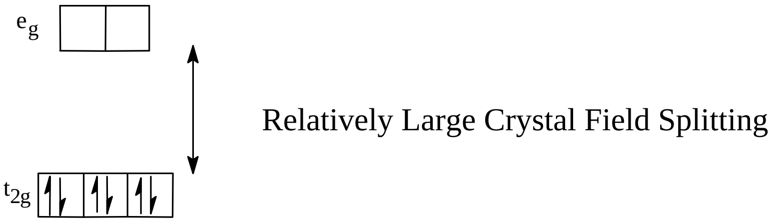


(iii)

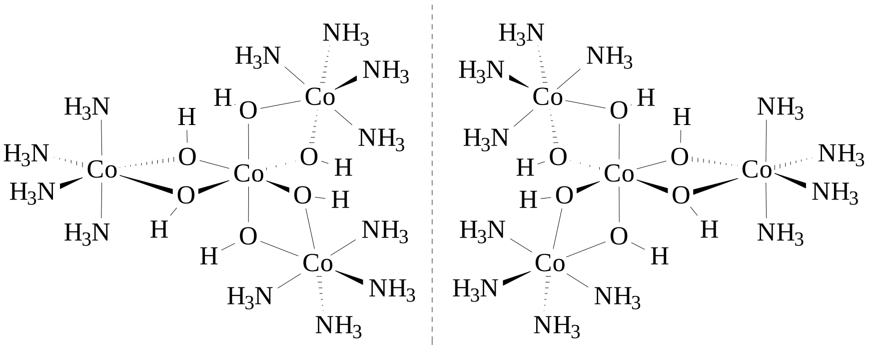
Only structure (iii), which has an ethylenediamine ligand connecting the diagonal corners of a face can give rise to optical isomers. Structure (iii) is highly unlikely, however, because the ethylenediamine ligand is simply too short to effectively span the diagonal distance across the face of the prism. Thus, barring any unusual stretching of the ethylenediamine ligand, a trigonal prismatic structure cannot account for the optical isomerism that was observed for $[Co(en)_3]^{3+}$.

65. (D) Assuming that each hydroxide ligand bears its normal 1– charge, and that each ammonia ligand is neutral, the total contribution of negative charge from the ligands is 6 –. Since the net charge on the complex ions is 6+, the average oxidation state for each Co atom must be +3 (i.e., each Co in the complex can be viewed as a Co^{3+} $3d^6$ ion surrounded by six ligands.) The five 3*d* orbitals on each Co are split by the octahedrally arranged ligands into three lower energy orbitals, called t_{2g} orbitals, and two higher energy orbitals, called e_g orbitals. We are told in the question that the complex is *low spin*. This is simply another way of saying that all six 3*d* electrons on each Co are paired up in the t_{2g} set as a result of the e_g and t_{2g} orbitals being separated by a relatively large energy gap (see below). Hence, there should be no unpaired electrons in the hexacation (i.e., the cation is expected to be diamagnetic).

Low Spin Co^{3+}
(Octahedral Environment):



The Lewis structures for the two optical isomers (enantiomers) are depicted below:

