Nature of the Interaction Coefficients.—No attempt appears to have been made to correlate observed ion-exchange interaction coefficients with known physical properties of ions. If such correlations exist they may be of significance in themselves and will be of value in permitting the calculation of mixed resin activity coefficients from pure activity coefficients. In Table VI are listed the experimentally measured values of α_{12} and those calculated using the empirical equation

$$|\alpha_{12}| = (r_1 - r_2/2)^3 \qquad (12)$$

where r_1 and r_2 refer to the crystal radii in ångströms of the two cations that compose the system. The two values agree fairly well over a considerable range. The most surprising fact about equation 12 is that crystal radii in ångströms give the value for the interaction coefficients needed in general equations 6 and 7. Since the interaction coefficients have the dimensions of liters per equivalent it is obvious that other terms are required in equation 12. The important implication does remain, however, that a knowledge of the osmotic coefficients of the pure salt forms probably will permit the ultimate calculation of monovalent ion selectivities for cross-linked exchangers.

TABLE VI

COMPARISON OF CALCULATED AND MEASURED α_{12} VALUES

System	Experimentally measured α_{12}	Calcd. $\lvert\alpha_{12}\rvert$ by eq. 12	System	Experimentally measured α_{12}	Calcd. α_{12} by eq. 12
Cs–Li	+0.16–0.18[a]	0.162	K–Na	+0.02	0.0068
Cs–Na	+ .052	.052	Cs–NH_4	+ .00346	.0012
Ag–Na	− .0066	.004	Na–Li	− .005	.005
Ag–H	+ .045[a]	.045	NH_4–Na	+ .0176	.0186
Ag–Cs	− .0095	.0099			

[a] α_{12} values calculated from measured values of α_{21} using equations 10 and 11.

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OAK RIDGE, TENN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The Hydrogen Electrode–Silver Chloride Electrode System at High Temperatures and Pressures[1]

BY M. H. LIETZKE

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A knowledge of the behavior of the hydrogen electrode at high temperatures and pressures will ultimately afford a means of measuring the *p*H of aqueous solutions above 100°. In the present paper it is shown how calculated curves can be plotted demonstrating the behavior of the hydrogen electrode–silver chloride electrode system at temperatures up to 250° and pressures up to 40 atmospheres. The agreement between calculated potentials, which are based on extrapolation of data obtained at lower temperatures, and experimental data obtained directly at the higher temperatures is shown and discussed. A mechanism is proposed to account for deviations between the calculated and experimental values at the higher temperatures and pressures.

Introduction

The behavior of the hydrogen electrode at high temperatures and pressures is of considerable importance since it will ultimately afford a means of measuring the *p*H of solutions above 100°. When the hydrogen electrode itself cannot be used in *p*H measurements, for example in solutions where the hydrogen gas might cause chemical reduction, other electrodes, such as metal, metal oxide or special glass electrodes, could be calibrated against the hydrogen electrode in stable solutions. In the present paper it is shown how a series of calculated curves can be plotted demonstrating the behavior of the hydrogen electrode–silver chloride electrode system at high temperaures and pressures in hydrochloric acid solution. The agreement between the calculated values and the experimental data of Choudhury and Bonilla[2] is also shown and discussed.

Theoretical

E^0 of the Electrode System.—In order to obtain E^0 values at temperatures above 100° the E^0 values obtained by Harned and Ehlers[3] for the hydrogen electrode–silver chloride electrode system were extrapolated. The equation used was

$$E^0 = 0.22239 - 645.52 \times 10^{-6}(t - 25) - 3.284 \times 10^{-6} (t - 25)^2 + 9.948 \times 10^{-9}(t - 25)^3 \quad (1)$$

where t is the temperature in degrees centigrade. Equation 1 was derived from data obtained between 0 and 60°. At 95° the E^0 value calculated agrees with the experimental value to within 0.1 mv. The value of E^0 decreases from 0.22239 v. at 25° to 0.02603 v. at 250°.

