cal. From these data the molal heat of transition of cubic into orthorhombic oxide is $\Delta H_{830} = +3240$ cal., and the molal heats of fusion are 26,250 cal. for the orthorhombic and 29,490 cal. for the cubic. For convenience of reference, vapor pressures as read from the chart of Fig. 2 are shown tabularly in Table III, which shows the vapor and sublimation pressures of the stable modification at 25°-temperature intervals over the determined range.

Summary

1. The vapor pressures of cubic and orthorhombic solid antimony trioxide have been measured between the temperatures 470 and 650° by the gas saturation method.

2. The vapor pressure of liquid antimony trioxide has been determined over the temperature range from 656 to 800°, using a new type of static balanced tensimeter. These values were checked by direct tensimeter measurement.

3. Heats of vaporization and transformation have been calculated from the vapor pressure data.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE IONIZATION CONSTANT OF WATER AT 25° FROM THE ELECTROMOTIVE FORCE OF CELLS WITHOUT LIQUID JUNCTION

BY ELLIOTT J. ROBERTS

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In view of the fact that all previous determinations of the ionization constant of water by the electromotive force method have involved cells containing liquid junctions, it appeared to be worth while to make a determination involving no liquid junctions. This has been accomplished by a new method, the basis of which consists of the measurement of two electrodes of the second kind, directly against each other in a common solution containing ions requisite to the reversibility of both electrodes.

In the present case, the two electrodes of the second kind were Pt,H_2,H_2O,OH^- and $Ag,AgCl,Cl^-$, and the solution in which they were measured was a mixture of sodium hydroxide and sodium chloride. Thus the complete cell was

$$Pt,H_2,NaOH\ (m_1) + NaCl\ (m_2),AgCl,Ag$$

The electromotive force of this cell at 25° may be represented by the equation

$$E = E^\circ_a - E^\circ_b - 0.05915 \log m_{Cl^-}/m_{OH^-} - 0.05915 \log \frac{\gamma_{Cl^-}\alpha_{H_2O}}{\gamma_{OH^-}} \qquad (1)$$

where E_a° is the normal potential of the electrode Pt,H_2,H_2O,OH^- and E_b° is the normal potential of the electrode Ag,AgCl,Cl^-. If, now, we define a quantity E' by the equation $E' = E + 0.05915 \log m_{Cl}/m_{OH^-}$, Equation 1 becomes

$$E' = E_a^\circ - E_b^\circ - 0.05915 \log \frac{\gamma_{Cl^-}\alpha_{H_2O}}{\gamma_{OH^-}} \tag{2}$$

and at zero concentration of ions

$$E' = E_a^\circ - E_b^\circ \tag{2*}$$

Furthermore, the extrapolation of the E' values to $m = 0$ should be linear with the ionic strength in dilute solutions, since the last term in Equation 2 contains a ratio of two activity coefficients. Thus, a series of determinations leading to E' at zero concentration will enable a calculation of E_a° if E_b° is known; but[1]

$$E_a^\circ = -0.05915 \log K_w \tag{3}$$

where K_w is the ionization constant of water in terms of activities. E_b° may be obtained from measurements of cells of the type Pt,H_2,HCl,AgCl,Ag by means of an extrapolation involving the use of the theoretical equation of Hückel.[2] Although measurements of the hydrochloric acid cells have been made at 25° by several investigators,[3] further measurements were deemed advisable to insure a uniformity of technique and to avoid possibility of error due to differences in electrodes. Accordingly, measurements on hydrochloric acid cells as well as sodium hydroxide–chloride cells have been made in the present investigation. These measurements furnish data for calculating E' at zero concentration and E_b°, from which E_a° and K_w follow by Equations 2* and 3.

Similar measurements with hydrogen and silver chloride electrodes on mixtures of sodium chloride with a weak acid and its sodium salt in equimolal proportions should lead to the ionization constant of that weak acid, provided that the constant has a value lying between 10^{-5} and 10^{-9}; or, if suitable corrections are made for ionization or hydrolysis, the range may be extended to 10^{-4} and 10^{-10}. The principal limitation to the use of this type of cell is that no change of phase shall occur at either of the electrodes due to reaction with the foreign ion.

Experimental Procedure

A Leeds and Northrup Type K potentiometer was used and the working standard cell was repeatedly checked against two cells recently standardized by the Bureau of

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[1] Taylor, "Treatise on Physical Chemistry," D. van Nostrand Co., New York, **1924**, p. 800.

[2] (a) Hückel, *Physik. Z.*, **26**, 93 (1925); (b) Scatchard, THIS JOURNAL, **47**, 2098 (1925); (c) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[3] (a) Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917); (b) Linhart, *ibid.*, **41**, 1175 (1919); (c) Scatchard, *ibid.*, **47**, 641 (1925); (d) Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926).

