

detect the liberated iodine. Both these methods gave results in agreement with the gravimetrically determined amounts of iridium present in the solutions. They show, moreover, that the iridium content of crystalline ammonium hexachloroiridate as determined volumetrically and gravimetrically is the same, within a fraction of one per cent., as that calculated from the formula $(\text{NH}_4)_2\text{IrCl}_6$.

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[CONTRIBUTION NO. 649 OF THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

ACIDITY IN NON-AQUEOUS SOLVENTS. CONDUCTIMETRIC AND ELECTROMETRIC TITRATIONS OF ACIDS AND BASES IN BENZENE

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I. Introduction

When we consider the remarkable successes which the theory of Arrhenius achieved in correlating such diverse properties of aqueous solutions as (a) conductivity, (b) osmotic properties, (c) acid and base catalysis, (d) hydrogen electrode potentials, and (e) indicator effects, it is quite natural that the degree of acidity should have been taken as synonymous with the concentration of hydrogen ions behaving osmotically as solute particles independent of the acid ionogen. In other words, it has been tacitly assumed that on passing from one solvent to another the purely thermodynamic properties like (b) and (d) will run parallel to properties like (a) and (c) which depend only indirectly upon thermodynamic relations. On this view the acidity of an acid dissolved in benzene should at best be very small, since its degree of dissociation as judged by conductivity is very minute.

The experimental work of Hantzsch,¹ of Brönsted,² and of Hall and Conant,³ is primarily responsible for demonstrating that this assumed

¹ (a) Hantzsch, *Z. Electrochem.*, 29, 230 (1923). Hammett, *THIS JOURNAL*, 50, 2666 (1928), gives complete references of Hantzsch's work up to 1928 and presents the salient features. Later papers of importance are (b) Hantzsch and Voigt, *Ber.*, 62, 975 (1929); (c) Hantzsch and Buroway, *ibid.*, 63, 1180 (1930).

² Brönsted, (a) *Z. physik. Chem.*, 108, 217 (1924), with Kai Pedersen, (b) *Rec. trav. chim.*, 42, 718 (1923) (definition of acids and bases). Similar views were presented independently by Lowry, *Trans. Faraday Soc.*, 20, 58 (1924); *Chemistry Industry*, 42, 43 (1923); (c) *J. Phys. Chem.*, 30, 777 (1926); (d) *THIS JOURNAL*, 49, 2554 (1927), with E. A. Guggenheim (catalysis by undissociated molecules); (e) *Ber.*, 61 2049 (1928) (indicators in benzene); (f) *Z. physik. Chem.*, 143, 301 (1929) (acidity and ion potentials); (g) *Chem. Rev.*, 5, 284 (1928) (review of subject).

³ (a) Hall and Conant, *THIS JOURNAL*, 49, 3047, 3062 (1927); (b) Hall and Werner, *ibid.*, 50, 2367 (1928); (c) Hall, *J. Chem. Ed.*, 7, 782 (1930); (d) *THIS JOURNAL*, 52, 5115 (1930).

parallelism between thermodynamic and non-thermodynamic properties does not hold. The lines of evidence which they have adduced in support of the view that the classical consideration of acids and bases must be modified if it is to apply to non-aqueous solvents and even certain properties of aqueous solutions as (2) below, are: (1) properly chosen indicators respond promptly to additions of acids and bases when dissolved in solvents like glacial acetic acid^{3a,4} or benzene,^{2e,1b} whereas the conductivity indicates extremely low ionization; (2) acid (or basic^{2a}) catalysis is produced by undissociated acids^{2d} (or bases), the catalysis being dependent primarily upon the facility with which protons can be transferred from catalyst to substrate (or *vice versa*); (3) the degree of dissociation^{2b,2c} as indicated by the conductance ratio in any given solvent depends not only upon the dielectric constant but also upon the extent of combination of the acid with the solvent acting as a base, yielding a highly dissociated electrolyte popularly called a salt.

As far as we are aware, the possibility of titrating acids and bases electrometrically in solvents like benzene whose role is that of an inert diluent has never been considered. It is obvious if an electrometric titration can be carried out that an important experimental method becomes available since electrometric titration presents in simplest form the essential features of the capacity and intensity factors of acidity.

II. Experimental

A. Conductimetric Titrations.—Walden and Gloy⁵ have demonstrated that certain salts like the tetra isoamyl ammonium halides, perchlorates, thiocyanates and picrates, (R_4NX), are appreciably soluble (iodide about 0.1 *m* at 72°) in benzene and conduct the current. No corresponding work has been reported for acids and bases.

