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REPRODUCIBILITY OF SILVER-SILVER HALIDE
ELECTRODES¹

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ABSTRACT

Tests of the reproducibility in potential of the electrolytic, thermal-electrolytic, and thermal types of silver-silver chloride, silver-silver bromide, and silver-silver iodide electrodes, in both acid and neutral solutions, are reported. All of these silver-silver halide electrodes show an aging effect, such that freshly prepared electrodes behave as cathodes towards electrodes previously aged in the solution. They are not affected in potential by exposure to light, but the presence of oxygen disturbs the potentials of the silver-silver chloride and silver-silver bromide electrodes in acid solutions, and of the silver-silver iodide electrodes in both acid and neutral solutions. Except in the case of the silver-silver iodide electrodes, of which the thermal-electrolytic type seems more reliable than the electrolytic or the thermal type, the equilibrium potential is independent of the type, within about 0.02 mv.

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I. INTRODUCTION

In a previous investigation on the reproducibility of the silver-silver chloride electrode in neutral solution of potassium chloride,² a significant aging effect, first noted by MacInnes and Parker,³ was measured and discussed. The origin of this aging effect was traced to concentration-polarization. It was found that freshly prepared electrodes always behave as cathodes towards aged electrodes. The initial difference in potential sometimes exceeds a millivolt, but when sufficient time is allowed, the electrolytic, thermal-electrolytic, and thermal types of the silver-silver chloride electrode finally attain the same potential, within about 0.02 mv, irrespective of the presence or absence of light and of air dissolved in the solution.

In this investigation the work on the reproducibility of silver-silver chloride electrodes was extended to include measurements of the effect of aging and of the effect of oxygen, in acid solutions. In addi-

¹ A part of the material included in this paper was submitted as a thesis by J. K. Taylor in partial fulfillment of the requirements for the degree of Master of Science at the University of Maryland. The interest and advice of Prof. M. M. Haring are gratefully acknowledged.

² E. R. Smith and J. K. Taylor, *J. Research NBS* **20**, 837 (1938) RP1108.

³ D. A. MacInnes and K. Parker, *J. Am. Chem. Soc.* **37**, 1445 (1915).

tion, silver-silver bromide and silver-silver iodide electrodes were studied with respect to aging, the effect of oxygen, and the influence of light, in both neutral and acid solutions.

II. APPARATUS AND MATERIALS

The measurements were made with the same apparatus, including the potentiometer, standard cell, galvanometer, thermostat, and vessels for the electrodes used in the previous work with silver-silver chloride electrodes.⁴

Potassium bromide and potassium iodide of reagent grade were recrystallized before use. Silver bromate was prepared by mixing solutions of silver nitrate and potassium bromate. The precipitated silver bromate was washed repeatedly and finally recrystallized from water. Silver iodate was prepared similarly from silver nitrate and potassium iodate, and was washed repeatedly before use. Hydrochloric and hydrobromic acids were prepared by diluting acids of reagent quality and adjusting the concentration to 0.05 *N*.

Nitrogen, for the removal of oxygen from the solutions, was freed from oxygen by passage through hot copper in a tubular electric furnace. It was then passed through solutions of sodium hydroxide, dilute sulfuric acid, and finally through a solution of the same composition as that in the cell.

III. SILVER-SILVER CHLORIDE ELECTRODES

It has been demonstrated previously⁵ that the aging effect results from concentration-polarization. This effect should, therefore, occur in acid solutions as well as in neutral solutions, and it is important to know how much time should be allowed after the preparation of silver-silver chloride electrodes to insure the attainment of their equilibrium potential.

The aging effect was found to occur in oxygen-free acid solutions and was measured by the following procedure. Eight silver electrodes of the thermal type and a large silver-silver chloride electrode were placed in a cell of the design shown in figure 1, containing 0.05 *N* hydrochloric acid solution. Nitrogen was bubbled continuously through the cell (except during the measurements) to remove oxygen, and two of the silver electrodes were chloridized, using the large silver-silver chloride electrode as a cathode. In this way, the silver-silver chloride electrodes were formed without contact with oxygen and without change in the composition of the solution. After waiting several days to allow the freshly formed electrodes to age, a second pair of the silver electrodes was chloridized and then compared in potential with the first two. On succeeding days the remaining two pairs of electrodes were chloridized and compared with the two aged electrodes. In figure 2 the points on the curve represent the average values of potential difference for each pair, with reference to the aged pair at the given time. The new electrodes were initially positive to aged electrodes, rapidly approached the latter in potential during the first several hours, and finally, after a period of from 1 to 2 days, attained an equilibrium potential in agreement with that of the older electrodes.