Standards. The two pyrex electrode vessels used were of the U-type, and were adapted to a vacuum technique by having an outlet tube at the base of the silver chloride electrode limb and an inlet tube about one-third of the way up on the hydrogen electrode limb. A three-way cock attached to the inlet tube allowed this to be used for the introduction of both hydrogen and solution. Auxiliary outlets through the rubber stoppers carrying the electrodes assisted in washing and removing gas bubbles. The electrode vessels were permanently mounted in an air thermostat maintained at 25 ± 0.02°, with the inlet and outlet tubes projecting, respectively, through the side and base of the thermostat. Hydrogen prepared by the electrolysis of a 15% solution of sodium hydroxide was passed through pure water at 25° before reaching the electrode vessels. Platinum strips, 0.5 by 2.5 cm. coated with platinum black for two to ten minutes at 150 milliamperes, served as hydrogen electrodes. After each determination they were heated to a white heat before re-use. The silver chloride electrodes were of the Noyes and Ellis type and were used for a number of measurements before being replaced. Recrystallized sodium chloride was added in the required amount to an 0.2 *M* solution of carbonate-free sodium hydroxide, prepared as described by Cornog,[4] and the resultant solution was analyzed for hydroxide and chloride ions. This solution was diluted with carbon dioxide-free distilled water as required. A carefully standardized 0.2 *M* solution of hydrochloric acid was prepared from distilled acid. The solutions used in the hydrochloric acid measurements were prepared by dilution, both the stock solution and the distilled water being weighed to one part in five thousand. All solutions were freed from dissolved oxygen by boiling *in vacuo* before being drawn into the electrode vessels, correction being made for the water lost. One liter of solution was used for each washing and filling of a cell. The capacity of each cell was 100 cc. The process of washing occupied about thirty minutes, which allowed considerable time for soaking out the silver chloride electrodes. Constant potential was reached one to two hours after starting the hydrogen. Three factors contributed to the elimination of error due to adsorption or reaction of the solutions with glass; namely, the use of pyrex vessels, the rapid attainment of equilibrium, and the approach of the determinations from both more concentrated and more dilute solutions. Removal of dissolved oxygen was shown by Güntelberg[5] to be necessary in the case of hydrochloric acid. In confirmation, results 0.3–0.4 mv. higher were obtained when 0.01 *M* solutions were introduced into the cells without boiling.

Experimental Results

Table I presents the results of measurements on sodium hydroxide–chloride cells in which the ratio of m_{Cl^-} to m_{OH^-} was within 1% of unity. Column 1 gives the total molality, $m_1 + m_2$; Col. 2, the observed e. m. f. corrected to 1 atm. partial pressure of hydrogen and to unity ratio of m_{Cl^-} to m_{OH^-}, the latter correction amounting to −0.29, −0.10 and −0.08 mv. in the three stock solutions made up.

Table II presents the results of measurements on hydrochloric acid cells. Column 1 gives the concentration of hydrochloric acid in moles per kilo of water *in vacuo*, Col. 2, the observed e. m. f. corrected to 1 atm. partial pressure of hydrogen, and Col. 3, the deviation of the individual E_b° values, as calculated by Equations 5 and 8, from the average of these values (−0.22239).

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[4] Cornog, This Journal, **43**, 2573 (1921).

[5] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

TABLE I

ELECTROMOTIVE FORCE IN VOLTS AT 25° OF THE CELLS $Pt,H_2,NaOH + NaCl,AgCl,Ag$

Total molality	E' observed	Total molality	E' observed	Total molality	E' observed
0.0126	1.05077	0.0326	1.05081	0.166	1.05101
.0168	1.05081	.0526	1.05081	.203	1.05083
.0170	1.05081	.0844	1.05089	.270	1.05085
.0212	1.05084	.130	1.05082		

