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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY[1]]

The Electromotive Force of the Cell H_2, HCl(g), AgCl(s), Ag(s) at 25°. Derived Values from 0 to 40°[2]

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The value of E_0° referred to the ideal gas state obtained from the aqueous cell is −0.1506. A method for measuring this value directly has been found leading to a value of −0.1509 abs. volt. Values are calculated from this result from 0 to 40°.

The value of the electromotive force of the cell

$$H_2(g),\ HCl(g),\ AgCl(s),\ Ag(s) \qquad (A)$$

at 25° can be calculated from difference between the standard free energies of HCl(g) and AgCl(s) as given in the Tables of Selected Values of Chemical Thermodynamic Properties issued by the National Bureau of Standards.[3] The difference is $\Delta F =$ 3455 cal. corresponding to an e.m.f. of −0.14977 international volt. The value which can be deduced directly from the results of Randall and Young[4] is −0.15076 international volt. The vapor pressure data used by these authors are open to reinterpretation but no new vapor pressure data have since become available to the authors' knowledge. The variation in values of E°[5] for the aqueous hydrogen chloride cell, which form the basis of the calculation, could only change the value from −0.15076 to −0.15059 so that the "Selected Value" must be based on a reinterpretation of the vapor pressure data or is an "indirect" value. Since an accurate value was needed for use in work described in the preceding paper[6] we therefore decided to measure the e.m.f. of the cell directly. This can be done simply by a study of the cell with the hydrogen chloride dissolved in acetic acid containing sufficient water to give the desired pressure of hydrogen chloride.

Experimental

Materials.—The acetic acid was prepared by distillation through a fractionating column with about 70 theoretical plates. This was saturated with dry hydrogen chloride (from sodium chloride and sulfuric acid) to make a stock solution from which those of lower vapor pressure were made by dilution with water. Standard aqueous hydrogen chloride was made by dilution of a weighed amount of constant boiling aqueous hydrochloric acid and checked by titration. The hydrogen and silver–silver chloride electrodes and other materials were made up as described in the previous paper.

Measurement of Electromotive Force.—The potentiometer, thermostat, electrodes, hydrogen and cell vessels were as previously described.[6] All results are reported in absolute volts. 0.059156 abs. volt eqt.$^{-1}$ was used for RTF^{-1} ln 10 at 25° (298.16°K.).

The Standard Electromotive Force for Unit Activity of Hydrochloric Acid in Water.—In all, sixty-one pairs of hydrogen, silver–silver chloride electrodes giving values of E° within 0.20 millivolt of the mean were measured at 25° with concentrations of hydrochloric acid ranging from 0.18 to 0.27 N with one concentration used for each electrode as tests of electrodes to be used in the following and the preceding work.[6] There was no previous saturation and no additional silver chloride was added to the silver–silver chloride compartment. The values were compared with the values of Harned and Ehlers.[5a,b] Any difference was attributed to a difference in E° since the activities of hydrogen chloride[4,5a,b] are not in doubt, and accordingly a value of E° was derived from each measurement. The mean value of E° thus obtained was 0.2221 ± 0.00008 abs. volt for the cell

$$H_2(g)\ HCl(aq),\ AgCl(s)\ Ag(s) \qquad (B)$$

The error given is the "standard error of estimate." The deviations from this value were essentially Gaussian. The values obtained by Randall and Young,[4] Carmody,[7] Harned and Ehlers[5a,b] and Harned and Paxton[5c] are, respectively, 0.2221, 0.2223, 0.22246 and 0.22239 abs. volt. Since the above electrodes were only followed until they seemed to be constant to 0.00002 volt, it is possible that only the higher values had come to true equilibrium. On the basis of unpublished work of Bates (National Bureau of Standards)[8a]

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[2] This research was in part supported by the Office of Naval Research, Contract N6 ONR-269 T. O. III.

[3] F. D. Rossini, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, p. 22 and p. 224, Washington, D. C.

[4] M. Randall and L. Young, THIS JOURNAL, **50**, 989 (1929).

[5] (a) H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932); (b) **55**, 2179 (1933); (c) H. S. Harned and T. P. Paxton, *J. Phys. Chem.*, **57**, 531 (1953).

[6] J. G. Aston and F. L. Gittler, *ibid.*, **77**, 3175 (1955).

[7] W. R. Carmody, *ibid.*, **54**, (88 (1932).

and Young (University of Chicago)[8b] together with the previous work we take the value as 0.2223 abs. volt.

The Standard Electromotive Force for Hydrogen Chloride at 1 Atm.—The silver–silver chloride compartment was not previously saturated with silver chloride and no additional silver chloride was added. For the electrolyte, a solution of hydrogen chloride in acetic acid was diluted with water to give a convenient vapor pressure of hydrogen chloride. The entering hydrogen was presaturated by passing through a solution identical with that in the cell. It entered the cell through a fritted disc as previously.[6] The weighed absorbers through which the hydrogen passed contained standard sodium hydroxide followed by activated alumina and the total acid concentration was determined by back-titration with standard sulfuric acid. The hydrochloric acid was determined by the Volhard method and the difference was equal to the acetic acid in the absorbers. The water was determined by difference. The accuracy was about 0.1%. The electromotive force was read every five minutes until the e.m.f. was constant to 0.2 mv. for three hours or more. About three liters of hydrogen was passed through the cell. The volume was measured to 0.2% by a calibrated wet test meter. The glycerol differential manometer on the cell together with a mercury barometer allowed the pressure in the cell to be read to 0.1 mm. of mercury. From these data the partial pressures of the hydrogen and hydrogen chloride could be evaluated to 0.02 and 0.2%, respectively. A value of E_g° was calculated from the four paired electrode readings for each partial pressure determination using the equation

$$E_g^\circ = E + 0.05916 \log P_{\mathrm{HCl}}/P_{\mathrm{H_2}}^{1/2} \qquad (1)$$

The experimental results for cell A are summarized in Table I. At these low pressures the fugacity of hydrogen chloride could be considered as equal to the pressure. The average value found for E_g° is −0.1509 volt.

