plicated and rather unstable molecules. Thus Jaeger[4] found, to give only a few examples, that ethyl acetate has a value of Ke between −74 and 0° of 2.50, which gradually falls to a value of 1.30 above 15°. A few cases show increasing values of Ke with rising temperature, *e. g.*, diethyloxalic acid has a value of 1.8 below 0°, which rises to 3.6 at temperatures above 146°. In still other cases the value of Ke passes through a minimum. While inaccuracies in measurement might be the cause of small variations in the value of Ke, as suggested by Livingston and Morgan,[10] they can scarcely be held to account for the gradual drift in the up or down value of Ke. In any case it appears that liquids composed of complicated molecules behave as do binary mixtures.

A satisfactory explanation of the foregoing will likely be found in a combination of surface absorption theories and that of orientation as put forward by Hunten and Maass.[11]

Summary

1. The freezing points, densities and surface tensions of pure sulfur dioxide and of sulfur dioxide and benzene solutions have been measured.
2. It has been shown that sulfur dioxide is associated at low temperatures.
3. The freezing-point curve shows no compound formation.
4. The values of the Eötvös constant for binary mixtures have been shown to be dependent upon concentration and temperature.

VANCOUVER, B. C., CANADA

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A COMPARISON METHOD FOR DETERMINING IONIZATION CONSTANTS WITH A QUINHYDRONE REFERENCE ELECTRODE

BY H. DARWIN KIRSCHMAN, BAKER WINGFIELD AND HOWARD J. LUCAS

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Introduction

Within recent years, the potentiometric method[1,2] of determining ionization constants of weak acids has begun to displace the conductivity method. One disadvantage of the latter is that it is necessary to make conductance measurements not only of solutions of the acid but also of those of a salt of the acid in order to compute Λ_0; another disadvantage arises from the fact that in order to obtain moderately accurate results very pure water must be used for the preparation of the dilute solutions.

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[10] Livingston and Morgan, THIS JOURNAL, **33**, 643 (1911).

[11] Hunten and Maass, *ibid.*, **51**, 153 (1929).

[1] Britton, *J. Chem. Soc.*, **127**, 1896 (1925); Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

[2] Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 31 (1928).

The usual potentiometric method in which the acid is titrated with a standard base to give a titration curve is not entirely satisfactory since (1) the accuracy of the constant is seriously affected by the difficulty of determining the inflection point in the voltage–ml. plot when the acid is weak, and (2) the liquid junction potentials vary while the titration is being carried on, due to the continued addition of water and of the positive ion. The method described in this paper has an advantage over the titration method in that the liquid junction potentials are for the most part eliminated.

Method

The method consists in determining the potential of the reference electrode represented at the left end of the cell below, first against a saturated solution of quinhydrone containing hydrochloric acid at various concentrations, and then against similar solutions containing the acid under investigation at a series of concentrations. The whole cell may be represented thus

$$\begin{array}{c}\text{Pt, KCl}(0.09\ N) + \text{HCl}(0.01\ N) + \text{Quinhydrone} \\ \text{KCl}(0.09\ N),\ \text{HA}(c\ N) + \text{Quinhydrone, Pt}\end{array}$$

HA represents hydrochloric acid in one series of measurements and the acid under investigation in the other series.

From the data obtained when hydrochloric acid is used a curve is drawn by plotting the measured voltages against the logarithms of the mean ion activities, $C\alpha$ of the hydrochloric acid. When any other acid is used as HA in the above cell, it is possible to obtain the logarithm of the mean ion activity of this acid at any concentration from the corresponding voltage.

It is difficult to evaluate the liquid junction potentials when the junction is being continuously renewed, but it seems certain that the difference between the liquid junction potential when hydrochloric acid is used and when an organic acid of the same mean ion activity replaces it will introduce an error in the constants well within the limit of experimental error of the measurements.

Calculation of the Constant.—The ionization constant is calculated from the experimental data by means of the expression

$$K_A = \frac{a_{\pm}^2}{\left(C - \frac{a_{\pm}}{\alpha}\right)}$$

where $a_{\pm}$ is the mean activity of the ions, C is the molal concentration of the acid, and α is the mean activity coefficient.

