[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

A Silver–Silver Bromide Electrode Suitable for Measurements in Very Dilute Solutions[1]

BY ALBERT S. KESTON

Carmody[2] has discussed the importance of and the difficulties involved in measurement of electromotive forces in dilute aqueous solutions and has measured the cell

$\mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm.}) \mid \mathrm{HCl}(m) \mid \mathrm{AgCl} \mid \mathrm{Ag}$[3]

at concentrations below 0.01 molar in quartz cells. In the following paper, a novel type of silver–silver halide electrode having many advantageous properties has been applied to the study of electromotive forces in dilute solutions. Measurements were made in both quartz and in Pyrex cells, of the cell

$$\mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm.}) \mid \mathrm{HBr}(m) \mid \mathrm{AgBr} \mid \mathrm{Ag}$$

at concentrations between 0.0001 and 0.005 *M*. The silver–silver bromide electrode was prepared by heating an intimate mixture of silver oxide and silver bromate to 650°. Electrodes prepared in this manner possess the following advantages over the type prepared by electrolyzing silver in a halide solution.[4] (1) They may be prepared easily and quickly. (2) Silver halides prepared in a dry way are not as sensitive to light as those prepared in the wet way.[5] (3) The solubility of fused halides is much lower than the precipitated forms.[6] (4) Electrodes prepared by fusion of the halide are well calculated to be reproducible in dilute solutions since there is no chance for electrolytes to be either occluded in them or adsorbed on them.

Electrodes and Materials

1. The silver–silver bromide electrode was prepared in the following manner. A platinum wire was sealed into a glass tube and a small spiral formed on the end of the metal. A mixture containing about 90% of silver oxide and about 10% of silver bromate was ground in an agate mortar. The intimate mixture was made into a paste with water and some of the paste transferred to the platinum spiral. The electrode was then placed in an electric furnace which had previously been heated to about 650° and was kept there for about seven minutes. The electrodes were removed from the furnace and allowed to cool. For this work on dilute solutions the mass of the silver–silver halide mixture was small (about 20–50 mg.). These electrodes were very reproducible.

Dozens of these electrodes were prepared under widely different conditions. The range of the percentage of the silver bromate was varied between 8 and 12%. The percentage of bromide was kept low because it was found that electrodes in which there was a large fraction of silver bromide did not perform satisfactorily. The time of heating was varied between four and fifteen minutes. The temperature was varied between 575 and 750°. Electrodes prepared within this range had the same potential in a given solution of hydrobromic acid.

Although some electrodes of the same type were prepared using silver bromide in place of the silver bromate, and which gave the same potential in a given solution of hydrobromic acid, the bromate was used in the preparation because it was easy to prepare pure by crystallization from water. Moreover, the oxygen liberated by its thermal decomposition tends to increase the porosity of the electrode. The electrodes used for the measurements in the dilute solutions were all prepared under the same conditions as described in the first paragraph of this section.

2. The hydrogen electrodes were of the platinum foil type and were coated with platinum black in the usual way.

3. Hydrogen used for the hydrogen electrode was purified by passing it, from the tank, over red hot copper.

4. The hydrobromic acid was Baker "C. P. Analyzed" grade which was distilled with a little tin from an all-glass still. An approximately 0.02 molal stock solution was prepared by diluting the distillate. This was standardized gravimetrically. All weights were corrected to vacuum.

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(1) The material in this communication was taken from part of a Dissertation presented by Albert S. Keston to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

(2) Carmody, THIS JOURNAL, **51**, 2905 (1929).

(3) Carmody, *ibid.*, **54**, 188 (1932).

(4) Jahn, *Z. physik. Chem.*, **33**, 545 (1900); Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917); Carmody, *ibid.*, **51**, 2905 (1929); Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922).

(5) Roscoe and Schorlemmer, "Treatise on Chemistry," 4th Ed., Vol. II, p. 466.

(6) Stas, *Compt. rend.*, **73**, 998 (1871).

5. Conductivity water with specific conductance below 1 × 10^{-6} was used.

6. Silver oxide was prepared by adding dilute sodium hydroxide to an excess of silver nitrate solution. The precipitate was washed about 25 times by decantation, then filtered off and dried in a vacuum desiccator.

