

Relative Partial Molal Heat Content and Heat Capacity.—Values of the relative partial molal heat content, \bar{L}_2 , computed from the data in Table I, have been expressed by the equation

$$\bar{L}_2 = \alpha + \beta T^2 \quad (4)$$

α and β are related to the constants in Table I by the expressions

$$\alpha = -23,074[(E_{25} - E_{6(25)}) - 298.1(a - a_0) + 88,864(b - b_0)] \quad (5)$$

$$\beta = 23,074[b - b_0] \quad (6)$$

respectively.³ \bar{L}_2 is in calories. α and β were smoothed by a graphical method. The fourth and fifth columns of the table contain the values obtained for \bar{L}_2 and $(\bar{C}_p - \bar{C}_p)$ at 25°.

TABLE III
PARAMETERS OF EQUATIONS (4) AND (7)
 \bar{L}_2 and $(\bar{C}_p - \bar{C}_p)$ at 25°

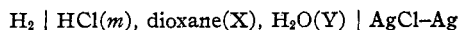
<i>m</i>	$-\alpha$	β	$\bar{L}_2(25)$	$(\bar{C}_p - \bar{C}_p)_{25}$
0.001	5190	0.0752	1493	44.8
.0015	5710	.0824	1612	49.1
.002	6550	.0930	1714	55.4
.003	7800	.1082	1815	64.5
.005	9240	.1258	1939	75.0
.007	10100	.1364	2021	81.3
.01	10500	.1418	2101	84.5
.015	10860	.1468	2185	87.5
.02	11000	.1488	2223	88.7
.03	11120	.1510	2298	90.0
.05	11240	.1538	2427	91.7
.07	11360	.1560	2503	93.0

(3) Harned and Thomas, *THIS JOURNAL*, **58**, 761 (1936); Harned and Donelson, *ibid.*, **60**, 339 (1938).

0.1	11480	0.1589	2640	94.7
.15	11630	.1624	2802	96.8
.2	11860	.1666	2945	99.3
.3	12200	.1742	3280	103.9
.5	12830	.1880	3876	112.1

Summary

1. Measurements of the electromotive forces of the cells



have been reported in 82% dioxane mixtures which possess a dielectric constant of approximately 10. The measurements cover an acid concentration range 0.001 to 0.5 *M*, and were obtained at 5° intervals from 5 to 45°. Their accuracy is of the order of ± 0.2 mv.

2. From these results and the standard potentials previously evaluated,² the activity coefficient, relative partial molal heat content and heat capacity have been evaluated. These results have an accuracy relative to a concentration where the electromotive force was measured comparable to that obtained with mixtures of higher dielectric constant. The greatest uncertainty lies in the estimation of the standard potentials. The extent of the error involved in the required extrapolation cannot be estimated accurately from our present knowledge. A general summary and critique of the thermodynamics of all these mixtures will be given in another communication.

NEW HAVEN, CONN.

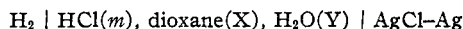
RECEIVED SEPTEMBER 13, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. X. General Summary and Critique

BY HERBERT S. HARNED, JOHN OWEN MORRISON, FLETCHER WALKER, JOHN G. DONELSON AND CALVIN CALMON

Our earlier contributions¹⁻¹² to this series contain the measurements of the electromotive forces of the cells



- (1) *Am. J. Sci.*, **33**, 161 (1937).
- (2) *THIS JOURNAL*, **58**, 1908 (1936).
- (3) **60**, 334 (1938).
- (4) **60**, 336 (1938).
- (5) **60**, 339 (1938).
- (6) **60**, 2128 (1938).
- (7) **60**, 2130 (1938).
- (8) **60**, 2133 (1938).
- (9) **61**, 44 (1939).
- (10) **61**, 48 (1939).
- (11) Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).
- (12) Owen and Waters, *ibid.*, **60**, 2371 (1938).

containing solvent mixtures of 20, 45, 70 and 82% dioxane, which correspond roughly to values of the solvent dielectric constant of 60, 40, 20 and 10, respectively. The measurements were carried out over as wide ranges of concentration of acid as was found practical and at 5° temperature intervals from 0 to 50°. All these results possess an accuracy comparable to that obtainable in aqueous solutions. In the previous communications, detailed descriptions of the technique,^{1,2} methods of extrapolation,^{2,4,7,9} and methods of computing the thermodynamic properties^{5,6,8,10} have been reported. In addition, the dielectric constant of

the mixtures,¹¹ densities,³ and dilute solution conductances¹² have been measured.

