[CONTRIBUTION FROM THE COLLEGE OF ST. THOMAS]

The Mercurous Bromide Electrode

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There are available in the recent literature only a few measurements from which the standard potential of the mercury–mercurous bromide electrode can be calculated. Gerke[1] measured the cell

$$H_2/HBr/Hg_2Br_2/Hg \qquad (1)$$

at an acid molality of 0.10015. Ishikawa and Ueda[2] measured cell (1) at a molality of 0.1012.

In the present study are presented data on the cell

$$Ag/AgBr,\ KBr,\ Hg_2Br_2/Hg \qquad (2)$$

at 20, 25, and 30°. These data allow the calculation of the standard potential of the mercury–mercurous bromide electrode, since the corresponding value for the silver–silver bromide electrode is well known at the various temperatures.[3] Harned[3e] has pointed out that $E^0 = 0.07115 \pm 0.00015$ v. includes the results of all the investigators listed in reference (3). The value of Harned and Donelson,[3e] namely, $E^0 = 0.07131 - 4.99 \times 10^{-4}(t - 25) - 3.45 \times 10^{-6}(t - 25)^2$ has been chosen for the calculation of the standard potentials reported in this paper.

Experimental

The cell vessels were of a modified H type arranged so that solutions free from air (and saturated with nitrogen) could be used in them. There was a stopcock between the two electrodes. Measurements were made with the stopcock open, but it was kept closed at all other times.

Mercury was purified by spraying through a tower of diluted nitric acid, and washing with water. It was then distilled in a slow current of air, and redistilled *in vacuo*.

Mercurous bromide was prepared by precipitation from approximately 0.1 *N* solutions of potassium bromide and mercurous nitrate. Br^- was kept in excess. Especial care was taken that no chloride was present in the potassium bromide; it was prepared from a chlorate and chloride-free preparation of potassium bromate by decomposition with heat followed by three crystallizations from "conductivity" water. The mercurous nitrate solution was made up without the addition of nitric acid.[4] Preliminary experiments showed that constant and reproducible e. m. f. readings could be obtained with aged mercurous bromide. Preparations of the salt allowed to stand in the dark under water for at least one week after thorough rinsing gave e. m. f. readings which were constant within a few hours after the cells were made up. The thickness of the layer of mercurous bromide on the mercury in the electrode made no difference in the values obtained.

The silver–silver bromide electrodes were prepared according to the directions of Keston[3b] for the thermal type electrodes. In order to compare an electrolytic type electrode, several silver–silver bromide electrodes were prepared according to Carmody[5] for silver–silver chloride electrodes. Electrodes prepared by these two methods had potentials which differed by about 0.1 mv. on the average. The greatest variation observed was 0.4 mv.

Electromotive force measurements were made with a L. & N. type K potentiometer and either a type R or a type 2520-c L. & N. galvanometer. An Eppley unsaturated Weston cell certified by the manufacturers was the standard of e. m. f. The cells were kept in a water thermostat. Temperature control at 25° was within 0.04° and within 0.06° at 20 and 30°. The temperatures were determined by reference to a mercury in glass thermometer certified by the Bureau of Standards, and were known to be accurate to within 0.05°.

Cells were measured for not less than five days, and some were kept for over a month. Any cell which showed wide variations in e. m. f. after the first few days was discarded.

Concentrations of the electrolyte, KBr, varied from 0.02 to 0.15 molar. No differences in e. m. f. due to concentration of the bromide were observed.

Results

The Standard Potential.—The measurement of eleven cells containing silver–silver bromide electrodes prepared electrolytically gave a mean value of 0.06831 v. at 25°. The average error was 0.15 mv. The greatest deviation from the mean value amounted to 0.38 mv. for these cells. For the cells containing thermally prepared silver–silver bromide electrodes, the e. m. f. was 0.06839 v. at 25°. The average error and greatest individual deviation from the mean for these latter cells were 0.11 mv. and 0.18 mv., respectively. Table I summarizes the results obtained at 20, 25, and 30°.

TABLE I

THE VALUES OF THE E. M. F. OF CELL (2) AT VARIOUS TEMPERATURES

Temp., °C.	E. m. f., volts	Number of cells	Type of AgBr electrode
20	0.06630 ± 0.00014	5	Thermal
25	.06831 ± .00015	11	Electrolytic
25	.06839 ± .00011	9	Thermal
30	.07048 ± .00012	5	Thermal

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[1] Gerke, *J. Phys. Chem.*, **31**, 886 (1927).

[2] Ishikawa and Ueda, *J. Chem. Soc. Japan*, **51**, 59 (1930).

[3] (a) Jones and Baeckstrom, THIS JOURNAL, **56**, 1524 (1934); (b) Keston, *ibid.*, **57**, 1671 (1935); (c) Harned, Keston and Donelson, *ibid.*, **58**, 989 (1936); (d) Owen and Foering, *ibid.*, **58**, 1575 (1936); (e) Harned and Donelson, *ibid.*, **59**, 1280 (1937).

