

until either the ether or ammonia has been displaced by the water. That the ammine reacts more slowly than the etherate is explainable by the fact that in the ammine both the gallium and nitrogen have completely shared octets, while in the etherate only the gallium has a completely shared octet, that of oxygen still having an unshared lone pair.

Summary

This article deals with the preparation and the properties of gallium triethyl monoetherate, gallium triethyl and gallium triethyl ammine. The behavior of the compounds upon hydrolysis is discussed in some detail, and evidence as to the existence of gallium diethyl hydroxide, a base, is presented. The latter substance is now being further investigated in the Cornell Laboratory.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF REED COLLEGE]

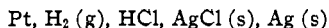
STUDIES IN THE MEASUREMENT OF ELECTROMOTIVE FORCE IN DILUTE AQUEOUS SOLUTIONS. II. THE SILVER CHLORIDE ELECTRODE

BY WALTER R. CARMODY

RECEIVED SEPTEMBER 21, 1931

PUBLISHED JANUARY 7, 1932

In a former paper¹ the writer discussed the importance of and difficulties involved in the measurement of electromotive force in dilute aqueous solutions and introduced a type of cell and a method designed to eliminate the relatively large variations in electromotive force encountered in such measurements. In the following paper this method has been applied to the measurement of the potential of the silver chloride electrode by means of the cell



with such modifications of cell design and method as the problem necessitated.

Three investigators² have made measurements on this cell which permit extrapolation to be made to infinite dilution. Their results, although checking very well in concentrated solutions, diverge as the dilution is increased until at zero concentration they differ by as much as 1.0 mv. In each case glass has been used as material for cell and containers. Kraus and Parker³ have shown that for strong acids, concentrations below 0.005 molar cannot be kept in glass containers without change, the relative effect of which increases with the dilution of the acid. Randall and

¹ Carmody, *THIS JOURNAL*, 51, 2905 (1929).

² Noyes and Ellis, *ibid.*, 39, 2532 (1917); Linhart, *ibid.*, 41, 1175 (1919); Nonhebel, *Phil. Mag.*, [7] 2, 1085 (1926).

³ Kraus and Parker, *THIS JOURNAL*, 44, 2429 (1922).

Young⁴ have pointed out the necessity of using quartz apparatus in determining the potential of the silver chloride electrode. They account for the discrepancy between results of electromotive force and freezing-point measurements by the action of the dilute acid solutions on the glass container which would cause a decrease in acid concentration and a corresponding increase in potential. Considering the electromotive force results to be high, they have estimated, from a summary of "freezing-point measurements of hydrochloric acid and the relation of these measurements to those of other salts," the value of the electrode potential to be $E_{298}^{\circ} = -0.2221$ volt. Results obtained from measurements made in quartz apparatus on eight concentrations of hydrochloric acid below 0.01 molar yield, upon extrapolation to infinite dilution, the value, -0.2223 volt.

I. Electrodes and Materials

1. The silver chloride electrodes were prepared and used, with slight modification, according to the directions given by Carmody.⁵ Platinum gauze electrodes 1.27 cm. square were electrolyzed as cathodes from a solution of potassium silver cyanide for a period of thirty hours with a current of two milliamperes per electrode. After being washed in distilled water for three weeks they were electrolyzed in the dark as anodes in dilute hydrochloric acid for one hour at a current of three milliamperes per electrode. This method usually produced pure white electrodes reproducible to 0.01 mv. On several occasions, for reasons undetermined, a light brown electrode was produced which gave a potential 0.2–0.3 mv. higher than that of the white electrodes. The brown electrodes corresponding to those produced and discarded by other investigators, were discarded in favor of the white electrodes, which have been found to be constant if kept in water or dilute hydrochloric acid from which oxygen has been removed. In acid solutions containing oxygen their potential lowers quite rapidly.

2. The hydrogen electrodes were prepared according to directions given by Popoff, Kunz and Snow.⁶

3. The hydrochloric acid solutions were prepared quantitatively from constant boiling acid distilled according to directions given by Foulk and Hollingsworth.⁷ The concentrations were checked by analysis.

4. Conductivity water, with specific conductance below 1.0×10^{-6} mhos, was used in preparing solutions. Water and all acid solutions below 0.05 molar were stored and used in quartz apparatus.

