

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

## The Standard Potential of the Silver-Silver Bromide Electrode in Anhydrous Methanol at 25°

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The standard potential of the silver-silver chloride electrode with methyl alcohol as the solvent for the dissolved hydrogen chloride has been measured by Nonhebel and Hartley<sup>2</sup> and with ethyl alcohol as solvent by Woolcock and Hartley.<sup>3</sup> In methyl alcohol, the value of  $E_0$  expressed on a molarity basis was found to be  $-0.0205 \pm 0.0003$  volt, and, in ethyl alcohol,  $-0.0883 \pm 0.0003$  volt.

In testing the applicability of the Debye-Hückel limiting law

$$-\log f = Ac^{1/2}$$

to these solutions of hydrogen chloride, it was found that  $A$  had a value in methyl alcohol solutions of 1.48 in contrast to the theoretical value of 2.11. By applying the extended form of the Debye-Hückel equation

$$-\log f = \frac{Ac^{1/2}}{1 + \alpha c^{1/2}} - Bc$$

it was found that  $\alpha$ , which is proportional to the ionic diameter, had to be assigned an unreasonably high value. In ethyl alcohol solutions of hydrogen chloride, the value of  $A$  was found to be 3.4, which was much higher than the theoretical value of 2.82. The constant  $\alpha$  in the extended equation would have to be given a negative value in ethyl alcohol solutions. A negative value for the ionic diameter would have no physical significance.

The standard potential of the silver-silver bromide electrode in an aqueous solution of hydrogen bromide has been found by Keston<sup>4</sup> to be  $-0.0711$  volt at 25°. In solutions from 0.0001 to 0.005 molar, good agreement with the Debye-Hückel limiting law was obtained. From the value of  $\alpha$ , the distance of closest approach was found by Keston to be 4.52 Å. By a later investigation by Harned, Keston and Donelson,<sup>5</sup> the mean value of  $\alpha$  over a wide range of concentration was found to correspond to a distance of closest approach of 4.40 Å.

(1) This paper is constructed from a dissertation presented by Arthur Wayne Campbell to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Nonhebel and Hartley, *Phil. Mag.*, [6] **50**, 734 (1925).

(3) Woolcock and Hartley, *ibid.*, [7] **5**, 1133 (1928).

(4) Keston, *THIS JOURNAL*, **57**, 1671 (1935).

(5) Harned, Keston and Donelson, *THIS JOURNAL*, **58**, 989 (1936).

The purpose of the investigation reported in this paper was to measure the value of the standard potential,  $E_0$ , at 25° for the cell



and to test the applicability of the Debye-Hückel limiting law to dilute solutions of hydrogen bromide in methanol.

**Materials.**—The alcohol was a pure grade of anhydrous synthetic methanol. It was freed from reducing impurities by a method adapted from that of Bates, Mullaly and Hartley.<sup>6</sup> The alcohol to be purified was divided into two equal portions. In one portion was dissolved 10 g. of sodium hydroxide for each liter of alcohol. In the other portion was dissolved 15 g. of iodine for each liter of the alcohol. Then the two portions were mixed and the mixture was allowed to stand for at least twenty-four hours. After refluxing for six hours, the alcohol was distilled off slowly. The first 10% and the last 15% of the distillate were discarded. The methanol purified in this manner gave a negative test for reducing agents when tested by the method of Hartley and Raikes.<sup>7</sup> The water was removed by the method of Lund and Bjerrum.<sup>8</sup> Finally, volatile bases were removed by refluxing and distilling the alcohol in the presence of a few grams of sulfanilic acid.

The silver bromide electrodes were prepared by the thermal method of Keston.<sup>9</sup> Silver oxide used in making these electrodes was prepared by adding a 0.1 *N* solution of sodium hydroxide to a 0.1 *N* solution of silver nitrate. The resulting precipitate was washed twenty times by decantation with distilled water and then dried at 95°. After drying, the precipitate was ground in an agate mortar and stored in a brown glass-stoppered bottle. The silver bromate was c. p. grade purchased from E. H. Sargent and Co. The hydrogen electrodes were platinized and treated according to the directions of Popoff, Kunz and Snow.<sup>10</sup>

The hydrogen used was commercial tank hydrogen and it was purified by passing over potassium hydroxide, hot copper gauze heated to 500–600° and, finally, over anhydrous calcium sulfate.

Dry hydrogen bromide was prepared by the action of bromine on tetrahydronaphthalene.<sup>11</sup> The bromine used was a commercial grade and it was purified by shaking with a few milliliters of concentrated aqueous sodium hydroxide solution and distilling. Water was removed by distilling the bromine from concentrated sulfuric acid. The tetrahydronaphthalene was a practical grade purchased from the Eastman Kodak Co. It was dried with metallic

(6) Bates, Mullaly and Hartley, *J. Chem. Soc.*, **123**, 401 (1923).