⁴ E. R. Smith and J. K. Taylor, *J. Research NBS* 20, 837 (1938) RP1108.

⁵ See footnote 4.

This behavior is practically identical with that found for these electrodes in neutral solution.

In the previous paper, oxygen was shown to have no significant effect on the potential of the silver-silver chloride electrode in neutral solutions, but it has long been known that in acid solutions the potential is disturbed by the presence of oxygen. Güntelberg⁶ attributed this disturbance to the reaction



If this reaction causes the disturbance, then in the presence of oxygen there should be a slight decrease in the concentration of hydrochloric acid within the interstices of the coating of silver chloride which envelops the silver, and such a decrease should cause an oxygen-saturated electrode to act as a cathode towards an oxygen-free electrode. The disturbing effect of oxygen in acid solution was confirmed, and a direct measurement of its sign and magnitude was accomplished in the following way:

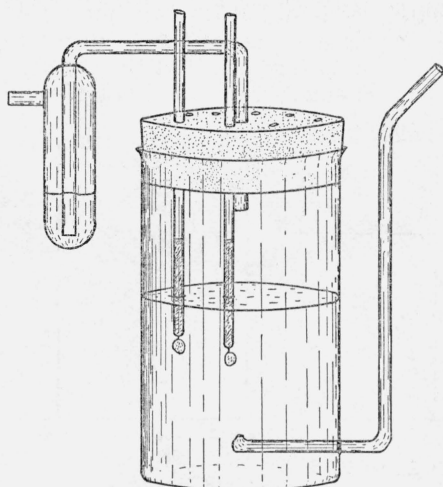
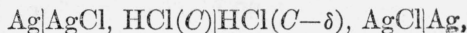


FIGURE 1.—Cell for comparison of electrodes.

Two cells, of the type shown in figure 1, each containing seven thermal silver-silver chloride electrodes immersed in 0.05 *N* hydrochloric acid solution, were connected by an inverted Y-tube of 5-mm bore, through which the cells could be connected at will by drawing up solution from them to form a liquid junction. After passing nitrogen through each cell to remove oxygen, the largest difference in potential between any two electrodes in each set was 0.02 mv and, on making the junction between the cells, the average potential difference between the electrodes in cell 1 and those in cell 2 was 0.05 mv. Those in cell 1 were cathodic by this amount with respect to those in cell 2. The junction between the cells was then disconnected and oxygen was bubbled through cell 1 while nitrogen was again passed through cell 2. After saturation with oxygen, the electrodes in cell 1 varied erratically in potential with respect to each other by as much as 0.19 mv, and on reforming the junction the average difference in potential between cell 1 and cell 2 increased to 0.21 mv. Cell 1, saturated with oxygen, acted as a cathode toward cell 2. The oxygen was then swept out of cell 1, and its electrodes returned to their original agreement among themselves and with those of cell 2.

The magnitude of the effective change in concentration resulting from the reaction given by eq 1 can be estimated from a consideration of the cell



⁶ E. Güntelberg, *Z. physik. Chem.* **123**, 199 (1926).

in which δ is the effective decrease in concentration of hydrochloric acid within the porous electrode in the oxygen-saturated solution. Since δ is small, the concentrations C and $C-\delta$ are nearly the same. Consequently, the variations in ionic mobilities between these concentrations may be assumed to be negligible, and the activity ratio may be taken as equal to the concentration ratio. The expression for the emf of the cell then becomes

$$E = 2N_{\text{H}} \left(\frac{RT}{F} \right) \ln \frac{C}{C-\delta}, \quad (2)$$

in which N_{H} is the cation transference number, and the other symbols have their usual meanings. Since $\ln C/(C-\delta) > 0$, $E > 0$, and the oxygen-saturated electrode is the cathode. Substituting the measured value of E (0.00021 v) and the appropriate values of the other quantities⁷ in eq 2, it is found that $\delta \approx C/200$. This means that the reaction with oxygen caused a change in the effective concentration of acid