5. Nitrogen for stirring cells was purified by being passed through acid permanganate, alkaline pyrogallol, water and finally through a solution of the same concentration as used in the cell.

6. Hydrogen used in the hydrogen electrode was prepared in a U-tube generator similar to that used by Lewis, Brighton and Sebastian.⁸ As an added precaution an auxiliary cathode was used in the anode compartment as suggested by Niese.⁹ The

⁴ Randall and Young, *THIS JOURNAL*, 50, 989 (1928).

⁵ Carmody, *ibid.*, 51, 2901 (1929).

⁶ Popoff, Kunz and Snow, *J. Phys. Chem.*, 32, 1056 (1928).

⁷ Foulk and Hollingsworth, *THIS JOURNAL*, 45, 1220 (1923).

⁸ Lewis, Brighton and Sebastian, *ibid.*, 39, 2245 (1917).

⁹ Niese, *Physik. Z.*, 24, 12 (1923).

auxiliary cathode serves to prevent diffusion of oxygen into the hydrogen supply and eliminates the necessity of using sand for that purpose.

II. Apparatus and Method

The cell (Fig. 1) was of quartz except for the central three-way stopcock, reservoir stoppers and cell electrodes, which were of Pyrex glass. Connections to the several parts of the cell were ground joints requiring no lubrication. During the interval necessary for the cell to reach equilibrium the solution came in contact at times with the end of the Pyrex tube to which the electrodes were sealed. Any change of concentration due to this slight contact was considered to be negligible. The cell was designed with small electrode compartments (25 cc.) with large connecting reservoirs (500 cc.). The electrodes were placed in separate compartments to permit the study of the silver chloride electrode independently of the hydrogen electrode. The method of measurement was as follows.

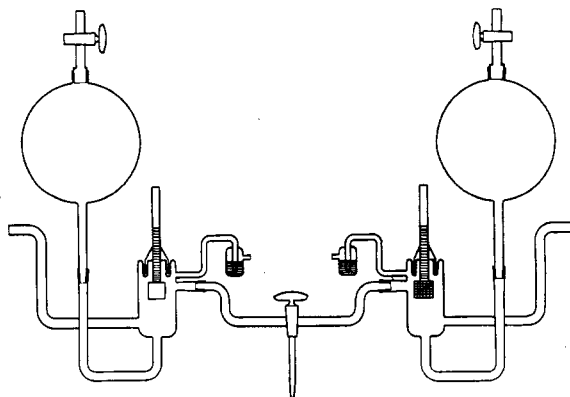


Fig. 1.—Quartz cell.

The cell, with electrodes in position, and reservoir are filled with the oxygen-free solution and seasoned by standing for several hours, when the solution is drawn off and the reservoirs filled with a new supply. The electrode compartments are then washed at intervals with this fresh solution. After final washing and filling the hydrogen is bubbled through the hydrogen electrode compartment while the silver chloride compartment is stirred with nitrogen. After the cell has reached equilibrium a second measurement may be made readily by filling the electrode compartments with a new supply of solution from the reservoir and obtaining a new equilibrium.

III. Experimental

To test the constancy of the potential of the silver chloride electrode in water and in hydrochloric acid three groups of electrodes were allowed to stand for two weeks: one group in water, one group in dilute hydrochloric acid freed from oxygen and one group in dilute hydrochloric acid in contact with air. Checking against a group of freshly prepared electrodes showed no change in the electrodes which had stood in water and in hydrochloric acid freed from oxygen, while those electrodes which had stood in hydrochloric acid in contact with air were 0.6 to 0.7 mv. positive. Throughout the experiment electrodes stored in water and used with

oxygen-free hydrochloric acid solution suffered no apparent change in appearance or potential.

With the hydrogen electrode at equilibrium a study was made of the time and conditions necessary to establish and maintain stable equilibrium in the silver chloride compartment. With pure hydrochloric acid in the compartment a period of about four hours was necessary to establish equilibrium, during which time the potential rose approximately 6.0 mv. This equilibrium, however, was quite unstable, being easily disturbed by any motion between electrode and surrounding solution, which would cause the potential to lower to nearly its original value. With hydrochloric acid that had been previously saturated with silver chloride, a somewhat shorter time was found necessary for equilibrium to be established. This equilibrium was relatively stable and independent of small motions between electrode and solution. In the measurements described below the hydrochloric acid was saturated with silver chloride before being introduced into the silver chloride compartment, and stable equilibrium was obtained in each measurement recorded.

