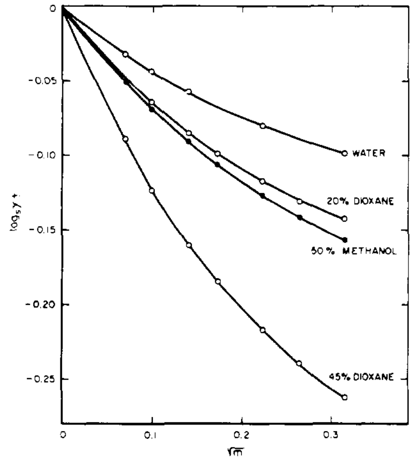

Figure 2. Values of log $_s\gamma_\pm$ for hydrochloric acid in water and in three mixed solvents at 25° plotted as a function of the square root of the molality of acid

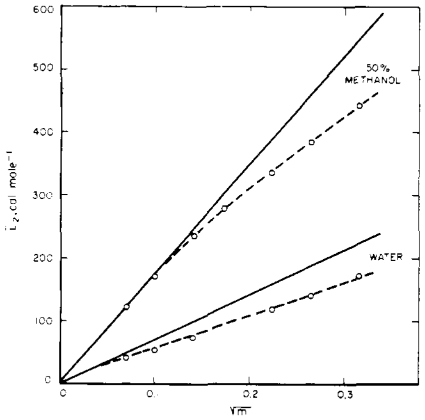

Figure 3. Comparison of $\overline{L_2}$ at 25° for hydrochloric acid in water and in 50 wt. % methanol. Solid lines are the theoretical slopes

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.

RECEIVED for review January 16, 1964. Accepted March 13, 1964.

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:

$$\text{Pt-H}_2/\text{HCl}\,(m),\ \text{mannitol}\ (5\ \text{wt.}\ \%),\ \text{H}_2\text{O}/\text{AgCl-Ag}$$

From these data and from data on the same cell containing no mannitol, the relative partial molal quantities ΔG°, ΔH° and ΔS° for the change in solvent are calculated. The value of ΔG° 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:

$$\text{Pt-H}_2/\text{HCl}\,(m)\ \text{in 5 wt. \% mannitol/AgCl-Ag},$$

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 highly purified sample used in previous work (*5*) and supplied by Atlas Chemical Industries, Ltd. Hydrochloric acid (Baker and Adamson) was distilled from the constant boiling solution, the first and last thirds being discarded. From this, a stock solution about 0.2*m* was prepared.

Solutions of mannitol and hydrochloric acid in conductance water were prepared by weighing the components (with vacuum corrections) and were deaerated with hydrogen. Concentrations are expressed in molality, *m*, (moles per kilogram of water + mannitol).

CELLS AND ELECTRODES

The cells were of borosilicate glass throughout except for "Teflon" stopcocks. The design was similar to that used by Harned and his coworkers (*8*) and by workers in this laboratory except for the following features. Presaturation of the hydrogen by portions of the same solution as that in the electrode compartments was achieved by a three-stage saturator with a sintered glass disperser in the middle stage. The glass joints were specially constructed with two seating surfaces separated by a groove 5 mm. wide to protect the solution from contamination by grease or by water from the water bath. The components of the cell and the filling tubes were so arranged that the previously conditoned and rinsed electrodes and the dry electrode compartments could be rinsed twice with the cell solutions prior to final filling. The rinse solutions were forced by hydrogen pressure into the saturators.

The platinum electrode was partially immersed in the solution, the upper half being exposed to the hydrogen above the solution. The silver-silver chloride electrodes were of the thermal-electrolytic type prepared according to the recommendations of Bates (*2*).

Voltage measurements were made on duplicate or triplicate cells, the results being generally within ±0.02mv. of the mean except at 55° and 60° where the spread was sometimes as much as ±0.05mv. The cells were allowed to stand for eighteen hours with the hydrogen flowing (about 100 ml. per hour) before any measurements were made. Thereafter, equilibrium was attained within 30 minutes of each temperature change, although measurements were continued for another 90 minutes to be certain that the equilibrium voltage was being measured. In a few cases, measurements were made at a given temperature for a further 14 hours without any significant change. Data were obtained at 5° intervals up to 60°, those at 0° being extrapolated from measurements at 0.2°. The temperature control was ±0.01° measured by a platinum resistance thermometer which, along with the potentiometer and the standard cell, has been recently calibrated by the National Bureau of Standards. The vapor pressures of the solutions, needed for correcting voltages to one atm. hydrogen pressure, were calculated from the data of Robinson and Stokes (*10*) at 25° with the assumption that p/p°, the ratio of the partial pressure of water over the mannitol solution to that of pure water, is constant over the temperature range 0° to 60°.