The Activity Coefficient of HCl at High Temperatures.—The mean ionic activity coefficient of hydrochloric acid was calculated by two methods. In the first method equation 2 was integrated over the interval from 0° to the desired temperature.

$$\left(\frac{\partial \ln \gamma\pm}{\partial T}\right)_m = -\frac{\bar{L}_2(T)}{\nu R T^2} \qquad (2)$$

$\bar{L}_2$ is the partial molal heat content of HCl in a solution of the specified concentration. The equation was solved only for a solution of HCl which was 0.01689 *m* at 25°. This value was taken so that a direct comparison could be made between the calculated potential values and the experimental values of Choudhury and Bonilla.

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[1] This paper is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] R. N. Choudhury and C. F. Bonilla, thesis submitted by R. N. Choudhury in partial fulfillment of the requirements for the degree of Master of Science, Columbia University, May 1, 1952.

[3] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933).

Equation 3 showing the temperature dependence of $\bar{L}_2$ was taken from Harned and Owen[4]

$$L_2(T) = \bar{L}_2(0) + \alpha(T - 273) + \beta(T - 273)^2 \quad (3)$$

Equation 3 is based on e.m.f. data taken from 0 to 60°. When equation 3 was substituted into equation 2 and the integration performed equation 4 was obtained

$$\nu \ln \frac{\gamma\pm}{\gamma\pm_0} = \left[\frac{\bar{L}_2(0)}{273RT} + \frac{273\beta - \alpha}{RT} + \frac{\beta}{R}\right](273 - T) + \left[\frac{546\beta - \alpha}{R}\right] \ln \frac{T}{273} \quad (4)$$

For 0.01689 *m* HCl $\alpha = 1.22$, $\beta = 0.004$, $\bar{L}_2(0) = 49$, and $\gamma\pm_0$, the $\gamma\pm$ at 0°, is 0.8870.[4] When these values were substituted into equation 4 and the conversion made to common logarithms equation 5 was obtained

$$\log \gamma\pm = 5.408 \times 10^{-3}\,\frac{T - 273}{T} - 4.370 \times 10^{-4}(t - 273) + 0.2426 \log T - 0.6431 \quad (5)$$

Equation 5 was solved to give activity coefficients at 25° intervals between 25 and 250°.

Activity coefficients were also calculated by solving the Debye–Hückel equation in the form

$$-\log \gamma\pm = \frac{1.8123 \times 10^6\sqrt{C}}{(DT)^{3/2}} \cdot \frac{1}{1 + 50.288 \times 10^8(DT)^{-1/2}a_i\sqrt{C}} \quad (6)$$

The value of a_i was taken as 5×10^{-8} cm. at all temperatures. Although this is probably not correct a twofold variation in a_i affects the value of $\gamma\pm$ by less than 1%. Wyman's[5] equation was used to calculate the change in the dielectric constant of water with temperature. This equation is

$$D = 78.54[1 - 0.00460(t - 25) + 0.0000088\,(t - 25)^2] \quad (7)$$

The decrease in the molar concentration of the HCl with increasing temperature was calculated by assuming the density of the solution changed in the same manner as did pure water. Equation 6 was solved to give activity coefficients at 25° intervals between 25 and 250°.

Table I shows values of the activity coefficients of an HCl solution 0.01689 *m* at 25° calculated by the two different methods.

TABLE I

THE ACTIVITY COEFFICIENT OF AN HCl SOLUTION 0.01689 *m* AT 25°

t, °C.	$\gamma\pm$ from $\bar{L}_2$ data	$\gamma\pm$ from D.-H. equation	*t*, °C.	$\gamma\pm$ from $\bar{L}_2$ data	$\gamma\pm$ from D.-H. equation
25	0.8835	0.8827	150	0.8519	0.8472
50	.8802	.8774	175	.8428	.8400
75	.8748	.8710	200	.8331	.8348
100	.8680	.8636	225	.8228	.8325
125	.8604	.8555	250	.8123	.8356

Up to 200° the activity coefficients calculated by the two methods differ by no more than 0.6% which causes a maximum variation in the calculated potentials of 0.4 mv. At 250° the discrepancy becomes 2.5 mv. It is to be noted that activity coefficients calculated by the Debye–Hückel equation pass through a minimum. Since the dielectric constant of water decreases much more slowly at higher temperatures, values of the *DT* product pass through a minimum; this behavior is then reflected in the values of the activity coefficient of the HCl.