Measurements were made first at concentrations above 0.01 molar to compare the silver chloride electrodes with those used by other investigators; then at concentrations from 0.01 molar to 0.0003 molar, which limit was determined by the apparatus available. Results are shown in Table I. The molalities are given in column 1, the two most dilute of which are corrected for the solubility of the silver chloride in hydrochloric acid. Calculations were based on the solubility measurements of Forbes and Cole.¹⁰

TABLE I
ELECTROMOTIVE FORCE AT 25° OF THE CELL: Pt, H₂(g), HCl, AgCl(s), Ag(s)

Molality, <i>m</i>	<i>E</i> measured	<i>E</i> ^o <i>E</i> + 0.1183 log <i>m</i>
0.1165	0.3449	-0.2344
.1083	.3483	- .2341
.1056	.3496	- .2341
.09425	.3552	- .2338
.04572	.3901	- .2316
.009582	.4660	- .2272
.004965	.4987	- .2261
.002799	.5271	- .2251
.001910	.5462	- .2245
.001129	.5727	- .2241
.0007280	.5950	- .2238
.0005518	.6090	- .2236
.0003288	.6353	- .2233

For purposes of extrapolation we may use the equation of Lewis and Randall, $E^{\circ} = E^{\circ'} + 0.1183 \log \gamma$ where $E^{\circ'} = E + 0.1183 \log m$. The

¹⁰ Forbes and Cole, THIS JOURNAL, 43, 2492 (1921).

third column of Table I contains the values of $E^{\circ'}$ calculated from experimental results. In Fig. 2 these are plotted against the square root of the molality. For comparison the numerous points of other investigators are indicated. Extrapolation to zero concentration of the new experimental values yields the result: Ag (s), AgCl (s), Cl⁻: $E_{298}^{\circ} = -0.2223$ volt. This value corresponds closely to that estimated by Lewis and Randall.⁴

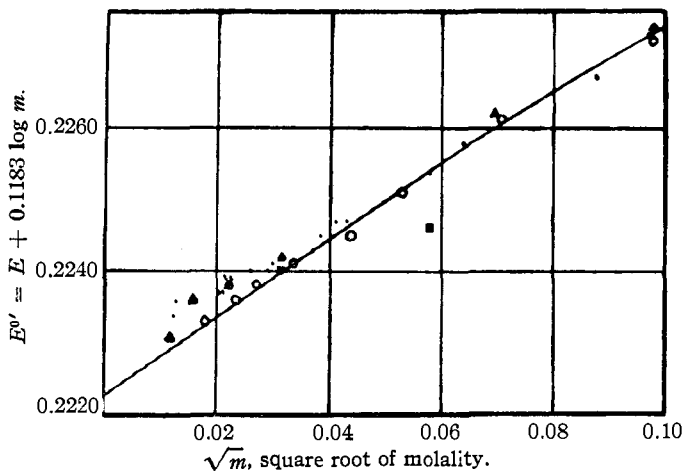


Fig. 2.—Curve showing \sqrt{m} plotted against $E^{\circ'}$ for the cell, Pt, H₂ (g), HCl, AgCl (s), Ag (s), at 25°: Δ , Linhart; \square , Noyes and Ellis; \bullet , Nonhebel; \circ , Carmody.

The writer is pleased to acknowledge his indebtedness to Dr. H. V. Tartar and to the Chemistry Department of the University of Washington for apparatus and materials and for the privileges of the laboratory in which the experimental work described in this paper was completed.

IV. Summary

1. The electromotive force of the cell, Pt, H₂ (g), HCl, AgCl (s), Ag (s), has been measured with quartz apparatus at eight concentrations below 0.01 molar.

2. From these measurements a new value for the potential of the silver chloride electrode has been obtained: $E_{298}^{\circ} = -0.2223$ v.

PORTLAND, OREGON