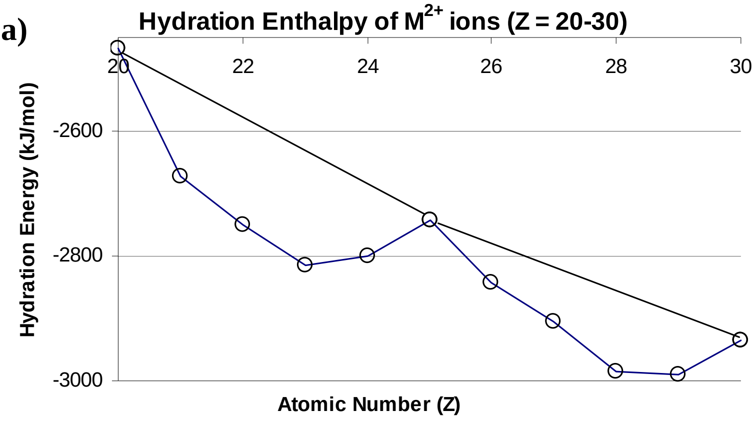


Non-superimposable mirror images of one another

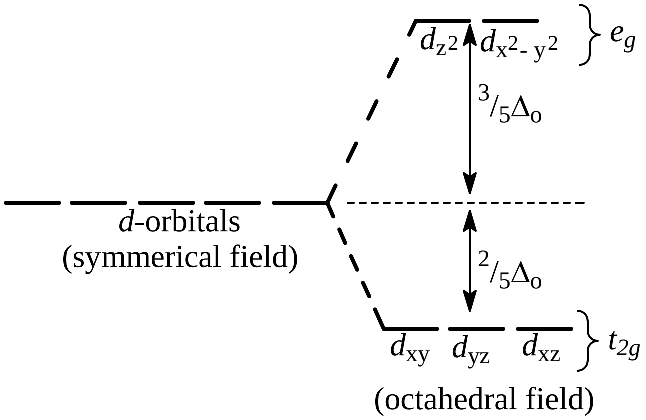
66. **(D)** The data used to construct a plot of hydration energy as a function of metal ion atomic number is collected in the table below. The graph of hydration energy (kJ/mol) versus metal ion atomic number is located beneath the table.

Metal ion	Atomic number	Hydration energy
Ca^{2+}	20	−2468 kJ/mol
Sc^{2+}	21	−2673 kJ/mol
Ti^{2+}	22	−2750 kJ/mol
V^{2+}	23	−2814 kJ/mol
Cr^{2+}	24	−2799 kJ/mol
Mn^{2+}	25	−2743 kJ/mol
Fe^{2+}	26	−2843 kJ/mol
Co^{2+}	27	−2904 kJ/mol
Ni^{2+}	28	−2986 kJ/mol
Cu^{2+}	29	−2989 kJ/mol
Zn^{2+}	30	−2936 kJ/mol

(a)



(b) When a metal ion is placed in an octahedral field of ligands, the five *d*-orbitals are split into e_g and t_{2g} subsets, as shown in the diagram below:



Since water is a weak field ligand, the magnitude of the splitting is relatively small. As a consequence, high-spin configurations result for all of the hexaaqua complexes. The electron configurations for the metal ions in the high-spin hexaaqua complexes and their associated crystal field stabilization energies (CFSE) are provided in the table below

Metal Ion	Configuration	t_{2g}	e_g	number of unpaired e$^-$	CFSE(Δ_o)
Ca^{2+}	$3d^{0}$	0	0	0	0
Sc^{2+}	$3d^{1}$	1	0	1	$-^{2}/_{5}$
Ti^{2+}	$3d^{2}$	2	0	2	$-^{4}/_{5}$
V^{2+}	$3d^{3}$	3	0	3	$-^{6}/_{5}$
Cr^{2+}	$3d^{4}$	3	1	4	$-^{3}/_{5}$
Mn^{2+}	$3d^{5}$	3	2	5	0
Fe^{2+}	$3d^{6}$	4	2	4	$-^{2}/_{5}$
Co^{2+}	$3d^{7}$	5	2	3	$-^{4}/_{5}$
Ni^{2+}	$3d^{8}$	6	2	2	$-^{6}/_{5}$
Cu^{2+}	$3d^{9}$	6	3	1	$-^{3}/_{5}$
Zn^{2+}	$3d^{10}$	6	4	0	0

Thus, the crystal field stabilization energy is zero for Ca^{2+}. Mn^{2+} and Zn^{2+}.