(7) Hartley and Raikes, *ibid.*, **127**, 524 (1927).

(8) Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

(9) Keston, *THIS JOURNAL*, **57**, 1673 (1935).

(10) Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

(11) See Booth, "Inorganic Syntheses," McGraw-Hill Book Co., New York, N. Y., 1939, Vol. I, p. 151.

sodium and distilled. Stock solutions of hydrogen bromide in anhydrous methanol were standardized gravimetrically by the precipitation and weighing of silver bromide. Solutions of lower concentration were prepared by weight dilution of this stock solution.

**Procedure.**—The measurements of cell potentials were made with a Leeds and Northrup type K-2 potentiometer, a type R galvanometer and an Eppley standard cell which was certified by the manufacturer and checked frequently with another certified cell.

The cell consisted of a Pyrex tube 4.5 cm. in outside diameter and 19 cm. in length fitted with a hydrogen inlet sealed in at the bottom. A molded paraffin or beeswax stopper served to close the cell and to support the hydrogen and silver bromide electrodes. In taking a measurement, the silver bromide electrodes were first prepared and sealed into the wax stopper and then placed for fifteen minutes in a solution of hydrogen bromide in methanol of the same concentration as that to be used in the cell. At the end of this period, the cell and a saturator were filled with solution and the stopper containing the silver bromide electrodes was waxed in place quickly. The assembly was then placed in a constant temperature bath (transformer oil) maintained at  $25 \pm 0.01^\circ$ . Hydrogen was passed and the electrodes were allowed to come to equilibrium. Then freshly prepared hydrogen electrodes were introduced into the cell through the wax stopper. For each experiment, four silver bromide and two or more hydrogen electrodes were used in the same cell solution. The silver bromide electrodes came to equilibrium rapidly, were constant for as long as twenty-four hours and gave a maximum deviation from the mean of 0.07 mv. The hydrogen electrodes were very reproducible and came to equilibrium within fifteen minutes, but were soon poisoned in the methanol solution. This is in agreement with the experience of Nonhebel and Hartley.<sup>2</sup> A few experiments were carried out with bright iridium electrodes prepared by the method of Lorch.<sup>12</sup> These electrodes proved to be less satisfactory than the platinum electrodes.

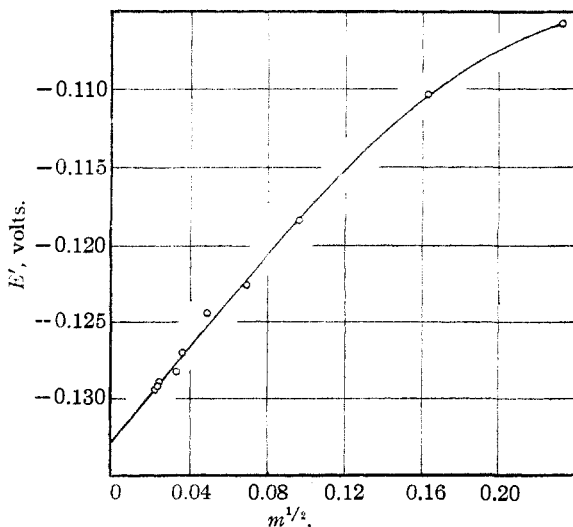


Fig. 1.—Plot of  $E' = E + 0.1183 \log m$  against  $m^{1/2}$ .

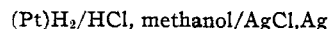
(12) Lorch, *Ind. Eng. Chem., Anal. Ed.*, **6**, 164 (1934).

**Data and Results.**—The data obtained from the measurements of the potential of the cell are summarized in Table I, where  $m$  is the molality of the hydrogen bromide solution,  $E$  the observed electromotive force of the cell and  $E'$  is defined by the equation

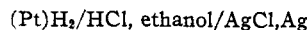
$$E' = E + 0.1183 \log m = E_0 - 0.1183 \log \gamma$$

The values of the observed potential are corrected for the barometric pressure and the vapor pressure of methanol, which was calculated to be 122.8 mm. at  $25^\circ$ .<sup>13</sup> Since the deviations between the potentials of the various electrode combinations were slight, in the order of 0.07–0.08 mv., the values of  $E$  recorded are averages of the possible combinations.