7. Silver bromate was prepared in a similar manner, using potassium bromate as the precipitating agent. After being thoroughly washed with water, the silver bromate was crystallized from hot water.

Description of Cells and Experimental Results

The measurements were made in both quartz and Pyrex cells. Each cell consisted of a 500-cc. flask at the bottom of which a hydrogen inlet was sealed. The outlet tube for the hydrogen was sealed in the neck of the flask. The incoming hydrogen was saturated with water vapor. The hydrogen and silver–silver bromide electrodes were held by a rubber stopper at the mouth of the flask. Since the solutions were dilute and not highly conducting the electrodes were fixed about 1 cm. apart.

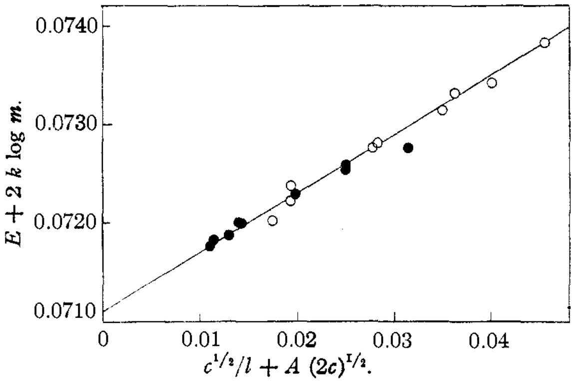

Fig. 1.—Plot of Debye–Hückel function: ●, quartz cells; ○, glass cells.

The cells were cleaned, washed and steamed. Conductivity water directly from a Kraus still was collected in the cell. The requisite quantity of an accurately analyzed 0.02 *M* stock solution of hydrobromic acid was introduced from a weight buret. The cell was stoppered and then the solution was mixed and saturated by the passage of a rapid stream of hydrogen. This stopper was removed and replaced by the stopper holding the electrodes which had previously been washed with a part of the solution in the cell. The cell solution was never allowed to make contact with the rubber stopper or the soft glass tubes which held the electrodes.

The cells were allowed to equilibrate for five to six hours and then readings were taken. After equilibrium had been obtained the electromotive forces remained constant to within 0.02 mv. for a long period of time. The reproducibility is estimated to be of the order of ±0.05 mv. A calibrated Leeds and Northrup Type K potentiometer was employed. The thermostatic control was ±0.01°. Table I contains the experimental results.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS H_2 | HBr(*m*) | AgBr | Ag AT 25°

I Quartz cells		II Pyrex cells	
m	*E*	*m*	*E*
0.0001262	0.53300	0.0003198	0.48469
.0001340	.53001	.0003968	.47561
.0001775	.51616	.0004042	.47381
.0002066	.50792	.0008444	.43636
.0002163	.50558	.0008680	.43499
.0004172	.47211	.0013554	.41243
.0006700	.44804	.001464	.40864
.0006708	.44799	.001850	.39667
.0010994	.42280	.002396	.38383
		.003719	.36173

Discussion

The accuracy of the results may be illustrated by employing the law of Debye and Hückel in the form

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} \qquad (1)$$

If this be substituted in the equation for the electromotive force of the cell[7]

$$E + 2\,k \log m = E_0 + \frac{2ku\sqrt{d_0 m}}{1 + A\sqrt{2d_0 m}} \qquad (2)$$

The parameter *A* was computed from measurements at higher concentrations which will be published in a subsequent communication. *A* was found to be 1.05, which corresponds to a "mean distance of approach" of 4.52 Å. In Fig. 1 the left side of this equation is plotted against $m^{1/2}/l + A(2c)^{1/2}$. The solid line possesses the theoretical slope. The dots represent measurements with quartz cells and the circles results obtained with the Pyrex cells. The experimental results are in excellent agreement with the theoretical. This result is particularly gratifying since it has been obtained at such high dilution. The value of the molal electrode potential of the

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[7] The symbols and constants used were those given by Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933) (*e. g.*, u = 0.506).

silver–silver bromide electrode is found to be 0.07111.