(c) The lines drawn between those ions that have a CFSE = 0 show the trend for the enthalpy of hydration after the contribution from the crystal field stabilization energy has been subtracted from the experimental values. The Ca to Mn and Mn to Zn lines are quite similar. Both line have slopes that are negative and are of comparable magnitude. This trend shows that as one proceeds from left to right across the periodic table, the energy of hydration for dications becomes increasingly more negative. The hexaaqua complexes become progressively more stable because the Z_{eff} experienced by the bonding electrons in the valence shell of the metal ion steadily increases as we move further and further to the right. Put another way, the Z_{eff} climbs steadily as we move from left to right and this leads to the positive charge density on the metal becoming larger and larger, which results in the water ligands steadily being pulled closer and closer to the nucleus. Of course, the closer the approach of the water ligands to the metal, the greater is the energy released upon successful coordination of the ligand.

(d) Those ions that exhibit crystal field stabilization energies greater than zero have heats of hydration that are more negative (i.e. more energy released) than the hypothetical heat of hydration for the ion with CFSE subtracted out. The heat of hydration without CFSE for a given ion falls on the line drawn between the two flanking ions with CFSE = 0 at a position directly above the point for the experimental hydration energy. The energy difference between the observed heat of hydration for the ion and the heat of hydration without CFSE is, of course, approximately equal to the CFSE for the ion.

(e) As was mentioned in the answer to part (c), the straight line drawn between manganese and zinc (both ions with CFSE = 0) on the previous plot, describes the enthalpy trend after the ligand field stabilization energy has been subtracted from the experimental values for the hydration enthalpy. Thus, Δ_o for Fe^{2+} in $[Fe(H_2O)_6]^{2+}$ is approximately equal to $^5/_2$ of the energy difference (in kJ/mol) between the observed hydration energy for $Fe^{2+}(g)$ and the point for Fe^{2+} on the line connecting Mn^{2+} and Zn^{2+}, which is the expected enthalpy of hydration after the CFSE has been subtracted out. Remember that the crystal field stabilization energy for Fe^{2+} that is obtained from the graph is not Δ_o, but rather $^2/_5\Delta_o$, since the CFSE for a $3d^6$ ion in an octahedral field is just $^2/_5$ of Δ_o. Consequently, to obtain Δ_o , we must multiply the enthalpy difference by $^5/_2$. According to the graph, the high-spin CFSE for Fe^{2+} is –2843 kJ/mol – (–2782 kJ/mol) or –61 kJ/mol. Consequently, $\Delta_o = {}^5/_2(-61 \text{ kJ/mol}) = -153$ kJ/mol, or 1.5×10^2 kJ/mol is the energy difference between the e_g and t_{2g} orbital sets.

(f) The color of an octahedral complex is the result of the promotion of an electron on the metal from a t_{2g} orbital $\rightarrow$ e_g orbital. The energy difference between the e_g and t_{2g} orbital sets is Δ_o. As the metal-ligand bonding becomes stronger, the separation between the t_{2g} and e_g orbitals becomes larger. If the e_g set is not full, then the metal complex will exhibit an absorption band corresponding to a $t_{2g} \rightarrow e_g$ transition. Thus, the $[Fe(H_2O)_6]^{2+}$complex ion should absorb electromagnetic radiation that has $E_{photon} = \Delta_o$. Since $\Delta_o \approx 150$ kJ/mol (calculated in part (e) of this question) for a mole of $[Fe(H_2O)_6]^{2+}(aq)$,

$$E_{\text{photon}} = \frac{1.5\times10^2\,\text{kJ}}{1\,\text{mol}[\text{Fe(H}_2\text{O)}_6]^{2+}}\times\frac{1\,\text{mol [Fe(H}_2\text{O)}_6]^{2+}}{6.022\times10^{23}[\text{Fe(H}_2\text{O)}_6]^{2+}}\times\frac{1000\,\text{J}}{1\,\text{kJ}}$$

$$= 2.5\times10^{-19}\ \text{J per ion}$$

$$\nu = \frac{E}{h} = \frac{2.5\times10^{-19}\ \text{J}}{6.626\times10^{-34}\ \text{J s}} = 3.8\times10^{14}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{h} = \frac{2.998\times10^{8}\ \text{m s}^{-1}}{3.8\times10^{14}\ \text{s}^{-1}} = 7.8\times10^{-7}\ \text{m (780 nm)}$$

So, the $[Fe(H_2O)_6]^{2+}$ ion will absorb radiation with a wavelength of 780 nm, which is red light in the visible part of the electromagnetic spectrum.