Calculation of E_0 (gas) from the Aqueous Cell Data.—Table II shows how the calculated value of E° at 298.16°K. was obtained from the smoothed values of ln $\gamma\pm$ and of the hydrogen chloride partial pressures derived by Randall and Young.[4] The latter are chiefly based on the vapor pressure data of Bates and Kirschmann.[9] The activity coefficients and vapor pressures were completely re-smoothed but the results did not produce significant changes in the values given by Randall and Young. Column 1 shows the pressure of hydrogen chloride above its aqueous solution at the concentration in column 2. Column 3 of the table gives the logarithm of the mean ionic activity coefficient corresponding to column 2, while column 4 gives the logarithm of $P^{1/2}/m_\pm\gamma_\pm$. The value of E_g° for cell (B) is given by

$$E_g^\circ = E^\circ - \frac{RT}{F} \ln \frac{m_\pm{}^2\gamma_\pm{}^2}{P} \qquad (2)$$

The value for $E^\circ{}_g$ of −0.1506 abs. volt, based on E° = 0.2223 volt, agrees satisfactorily with the directly measured of −0.1509 ± 0.0003 abs. volt value in Table I. The value finally adopted is −0.1508 ± 0.0002 abs. volt. To obtain the values of E° (gas) at other temperatures from 0 to 40° the relation was used

$$-\Delta F_T^\circ + \Delta F_{298.16}^\circ = NF(E_T^\circ - E_{298.16}^\circ) = \int_{298.16}^{T} \Delta S^\circ \mathrm{d}T \qquad (3)$$

TABLE I

E_g° OF THE GASEOUS HYDROGEN CHLORIDE CELL

P_{HCl}, 10^3 atm.	$P_{\mathrm{H_2}}$, atm.	E.m.f., abs. volts	$-E_g^\circ$, abs. volts
1.804	0.9168	0.00986	0.1513
1.804	.9168	.00983	.1513
1.804	.9168	.00994	.1513
1.804	.9168	.00992	.1513
1.169	.9202	.02172	.1507
1.169	.9202	.02188	.1505
1.169	.9202	.02153	.1509
1.169	.9202	.02154	.1508
1.170	.9202	.02172	.1507
1.170	.9202	.02188	.1505
1.170	.9202	.02153	.1509
1.170	.9202	.02154	.1508
		Av.	0.1509 ± 0.0003

TABLE II

CALCULATION OF E_g° FOR THE GASEOUS HYDROGEN CHLORIDE CELL AT 25°[a]

P_{HCl}, 10^7 atm.	m, moles/1000 g. solvent	log $\gamma\pm$	$\log \left(p_{\mathrm{HCl}}^{1/2}/m_\pm\gamma_\pm\right)$
5.08	1.2	−0.0743	−3.1519
7.61	1.4	− .0556	−3.1498
10.77	1.6	− .0359	−3.1521
14.99	1.8	− .0153	−3.1521
20.6	2.0	+ .0080	−3.1521
41.1	2.5	+ .0610	−3.1520
77.8	3.0	+ .1205	−3.1521
140.5	3.5	+ .1818	−3.1520
246	4.0	+ .2460	−3.1523
		Av.	−3.1518

[a] E_g° calculated, −0.1506 abs. volt.

TABLE III

CALCULATION OF E_g° AT OTHER TEMPERATURES

T, °K.	S°_{AgCl}, e.u.	S°_{Ag}, e.u.	S°_{HCl}, e.u.	$S^\circ_{\mathrm{H_2}}$, e.u.	E_g°, abs. volts
273.16	21.91	9.67	44.01	15.34	−0.1685
278.16	22.13	9.78	44.15	15.39	− .1649
283.16	22.35	9.89	44.27	15.45	− .1614
288.16	22.56	10.00	44.39	15.51	− .1578
293.16	22.77	10.10	44.50	15.56	− .1543
298.16	22.97	10.21	44.62	15.61	− .1508
303.16	23.17	10.31	44.73	15.67	− .1472
308.16	23.37	10.42	44.85	15.72	− .1437
313.16	23.57	10.53	44.96	15.77	− .1395

Table III summarizes the values of the entropies used in the calculation and the values obtained for E_0 from 0 to 40°. Except in the case of silver chloride, the extropies were obtained from the published values[10] by interpolation or short extrapolation. The entropy of silver chloride was obtained by integrating the heat capacity data of Eastman and Milner.[11]

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(8) (a) R. C. Bates and V. E. Bower, *J. Research Natl. Bur. Standards*, forthcoming publication; (b) T. F. Young, private communication.

(9) S. J. Bates and H. D. Kirschmann, THIS JOURNAL, **41**, 1991 (1919).

(10) (a) For Ag(s): P. F. Meads, W. R. Forsythe and W. F. Giauque, *ibid.*, **63**, 1902 (1941); (b) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C. (1952); (c) For HCl(g): R. H. Sherman and W. F. Giauque, THIS JOURNAL, **75**, 2007 (1953); (d) For H_2(g): H. W. Wooley, R. B. Scott and F. G. Brickwedde, *J. Natl. Bur. Standards*, **41**, 379 (1948).

(11) E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 450 (1933).