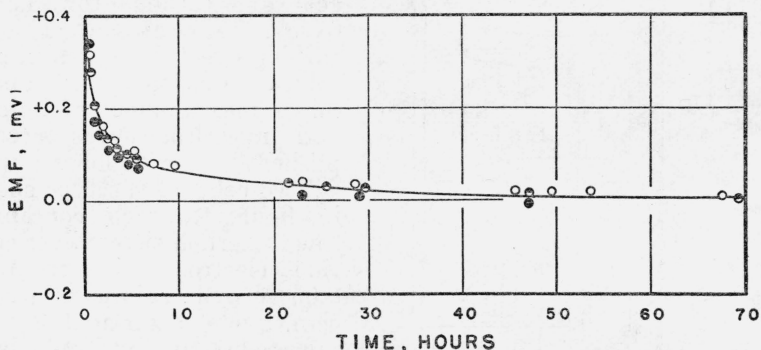


FIGURE 2.—Aging effect with the thermal-electrolytic type of silver-silver chloride electrodes in 0.05 *N* air-free solution of hydrochloric acid.

within the pores of the electrode of about 0.5 percent. The total amount of solution within the pores is, however, relatively so small that, after removal of the oxygen and reattainment of equilibrium with the bulk of the solution, the net change in concentration is insignificant, and the electrodes readily return to their initial potential. The figure of 0.5 percent is, of course, only an order of magnitude, since in any given case the value will depend on the time of contact, concentration of oxygen, and the porosity of the electrodes.

IV. SILVER-SILVER BROMIDE ELECTRODES

Silver-silver bromide electrodes of the electrolytic type were prepared by electroplating silver on rectangular pieces of platinum gauze, 0.5 by 1 cm, washing them for 10 days in frequently changed distilled water, to eliminate contamination by the plating solution,⁸ and bromidizing them electrolytically in 1 *N* hydrobromic acid solution with a current of 4 ma per electrode for 1 hour. These electrodes were first soaked for 1 hour in 0.05 *N* potassium bromide solution and

⁷ The cation transference number in 0.05 *N* HCl at 25° C is 0.829, according to L. G. Longworth, *J. Am. Chem. Soc.* 54, 2741 (1932).

⁸ W. R. Carmody, *J. Am. Chem. Soc.* 51, 2901 (1929).

then placed in a cell containing 0.05 *N* potassium bromide solution. After 1 week, to allow for aging, during which time nitrogen was passed through the cell, their differences in potential were recorded.

Thermal-electrolytic electrodes were made by heating a paste of silver oxide and water, supported on spirals of platinum wire, and electrolytically coating the resulting porous beads of silver with bromide from a large silver-silver bromide electrode. The latter operation was performed after placing the electrodes in a second cell containing 0.05 *N* potassium bromide, through which nitrogen was passed. After allowing 1 week for aging, their differences in potential were measured.

Thermal electrodes were prepared by heating to decomposition in an electric furnace a paste of silver oxide and silver bromate in water, supported on spirals of platinum wire.⁹ These were placed together in a third cell containing 0.05 *N* potassium bromide solution, from which oxygen was excluded by nitrogen, and after 1 week their differences in potential were recorded.

The results of the reproducibility tests on these three types of silver-silver bromide electrodes, exposed to light in neutral (0.05 *N*) air-free potassium bromide solution, are shown in table 1. From this table it is seen that under these conditions the individual electrodes of any one type agree among themselves within a few hundredths of a millivolt.

TABLE 1.—*Reproducibility of different types of silver-silver bromide electrodes exposed to light in neutral air-free 0.05 N potassium bromide solution*

Electrode number	Electrolytic type	Thermal-electrolytic type	Thermal type
	<i>mv</i>	<i>mv</i>	<i>mv</i>
1-2.....	0.00	-0.03	+0.01
1-3.....	+ .04	+ .02	.00
1-4.....	+ .05	.00	.00
1-5.....	- .01	+ .01	- .04
1-6.....	- .02	.00	- .04
1-7.....	- .02	+ .02	.00
Average deviation.....	0.02	0.01	0.02

To determine the agreement of the different types, six electrolytic and six thermal silver-silver bromide electrodes were compared with a group of five thermal-electrolytic electrodes. The results are given in table 2 and show that the different types attain the same final value of potential within a few hundredths of a millivolt.

⁹ A. S. Keston, *J. Am. Chem. Soc.* **57**, 1671 (1935).