SELF-ASSESSMENT EXERCISES

67. **(E) (a)** Coordination number is the number of ligands coordinated to a transition metal complex.
(b) Δ_0 is the crystal field splitting parameter which depends on the coordination geometry of a transition metal complex.
(c) Ammine complex is the complex that contains NH_3 ligands.
(d) An enantiomer is one of two stereoisomers that are mirror images of each other that are "non-superposable" (not identical).

68. **(E) (a)** A spectrochemical series is a list of ligands ordered on ligand strength and a list of metal ions based on oxidation number, group and identity.
(b) Crystal field theory (CFT) is a model that describes the electronic structure of transition metal compounds, all of which can be considered coordination complexes.
(c) Optical isomers are two compounds which contain the same number and kinds of atoms, and bonds (i.e., the connectivity between atoms is the same), and different spatial arrangements of the atoms, but which have non-superimposable mirror images.
(d) Structural isomerism in accordance with IUPAC, is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

69. **(E) (a)** Coordination number is the number of ligands coordinated to a transition metal complex. Oxidation number of a central atom in a coordination compound is the charge that it would have if all the ligands were removed along with the electron pairs that were shared with the central atom.
(b) A monodentate ligand has one point at which it can attach to the central atom. Polydentate ligand has many points at which it can coordinate to a transition metal.
(c) Cis isomer has identical groups on the same side. In trans isomer, on the other hand, identical groups are on the opposite side.
(d) Dextrorotation and levorotation refer, respectively, to the properties of rotating plane polarized light clockwise (for dextrorotation) or counterclockwise (for levorotation). A compound with dextrorotation is called dextrorotary, while a compound with levorotation is called levorotary.
(e) When metal is coordinated to ligands to form a complex, its "d" orbital splits into high and low energy groups of suborbitals. Depending on the nature of the ligands, the energy difference separating these groups can be large or small. In the first case, electrons of the d orbital tend to pair in the low energy suborbitals, a configuration known as "low spin". If the energy difference is low, electrons tend to distribute unpaired, giving rise to a "high spin" configuration. High spin is associated with paramagnetism (the property of being attracted to magnetic fields), while low spin is associated to diamagnetism (inert or repelled by magnets).

70. **(E)** (d)

71. **(E)** (e)

72. **(E)** (b)

73. **(E)** (a)

74. **(E)** (d)

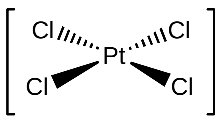
75. **(E)** (c)

76. **(E)** (b)

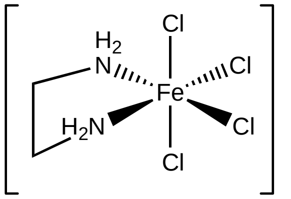
77. **(M)** **(a)** pentaamminebromocobalt(III)sulfate, no isomerism.
(b) hexaamminechromium(III)hexacyanocobaltate(III), no isomerism.
(c) sodiumhexanitrito-N-cobaltate(III), no isomerism
(d) tris(ethylenediamine)cobalt(III)chloride, two optical isomers.

78. **(M)** **(a)** $[Ag(CN)_2]^-$; **(b)** $[Pt(NO_2)(NH_3)_3]^+$; **(c)** $[CoCl(en)_2(H_2O)]^{2+}$; **(d)** $K_4[Cr(CN)_6]$

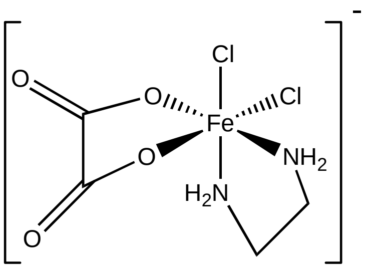
79. **(M)**



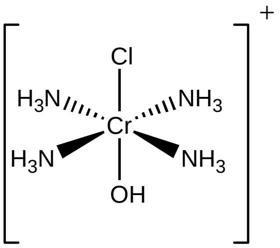
(a)