TABLE II

ELECTROMOTIVE FORCE IN VOLTS AT 25° OF THE CELLS $Pt,H_2,HCl,AgCl,Ag$

Molality	E observed	$-E^\circ_b$ (Eq. 8) -0.22239 in mv.	Molality	E observed	$-E^\circ_b$ (Eq. 8) -0.22239 in mv.	Molality	E observed	$-E^\circ_b$ (Eq. 8) -0.22239 in mv.
0.001637	0.55424	+0.00	0.010525	0.46156	−0.02	0.03117	0.40871	+0.11
.001932	.54597	+ .04	.010759	.46042	− .08	.03340	.40530	+ .05
.002128	.54116	+ .12	.010965	.45947	− .09	.03358	.40512	+ .13
.002861	.52621	− .02	.011127	.45866	− .18	.03661	.40074	− .08
.003897	.51070	− .09	.011460	.45741	− .01	.04045	.39612	+ .14
.004222	.50695	+ .16	.011708	.45628	− .05	.04130	.39485	− .13
.006073	.48874	+ .01	.014364	.44646	+ .14	.04223	.39396	+ .05
.006117	.48838	+ .01	.015221	.44358	+ .09	.04253	.39363	+ .06
.009159	.46838	− .05	.020542	.42875	− .11	.05076	.38500	− .02
.009395	.46725	+ .08	.020635	.42871	+ .08	.05135	.38444	− .02
.009517	.46659	+ .04	.020684	.42854	+ .02	.06147	.37577	− .02
.009729	.46558	+ .14	.020844	.42826	+ .12	.06230	.37508	− .06
.009736	.46536	− .07	.020891	.42817	+ .14	.08322	.36122	+ .06
.009977	.46408	− .13	.02171	.42608	− .07	.08336	.36097	− .14
.010222	.46287	− .16	.02265	.42425	+ .15	.09018	.35729	+ .01
.010300	.46256	− .09	.02273	.42398	+ .07	.10757	.34887	+ .10
.010400	.46209	− .09	.02653	.41641	+ .00	.13544	.33762	+ .01
.010430	.46191	− .13	.02981	.41062	− .15	.13820	.33679	+ .17

Calculation of Results

The extrapolation of the E' values of Table I to $m = 0$ gives 1.05080 volts. Values of E°_b were calculated by means of the equation

$$-E^\circ_b = E_{\text{obs.}} + 0.1183 \log m + 0.1183 \log \gamma_\pm \qquad (5)$$

The values of $\log \gamma_\pm$ were calculated by means of Hückel's equation, using three different combinations of constants, as follows

$$\text{(a)} \quad \log \gamma_\pm = -\frac{0.5000\sqrt{c}}{1 + 1.4\sqrt{c}} + 0.136\, c - \log (1 + 0.036\, m) \qquad (6)$$

which is the formula used by Güntelberg[5] for his results at 20°

$$\text{(b)} \quad \log \gamma_\pm = -\frac{0.5049\sqrt{c}}{1 + 1.329\sqrt{c}} + 0.1426\, c - \log (1 + 0.036\, m) \qquad (7)$$

which is the formula used by Scatchard[6] for results at 25°

$$\text{(c)} \quad \log \gamma_\pm = -\frac{0.5044\sqrt{c}}{1 + 1.45\sqrt{c}} + 0.1338\, c - \log (1 + 0.036\, m) - N \qquad (8)$$

where N is the second term of formula No. 107 of Gronwall, La Mer and

[6] Scatchard, THIS JOURNAL, 47, 2098 (1925).

Sandved,[7] and has a maximum value of 0.09 mv. The two constants 1.45 and 0.1338 were determined by trial, with the aid of Scatchard's[8] results above 0.1 M. The values of c were calculated by means of the equation

$$c_{25^\circ} = M - M\,(0.0029 + 0.0184\,M + 0.0001\,M^2) \qquad (9)$$

which was derived from data in the "International Critical Tables."

The average values for E°_b as calculated by means of the three equations are -0.22247, -0.22235 and -0.22239 volt, respectively, with mean deviations from the average of 0.08, 0.09 and 0.08 millivolt, respectively. The average of the three values, -0.22240 volt, may therefore be used for E°_b (E° of the silver chloride electrodes used). By Equation 2*

$$\mathrm{Pt,H_2,H_2O,OH^-};\ E^\circ = 0.82840 \text{ volt } \pm 0.10 \text{ mv.}$$

Therefore, by Equation 3

$$K_w = (0.988 \pm 0.004) \times 10^{-14}$$

Summary

The ionization constant of water has been determined at 25° from the electromotive force of cells without liquid junction and found to be equal to $(0.988 \pm 0.004) \times 10^{-14}$.

A new method has been outlined for the determination of the ionization constants of weak electrolytes from the electromotive force of cells without liquid junction.

New Haven, Connecticut

[Contribution from the Division of Inorganic Chemistry, Department of Chemistry, University of Wisconsin]

THE AMMONATES OF COPPER SELENITE[1]

By Loren C. Hurd, George I. Kemmerer and V. W. Meloche

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As a part of the study of selenium and its compounds being made at this Laboratory, it was thought that an investigation of the compounds formed by the action of ammonia on the metallic selenates and selenites might yield results of interest. The present report deals with the compounds formed by the action of ammonia on copper selenite.

During the course of an investigation of a number of ammonates of metallic salts, Boutzaureanu[2] prepared a monammonate monohydrate of

[7] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[8] Scatchard, This Journal, **47**, 641 (1925).

[1] Abstracted from a portion of a thesis submitted to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929. This work was started under the direction of the late Victor Lenher, continued under the supervision of the late George Kemmerer, and completed under the guidance of Professor V. W. Meloche.

[2] Boutzaureanu, *Ann. chim. phys.*, **6**, 18, 346 (1889).