RESULTS

The first part of Table I presents the observed e.m.f. values (${}_sE$) of the cell; the second part presents e.m.f. values of a few cells in which the mannitol was replaced by sorbitol. The third part of the table gives the e.m.f. (${}_wE$) of the cell with 0.01*m* HCl in aqueous solution (without mannitol or sorbitol). These latter measurements were made as a calibration procedure (*3*) because the potential of the cell is known to depend somewhat on the mode of preparation of the silver-silver chloride electrode.

Table II presents the standard potentials of the silver-silver chloride electrode on the molal scale, ${}_sE^\circ(m)$, with

Table I. Electromotive Forces[a]

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
(a) Electromotive Force of the Cell Pt-H_2/HCl(*m*) in 5% mannitol/AgCl-Ag													
0.005000	0.48656	0.48876	0.49069	0.49248	0.49411	0.49557	0.49695	0.49814	0.49920	0.50010	0.50090	0.50157	0.50211
0.01000	0.45527	0.45682	0.45820	0.45946	0.46048	0.46137	0.46212	0.46277	0.46331	0.46369	0.46391	0.46402	0.46413
0.01500	0.43698	0.43815	0.43921	0.44011	0.44085	0.44144	0.44187	0.44221	0.42240	0.44245	0.44237	0.44212	0.44177
0.02000	0.42405	0.42498	0.42582	0.42651	0.42702	0.42739	0.42759	0.42770	0.42768	0.42748	0.42719	0.42667	0.42607
0.02500	0.41404	0.41491	0.41554	0.41604	0.41638	0.41656	0.41660	0.41653	0.41631	0.41598	0.51550	0.41491	0.41417
0.03500	0.39902	0.39965	0.40001	0.40022	0.40027	0.40020	0.39997	0.39968	0.39919	0.39860	0.39886	0.39709	0.39602
0.05000	0.38322	0.38355	0.38369	0.38360	0.38338	0.38304	0.38253	0.38193	0.38120	0.38032	0.37931	0.37817	0.37694
(b) Electromotive Force of the Cell Pt-H_2/HCl(*m*) in 5% sorbitol/AgCl-Ag													
0.01000	0.45542	0.45697	. . .	0.45960	. . .	0.46151	0.46226	0.46293	. . .	0.46376	. . .	0.46420	. . .
0.02000	0.42424	0.42525	. . .	0.42674	. . .	0.42760	0.42783	0.42791	. . .	0.42766	. . .	0.42695	. . .
(c) Electromotive Force of the Cell Pt-H_2/HCl (0.01*m*) in water/AgCl-Ag													
0.01000	0.45803	0.45962	0.46098	0.46222	0.46331	0.46425	0.46501	0.46571	0.46618	0.46656	0.46684	0.46702	0.46706

[a] All e.m.f.'s are in absolute volts.

Table II. Standard Potentials and Thermodynamic Quantities

t, °C.	${}_sE^\circ(m)$ By Eq. 1	${}_sE^\circ(m)$ Experimental	${}_sE^\circ(N)$ (abs. v.)	${}_uE^\circ(N)$ (abs. v.)	ΔG° j. mole^{-1}	ΔH° j. mole^{-1}	ΔS° j. deg.$^{-1}$ mole^{-1}
0	0.23388	0.23392	0.04701	0.04769	66	264	0.73
5	0.23133	0.23133	0.04100	0.04164	62	233	0.72
10	0.22860	0.22859	0.03484	0.03545	59	203	0.51
15	0.22576	0.22571	0.02853	0.02912	57	172	0.40
20	0.22271	0.22268	0.02209	0.02266	55	140	0.29
25	0.21950	0.21950	0.01548	0.01604	54	108	0.18
30	0.21617	0.21618	0.00875	0.00930	53	74	0.07
35	0.21270	0.21272	0.00186	0.00241	53	42	−0.04
40	0.20909	0.20910	−0.00517	−0.00462	53	−8	−0.20
45	0.20532	0.20535	−0.01235	−0.01179	54	−27	−0.25
50	0.20143	0.20145	−0.01967	−0.01909	56	−62	−0.36
55	0.19738	0.19739	−0.02714	−0.02654	58	−97	−0.47
60	0.19325	0.19320	−0.03476	−0.03413	61	−133	−0.58

5% mannitol as solvent. These were obtained by extrapolation (using the method of least squares) of the function:

$$ {}_sE + 2k \log m - 2kA\sqrt{m}/(1 + Ba\sqrt{m}), $$

where A and B are parameters of the Debye-Hückel equation and a, the ion-size parameter, was taken as 4.3 A. Raising a to 5.0 A. increases the value of ${}_sE^\circ(m)$ by 0.03 mv. Values of the dielectric constant of a 5% mannitol solution, needed for the calculation of A and B, were taken from the literature (*1*).

