Standard Electromotive Force of the Hydrogen-Silver Chloride Cell and the Thermodynamics of Solutions of Hydrochloric Acid in 50 Wt. % Methanol from 10 to 40° C.

MAYA PAABO, R. A. ROBINSON, and ROGER G. BATES
National Bureau of Standards, Washington, D. C.

The standard electromotive force of the cell Pt/H_2 (*g.*, 1 atm.): HCl(*m*) in 50 wt. % methanol-water: AgCl/Ag has been determined at seven temperatures from 10° to 40° C. The activity coefficients of hydrochloric acid in 50% methanol for molalities in the range 0.005 to 0.1 have been derived from the e.m.f. measurements. From the variation of the activity coefficient with temperature, the relative partial molal enthalpy of hydrochloric acid at 25° was calculated for comparison with the value in the aqueous medium.

WHILE THE STANDARD POTENTIAL of the silver-silver chloride electrode has been determined in many nonaqueous and partially aqueous solvents, the measurements have usually been limited to a temperature of 25° C. Data obtained over a range of temperatures, with two exceptions, have been confined to solvent mixtures of comparatively high dielectric constant, for example, 20 wt. % isopropanol ($\epsilon = 64.1$) (*8*) or 50% glycerol ($\epsilon = 64.0$) (*7*). These exceptions are the comprehensive study of water-dioxane solvents of dielectric constants as low as 9.5 (*6*), and the recent study of 1-propanol-water mixtures at 0°, 25°, and 40°, which included media of dielectric constant as low as 26.1 (*4*). These dielectric constants refer to a temperature of 25° C. Parton and coworkers have also made measurements in solvents of high methanol content. Their standard potentials have been reported as a "private communication" (*9*), but none of the associated thermodynamic quantities have been published.

Electromotive force measurements of the cell:

Pt/H_2 (g., 1 atm.): HCl(*m*) in 50 wt. % methanol: AgCl/Ag

have now been made at seven temperatures from 10° to 40° C. and for molalities (*m*) of hydrochloric acid from 0.01 to 0.1. The mixed solvent, composed of equal weights of water and methanol (35.99 mole % methanol), has a dielectric constant of 56.3 at 25° which is comparable with that of 25% dioxane. The standard electromotive force of the cell and the activity coefficient of hydrochloric acid from 10° to 40° C. have been determined from the measurements. The relative partial molal enthalpy of hydrochloric acid in 50 wt. % methanol at 25° was derived from the change of the activity coefficient with temperature.

EXPERIMENTAL

Methanol (Spectro Grade) was used without further purification, after preliminary measurements had shown that the difference between the e.m.f. for solutions made with distilled methanol and for solutions made from the untreated methanol was random and no greater than the experimental error (0.05 mv.). The stock solution of hydrochloric acid was prepared from a twice-distilled sample of the acid. Its chloride content was determined gravimetrically as silver chloride. All of the cell solutions were prepared by weight methods by diluting the aqueous stock solutions with methanol and water. The hydrogen electrodes and the silver-silver chloride electrodes were prepared by methods described elsewhere (*2*).

The cells have been described by Bates and Rosenthal (*3*). An additional triple saturator containing about 150 ml. of the solution was connected to the cell in order to reduce the rate of evaporation of the cell contents. For the measurements from 10° to 35°, the cells were brought to initial equilibrium at either 10° or 25°. This procedure led to reproducible results at these six temperatures. Reproducible results at 40°, however, were obtained only with fresh solutions.

RESULTS AND CALCULATIONS

All of the observed e.m.f. data were corrected to a partial pressure of hydrogen of 1 atm. with the aid of vapor pressure data given in the literature. The corrected e.m.f. is summarized in Table I, and the estimated vapor pressures of the aqueous methanol solvent at the seven temperatures studied are listed at the foot of the table. These were read from a smoothed curve plotted from information given in seven different sources.