Since the two methods gave activity coefficients which agreed so closely one method could be discarded in the subsequent calculations. The activity coefficients used were calculated by use of the Debye–Hückel equation.

The Fugacity of the Hydrogen.—The partial pressure of the hydrogen in the system was obtained at each temperature and pressure merely by taking the difference between the total pressure on the system and the vapor pressure of water at the given temperatures. It was assumed that the vapor pressure of the dilute HCl solution did not differ appreciably from that of water at the same temperature. The hydrogen pressures were then converted to fugacities using the data of Deming and Shupe[6] assuming the water vapor does not affect the H_2 fugacity. At the highest hydrogen partial pressures the correction amounted to about 3%.

Calculation of the Potentials by Means of the Nernst Equation.—When the hydrogen electrode is used in conjunction with the silver chloride electrode the cell reaction is

$$^1/_2H_2 + AgCl \rightleftharpoons Ag + H^+ + Cl^-$$

In this case the potential of the cell combination is given by the Nernst equation in the form

$$E = E^0 - \frac{RT}{F} \ln \frac{(m\gamma\pm)^2}{p'^{1/2}} \quad (8)$$

where p' is the fugacity of the hydrogen. Equation 8 was solved at 25° intervals from 25 to 250° at total pressures of 1, 7.80, 18.01 and 41.82 atmospheres. The resulting curves are shown in Fig. 1. The experimental data of Choudhury and Bonilla are also plotted on the same figure. The potentials decrease at the higher temperatures because at a constant total pressure the fugacity of the hydrogen in the system decreases with increasing temperature.

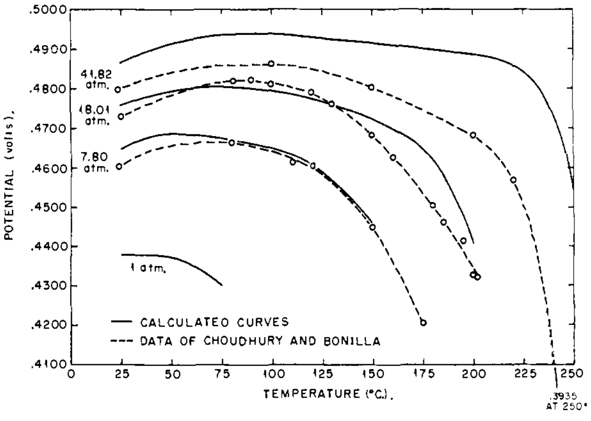

Fig. 1.

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[4] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950.

[5] J. Wyman, Jr., *Phys. Rev.*, **35**, 623 (1930).

[6] W. E. Deming and L. E. Shupe, *ibid.*, **40**, 848 (1932).

Discussion

From Fig. 1 it can be seen that the calculated and experimental potentials differ at 7.80 and 18.01 atm. total pressure by no more than a few millivolts up to 150°. This is probably within experimental error. At higher temperatures the deviation becomes as large as 10 mv. The experimental points at 41.82 atm. total pressure are lower than the calculated curve by 6 to 10 mv. up to 150° and then drop increasingly farther below the calculated curve until the value at 250° is 58 mv. below the calculated value.

Two possible explanations of the discrepancy between the calculated and experimental potentials at the higher temperatures and pressures are: (1) Hydrogen reduction of part of the AgCl of the Ag, AgCl electrode. This would increase the acid concentration and hence lower the potential of the system. Also the silver thus formed could poison the platinum electrode.

(2) A lowering of the silver chloride electrode potential by hydrogen. The fact that this effect can be very appreciable was experimentally demonstrated by Choudhury and Bonilla.[2] The mechanism of the potential lowering would probably involve the extablishment of hydrogen electrode sites on the silver metal of the silver, silver chloride electrode. This effect would be most pronounced at higher temperatures at constant pressure and at higher hydrogen pressures at constant temperature. Figure 1 shows that the deviations between the experimental and calculated values are in these directions.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OREGON STATE COLLEGE]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. IV. Kinetics of the Catalyzed S^{35}-Exchange between Thionyl Chloride and Sulfur Dioxide[1]

