The Electromotive Force of the Mercurous Bromide Electrode

BY WILLIAM R. CROWELL, RICHARD W. MERTES AND SIMPSON S. BURKE

The present paper deals with the effects of hydrogen, nitrogen, and air on the e. m. f. of the mercurous bromide electrode at 25° in 0.1002 m hydrobromic acid, and with measurements of the electrode e. m. f.'s in approximately 1, 2, and 3 normal hydrobromic acid solutions at 25° and 35°. The reference electrode consists of a hydrogen half cell using hydrobromic acid of the same concentration as that in the mercurous bromide compartment. Because of the differences in the values of the molal reduction e. m. f. of the mercurous bromide electrode reported by different investigators and because of the oxygen effect on the calomel electrode e. m. f. reported by Randall and Young[1] it was thought that there might also be a similar oxygen effect in the case of the mercurous bromide. While the mercurous bromide electrode is more sensitive to light than the calomel electrode, if properly prepared it is quite satisfactory in reproducibility and constancy. Although there is considerable formation of bromide complexes in solutions one normal or higher in hydrobromic acid, equilibria are easily obtained in solutions as high as three normal, and electrodes employing concentrations of acid from 0.1–3 N may be found to be convenient in certain cases where hydrobromic acid is used and when it is desired to eliminate unknown solution contact potentials.

Experimental

Reagents.—The hydrobromic acid was prepared from three times recrystallized potassium bromide dissolved in sulfuric acid solution. The hydrobromic acid was distilled from this solution, the portion going over between 110° and 127° again distilled and the constant boiling fraction retained.

The hydrogen was generated by electrolysis of a solution of sodium hydroxide. Tank nitrogen obtained from fractionation of liquid air was the source of the nitrogen. Both the hydrogen and the nitrogen were freed of oxygen by passage through chromous chloride solution. The mercury was passed through a dilute nitric acid tower and distilled *in vacuo*.

The mercurous bromide was prepared electrolytically by use of an apparatus which included a gas-stirred mercury anode and a platinum cathode with hydrobromic acid as the electrolyte. With this device the salt was prepared from and washed with acid which was of the same concentration as that used in the cell and which had been previ-

ously treated with the gas under investigation. The solution and mixture of mercury and mercurous bromide were then transferred to the mercurous bromide electrode chamber through which the gas being studied had been previously passed for twenty minutes to an hour. Finally the half cell was stoppered and rotated in a thermostat for several hours or until the solution was in equilibrium with the mercury and mercurous bromide. During these processes as well as during the cell measurements described later all light was excluded except that from a red light bulb which was used only when observations and experimental procedures made it necessary.

Cell Measurements.—A diagram of the complete cell is shown in Fig. 1. The mercurous bromide half cell was joined to the hydrogen electrode by means of a ground glass joint. The passages between the two half cells were flushed with hydrogen by use of the float which permitted the flow of gas before establishment of the liquid junction in the three-way stopcock. This junction was then established by sinking the float which was best accomplished by increasing somewhat the flow of hydrogen. Immediately before entering the hydrogen electrode chamber the hydrogen was bubbled through a solution of hydrobromic acid of the same concentration as that in the cell.
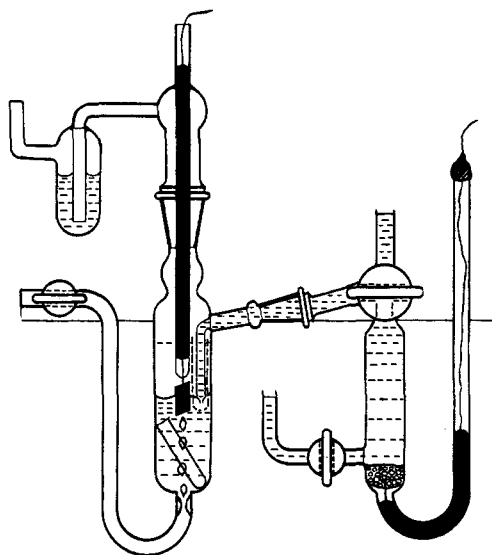

Fig. 1.—Schematic diagram of mercurous bromide–hydrogen cell.

Cell e. m. f.'s were measured by means of a Leeds and Northrup Type K potentiometer. The Weston cell used in adjusting the potentiometer current was checked against an Eppley cell which in turn had been standardized by the Bureau of Standards.

Results

Results are recorded in Tables I and II and are representative averages of several runs made over

(1) Randall and Young, THIS JOURNAL, **50**, 993 (1928).

TABLE I

EFFECT OF AIR ON THE ELECTROMOTIVE FORCE OF THE MERCUROUS BROMIDE ELECTRODE

| | Cell e. m. f. at 25° in 0.1002 m hydrobromic acid and 1 atm. of hydrogen. | | | Molal reduction e. m. f. at 25° | | |
	Hydrogen	Nitrogen	Air	Hydrogen	Nitrogen	Air
Gerke and Geddes[4]	0.2685			−0.1392		
Ishikawa and Ueda[5]			0.2688₃			−0.1395
Larson[6]						− .1397
Authors	.2684₁	0.26841	.26889	− .1391	−0.1391	− .1396

a period of more than two years, using independently prepared reagents. Results in 0.1 N hydrobromic acid were reproducible within 0.05 millivolt and in the higher acid concentrations within 0.1 millivolt. The e. m. f. readings remained constant for periods ranging from twenty-four to sixty hours. Equilibrium was usually attained in less than three hours.