Each of the above contributions contains some specialized part of the most comprehensive study yet made of the thermodynamic properties of a single electrolyte as a function of its concentration, the temperature and the dielectric constant. We have postponed a general discussion until all the measurements and specialized computations were complete. In addition to such a summary, the present communication contains a critique in which limits of experimental accuracy and uncertainties in the calculations will be discussed and if possible estimated. Such a discussion should serve as a basis for future progress.

Cell Measurements

The reproducibility of the cell measurements is ± 0.1 mv. with the exception of that obtained in 82% dioxane solutions which at some acid concentrations is ± 0.2 mv., and at 0.0006 and 0.001 molal acid in 70% dioxane mixtures where the error is of the order of 0.5 mv. The absolute accuracy will depend on the purity of the sample of dioxane. The dioxane after refluxing and distillation was purified by fractional freezing and the freezing point of all material used was within 12.76–12.78°. We doubt if the error caused by impurities in this material is greater than that of cell reproducibility. In any case, the values of the dielectric constant used were from measurements of the same material.

The ranges of acid concentrations reported are as follows: 20 and 45% dioxane, 0.003 to 3 *M*; 70% dioxane, 0.0008 to 1.5 *M*; 82% dioxane, 0.001 to 0.5 *M*. After considerable preliminary investigations, two kinds of silver chloride electrodes were selected, one made electrolytically and the other by heating a mixture of silver oxide and chlorate. At acid concentrations from 0.003 *M* and higher, both electrodes gave the same result. In general, however, those prepared from the chlorate were more reproducible in solutions containing acid at 0.01 *M* and less. No electrolytically prepared electrodes functioned properly in solutions containing less than 0.003 *M* acid, and neither electrode was reproducible at lower concentrations of acid than 0.0008 *M* although many attempts to obtain such results were made. Some measurements were made in 90% dioxane solutions at acid concentrations in the region of 0.01 to 0.1 *M* and found reproducible. But in this me-

dium, the ionization constant of the acid is of order of 10^{-8} and, consequently, results in the above region of high concentration do not appear to be particularly valuable.

We emphasize at this point that the principal criterion of accuracy has been the agreement of results at 25° before and after measurements were made at other temperatures. The cells were measured at one-half to one hour intervals over periods of time varying from twenty-four to sixty hours. Final readings at 25° agreed with initial readings to within the limits of error mentioned previously. Results consistent to within smaller limits (± 0.02 mv.) can be obtained at one temperature under conditions where the electrodes receive less severe treatment.

Extrapolations and Standard Potentials

The uncertainties involved in the extrapolations increase as the concentration of dioxane in the solvent mixture increases. Therefore, in summarizing the situation, it is best to discuss separately the results obtained in each medium.

1. In the case of the 20% dioxane mixtures, extrapolations which employed the Debye and Hückel limiting equation without the term for the mean distance of approach,² and the Gronwall-La Mer extension of this theory^{4,5} were made. Both methods gave practically the same result (within 0.2 mv.) for the standard potential. The Gronwall-La Mer method is considered the better and from all indications standard potentials in this medium are known to within 0.1 mv.

2. The extrapolations in the 45% dioxane mixtures by the two methods mentioned above^{2,4} differ from each other by a greater amount than in mixtures of higher dielectric constant. At 0° both extrapolations yielded the same value for the standard potentials while at 50° the extended theory led to a value 0.7 mv. lower. The values derived by the extended theory are unquestionably better and are believed to be correct to within 0.1 mv.