TABLE 2.—Comparison of different types of silver-silver bromide electrodes in neutral, air-free 0.05 N potassium bromide solution

Electrode number	Description ¹	Potential difference
		<i>mv</i>
1-2	TE-TE	0.00
1-3	TE-TE	-.01
1-4	TE-TE	-.01
1-5	TE-TE	-.01
1-6	TE-E	.00
1-7	TE-E	+.04
1-8	TE-E	+.05
1-9	TE-E	-.01
1-10	TE-E	-.02
1-11	TE-E	-.02
1-12	TE-T	+.01
1-13	TE-T	.00
1-14	TE-T	.00
1-15	TE-T	-.04
1-16	TE-T	-.04
1-17	TE-T	.00

¹ E, TE, and T symbolize electrolytic, thermal-electrolytic, and thermal types, respectively.

The time required for silver-silver bromide electrodes to come to equilibrium was determined by measuring the aging effect according

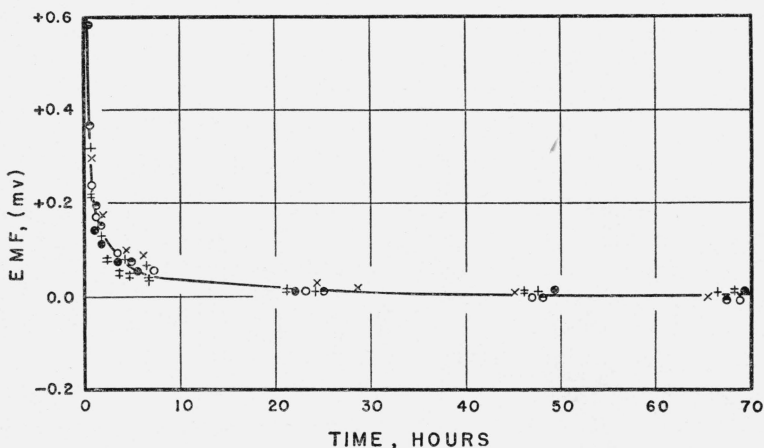


FIGURE 3.—Aging effect with the thermal-electrolytic type of silver-silver bromide electrodes in 0.05 N air-free solution of potassium bromide.

to the procedure used with the silver-silver chloride electrodes. The results obtained with the thermal-electrolytic type, in air-free 0.05 N potassium bromide solution, are shown in figure 3. The several kinds of crosses represent the measurements with electrodes prepared and measured with light excluded. The several kinds of circles represent the results with electrodes exposed to light. It is apparent that light has no effect on the aging of these electrodes. Also, that light has no effect on their equilibrium potential was shown by interchanging some of the electrodes between the blackened and the transparent cell. This interchange was made in a dark room and, on comparing the potentials of the light-protected and light-exposed electrodes, no significant differences were found.

The aging of the thermal type of silver-silver bromide electrodes in neutral air-free solution of potassium bromide is shown in figure 4. These data were obtained by placing electrodes, freshly prepared on succeeding days, in a cell containing aged electrodes, and, at definite intervals of time, comparing the potentials of the newer electrodes with those of the aged ones.

The effect of oxygen on the potential of silver-silver bromide electrodes was measured by the procedure used for the silver-silver chloride electrodes. In neutral solution (0.05 *N* KBr) no effect was observed, but in acid solution (0.05 *N* HBr) a marked effect was found. In the latter case, with seven thermal-electrolytic electrodes in each of the two cells connected by the inverted Y-tube, an average difference of 0.01 mv was obtained between the electrodes in cell 1 and those in cell 2, when oxygen was excluded from both. When oxygen was passed into cell 1, the individual electrodes varied errati-

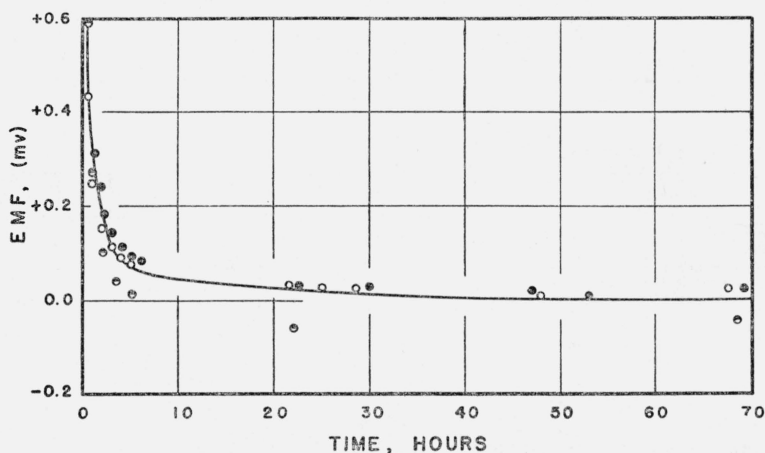


FIGURE 4.—Aging effect with the thermal type of silver-silver bromide electrodes in 0.05 *N* air-free solution of potassium bromide.