Table I shows results obtained from measurements made in approximately 0.1 m hydrobromic acid using mercurous bromide which had been prepared in an atmosphere of hydrogen, nitrogen, and air. Data of other investigators are shown for comparison with those of the authors. To put all results on the same basis they are corrected to 0.1002 m hydrobromic acid and one atmosphere of hydrogen. The molal reduction e. m. f., E^0, was calculated by use of the value of Harned, Keston and Donelson[2] for the mean ion activity coefficient of hydrobromic acid, namely, 0.805, employing the expression

$$E^0 = E - 0.1183 \log C\gamma^{\pm}$$

where E is the e. m. f. of the cell

H₂ (1 atm.), HBr (0.1002 m), Hg₂Br₂, Hg
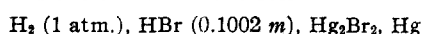
C the concentration of the hydrobromic acid in moles per 1000 g. of water, and $\gamma^{\pm}$ the mean ion activity coefficient of the hydrobromic acid. In the term "molal reduction e. m. f." the sign convention and activity units were the same as those used by Latimer.[3]

A study of the procedures of the different workers indicates that Ishikawa and Ueda, and Larson probably did not insure the complete removal of all air from the solutions used in the preparation of the mercurous bromide, while Gerke and Geddes displaced all air with hydrogen. For this reason, the results of Ishikawa and Ueda and of Larson are placed in the column with the air values and the results of Gerke and Geddes are recorded in the column with the hydrogen values.

(2) Harned, Keston and Donelson, THIS JOURNAL, **58**, 992 (1936).
(3) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 2 and 3.
(4) Gerke and Geddes, J. Phys. Chem., **31**, 886 (1927).
(5) Ishikawa and Ueda, J. Chem. Soc. Japan, **2**, 59–66 (1930).
(6) W. D. Larson, THIS JOURNAL, **62**, 765 (1940).

A comparison of the results in the table indicates that the electrode molal reduction e. m. f. has an accurately reproducible air free value of −0.1391 ± 0.0001 volt and an air value also accurately reproducible of −0.1396 ± 0.0001 volt. The 0.3 millivolt deviation of the results of Ishikawa and Ueda from those of Gerke and Geddes is probably due to this fact rather than because of greater experimental accuracy as claimed by the former.

Table II shows results of measurements of cell e. m. f.'s at 25 and 35° in approximately one, two, and three normal hydrobromic acid calculated on the basis of one atmosphere of hydrogen. In all these cases the mercurous bromide was prepared from and washed with hydrogen treated acid.

Since the main purpose of these measurements was to obtain data whereby the mercurous bromide electrode could be used as a reference electrode in cells requiring hydrobromic acid at these concentrations, the e. m. f. of the mercurous bromide half cell including a small solution contact e. m. f. was determined for each acid concentration. These e. m. f.'s at 25°, which are not to be confused with the molal reduction e. m. f.'s shown in Table I, are shown in Table II column 5 and were calculated by use of the cell data and hydrobromic acid mean ion activity coefficient values obtained from a curve plotted from data quoted by Harned,[7] employing the expression

$$E_{Hg, Hg_2Br_2 \text{(meas.)}} = -E_{cell} - 0.05913 \log C\gamma^{\pm}$$

The values in column 6 which we term "calculated" are those for the half cell which one would obtain by use of the molal reduction e. m. f., E^0, and the activity of the hydrobromic acid, employing the expression

$$E_{Hg, Hg_2Br_2 \text{(calcd.)}} = -0.1391 + 0.05913 \log C\gamma^{\pm}$$

TABLE II

E. M. F. OF MERCUROUS BROMIDE ELECTRODE AT HIGHER ACID CONCENTRATIONS

| Concn. of HBr | | Cell e. m. f. 1 atm. hydrogen | | Electrode e. m. f. at 25°C. | |
Molal	Normal	25°	35°	Measured	Calculated
1.029	1.000	0.14388	0.14310	−0.14130	−0.14168
2.117	2.002	.09058	.08867	− .11489	− .11480
3.246	2.987	.04845	.04524	− .09402	− .09353

(7) Harned, THIS JOURNAL, **57**, 1867 (1935).

The activity coefficient values taken from the curve were 0.879 for 1.000 N acid, 1.217 for 2.002 N acid, and 1,816 for 2.987 N acid.