The standard electromotive force, ${}_sE^\circ$, was calculated by means of the equations:

$$ {}_sE^\circ = E + \frac{4.6052RT}{F} \log (m \cdot {}_s\gamma_\pm) \qquad (2)$$

and

$$ -\log {}_s\gamma_\pm + \beta m = \frac{A(m)^{1/2}}{1 + Ba(m)^{1/2}} \text{ (Ext.)} + \log (1 + 0.04612m) \qquad (3)$$

In Equation 3, A and B are the Debye-Hückel constants, converted to the molal scale by multiplying by the square root of the density (d_0) of the solvent; a, the ion size parameter, was taken to be 4.3 A. at each temperature. The coefficient of m in the last term of Equation 3 is $(2G_0/1000)$, where G_0 is the weighted mean molecular weight of the solvent mixture, namely 23.06.

The dielectric constants (ϵ) used to calculate A and B were taken from the paper of Albright and Gosting (*1*), and d_0 was estimated from previously published density measurements as given in seven different sources. The values of ϵ and d_0 are collected at the foot of Table 1, together with the constants A and B derived with their aid. The extended terms (Ext.) were obtained from the tables of Gronwall, LaMer, and Sandved (*5*).

The standard e.m.f. ${}_sE^\circ$ at each temperature is the limit of $({}_sE^\circ - 4.6052RT\beta m/F) \equiv {}_sE^{\circ\prime}$ as m approaches zero.

Table I. Electromotive Force of the Cell Pt/H_2 (*g.*, 1 atm.): HCl(*m*) in 50 Wt. % Methanol: AgCl/Ag from 10° to 40° (in volts)

m	10°	15°	20°	25°	30°	35°	40°
0.009983	0.43385	0.43462	0.43518	0.43555[a]	0.43561	0.43556	0.43499
0.01998	0.40255	0.40287[a]	0.40287[b]	0.40252[a]	0.40216	0.40153	0.40066[a]
0.02999	0.38438	0.38428	0.38390	0.38332[a]	0.38283	0.38193	0.38071
0.03994	0.37154	0.37109	0.37072[a]	0.37003[a]	0.36919[a]	0.36806	0.36676
0.04091	0.37050	0.36013	...	0.36892	0.36806	0.36698	0.36559
0.04991	0.36156[a]	0.36108[a]	0.36047	0.35954[a]	0.35860	0.35732[a]	0.35578[a]
0.05994	0.35353	0.35298	0.35221[a]	0.35119	0.35006	0.34861	0.34712
0.07003	0.34663	0.34593	0.34497[a]	0.34384[a]	0.34273[a]	0.34122	...
0.08000	0.34077	0.34003[a]	0.33907[b]	0.33781	0.33659	0.33482	0.33318
0.09006	0.33557[a]	0.33467[a]	0.33356[a]	0.33229[a]	0.33099	0.32928[a]	0.32746[a]
0.1002	0.33084	0.32985	0.32874	0.32750[a]	0.32591	0.32420	0.32227
P_{total}, mm. Hg	29.2	39.4	54.1	71.8	91.0	117.0	154.0
ϵ	61.2	59.5	57.9	56.3	54.8	53.2	51.8
d_0, g./ml.$^{-1}$	0.9222	0.9187	0.9155	0.9125	0.9805	0.9045	0.9005
A, Kg.$^{1/2}$ mole$^{-1/2}$	0.7681	0.7791	0.7895	0.8015	0.8122	0.8268	0.8381
10^{-8} *B*, Kg.$^{1/2}$ mole$^{-1/2}$ cm.$^{-1}$	0.3668	0.3682	0.3693	0.3708	0.3719	0.3736	0.3747

[a] Mean value of two cells. [b] Mean value of three cells.

The plots of $_sE^{\circ\prime}$ as a function of *m* were straight lines at each temperature, as can be seen in Figure 1. The intercepts were obtained by the method of least squares. The values of $_sE^\circ$ and of the standard deviations of the intercepts (σ_i) are summarized in Table II. The standard e.m.f. is given on two scales, namely the molal scale ($_sE^\circ_m$) and the mole fraction scale ($_sE^\circ_N$). The former is expressed as a function of *t*, the temperature in degrees C., by:

$$_sE^\circ_m = 0.19067 - 8.0621 \times 10^{-4} (t - 25) - 4.8238 \times 10^{-6} (t - 25)^2 \qquad (4)$$

The values calculated by this equation are listed in the last column of Table II. The standard deviation of an "experimental" value from that calculated by Equation 4 is 0.05 mv.