3. With the 70% dioxane mixtures, the extended theory⁷ yielded values from 2 to 3 mv. lower than the simple Debye and Hückel equation² and without question is the better method. The uncertainty of the extrapolation is greater than in the media of lower dioxane content but we do not believe it to be large. Although at present an exact numerical estimate of the error in the determination of the standard potential cannot be given,

we believe that it is not greater than 0.2 or 0.3 mv.

4. With the 82% mixtures, neither the Debye and Hückel nor the extended theory extrapolations can be used with a high degree of certainty, so that it became necessary to employ a method of extrapolation which utilized ionization data derived from conductance measurements. Too little is known about this method to estimate the accuracy of the determination of the standard potential. The results may be in error to the extent of a few millivolts. This situation will be difficult to improve since reliable results at concentrations of acid from 0.00001 to 0.001 M are extremely hard if not impossible to obtain.

Activity Coefficient

The behaviors of the activity coefficient in water and in the mixtures is illustrated in Fig. 1

where all the results at 25° are plotted. Further values at 0 and 50° in the cases of the 45 and 70% dioxane mixtures, and values at 5 and 45° in the case of the 82% mixtures are plotted. The straight lines represent the Debye and Hückel limiting law at 25°. The values of the limiting slopes throughout the temperature ranges employed are given in the earlier communications.^{2,9}

The effect of the increase of ionic association with decreasing dielectric constant is illustrated by the results in dilute solution. In water, the activity coefficient curve lies above the limiting slope at all concentrations. As the dielectric constant decreases, the activity coefficient plot in dilute solutions approaches the limiting plot of the interionic attraction theory until in the case of the 70% dioxane mixture it superimposes, at acid concentrations below 0.002 M , and in the