cally in potential with respect to each other by as much as 0.23 mv and the average difference in potential between electrodes in cell 1 and cell 2 became 0.30 mv. The oxygen-saturated set acted as a cathode toward the oxygen-free set of electrodes. After removal of the oxygen, the electrodes returned to their initial agreement. The influence of oxygen is thus in the direction to be expected from the reaction.



which causes an effective decrease in the concentration of the acid within the pores of the electrode.

V. SILVER-SILVER IODIDE ELECTRODES

A number of sets of the electrolytic, thermal-electrolytic¹⁰ and thermal¹¹ types of silver-silver iodide electrode were prepared by methods analogous to those used for the chloride and bromide electrodes. They were tested for reproducibility and agreement of the different types. The thermal-electrolytic type showed a reproduci-

¹⁰ G. Jones and M. L. Hartman, *J. Am. Chem. Soc.* **37**, 756 (1915).

¹¹ B. B. Owen, *J. Am. Chem. Soc.* **57**, 1526 (1935).

bility of about 0.02 mv, comparable to that of the other halide electrodes, but the thermal and the electrolytic types were not as satisfactory. Occasionally, self-consistent groups of the latter two types were obtained, but more often the reproducibility was no better than 0.1 to 0.2 mv, particularly between electrodes prepared at different times. When the three types were intercompared, the thermal and the electrolytic type were always positive (i. e., cathodic) toward the thermal-electrolytic type by 0.1 to 0.2 mv. Since the cause of this behavior was not discovered, the experiments on the effects of light, oxygen, and aging on the potential of the silver-silver iodide electrode were confined to the thermal-electrolytic type.

The aging effect of the silver-silver iodide electrodes in neutral solution of 0.05 *N* potassium iodide in the presence and absence of light was measured according to the procedure used for the thermal-

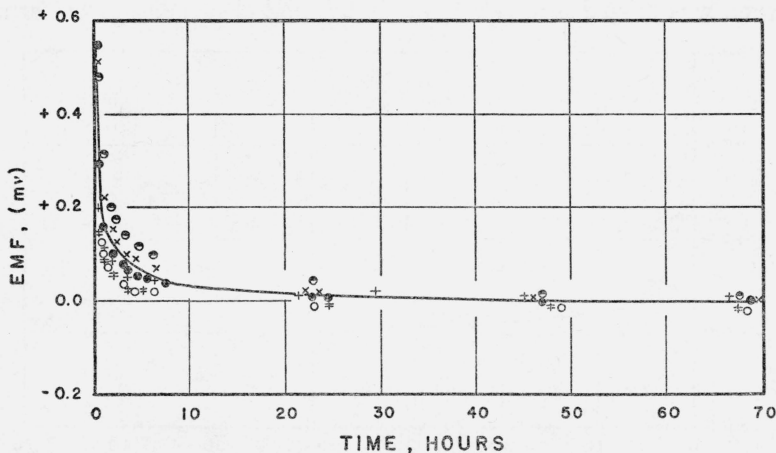


FIGURE 5.—Aging effect with the thermal-electrolytic type of silver-silver iodide electrodes in 0.05 *N* air-free solution of potassium iodide.

electrolytic type of silver-silver chloride and silver-silver bromide electrodes. The results are shown in figure 5, in which the circles and crosses of various types represent, respectively, electrodes protected from and exposed to light. By interchanging electrodes between the blackened and the transparent cell, the interchange being made in a dark room, it was found that all the electrodes had the same potential within about 0.02 mv.

The effect of oxygen on the potentials of the silver-silver iodide electrodes was tested in neutral solution of 0.05 *N* potassium iodide, using two cells connected by an inverted Y-tube, as in the tests with the other electrodes. With oxygen excluded from both cells, the average difference in potential between the electrodes in cell 1 and in cell 2 was 0.02 mv. As soon as oxygen was admitted to cell 2, its electrodes behaved erratically and became, on the average, 1.5 mv positive with respect to the electrodes in the oxygen-free cell. This effect is so marked in neutral solutions that it was considered unnecessary to make the same test in solutions of hydriodic acid, since the instability of the latter substance in the presence of oxygen is well known.