the molecular weight of triphenylmethane in sulfur monochloride. Application of the formula $K = 0.02\,T^2/L$, in which K is the molecular elevation, T the boiling point on the absolute scale and L the heat of vaporization (63.9) gives the value 52.9 which substantiates that of the above investigators.

Summary

1. The vapor pressure of sulfur monochloride has been determined through the temperature range 0° to its boiling point. The equation for the corresponding curve is $\log P = (7.4550) - (1880.1/T)$.

2. Sulfur monochloride is a stable, well-defined compound at these and intermediate temperatures.

3. The heat of vaporization has been determined and found to be at variance with previously reported values.

4. The molecular elevation agrees with that calculated from boiling-point data by other investigators.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 182]

THE IONIZATION OF WEAK ELECTROLYTES

BY D. A. MACINNES

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Arrhenius' theory that the degree of ionization can be obtained from the conductance ratio, Λ/Λ_0, is now quite generally conceded to be untrue for strong electrolytes, since it involves the assumption that the mobilities of the ions do not change from infinite dilution to the concentration in question. The properties of a large group of strong electrolytes can, in fact, be most readily explained by the theory that they are completely ionized. The decrease in the value of the equivalent conductance with concentration is, almost certainly, due to decrease in the ionic mobilities, caused by an inter-ionic attraction which steadily gains strength as the concentration increases. If, therefore, Arrhenius' method for computing the degree of dissociation is not valid for strong electrolytes, it seems improbable that it can be used without modification for weak electrolytes since, as will be shown below, the ion concentrations can attain values large enough to cause appreciable changes in the mobilities of the ions.

It has appeared to me, however, that a more nearly correct degree of dissociation can be obtained by comparing the measured equivalent conductance with that of an equivalent of the ions *at the same ion concentration*, a quantity which will be represented by Λ_e. Thus the degree of dissociation of acetic acid at 0.01 N may be computed by dividing the Λ value for that concentration by the equivalent conductance of completely dissociated acetic acid at the ion concentration existing in the 0.01 N solution. Now if solutions of hydrogen chloride, sodium chloride and sodium acetate are all completely dissociated, Λ_e for acetic acid can be computed by the simple relation $\Lambda e_{\mathrm{HAc}} = \Lambda_{\mathrm{HCl}} - \Lambda_{\mathrm{NaCl}} + \Lambda_{\mathrm{NaAc}}$, the Λ values all being interpolated for the ion concentration of the solution under consideration. This involves a short series of approximations since the value of Λ_e for the solution must be known before the value of the ion concentration, $C{\cdot}\Lambda/\Lambda_e$, can be obtained. Plots of Λ as ordinates against $C^{1/2}$ as abscissas were found useful for this interpolation as they give nearly straight lines.

If degrees of dissociation, α, calculated from the relation Λ/Λ_e are substituted in the familiar Ostwald dilution law, $K' = \alpha^2C/(1-\alpha)$, the values of K' are found to increase with the concentration. This is shown in Col. 5 of Table I, which is based on Kendall's[1] excellent conductance work. However, it must be recalled that although the product $C{\cdot}\Lambda/\Lambda_e$ gives the correct concentrations of the ions, and $(1-\Lambda/\Lambda_e)C$ that of the undissociated portion, each of these must be multiplied by the appropriate activity coefficient if the law of mass action is to hold. The modified Ostwald dilution law thus becomes,[2] for the acid HA

$$K = \frac{\alpha\gamma_{\mathrm{H}^+} \cdot \alpha\gamma_{\mathrm{A}^-} \cdot C}{(1-\alpha)\ \gamma_{\mathrm{HA}}}.$$