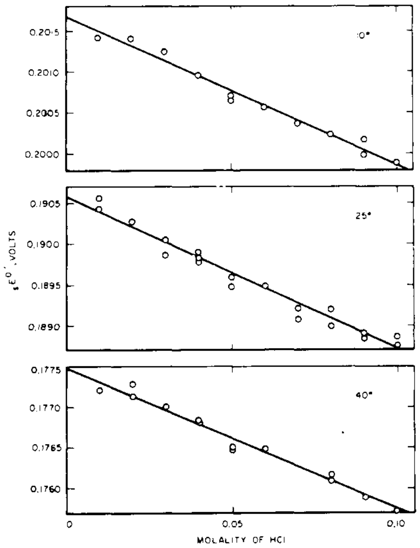

Figure 1. Plots of the extrapolation function $_sE^{\circ\prime}$ as a function of the molality of hydrochloric acid at 10°, 25°, and 40°

Table II. Standard Potential of the Cell Pt/H_2(*g.*, 1 atm.): HCl(*m*) in 50 wt. % Methanol: AgCl/Ag from 10° to 40° C.

t	$_sE^\circ_m$ (v.)	σ_i (mv.)	$_sE^\circ_N$ (v.)	$_sE^\circ_m$ (Eq. 4)
10	0.20167	0.05	0.01770	0.20167
15	0.19826	0.06	0.01106	0.19825
20	0.19463	0.06	0.00418	0.19458
25	0.19058	0.05	−0.00312	0.19067
30	0.18654	0.03	−0.01041	0.18652
35	0.18271	0.04	−0.01802	0.18213
40	0.17747	0.05	−0.02597	0.17749

THERMODYNAMIC QUANTITIES

The mean molal activity coefficient of hydrochloric acid, $_s\gamma_\pm$, at round molalities from 0.005 to 0.1 was calculated by Equation 3. The values of β at the seven temperatures obtained from the slopes of the extrapolation lines (compare Figure 1) are as follows:

t, ° C.	β	*t*, ° C.	β
10	0.161	30	0.153
15	0.168	35	0.159
20	0.172	40	0.138
25	0.158		

The value of $-\log {_s\gamma_\pm}$ at 10°, 25°, and 40° is given in Table III, together with $-\log \gamma_\pm$ in water at 25°. In Figure 2, this quantity is compared with the corresponding values in water ($\epsilon = 78.3$), in 20 wt. % dioxane ($\epsilon = 60.8$), and in 45% dioxane ($\epsilon = 38.5$).

The temperature variation of the activity coefficient was utilized to calculate the relative partial molal enthalpy, $\bar{L}_2$, of hydrochloric acid in 50 wt. % methanol at 25°. A comparison of $\bar{L}_2$ in water and in the methanolic solvent is also made in Table III. The values are given in thermochemical calories per mole (1 thermochemical calorie = 4.1840 joules). In Figure 3, the values of $\bar{L}_2$ in water and in 50 wt. % methanol (dotted lines) are compared with the theoretical slopes (solid lines) derived from the Debye-Hückel limiting law.

Table III. Activity Coefficients and Relative Partial Molal Enthalpy of Hydrochloric Acid in 50 Wt. % Methanol

	$-\log {_s\gamma_\pm}$ in				$\bar{L}_2$ at 25° (Cal. Mole^{-1})	
	50 % MeOH			Water		
m	10°	25°	40°	25°	50% MeOH	Water
0.005	0.0490	0.0511	0.0536	0.0323	124	42
0.01	0.0661	0.0690	0.0725	0.0436	172	54
0.02	0.0876	0.0915	0.0961	0.0578	234	73
0.03	0.1021	0.1067	0.1123	0.0675	279	...
0.05	0.1220	0.1274	0.1343	0.0805	336	120
0.07	0.1357	0.1418	0.1497	...	384	140
0.1	0.1501	0.1568	0.1662	0.0987	442	172