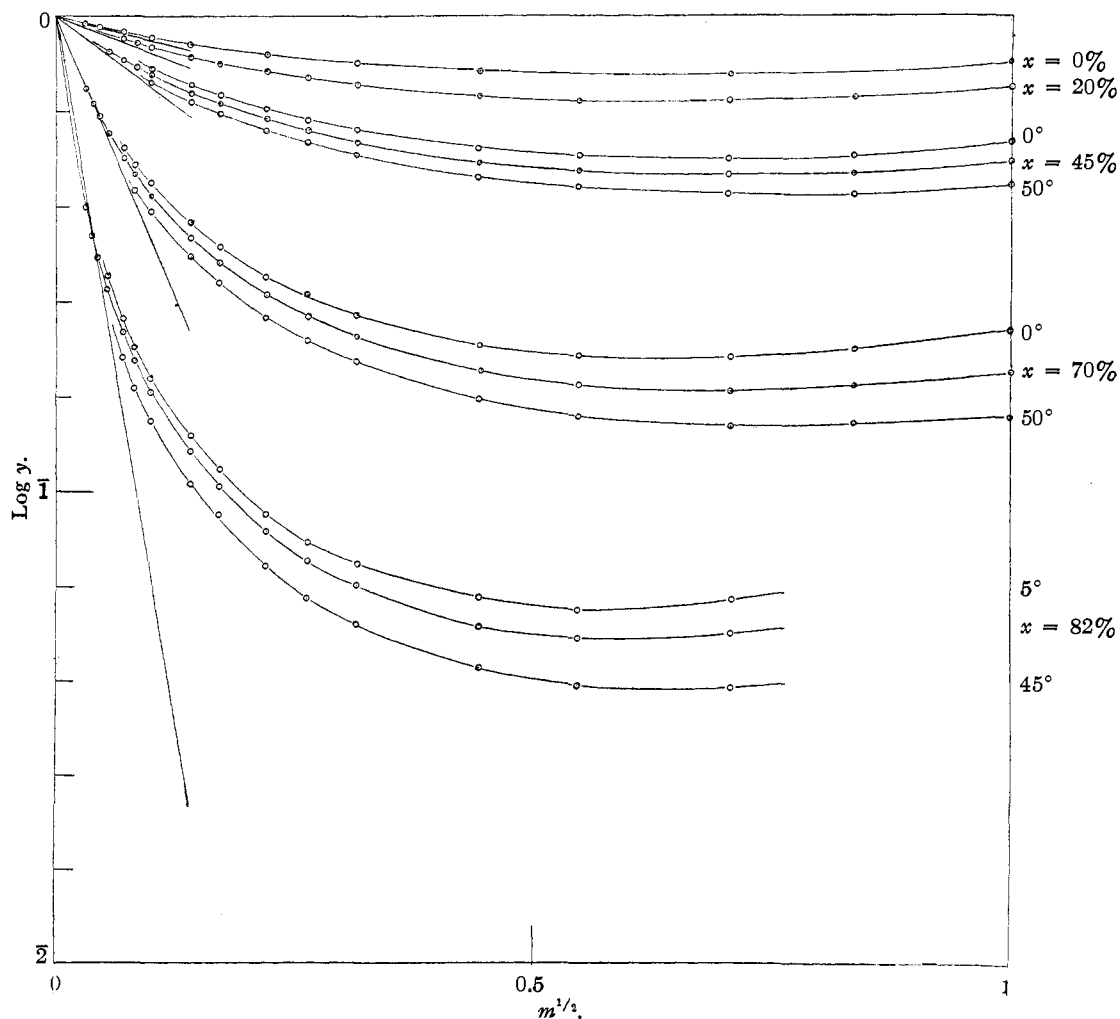


Fig. 1.—Activity coefficient,

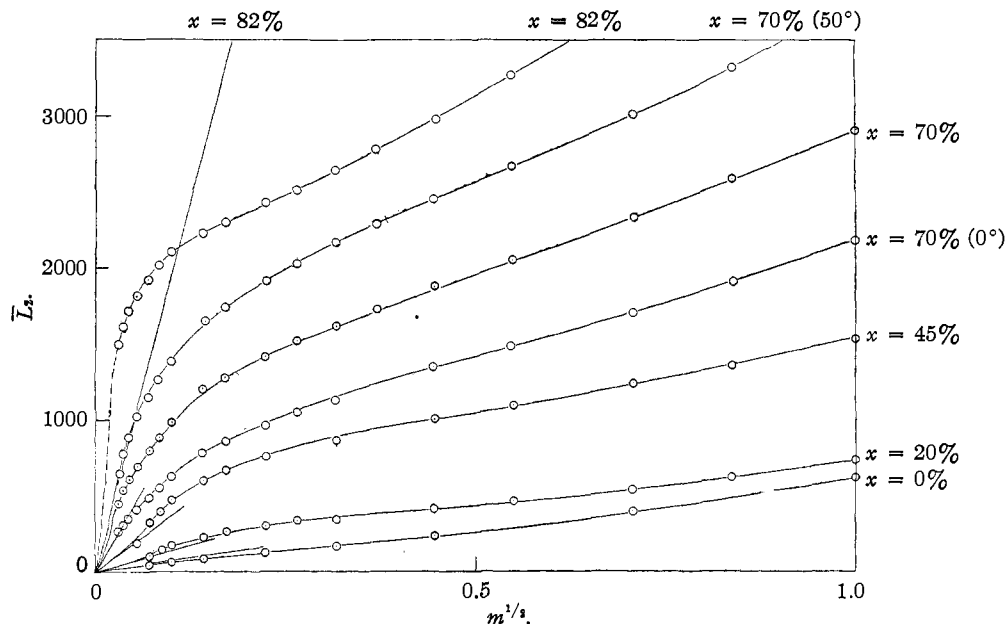


Fig. 2.—Relative partial molal heat content.

case of the 82% dioxane mixture, it lies slightly below the Debye and Hückel plot at 0.001 to 0.0015 M .

The activity coefficients of the acid at all concentrations and temperatures decrease with increasing temperature. Consequently, the relative partial molal heat content is always positive. In the more concentrated solutions, all these curves possess minima which are characteristic of strong electrolytes in aqueous solutions. Indeed, in spite of ionic association and the large effect of interionic attraction, minima appear in the plots of the 82% mixtures.