For the undissociated portion the activity coefficient, γ_{HA}, has been assumed to be unity, except as mentioned below, since this portion of the solute carries no charge and is otherwise similar to substances that are nearly perfect solutes in aqueous solution, at least at moderate concentrations. The activity coefficients of the ions γ_{H^+} and γ_{A^-} would be expected to change with ion concentration in very nearly the same manner that the activity coefficients of hydrochloric acid solutions vary with the *total* concentration, since the latter substance is completely dissociated. The mean activity coefficients γ have been computed from the Debye-Hückel limiting equation $-\log \gamma = 0.5\sqrt{C}$ with the exception of values at the higher ion concentrations which were interpolated from the values given by Scatchard.[3] The last column of the table gives values of the expression: $K = \alpha^2\gamma^2C/(1-\alpha)$. With the possible exception of the figures for acetic acid, the value of K is substantially the same throughout the range of concentrations, being more nearly constant in the more concentrated solutions of the stronger acids where the "ionization constant" computed on the Arrhenius assumptions changes rapidly with the concentration. The agreement of the theory with the computations is the more striking

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[1] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

[2] After the computations for this paper were completed I learned that Sherrill and Noyes had independently arrived at this equation, in a paper at that time unpublished.

[3] Scatchard, THIS JOURNAL, **47**, 641 (1925).

because in each case an error in any one of four series of conductance measurements will affect the value of the constant. Furthermore the constant K is the only empirical constant obtained from the data. Kendall's[4] computations involve two empirical constants, namely, the value of Λ_0 and the "ionization constant," and even so, the equation based on Arrhenius' assumption fails to fit the data for the stronger acids and the higher concentrations. In my computations the data for the lowest concentrations of

TABLE I

Concn.	Λ	Λ_e	"Ionization constant" $\times 10^4$	$K' \times 10^4$	$K \times 10^4$
ACETIC ACID					
0.07369	6.086	385.7	0.1845	0.1868	*0.1743*
.03685	8.591	386.5	.1851	.1862	*.1755*
.01842	12.09	386.9	.1849	.1857	*.1765*
.009211	16.98	388.1	.1849	.1844	*.1769*
.004606	23.81	388.9	.1851	.1840	*.1775*
.002303	33.22	389.2	.1849	.1838	*.1784*
o-CHLOROBENZOIC ACID					
0.006662	134.6	375.8	12.93	13.31	*12.03*
.003331	174.0	377.5	12.86	13.16	*12.11*
.001666	218.0	378.9	12.84	13.04	*12.23*
.0008327	262.6	380.3	12.84	12.86	*12.22*
.0004163	302.1	381.1	12.79	12.54	*12.16*
3,5-DINITROBENZOIC ACID					
0.003929	175.7	373.2	16.14	16.45	*15.03*
.001860	219.0	374.9	15.99	16.12	*15.08*
.0009822	262.7	376.1	15.94	15.90	*15.04*
.0004922	301.5	377.1	15.99	15.69	*15.05*
CYANO-ACETIC ACID					
0.05946	88.0	372.7	40.0	43.39	*34.9*
.02972	117.0	375.3	39.2	42.64	*34.9*
.01487	152.5	377.9	38.3	40.61	*34.9*
.007435	193.9	380.0	37.8	39.53	*34.9*
.003716	238.7	382.0	37.2	38.68	*35.0*
.001858	282.6	384.0	37.2	38.12	*35.2*
.0009290	320.0	385.4	37.3	37.62	*35.6*
.0004645	347.1	387.0	37.3	36.25	*34.7*
o-NITROBENZOIC ACID					
0.03125	139.7	367.0	67.2	73.11	*59.7*
.01562	179.0	369.8	66.0	70.99	*60.0*
.007812	221.9	372.3	64.5	68.70	*60.0*
.003906	265.0	374.6	63.3	66.81	*59.9*
.001953	303.6	376.2	62.8	65.91	*60.5*
.0009765	333.5	378.7	62.7	63.45	*59.6*

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[4] The values in the columns headed "ionization constant" are from Kendall's paper.

the acids were not used since it would have been necessary to extrapolate the corresponding conductance data for the sodium salts. I have not found other data than those given of sufficient accuracy to test the questions involved in this paper. It seems fitting to express appreciation of the recent, very accurate measurements of the conductance of dilute solutions of hydrochloric acid by Parker,[5] without which these computations would not have been possible.