[4] Kolthoff and Larson, *ibid.*, **56**, 1881 (1934).

[5] Carmody, *ibid.*, **54**, 188 (1932).

The cells with thermal type silver–silver bromide electrodes gave better agreement among themselves than those containing electrolytically prepared electrodes. For this reason the calculations are based on the cells made with thermal silver bromide electrodes.

At 20, 25, and 30°, the standard potential of the mercury–mercurous bromide electrode has the values 0.14001, 0.13970, and 0.13921 v., respectively. These figures are obtained by adding the standard potentials of the silver–silver bromide electrode as reported at these temperatures by Harned and Donelson[3e] to the observed electromotive forces. These results may be expressed by the equation

$$E^0 = 0.13970 - 8.1 \times 10^{-5}(t - 25) - 3.6 \times 10^{-6}(t - 25)^2 \qquad (3)$$

Values calculated by means of this equation agree with the experimental ones to less than 0.1 mv.

The value 0.1397 v. at 25° obtained in this study may be compared with 0.1396 v. reported by Gerke[1] and 0.1395 v. which may be calculated from the measurements of Ishikawa and Ueda[2] if one uses the activity coefficient for 0.1 molal hydrobromic acid given by Harned, Keston and Donelson.[3c] Latimer[6] gives 0.1397 v., based also on the measurement of Ishikawa and Ueda. It seems likely that a somewhat different activity coefficient may have been used by Latimer in this computation. In addition, there is the value 0.1385 v. given by Gerke in the "I. C. T."[7] This value apparently is based on Gerke's own measurement.[1] Finally, there are the values of the author[8] from measurements of cell (1) over a wide concentration range at 25°. When these results are recalculated using the activity coefficients of Harned, Keston and Donelson, one obtains 0.1389 v. as the standard potential at 25°.

Since the cells measured in this study were not as sensitive to oxygen or to light as are cells containing mercurous bromide in an acid solution, and in view of the agreement between the result obtained in this study and the value calculated from thermal measurements (see Latimer[6]), it seems reasonable that the most reliable value for the standard potential is 0.1397 v.

The Entropy of Mercurous Bromide.—From the value of the temperature coefficient of the standard electrode potential, which may be computed from eq. (3) by differentiation, one may calculate the standard entropy change for the reaction $2Hg + 2H^+ + 2Br^- \rightarrow Hg_2Br_2 + H_2$, using the familiar equation

$$\Delta S^0_{298} = nF(\mathrm{d}E/\mathrm{d}T) = 2 \times 23070 \times 0.000081 = 3.7 \text{ e. u.}$$

ΔS^0_{298} is also given by

$$\Delta S^0_{298} = S^0_{H_2} + S^0_{Hg_2Br_2} - 2S^0_{Hg} - 2S^0_{H^+} - 2S^0_{Br^-}$$

Using the values for the entropy of the substances involved which are given by Latimer,[6] the value of $S^0_{Hg_2Br_2}$ is found to be 48.9 e. u. at 25°.

To be compared with this is the value 52.8 given by Latimer. This value is based on the measurement of Ishikawa and Ueda[2] and on the thermal data of Kelley.[9] The temperature coefficients obtained in this study agree very well with those of Ishikawa and Ueda. Since Kelley also used the entropies of liquid mercury and of liquid bromine in computing the entropy of mercurous bromide, it is well to compare the entropy calculated on the basis of the reaction $2Ag + Hg_2Br_2 \rightarrow 2AgBr + 2Hg$ which is the cell reaction of cell (2). The e. m. f. of cell (2) is given by $E = 0.06839 + 0.000418(t - 25)$ over the range 20–30°. From this, the value of the temperature coefficient is 0.000418, giving for the standard entropy change of the reaction $2Ag + Hg_2Br_2 \rightarrow 2AgBr + 2Hg$, 19.3 e. u. If this value is combined with the entropies of AgBr, Hg, and Ag given by Latimer, one finds that the standard entropy of mercurous bromide is 48.5 e. u. This is in excellent agreement with the value calculated using the values given by Latimer for the entropy of Br^-, H_2, and Hg. This result would seem to indicate that the discrepancy may be due to the value of the entropy of liquid bromine used by Kelley.

Summary

1. The standard potential of the mercury–mercurous bromide electrode was determined by measurements of the cell Ag / AgBr, KBr, Hg_2Br_2 / Hg. The standard potential of the mercury–mercurous bromide electrode is 0.1397 v. at 25°.

2. From temperature coefficient measurements the standard entropy of mercurous bromide was computed. The standard entropy of solid mercurous bromide computed was 48.7 cal. deg.$^{-1}$ mole^{-1}.

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[6] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

[7] "I. C. T.," Vol. VI, McGraw-Hill Book Co., New York, N. Y., 1930, p. 332.

[8] W. D. Larson, M. S. Thesis, Michigan State College, 1931.

[9] Kelley, U. S. Bureau of Mines Bull. 394 (1935).