The Relative Partial Molal Heat Content

From the density data⁸ and the dielectric constant of the dioxane-water mixtures,¹¹ we have computed the limiting slopes of the relative partial molal heat content, \bar{L}_2 , from the theory of Debye and Hückel. According to this theory

$$\bar{L}_2 = u' \sqrt{c} = -\frac{3}{2} \frac{\omega}{D^{3/2} T^{1/2}} \left[1 + \frac{T}{D} \frac{dD}{dT} - \frac{1}{3} \frac{T}{c} \frac{dc}{dT} \right] \quad (1)^{13-15}$$

where

$$\omega = 2 \left(\frac{\pi^{1/2} e^3 N^{3/2} 2^{1/2}}{k^{1/2} 1000^{1/2}} \right) \quad (2)$$

Values of u' covering the temperature range under consideration are given in Table I.

In Fig. 2, the values of \bar{L}_2 at 25° for pure aque-

(13) Scatchard, *THIS JOURNAL*, **53**, 2037 (1931).

(14) Gatty, *Phil. Mag.*, [7] **11**, 1082 (1931).

(15) Harned and Ehlers, *THIS JOURNAL*, **55**, 2179 (1933).

TABLE I

	LIMITING SLOPES FOR \bar{L}_2 (CAL.)				
	$X = 0$	$X = 20$	$X = 45$	$X = 70$	$X = 82\%$
0	433	945	2480	7480	...
10	537	1147	2930	8940	14630
20	654	1364	3440	10570	17610
25	717	1485	3720	11470	19210
30	785	1605	4010	12410	20910
40	931	1872	4640	14450	24520
50	1090	2173	5340	16730	...

ous solutions and for all the dioxane mixtures are plotted against the square root of the acid concentration. The straight lines drawn from the origin represent values computed by equation (1). We note that there is an increasing tendency for the experimental curve to be higher than the limiting values in dilute solution as the dioxane content increases. The curves have similar characteristics. After the first rapid rise in dilute solution, their slope decreases and rises again as the solutions become more concentrated. The temperature effect is illustrated by the 70% mixtures for which curves are given at 0 and 50°.

The accuracy of this estimation of \bar{L}_2 has been discussed previously. The uncertainty of the extrapolation and, consequently, the values of \bar{L}_2 increase with increasing dioxane concentration. In the 82% mixtures, this may amount to a few hundred calories. The accuracy relative to a given concentration is better than this and is estimated to be of an order of less than 100 cal.

The Relative Partial Molal Heat Capacity

Values of the relative partial molal heat capacity of the acid at 25° in water and the dioxane-water mixtures are plotted against $m^{1/2}$ in Fig. 3. The straight lines represent the limiting equations of the theory of Debye and Hückel which were calculated from the data in Table I. Relative to a given concentration, these results are valid to within one to four calories. The extrapolation in the case of the 82% dioxane mixtures, represented by the dashed line, may be subject to a large error (~ 10 cal.). The large increase in this quantity with increasing acid concentration in the media of low dielectric constant is illustrated strikingly by these results. It is also interesting that, with the exception of the 82% mixtures, the slopes of these curves are of the same order of magnitude in the more concentrated solutions.

General Considerations

The determination of the mean distance of approach of the ions of the acid, a , is of interest. This was accomplished by employing the extended interionic attraction theory for the extrapolations and assuming that no other effect was present in the dilute acid solutions ($m < 0.01$). This method leads to higher values of " a " than the method which employs the interionic attraction equation with an additional linear term. Thus in aqueous solution Shedlovsky and MacInnes¹⁶ obtained 5.6 Å. for " a " by using the Debye and Hückel equation whereas Harned and Ehlers¹⁷ obtained 4.3 Å. by use of this equation with an additional linear term. Using the first method, we obtained 5.0, 5.4 and 5.6 Å. for " a " at 25° in the 20, 45 and 70% dioxane-water mixtures, respectively. Since this determination is very sensitive, there is no indication of a change in this quantity with dioxane content. In the case of the 82% mixtures, this method of evaluation of " a " is unsatisfactory. On the other hand, ionization constants from conductance measurements lead to a value of 6.0 Å. for " a " according to Bjerrum's

(16) Shedlovsky and MacInnes, *THIS JOURNAL*, **58**, 1970 (1936).