(b)

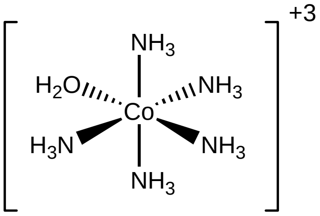


(c)

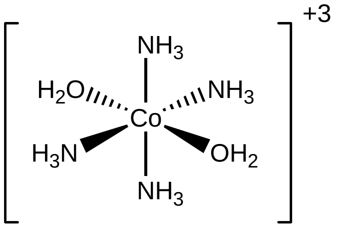


(d)

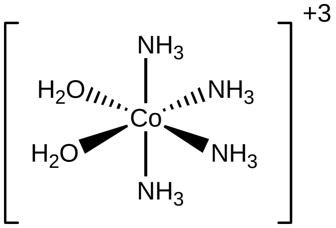
80. **(M)** **(a)** one structure only (all positions are equivalent for the H_2O ligand; NH_3 ligands attach at the remaining five sites).



(b) two structures, *cis* and *trans*, based on the placement of H_2O.

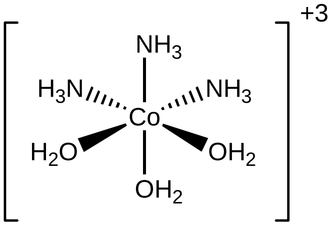


trans

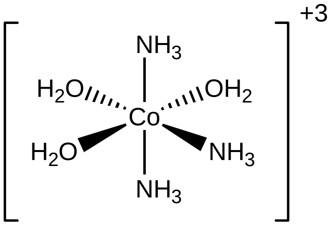


cis

(c) two structures, *fac* and *mer*.

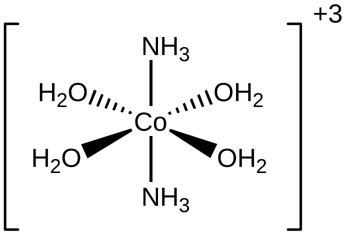


fac

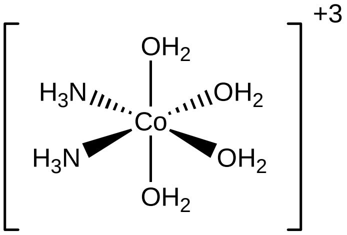


mer

(d) two structures, *cis* and *trans*, based on the placement of NH_3.



trans



cis

81. **(M) (a)** coordination isomerism, based on the interchange of ligands between the complex cation and complex anion.
(b) linkage isomerism, based on the mode of attachment of the SCN^- ligand (either $–SCN^-$ or $–NCS^-$).
(c) no isomerism
(d) geometric isomerism, based on whether Cl^- ligands are *cis* or *trans*.
(e) geometric isomerism, based on whether the NH_3 or OH^- ligands are *fac* or *mer*.

82. **(M) (a)** geometric isomerism (*cis* and *trans*) and optical isomerism in the *cis* isomer.
(b) geometric isomerism (*cis* and *trans*), optical isomerism in the *cis* isomer, and linkage isomerism in the thiocyanate ligand.
(c) no isomers.
(d) no isomers for this square-planar complex.
(e) two geometric isomers, one with the tridentate ligand occupying meridional positions and the other with the tridentate ligand occupying facial positions.

83. **(M)** Because ethylenediamine (en) is a stronger field ligand than H_2O, more energy must be absorbed by $[Co(en)_3]^{3+}$ than by $[Co(H_2O)_6]^{3+}$ to simulate an electronic transition. This means that $[Co(en)_3]^{3+}$(aq) absorbs shorter wavelength light and transmits longer wavelength light than does $[Co(H_2O)_6]^{3+}$(aq). Thus $[Co(en)_3]^{3+}$(aq) is yellow and $[Co(H_2O)_6]^{3+}$(aq) is blue.