From the values in columns 3 and 4 the following expressions were derived for the cell e. m. f., E_t, at any temperature t from the vicinity of 25 to that of 35°

In 1.000 N hydrobromic acid E_t =
$$0.14388 - 0.000078(t - 25)$$
In 2.002 N hydrobromic acid E_t =
$$0.09058 - 0.000191(t - 25)$$
In 2.897 N hydrobromic acid E_t =
$$0.04845 - 0.000321(t - 25)$$

In these acid solutions as the concentration increases there is a tendency for the mercurous bromide electrode reduction e. m. f. to become increasingly less than the calculated value because of the decrease in activity of the bromide ions due to the formation of bromide complexes. This decrease in reduction e. m. f. is more or less compensated for by an opposing liquid junction potential at the zone of contact of the hydrobromic acid solutions of the two electrodes. Such behavior probably is responsible for the fairly close agreement between the experimental and theoretical values.

Summary

Determinations of the molal reduction e. m. f. of the mercurous bromide electrode at 25° in 0.1002 m hydrobromic acid solutions show that the values obtained in solutions free from air are about 0.5 millivolt higher than those in which air is not completely removed. Both values are accurately reproducible and are −0.1391 volt in air free solutions and −0.1396 volt in solutions containing air, using hydrogen as the reference electrode. Results of e. m. f. measurements made at 25 and 35° in approximately one, two, and three normal hydrobromic acid are also shown.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Molar Dispersion and Refraction of Free and Bonded Ions[1]

BY NORMAN BAUER[1a] AND KASIMIR FAJANS

Introduction

This paper is a continuation of the series of "Refractometric Investigations,"[2] the main goal of which has been an understanding of the changes occurring in the electronic systems of ions, atoms and molecules when they combine with each other. Since the "valence" electrons are identical with those responsible for the optical behavior in the visible and near ultraviolet, it was justified to expect that optical properties would be especially suited to a study of this problem which is so closely connected with the nature of chemical forces. In fact, for substances having electronic systems of the noble gas type,[3] these refractometric investigations have revealed (see especially I, VII, XXX) the existence of two effects which prove to have great influence on the physical[4] and chemical behavior of substances:

(1) From a doctoral dissertation submitted by N. Bauer at the University of Michigan in June, 1941. The paper was presented in part at the 101st Meeting of the American Chemical Society, April 9, 1941.

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(2) This is paper number LV in the series. The following of the former papers will be referred to by the corresponding Roman numerals. I. K. Fajans and G. Joos, Z. Physik, 23, 1 (1924); VII. K. Fajans, Z. Elektrochem., 34, 502 (1928); IX. H. Kohner, Z. physik. Chem., B1, 427 (1928); X. W. Geffcken and H. Kohner, ibid., B1, 456 (1928); XI. W. Geffcken, ibid., B5, 81 (1929); XII. H. Kohner and M. L. Gressmann, ibid., A146, 137 (1930); XIV. K. Fajans and H. Kohner, ibid., A147, 241 (1930); XX. Z. Shibata and P. Hoelemann, ibid., B13, 347 (1931); XXI. K. Fajans, P. Hoelemann and Z. Shibata, ibid., B13, 353 (1931); XXIII. W. Geffcken, C. Beckmann and A. Kruis, ibid., B20, 398 (1933); XXV. P. Wulff, ibid., B21, 367 (1933); XXVI. A. Kruis and W. Geffcken, ibid., A166, 16 (1933); XXVII. P. Wulff and D. Schaller, Z. Krist., A87, 43 (1934); XXIX. W. Geffcken and A. Kruis, Z. physik. Chem., B23, 175 (1933); XXX. K. Fajans, ibid., B24, 103 (1934); XXXV. P. Hoelemann and H. Goldschmidt, ibid., B24, 199 (1934); XXXVIII. P. Wulff, ibid., B25, 177 (1934); XL. G. Damkoehler, ibid., B27, 130 (1934); XLI. P. Wulff and T. Anderson, Z. Physik, 94, 28 (1935); XLII. R. Luehdemann, Z. physik. Chem., B29, 133 (1935); XLIII. K. Fajans and R. Luehdemann, ibid., B29, 150 (1935); XLVII-LI. A. Kruis and W. Geffcken, ibid., B34, 1-95 (1936).

(3) It has been shown (see, e. g., K. Fajans, "Chemical Forces and Optical Properties of Substances," (Cornell Lectures), McGraw-Hill Book Co., Inc., New York, N. Y., 1931) on the basis of properties such as lattice distances, lattice energies, crystal structure, solubility, formation of complex compounds, color, etc., that deformation phenomena are more pronounced in substances formed from non-rare gas cations (Class II, e. g., AgCl) than in substances derived solely from noble gas ions (Class I, e. g., NaCl). However, the refractometric method has not yet given clear results for the former class of compounds (see XXX, p. 147-151); this seems to have the following reason. For most cases in Class I the refractometric effect caused by anion tightening is very much stronger than the opposite effect. In Class II, because of the deeper mutual interpenetration of the ions, and also because of the larger polarizability of non-rare gas cations, both effects are of the same order of magnitude and partly cancel each other.

(4) See, e. g., K. Fajans, Phys. Rev., 61, 543 (1942).