(17) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

theory of ionic association which agrees as well as could be expected with the above values. In general, there is little evidence that this parameter varies with temperature. In water, Harned and Ehlers obtained values nearly constant from 0 to 60°. In 20 and 45% dioxane solutions, " a " ap-

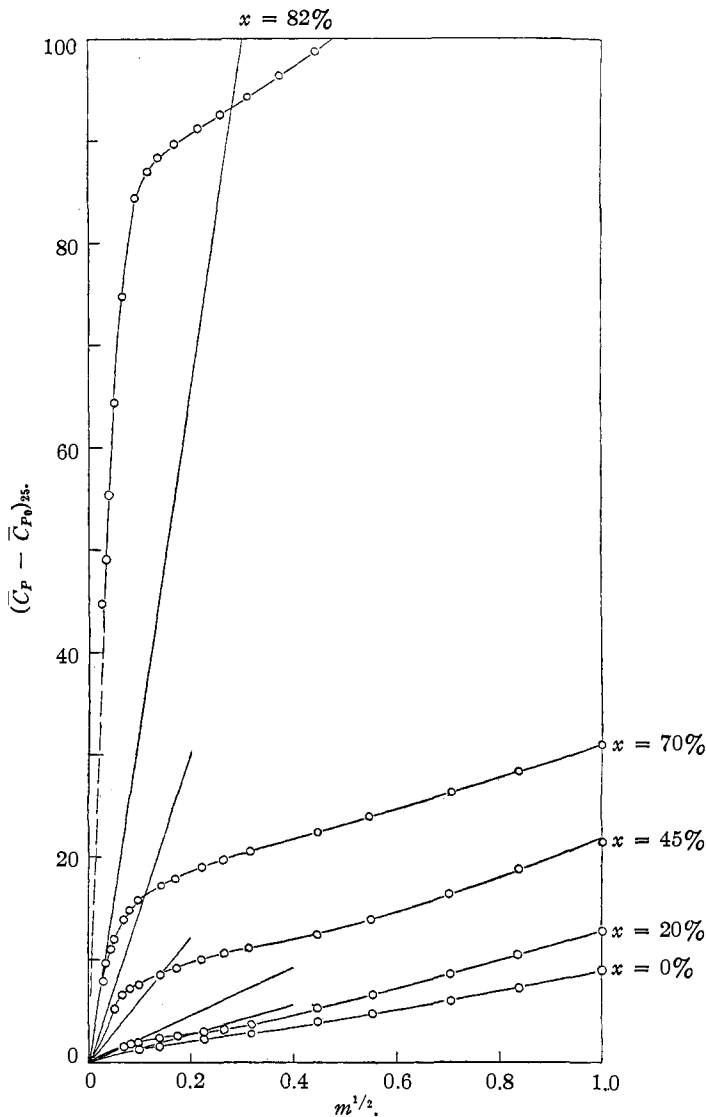


Fig. 3.—Relative partial molal heat capacity.

peared to decrease somewhat from 0 to 50° but we do not regard this as significant. In the 70% dioxane mixtures, a constant value of 5.6 Å. from 0 to 50° was suitable for extrapolation. Conductance measurements in the 82% dioxane mixtures indicate a slight decrease with temperature. From these results, it appears that any change in redistribution of the solvent molecules with the proton is not sufficient to cause the thermodynamic prop-

erties to vary much from those to be expected upon the basis of a constant value of " a_i ."