The author extends his thanks to Professor Herbert S. Harned for advice and suggestions during the course of this work.

Summary

1. A type of silver–silver bromide electrode prepared in a novel manner has been described.

2. Measurements of the cell

$$H_2 \text{ (1 atm.)} \mid HBr(m) \mid AgBr \mid Ag$$

have been made at concentrations from 0.0001 to 0.02 *M* in quartz and Pyrex glass cells of very simple design.

3. Agreement with the limiting law of Debye and Hückel has been obtained.

4. The value of the molal electrode potential of the silver–silver bromide electrode has been found to be 0.0711 volt.

NEW HAVEN, CONN. RECEIVED JUNE 28, 1935

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Absorption Spectra of Free Radicals

BY LEIGH C. ANDERSON

The cause of the color of solutions of free radicals has been the subject of considerable discussion.[1] Most investigators agree that the color is associated with the free radical, for example, triphenylmethyl, rather than the dimolecular form, hexaphenylethane. For a number of years after the discovery of free radicals, many writers thought that the presence of trivalent carbon in the triarylmethyl radicals produced by dissociation of the hexaphenylethane was sufficient reason alone for the color of such solutions. However, after Gomberg[2] demonstrated the reactivity of para substituted halogens in triarylmethyl halides, the question of quinonoidation of the free radicals was given more consideration. In 1923, Gomberg and Blicke[3] published some studies on the chemical reactions of para halogenated triarylmethyls and presented data which also indicated in a conclusive manner the existence of a quinonoid modification of the free radical. Visual comparison of the color of the solutions, as well as qualitative absorption spectra, have indicated the similarity of light absorption of sulfur dioxide solutions of a triarylmethyl radical to the light absorption of corresponding solutions of the triarylmethyl halides and sulfate.[4] The qualitative absorption spectrum of the negative triphenylmethyl ion was reported by Hein[5] and the spectrum was shown to be quite different from that of the corresponding free radical or that of the cation. In this paper we are presenting conclusions based on data obtained from quantitative absorption spectra of free radical solutions.

Previous investigators[6] have shown that the triphenylmethyl halides are electrolytes when dissolved in sulfur dioxide. The quantitative absorption spectrum curve for a solution of triphenylbromomethane (Curve 2, Fig. 1) in sulfur dioxide is, therefore, the curve for the triphenylmethyl cation. It is very similar to the curve for the triphenylmethyl cation in solution in sulfuric acid, perchloric acid or dimethyl sulfate.[7] In sulfur dioxide the frequencies of maximum absorption for the triphenylmethyl cation are shifted toward the longer wave lengths but otherwise the shape and height of the curves are almost identical with those in the above-named solvents. In the publication just referred to, we presented evidence, based on quantitative absorption spectra data, that the triphenylmethyl cation exists in a quinonoid modification in solvents like sulfuric acid, and the present data indicate that this cation exists in a quinonoid modification in sulfur dioxide as well.

The curve for a solution of the free radical, triphenylmethyl, in ether (Curve 1) has a group of narrow bands in the visible region near the ultraviolet. When this curve is compared with the

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[1] A more complete discussion of the early work on this subject than is included in this paper is presented in Schmidlin, "Das Triphenylmethyl," Verlag von F. Enke, Stuttgart, 1914; and Walden, "Chemie der freien Radikale," Verlag von S. Hirzel, Leipzig, 1924.

[2] Gomberg, *Ber.*, **40**, 1851 (1907).

[3] Gomberg and Blicke, THIS JOURNAL, **45**, 1765 (1923).

[4] Meyer and Wieland, *Ber.*, **44**, 2557 (1911); Schmidlin and Garcia-Banùs, *ibid.*, **45**, 3187 (1912); Tschitschibabin, *J. prakt. Chem.*, **88**, 511 (1913).

[5] See Hantzsch, *Ber.*, **54**, 2619 (1921).

[6] Walden, *ibid.*, **35**, 2018 (1902); Gomberg, *ibid.*, **35**, 2403 (1902).

[7] Anderson, THIS JOURNAL, **52**, 4567 (1930).