This assumes (1) that the activity of the undissociated acid is equal to its concentration, (2) that the mean ion activity in the organic acid solution is the same as the mean ion activity in that hydrochloric acid solution which gives the same potential against the reference cell and (3) that the quinhydrone will affect the mean ion activity to the same extent in solutions of the same mean ion activity.

The work of Randall and others[3] shows that at the concentrations of acid (0.02–0.0003 M) used in these measurements the first assumption is fully justified. Since the determination of the individual ion activities is a difficult operation, it is desirable to make the second assumption, which seems justifiable at the low concentrations of ions prevailing.

The solubility of the quinhydrone is small,[4] 0.018 mole per liter at 25°, and presumably about the same in the various solutions so that the last assumption is a reasonable one.

Apparatus and Materials

The cell used was similar to the type proposed by Köhn[5] and is shown in the figure. The inner cell containing the reference solution consisted of a glass tube 1.5 cm. in diameter and 15 cm. in length fitted with a ground-on glass cap and a removable electrode carrying a piece of bright platinum foil. The outer cell consisted of a 400-cc. beaker fitted with a rubber top through which passed the mechanical stirrer, the nitrogen bubbling tube, the inner cell and a glass tube carrying a piece of bright platinum foil which served as the second electrode.

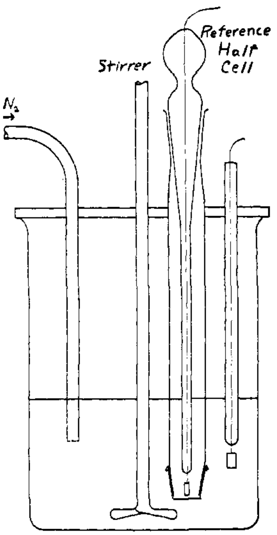

Fig. 1.

The e.m.f. measurements were made with a Leeds and Northrup Type K potentiometer. The cell was immersed in an oil thermostat maintained at 25 ± 0.02°.

Eastman's quinhydrone was recrystallized twice from water at 70° and was dried over sulfuric acid in a vacuum desiccator.

Constant boiling hydrochloric acid was prepared by the distillation in an all-pyrex apparatus of concentrated C. P. hydrochloric acid previously diluted to a specific gravity of 1.11. At the observed pressure of 744.6 mm.[6] one mole of hydrogen chloride is contained in 179.864 g. of solution. A tenth-normal solution was prepared by diluting a weighed amount of this standard acid with a weighed amount of water. Lower concentrations were made by volume dilutions from this solution.

The potassium chloride was recrystallized four times from hot water and fused to dryness.

Benzoic acid of standard quality was purified by three crystallizations from hot water and a subsequent sublimation.

The *p*-cyanobenzoic acid was the same as that used in the research of Valby and Lucas.[7] A stock solution was prepared by dissolving a weighed quantity of the solid organic acid in water to a definite volume. This stock solution was diluted by volume to obtain the lower concentrations.

The water used in the preparation of all solutions was obtained by distillation of distilled water from sodium carbonate and potassium permanganate in an all-pyrex

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[3] Randall and Failey, *Chem. Reviews*, **4**, 291 (1927).

[4] Biilman, *Ann. chim.*, **15**, 113 (1921).

[5] Köhn, *Z. angew. Chem.*, **39**, 1073 (1926).

[6] Foulk and Hollingsworth, THIS JOURNAL, **45**, 1225 (1923).

[7] Valby and Lucas, *ibid.*, **51**, 2718 (1929).

apparatus in an atmosphere of nitrogen. Care was taken to prevent absorption of carbon dioxide and oxygen from the atmosphere.