In order to explore to what extent salt formation may proceed in benzene, we determined the changes in conductivity produced on alternate additions of acids and bases. A very low resistance cell consisting of two platinum electrodes having an area of about 8 sq. cm. held rigidly about 2 mm. apart by glass supports contained the solutions studied. The resistance was measured by noting the deflections on a Leeds and Northrup galvanometer, type 2500, when the cell and galvanometer were placed in series with the 110-volt direct current line. By shunting a variable resistance across the galvanometer, the range of measurement can be greatly extended. Cady and Lichtenwalter,⁶ using this method, noted that polarization effects of a few tenths of a volt were present. In our work all

⁴ Nicholas Dietz, Dissertation, Columbia University, 1930 (formic acid as solvent); Hammett and Dietz, *THIS JOURNAL*, **52**, 4795 (1930).

⁵ Paul Walden, "Acids, Bases and Salts," McGraw-Hill Book Company, Inc., New York, 1929. Gloy, Dissertation, Rostock, 1927; *Chem. Abst.*, **23**, 5088 (1929).

⁶ Cady and Lichtenwalter, *THIS JOURNAL*, **35**, 1434 (1913).

readings were checked by reversing the direction of the current through the cell. We found that the deflections in either direction were sensibly identical and reproducible within the accuracy of the measurement.

In one typical run we employed 1.11 *M* trichloroacetic acid and 0.834 *M* diethylamine as the acid and base. The results are plotted in Fig. 1: the ordinates are in reciprocal ohms times 10^{11} and the abscissas in cc. of added base or acid calculated to molar values. The solid dots represent a repetition of the experiment and give a measure of the reproducibility. The arrows indicate the equivalence points where stoichiometrically equal quantities of acid and base were present. The conductivity appears to be

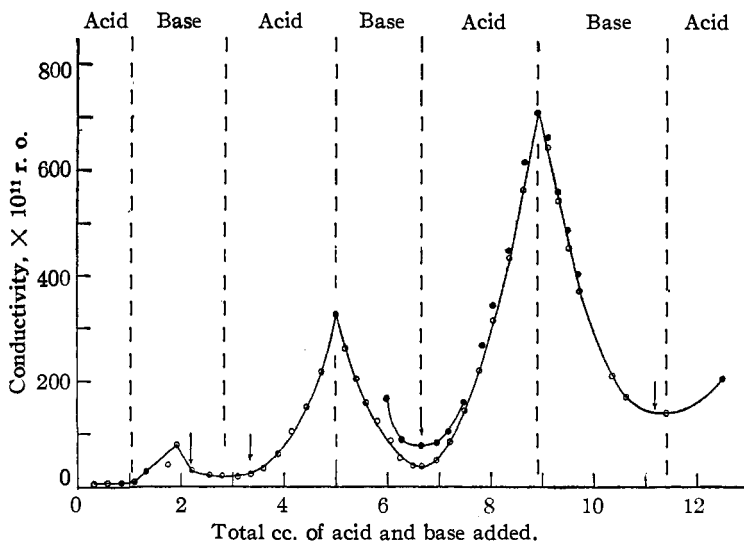


Fig. 1.—Conductimetric titration of diethylamine by trichloroacetic acid.

unchanged on addition of trichloroacetic acid to benzene, at least up to 0.04 *M*. At that point diethylamine was added; the conductivity rose sharply, reaching a maximum and then decreasing to a value very little greater than that for benzene, when the equivalence point was reached. The equivalence point in the titration corresponds closely with a region of minimum conductivity.

In another run (not shown) where diethylamine was first added to benzene, the conductivity remained sensibly constant (80×10^{-11} r. o.) up to about 0.05 *M*, when it rose sharply to a maximum at about 0.06 *M*, then decreased to a value which remained constant on addition of trichloroacetic acid until the equivalence point was passed. Further additions of acid then produced relatively rapid increases in conductivity, reaching a value of 1290×10^{-11} r. o. for a solution containing 0.220 *M* acid and 0.08 *M* base.

Paul Walden⁷ states that "*the equivalent conductivity in benzene decreases with increasing dilution.*" A plausible explanation for these curious anomalies has been presented by Gross and Halpern⁸ in a paper which has received scant attention to date. Their argument may be stated as follows. The addition of an electrolyte like potassium nitrate increases the dissociation of a weak acid like acetic acid in water, by reducing the activity coefficients of the hydrogen and acetate ions by the now well-established mechanism of interionic attraction. In a low dielectric solvent like benzene the dissociation of acids is extremely minute but nevertheless exists, as demonstrated by our own conductivity measurements.

When the electrolyte concentration is increased either by adding excess acid or better by adding base leading to salt formation, the values of the activity coefficients of the dissociated ions of the acids are reduced more than the corresponding conductivity coefficients. Increased equivalent conductance should therefore result.

The Debye-Hückel limiting law predicts that the value $-\log f$ should increase at a rate $(78/2.29)^{3/2} = 200$ times greater in benzene than in water; *i. e.*, the logarithm of the stoichiometric equilibrium constant would be increased 200 times more in benzene than in water at the same ionic strength.