One of the very valuable results of this study is the knowledge of the standard potentials in these media of varying dielectric constant since they may be used for the accurate determination of the ionization constants of weak electrolytes according to the method employed in this Laboratory.^{18,19} For purposes of convenience, the following equations for the standard potentials which summarize all these results are given below.

$$\begin{aligned}
 X = 0; E_0 &= 0.22237 - 639.64 \times 10^{-6}(t - 25) - \\
 &\quad 3.181 \times 10^{-8}(t - 25)^2 \\
 X = 20; E_0' &= 0.20303 - 760.5 \times 10^{-6}(t - 25) - \\
 &\quad 3.70 \times 10^{-8}(t - 25)^2 \\
 X = 45; E_0' &= 0.16352 - 1135 \times 10^{-6}(t - 25) - \\
 &\quad 3.70 \times 10^{-8}(t - 25)^2 \\
 X = 70; E_0' &= 0.06395 - 1767 \times 10^{-6}(t - 25) - \\
 &\quad 3.70 \times 10^{-8}(t - 25)^2 \\
 X = 82; E_0' &= -0.0413 - 2370 \times 10^{-6}(t - 25) - \\
 &\quad 8.80 \times 10^{-8}(t - 25)^2
 \end{aligned}$$

These have a range of validity from 0 to 50° inclusive. The uncertainties involved in these values have been discussed previously.

(18) Harned and Ehlers, *THIS JOURNAL*, **54**, 1350 (1932).

(19) Owen, *ibid.*, **56**, 24, 1695 (1934).

Summary

1. The thermodynamic properties of hydrochloric acid in dioxane-water mixtures covering a temperature from 0 to 50° and a dielectric constant range from 80 to 9 have been summarized and discussed. This is the most comprehensive study of such properties of a single electrolyte as a function of the electrolyte concentration, temperature and dielectric constant.

2. The results and calculations have been submitted to a critical survey. The ranges of acid concentration, temperature and dielectric constant within which accurate results may be obtained with the electrodes employed have been determined. Experimental errors have been estimated, and uncertainties in the extrapolations pointed out.

3. The results have been discussed in relation to the extended interionic attraction theory and Bjerrum's theory of ionic association.

4. Equations for the standard potentials of the cells $H_2 | HCl(m), \text{dioxane}(X), H_2O(Y) | AgCl-Ag$ in media containing 0, 20, 45, 70 and 80% dioxane are given.

NEW HAVEN, CONN.

RECEIVED SEPTEMBER 13, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 660]

A Comparative Method of Measuring Vapor Pressure Lowering with Application to Solutions of Phenol in Benzene

BY EDWIN N. LASSETTRE AND ROSCOE G. DICKINSON

Dilute solutions of many organic compounds in inert solvents have properties which may be explained on the basis of equilibria between the un-polymerized solute and polymers of all orders.¹ These solutions have been investigated either by studying the lowering of the freezing point, raising of the boiling point, or by studying the distribution of solute between water and the inert solvent. The first two of these methods do not permit a study to be made over an arbitrary temperature range; moreover, the determinations are not isothermal. The results from the third method are often difficult to interpret because of reaction of the solute with water which has been demonstrated in some cases to have an important influence on the equilibrium.²

(1) Lassettre, *THIS JOURNAL*, **59**, 1383 (1937); *Chem. Rev.*, **20**, 259 (1937).

(2) Szyzkowski, *Z. physik. Chem.*, **131**, 175 (1927); Cohen and Sabaro Miyake, *ibid.*, **119**, 247 (1926); Cohen and Van Dobbentburgh, *ibid.*, **118**, 37 (1925).

These objections are overcome by studying the distribution of a volatile solvent between two non-volatile solutes; one solute is the substance under investigation and the other, a comparison substance of known behavior. The procedure consists in preparing two solutions of the different solutes and connecting them through the vapor phase. Solvent then distills from the solution of high vapor pressure to the solution of low vapor pressure. The distillation is followed by measuring the volumes of the two solutions; the equilibrium volumes are determined by approach from both sides. This principle has been used by other investigators for special purposes³ but the methods employed were not well adapted to our needs.

Apparatus and Experimental Procedure.—The essential features of the apparatus are shown in Fig. 1. Solutions are introduced through the tubes H, a solution containing

(3) Barger, *J. Chem. Soc.*, **87**, 1042 (1905); Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).