Table II also contains some further thermodynamic data. The standard potentials, ${}_sE^\circ(m)$, have been fitted by the method of least squares to the equation:

$$ {}_sE^\circ(m) = a + b(t - 30) + c(t - 30)^2, \qquad (1) $$

where t is temperature in °C., to give $a = 0.21618$, $b = -6.786 \times 10^{-4}$ and $c = -2.910 \times 10^{-6}$. The values of ${}_sE^\circ(m)$ thus calculated and smoothed by Equation 1 are given in the third column. These were converted to standard potentials on the mole fraction scale, ${}_sE^\circ(N)$, and are recorded in the fourth column.

The standard potential, ${}_uE^\circ(m)$, of the cell with water as solvent was calculated at each temperature by the equation:

$$ {}_uE^\circ(m) = {}_uE + 2k \log \gamma m, \qquad (2) $$

where the value of ${}_uE$, the e.m.f. of the cell with 0.01m HCl, is taken from Table 1c, and the value of γ, the activity coefficient of hydrochloric acid, is taken from the work of Bates and Bower (*4*), whose values agree well with those of Harned and Ehlers (*7*). These standard potentials can also be represented by Equation 1 with $a = 0.21914$, $b = -6.714 \times 10^{-4}$ and $c = -2.797 \times 10^{-6}$. The smoothed potentials expressed on the mole fraction scale, ${}_uE^\circ(N)$, are given in the fifth column of Table II.

The relative partial molal quantity $\Delta G^\circ = F[{}_uE^\circ(N) - {}_sE^\circ(N)]$ is the change in free energy when a mole of hydrochloric acid is transferred from its hypothetical standard state in water to the corresponding state in 5% mannitol. It is thus a measure of the medium effect when the transfer occurs without the interference of interionic forces. The corresponding relative partial molal enthalpy and entropy changes are given by:

$$ \Delta H^\circ = -T^2 \frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{T}\right), \quad \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T. $$

Values of these functions are given in the last three columns of Table II.

There is a small but significant difference between mannitol and sorbitol in the effect which they have on the standard potential of the Ag-AgCl electrode. At 25° C. the standard potential in 5% mannitol is found to be 0.21950v. From the data (2 cells only) in Table Ib we estimate the standard potential of the sorbitol cell to be 0.18 mv. higher, i.e., 0.21968v. [This is somewhat lower than the value 0.22013v. found by Crockford and coworkers (*6*) in the same solvent].

Viewed in terms of the quantity ΔG°, discussed above, we find the value 54 j. mole^{-1} for HCl in 5% mannitol, compared with 37 j. mole^{-1} calculated from our measurements in 5% sorbitol. Paabo and Robinson (*12*) have reported 0.21948v. for the standard potential of the Ag-AgCl electrode in 5% mannitol and a ΔG° value of 47 j. mole^{-1} based upon the value ${}_uE^\circ(m) = 0.22234$v. as given by Bates and Bower (*4*) and not 0.22244, the value obtained from Equation 2 and used in the present calculation.

A further comparison may be made with 8 j. mole^{-1} for the transfer of a mole of sodium chloride from water to 5% mannitol (*9*) and 5 j. mole^{-1} for the corresponding transfer of potassium chloride (*11*).

LITERATURE CITED

(1) Akerlöf, G., *J. Am. Chem. Soc.* **54**, 4125 (1932).

(2) Bates, R.G., "Electrometric pH Determinations," John Wiley, New York, 1954.

(3) Bates, R.G., and coworkers, *J. Chem. Phys.* **25**, 361 (1956).

(4) Bates, R.G., Bower, V.E., *J. Res. Natl. Bur. Std.* **53**, 283 (1954).

(5) Bower, V.E., Robinson, R.A., *Ibid.* **67**, 1540 (1963).

(6) Crockford, H.D., Alley, B.J., Patterson, C.S., *J. Elisha Mitchell Sci. Soc.* **73**, 284 (1957).

(7) Harned, H.S., Ehlers, R.W., *J. Am. Chem. Soc.* **55**, 2179 (1933).

(8) Harned, H.S., Morrison, J.O., *Am. J. Sci.* **33**, 161 (1937).

(9) Kelly, F.J., Robinson, R.A., Stokes, R.H., *Ibid.* **65**, 1958 (1961).

(10) Robinson, R.A., Stokes, R.H., *J. Phys. Chem.* **65**, 1954 (1961).

(11) Robinson, R.A., Stokes, R.H., *Ibid.* **66**, 506 (1962).

RECEIVED for review January 13, 1964. Accepted March 25, 1964.