BY B. J. MASTERS[2] AND T. H. NORRIS

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Extending earlier work, a study has been made of the kinetics of the chloride-catalyzed S^{35} exchange reaction between liquid sulfur dioxide and thionyl chloride. Whereas rubidium and tetramethylammonium chlorides are effective catalysts, acid chlorides (aluminum and hydrogen chlorides) are found to be far less, if at all, active. A basic catalysis by chloride ion is proposed. Experiments both in excess sulfur dioxide and in excess thionyl chloride indicate the rate law Rate $= k_3$ (catalyst)($SOCl_2$)(SO_2). With tetramethylammonium chloride in excess sulfur dioxide the rate constant is about 0.06 l.^{2} mole^{-2} hr.$^{-1}$ (0°), while rubidium chloride gives *ca.* 0.03 l.^{2} mole^{-2} hr.$^{-1}$; in a large excess of thionyl chloride tetramethylammonium chloride gives about 0.22 l.^{2} mole^{-2} hr.$^{-1}$. For these three systems, activation energies are, respectively, 14.7, 14.7 and 13.6 kcal./mole and entropies of activation are -28.1, -29.5, and -29.6 cal. deg.$^{-1}$ mole^{-1}. A mechanism for the reaction is suggested. Comparison with the thionyl bromide–sulfur dioxide exchange reveals that, whereas the latter system shows, with tetramethylammonium bromide, a comparable activation energy of 13.2 kcal./mole, the rate is only about one-seventh as great as in the present case, possibly explicable in terms of a greater basicity for chloride than for bromide ion.

Whereas in pure liquid sulfur dioxide, thionyl halides do not exchange S^{35} at a significant rate with the solvent,[3] similar solutions containing certain soluble halide salts exhibit a rapid exchange. This observation, previously reported, led to an investigation of the kinetics of the catalysis involving the solute thionyl bromide.[4] The present research consists of a study of the kinetics of the catalyzed exchange reaction in the related thionyl chloride–sulfur dioxide system. The experiments, more extensive than the earlier ones, include results for solutions over the entire range from excess sulfur dioxide to excess thionyl chloride.

Experimental

Techniques were generally similar to those of previous work.[3,4] Radiosulfur, S^{35}, was obtained from the Atomic Energy Commission in the form of neutron-irradiated potassium chloride. Samples were counted as thin deposits of barium sulfate with an end window counter, all appropriate corrections being applied. In general, planchets were prepared and counted in duplicate.

Preparation of Reactants.—**Sulfur dioxide** was purified as previously described.[4] In addition a final rough fractional distillation of the liquid was done (*in vacuo*), only the middle third being retained.

Labeled sulfur dioxide was prepared as previously described,[5] and was generally shaken with concentrated sulfuric acid and then passed through phosphorus pentoxide. The resulting high specific activity material was either used directly to prepare labeled thionyl chloride, or was diluted several hundredfold with inactive sulfur dioxide to *ca.* 1000 c./min./mg. (as $BaSO_4$).

Thionyl chloride (Matheson, Coleman and Bell, b.p. range 75–76°) was distilled successively from quinoline and boiled linseed oil.[6] The resulting clear, colorless product was fractionated in the vacuum system, the middle third being collected in sealed glass tubes provided with break tips, in which it was stored in darkness until used.

Labeled thionyl chloride was prepared by an exchange, in which 100 mmoles of inactive material, 10 mmoles of high activity dioxide, and 3 mmoles of tetramethylammonium chloride catalyst were left together in a sealed tube in darkness for three days at room temperature. The volatile material, after complete distillation from the catalyst, was then fractionated in the vacuum system, the middle third, about 4 ml., being retained and diluted about tenfold with inactive thionyl chloride to give a final specific activity of *ca.* 4,000 c./min./mg. Traces of $S^{35}O_2$ left by this procedure were almost completely eliminated by a process of further fractionation, used in filling the exchange bombs.

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[1] Presented before the Physical and Inorganic Division of the American Chemical Society in New York, September, 1954. Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 259, Department of Chemistry, School of Science.

[2] Taken from the thesis of B. J. Masters, submitted in partial fulfillment of the requirements for the Ph.D. degree, at Oregon State College, June, 1954.

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