Experimental Method

The glass cap of the reference half-cell was filled with 0.09 *N* potassium chloride solution and fastened to the cell with a rubber band. This provided a bridge of 0.09 *N* potassium chloride through the ground-glass joint. The excess liquid was removed by three washings with the reference solution and the half-cell filled to a depth of 3–4 cm. with the reference solution. The liquid levels were kept about the same in the outer and inner half-cells to minimize the drift in potential due to diffusion through the ground-glass joint during the measurements. To the 400-cc. beaker which served as the outer half-cell was added about 200 cc. of the hydrochloric or organic acid solution. The outer parts of the reference half-cell were washed with a small amount of the same solution, the two half-cells were assembled in the oil thermostat and connected to the potentiometer. Stirring was carried on at a slow rate by the motor-driven stirrer while purified nitrogen was passed through the outer half-cell at the rate of about 20 bubbles a minute. Voltage readings were made at five-minute intervals until equilibrium to within 0.1 millivolt was attained, which generally took from ten to fifteen minutes. This equilibrium value was usually about one millivolt lower than the initial reading. The bright platinum foil electrodes were found to give reproducible results throughout the entire series of measurements.

The reference half-cell was filled anew before each determination, since otherwise the observed voltage on a succeeding run would be materially lower.

All solutions used were saturated with quinhydrone at 45° by vigorous shaking for fifteen minutes in the presence of a small excess of the solute. The solutions were then brought to 25° by immersion in the thermostat and were shaken at intervals to aid crystallization of the excess quinhydrone.

Reference Curve.—Using the apparatus and methods described, measurements were made of the voltages produced by solutions of known concentrations of hydrochloric acid saturated with quinhydrone against the reference solution 0.09 *N* in potassium chloride and 0.01 *N* in hydrochloric acid, saturated with quinhydrone. The results are given in Table I.

TABLE I

DATA FOR THE CONSTRUCTION OF THE REFERENCE CURVE

Concn. of HCl, moles per liter	Log α	Log αC	Observed e.m.f., volts	Concn. of HCl, moles per liter	Log α	Log αC	Observed e.m.f., volts
0.01023	−0.0432	$\bar{3}.9669$	+0.0020	0.000511	−0.0110	$\bar{4}.6974$	−0.0725
.01023	− .0432	$\bar{3}.9669$	+ .0026	.000204	− .0075	$\bar{4}.3021$	− .0963
.01023	− .0432	$\bar{3}.9669$	+ .0021	.000204	− .0075	$\bar{4}.3021$	− .0950
.01023	− .0432	$\bar{3}.9669$	+ .0025	.0001023	− .0050	$\bar{4}.0051$	− .1126
.00511	− .0325	$\bar{3}.6759$	− .0142	.0001023	− .0050	$\bar{4}.0051$	− .1157
.001023	− .0151	$\bar{4}.9950$	− .0544	.0001023	− .0050	$\bar{4}.0051$	− .1161
.001023	− .0151	$\bar{4}.9950$	− .0543	.0001023	− .0050	$\bar{4}.0051$	− .1174
.001023	− .0151	$\bar{4}.9950$	− .0533	.00001023	− .0009	$\bar{5}.0090$	− .1745
.001023	− .0151	$\bar{4}.9950$	− .0568				

The activity coefficients at the higher concentrations are those of Randall and Young.[8] At concentrations below 0.001 *N* the activity coefficients

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[8] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

were calculated by means of the Debye–Hückel equation.[9] The observed voltages were plotted against the corresponding values of log αC and a straight line was drawn through the points. The curve may be reproduced from the values given in Table II.

TABLE II

INTERPOLATED VALUES OF VOLTAGE AND LOG αC FROM REFERENCE CURVE

Log αC	$\bar{2}.000$	$\bar{3}.000$	$\bar{4}.000$	$\bar{5}.000$
Voltage	+0.0045	−0.0545	−0.1138	−0.1728

The small amount of carbon dioxide which may have contaminated the solution in spite of the precautions taken would not modify the curve appreciably in the region employed.

Application of the Method

In Table III are tabulated the data obtained with benzoic and *p*-cyanobenzoic acids, using the apparatus and experimental technique previously described.