By plotting the values of the observed potential,  $E$ , against  $\log m$ , it was found by interpolation that the limiting value of the slope of the curve was  $-0.115$  as compared with the theoretical value of  $-0.1183$ . The deviation in these values may be attributed to the incomplete dissociation of hydrogen bromide in the methanol solutions. In Fig. 1 the values of  $m^{1/2}$  are plotted against the values of  $E'$ . By extrapolation to  $m^{1/2} = 0$ , the standard potential of the silver bromide electrode on the molality basis was found to have the value  $-0.1328$  volt. A plot of  $E' = E + 0.1183 \log c$  against  $c^{1/2}$  gave a value of  $-0.1452$  volt, which converted to the molality basis gives  $-0.1329$  volt. The value of the standard potential also was determined by plotting the data in accordance with the method of Hitchcock<sup>14</sup> in which values of the term  $E' - (2ARTm^{1/2}/F)$  are plotted against  $(E' - E_0)m^{1/2}$ . The relationship was found to be linear only in the very dilute range. However, a good extrapolation to  $m = 0$  was possible to give  $-0.1328$  volt for the  $E_0$  value. Considering the good agreement among the three different extrapolations,  $-0.1328$  volt is considered the best value of the standard potential of the silver-silver bromide electrode in methyl alcohol at  $25^\circ$ . The error in extrapolation is probably less than 0.5 mv. The difficulty of obtaining a better degree of precision is realized when the effect of water on the potential of the cell is considered. Hartley and his co-workers determined the effect of water on the cells



and



(13) "Int. Crit. Tables," Vol. III, p. 216.

(14) Hitchcock, *THIS JOURNAL*, **50**, 2076 (1928).

In each case it was found that the addition of 0.01% by weight of water to a 0.01 *m* solution of hydrochloric acid caused an increase in the cell potential of about one millivolt. The effect of moisture was found to be greater the more dilute the solution. A similar effect of moisture was observed in this work on the potential of the silver bromide electrode.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL (Pt)H<sub>2</sub>/HBr, METHANOL/AgBr, Ag OVER THE CONCENTRATION RANGE 0.000474 *m* TO 0.0543 *m*

<i>m</i>	<i>E</i>	<i>E'</i>
0.05430	0.04393	-0.10574
.02650	.07621	- .11032
.00936	.12174	- .11826
.00486	.15107	- .12261
.00232	.18738	- .12428
.001274	.21553	- .12689
.001064	.22350	- .12822
.000573	.25456	- .12894
.000527	.25860	- .12921
.000474	.26385	- .12942

Considering the density of methyl alcohol, the standard potential of the cell expressed on the molarity basis is calculated as follows. The equations for *E*<sub>0</sub> on the two concentration systems are

$$E_{0m} = E + 0.1183 \log m + 0.1183 \log \gamma$$

and

$$E_{0c} = E + 0.1183 \log c + 0.1183 \log f$$

From the values of the densities of solutions of hydrogen bromide in methanol given by Goldschmidt and Aarflat,<sup>15</sup> the molality, *m*, and the molarity, *c*, may be related by the density of pure methanol, *D*, over the concentration range studied by the expression

$$c = Dm$$

(15) Goldschmidt and Aarflat, *Z. physik. Chem.*, **122**, 371 (1926).

Substituting in the expression for *E*<sub>0c</sub>

$$E_{0c} = E + 0.1183 \log m + 0.1183 \log D + 0.1183 \log f$$

Extrapolation to *m* = 0 and *f* = 1 yields

$$E_{0c} = E_{0m} + 0.1183 \log D$$

The value of *D* for pure methanol is 0.78662<sup>16</sup> and the value of the term 0.1183 log *D* is -0.01233. The standard potential of the silver bromide electrode on the molarity basis calculated in this manner is -0.1451 volt.

The slope of the curve in Fig. 1 is given by the expression

$$\frac{d E'}{d m^{1/2}} = -0.1183 \frac{d \log \gamma}{d m^{1/2}}$$

Substituting *c/D* for *m*

$$\frac{d E'}{d m^{1/2}} = 0.1183 D^{1/2} A$$

The value of the constant *A* in the Debye-Hückel limiting law was found by interpolation from the curve to be 1.42 for hydrobromic acid in methanol, as compared with the theoretical value of 2.11.

### Summary

The potential of the cell (Pt) H<sub>2</sub>/HBr, methanol/AgBr, Ag was measured at 25° over the concentration range, 0.000474*m* to 0.0543*m*.

The standard potential of the silver bromide electrode in methanol solution of hydrogen bromide expressed on the molality basis was found to be -0.1328 volt, and on the molarity basis, -0.1451 volt.

Deviations from the Debye-Hückel limiting law for the solutions studied are indicated by a value of 1.42 for the constant, *A*, as compared to the theoretical value of 2.11.

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(16) "Int. Crit. Tables," Vol. III, p. 27.