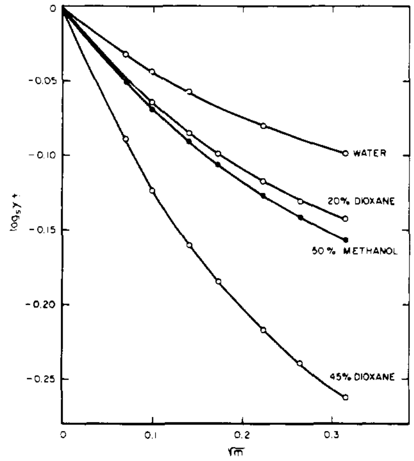

Figure 2. Values of log $_s\gamma_\pm$ for hydrochloric acid in water and in three mixed solvents at 25° plotted as a function of the square root of the molality of acid

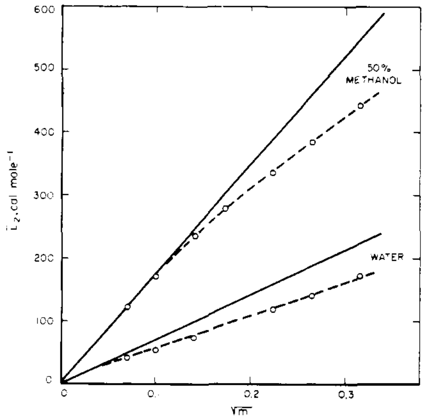

Figure 3. Comparison of $\bar{L}_2$ at 25° for hydrochloric acid in water and in 50 wt. % methanol. Solid lines are the theoretical slopes

LITERATURE CITED

(1) Albright, P.S., Gosting, L.J., *J. Am. Chem. Soc.* **68**, 1061 (1946).
(2) Bates, R.G., "Determination of pH," pp. 241, 282, John Wiley, New York, 1964.
(3) Bates, R.G., Rosenthal, D., *J. Phys. Chem.* **67**, 1088 (1963).
(4) Gentile, P.S., Eberle, L., Cefola, M., Celiano, A.V., J. CHEM. ENG. DATA **8**, 420 (1963).
(5) Gronwall, T.H., LaMer, V.K., Sandved, K., *Physik. Z.* **29**, 358 (1928).
(6) Harned, H.S., Morrison, J.O., Walker, F., Donelson, J.G., Calmon, C., *J. Am. Chem. Soc.* **61**, 49 (1939).
(7) Harned, H.S., Nestler, F.H.M., *ibid.* **68**, 665 (1946).
(8) Moore, R.L., Felsing, W.A., *ibid.* **69**, 1076 (1947).
(9) Robinson, R.A., Stokes, R.H., "Electrolyte Solutions," 2nd Ed., p. 470, Butterworths, London, 1959.

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Standard Potential of the Ag-AgCl Electrode in 5% Aqueous Mannitol

ROBERT GARY and R. A. ROBINSON
National Bureau of Standards, Washington, D. C.

The standard potential of the Ag-AgCl electrode from 0° to 60° has been determined by e.m.f. measurements on the cell:

Pt-H_2/HCl (m), mannitol (5 wt. %), H_2O/AgCl-Ag

From these data and from data on the same cell containing no mannitol, the relative partial molal quantities $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the change in solvent are calculated. The value of $\Delta G°$ for HCl in 5% mannitol at 25° is found to be 54 j. mole^{-1}. There is a small but significant change in the e.m.f. of the cell if mannitol is replaced by its diastereoisomer, sorbitol.

RECENT ISOPIESTIC STUDIES (*9, 10, 11*) have demonstrated the effect of mannitol on the thermodynamic properties of aqueous solutions of sodium chloride and potassium chloride. As the isopiestic method is not applicable to hydrochloric acid solutions, the effect of mannitol on such solutions has now been studied by means of the cell:

Pt-H_2/HCl (m) in 5 wt. % mannitol/AgCl-Ag,

and measurements have been made over the temperature range 0° to 60°. .A few measurements have been made with the corresponding cell in which sorbitol replaced mannitol.

MATERIALS

Mannitol (Fisher Certified Reagent grade) was recrystallized from conductance water and dried in vacuo at room temperature. M.p. 166.2-167.3°. Sorbitol was part of a