TABLE III

RESULTS WITH BENZOIC AND *p*-CYANOBENZOIC ACIDS

Benzoic Acid				*p*-Cyanobenzoic Acid			
Acid concn., moles per liter	Observed e.m.f.	Log $\alpha_{\pm}$	$K_A \times 10^5$	Acid concn., moles per liter	Observed e.m.f.	Log $\alpha_{\pm}$	$K_A \times 10^5$
0.02129	−0.0511	$\bar{3}.057$	6.47	0.007294	−0.0465	$\bar{3}.135$	3.17
.01065	− .0598	$\bar{4}.910$	6.73	.007294	− .0465	$\bar{3}.135$	3.17
.01065	− .0595	$\bar{4}.915$	6.90	.003647	− .0570	$\bar{4}.960$	3.08
.004258	− .0719	$\bar{4}.706$	6.90	.003647	− .0570	$\bar{4}.960$	3.08
.004258	− .0720	$\bar{4}.705$	6.87	.001459	− .0707	$\bar{4}.727$	3.01
.002129	− .0819	$\bar{4}.538$	6.72	.001459	− .0704	$\bar{4}.732$	3.12
.02032	− .0517	$\bar{3}.047$	6.49	.0007294	− .0823	$\bar{4}.531$	3.02
.02032	− .0511	$\bar{3}.057$	6.64	.0007294	− .0823	$\bar{4}.531$	3.02
.01016	− .0606	$\bar{4}.888$	6.38	.0003647	− .0946	$\bar{4}.325$	2.99
.01016	− .0603	$\bar{4}.902$	6.82		Av. 3.10 ± 0.10 × 10^{-4}		
.004064	− .0725	$\bar{4}.695$	6.90				
.001016	− .0926	$\bar{4}.351$	6.38				
	Av., 6.68 ± 0.25 × 10^{-5}						

The values of the logarithm of the mean ion activity in the organic acid solutions were obtained from the plot of the data of Table I. The values of the constant were calculated from the expression $K = a_{\pm}/(C - (a_{\pm}/\alpha))$. These values were then plotted against the logarithm of the concentration to obtain the constants at round concentrations which were compared in the case of benzoic acid in Table IV with those of some previous investigators obtained from conductance measurements.

It is seen that the values obtained by any one investigator agree very well but the divergence of the results of different investigators is quite con-

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[9] Noyes, THIS JOURNAL, **46**, 1080 (1924).

siderable. These constants were calculated using ion concentrations rather than mean ion activities, but this difference is much less than the variation in results.

Table IV

K_A of Benzoic Acid by Different Investigators[10]

Concn.	Ostwald	Euler	Schaller	Kortright	White and Jones	This paper
0.02	5.98	6.68	6.80	6.19	6.70	6.63
.01	5.98	6.67	6.77	6.30	6.77	6.84
.004	6.04	6.70	6.84	6.31	6.87	6.86
.002	6.05	6.69	6.77	6.34	6.83	6.76
.001	5.89	6.69	6.61	6.41	6.51	6.50

The maximum deviation from the mean in the values for the ionization constant of *p*-cyanobenzoic acid is 3%. The mean value agrees with the value of 3.09×10^{-4} which Valby and Lucas[7] obtained by the conductance method.

Summary

Ionization constants of organic acids may be determined by means of a quinhydrone cell in which the reference half-cell is standard hydrochloric acid solution saturated with quinhydrone and containing potassium chloride.

The method is tested in the case of benzoic acid by a comparison of the values herein obtained with those reported by previous investigators and found to be in satisfactory agreement.

The ionization constant of *p*-cyanobenzoic acid is found to be $3.10 \pm 0.10 \times 10^{-4}$. This result likewise agrees well with the value recently obtained by the conductance method.

Pasadena, California

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[10] Ostwald, *Z. physik. Chem.*, **3**, 241 (1899); Euler, *ibid.*, **21**, 257 (1896); Schaller, *ibid.*, **25**, 497 (1898); Kortright, *ibid.*, **21**, 311 (1896); White and Jones, *Am. Chem. J.*, **44**, 159 (1910).