The only case in which there is a definite trend in the value of the constant K is that of acetic acid in which there is a change of 2.2% from 0.07 to 0.002 N. This is probably due to the fact that the conductance data for the acid and its sodium salt were obtained by different workers.[6] In all the other cases cited Kendall measured both types of data. The trend of the constant for acetic acid is not due to a variation from unity of the activity coefficient γ_{HA}, of the undissociated acid. Using the method and data given by Lewis and Randall[7] for computing this factor from the freezing points of the more concentrated aqueous solutions of the acid it was found that this activity coefficient at 0.07 N is 0.996 and is progressively nearer unity for lower concentrations. This small correction has been applied to values of K in Table I. A similar computation of the values of this coefficient for the other acids should, of course, be made but the freezing-point data are not at present available. In any case it probably differs very slightly from unity. Another factor, called to my attention by Professor George Scatchard, which is sufficient to cause deviations of the magnitude observed, and which must certainly be considered in a complete theory for these solutions, is an effect on the activities of the ions produced by the change of the dielectric constant with the concentration. This change is not known for conducting solutions, but computations based on the Debye-Hückel theory indicate that for substances similar in composition to acetic acid a variation in K of the magnitude and sign of that observed may be expected. Similar effects might be present for the other acids, but the computations given above do not indicate their presence.

Summary

Computations, based mainly on Kendall's measurements, show that the mass law holds for a series of organic acids of various strengths, throughout the complete range of concentrations on which conductance measurements have been made, provided (a) that the degrees of ionization are computed in a manner which allows for inter-ionic attraction, and (b) that the resulting ion concentrations are multiplied by the appropriate activity co-

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[5] Parker, THIS JOURNAL, **45**, 2027 (1923).

[6] The published values for the conductance of sodium acetate show a wide divergence. I have used the data of Lorenz and Osswald, *Z. anorg. Chem.*, **114**, 209 (1920).

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, pp. 284–290.

efficients. The agreement hitherto found with Ostwald's dilution law, for weak electrolytes and for the lower concentrations of "transition" electrolytes, has been found to be due to a compensation of two effects. Arrhenius' method for computing degrees of dissociation yields too low values, and the activity coefficients have been tacitly assumed to be unity, whereas at all low concentrations such coefficients are less than one.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. III. COBALT SALTS AS PROMOTERS IN THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY POTASSIUM DICHROMATE

BY ALFRED C. ROBERTSON[1,2]

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In a previous study,[3] wherein hydrogen peroxide was decomposed catalytically by cupric and ferric salts, the cause for the "promotion" effect was demonstrated to be due to the formation of cupric acid by the intermediate compound of this catalysis (ferric acid). The mechanism of promotion was provisionally defined as a change in the path of the catalytic reactions, with a concomitant displacement of the region of the steady state. It was felt that other systems should be studied in order to test this hypothesis more fully. Since no other promoters had been found for the system using ferric salts as a catalyst, a new system was sought. This was found in the catalytic decomposition of hydrogen peroxide by potassium dichromate.

This reaction has been known for some time. As a product of this reaction, there are distinguished two different perchromic acids. The blue perchromic acid has been studied more than the red, probably due to its use in analysis. However, it will not be considered here, since whenever it is formed there is reduction of chromium and the reaction is no longer catalytic.

Schönbein[4] considered the brown color formed when potassium dichromate was added to a hydrogen peroxide solution to be a chromium chromate. Berthelot[5] also held this view, but in addition showed that the reaction is catalytic in character. This was done by means of a calorimetric study, which showed that the heat of the catalytic reaction is 20.8 Calories. The heat of formation of hydrogen peroxide is —21.6 Calories,

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[1] Du Pont Fellow.

[2] Part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Robertson, THIS JOURNAL, **47**, 1300 (1925).

[4] Schönbein, *J. prakt. Chem.*, **80**, 257 (1860).

[5] Berthelot, *Compt. rend.*, **108**, 24 (1889).