The complete solution of the Poisson-Boltzmann equation given by Gronwall, La Mer and Sandved⁹ show, contrary to the case in water, that in a solvent of low dielectric constant the terms of higher order than the first are of sufficient magnitude in the case of uni-univalent salts to completely overwhelm and change the sign of the contribution for ion size yielded by the Debye first approximation since D appears in the denominator to progressively higher powers for each order of approximation.¹⁰ The relative increase in equilibrium constant in benzene as compared to water must be very much greater than any prediction based on the limiting law alone. The general solution consequently strengthens the proposal advanced by Gross and Halpern.

B. Electrometric Titrations.—The cell consisted of a Jena glass

⁷ Ref. 5, p. 266.

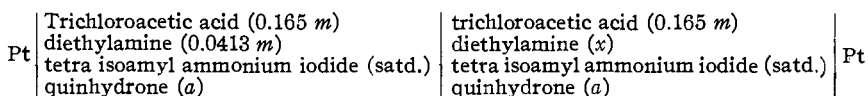
⁸ Gross and Halpern, *Physik. Z.*, **26**, 636 (1925).

⁹ Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

¹⁰ Detailed computations by V. K. La Mer on the magnitudes of the contributions of the higher terms and their ability to account for the striking data of Kraus and Seward for the solubility of sodium chloride in isopropyl alcohol $D = 16$ and the data of A. L. Robinson for various salts in acetone $D = 21.3$ were presented at the Columbus (April, 1929) Meeting of the American Chemical Society (see V. K. La Mer, "Annual Survey of American Chemistry, 1928-1929," 1930, Vol. IV, p. 12). Bjerrum's hypothesis of ion association yields the same qualitative result but at the expense of an additional and unnecessary hypothesis. For more recent data on solubility in ethyl alcohol, see Seward and Schumb, *THIS JOURNAL*, **52**, 3962 (1930).

crucible with a porous bottom of sintered glass rested in a small beaker. The electrodes were of platinum and placed close to both sides of the glass diaphragm. Even after saturating the benzene with tetra isoamyl ammonium iodide, the resistance of the cell is far too high for the sensitivity of the ordinary galvanometer. The method of discharging a condenser through a ballistic galvanometer as described by Beans and Walden¹¹ is admirably suited for the purpose. We have found that potential differences could be measured to ± 0.1 mv. with a 10 microfarad condenser, using the apparatus as a null point instrument. This procedure does not require the complete charging of the condenser and is almost as rapid as the method using the type 2500 galvanometer. Thiophene-free benzene was employed without any special effort to dry it completely since exposure to air could not be eliminated with a cell of this construction.

A typical cell may be represented as



where x is initially 0.0413 M but is increased by addition of base in the course of the experiment; (a) is undetermined but constant. The cell was assembled by saturating a quantity of benzene with tetra isoamyl ammonium iodide, then adding quinhydrone. A measured amount of this solution was put into the beaker and the desired amount of acid-base mixture (2 to 1 ratio of acid to base) added to it. A known aliquot was then pipetted into the crucible compartment which served as the titration vessel.

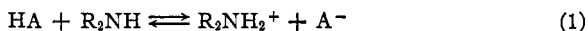
The saturating salt was washed with ether and recrystallized from benzene. The acid and base solutions were made up in benzene, roughly 1.0 molar and standardized against aqueous sodium hydroxide and hydrochloric acid with continuous shaking until the indicator change occurred in the water layer. The titrating solutions in this experiment were trichloroacetic acid, 1.111 ± 0.002 molar and diethylamine, 0.834 ± 0.001 molar.

Unless the initial potential was zero to within 3 mv., the electrodes were cleaned and the cell reassembled. Diethylamine was then added (about 1.2 milliequivalents at a time) and the potential measured after each addition until a large increase in potential, followed by a relatively slow increase, was observed. In some cases additions of trichloroacetic acid were made to the solution containing excess base. The potential returned to a value approximating the initial one. When the solution was strongly basic the color changed rapidly from pale yellow to red which we attribute

¹¹ H. T. Beans and George Walden, *THIS JOURNAL*, 50, 2673 (1928); George Walden, Dissertation, Columbia University, 1924.

to reaction with the quinhydrone. It was for this reason that we made up the standard solution by adding a 2 to 1 mixture of trichloroacetic acid and diethylamine rather than adding the pure components. A small amount of iodine dissolved in benzene gave a strong test for iodine with starch, but since the red solution gave no test with starch we could not attribute the color to iodine formed by reaction of the quinhydrone with the iodide. In strongly acid solution the same color change was observed, although it did not proceed as rapidly.

The reaction may be formulated¹² as follows



where HA is trichloroacetic acid and R₂NH is diethylamine. For the quinhydrone electrode where $C_{\text{quinone}} = C_{\text{hydroquinone}}$

$$E = E'_0 + RT/NF \ln a_{\text{H}^+} \quad (2)$$

The activity coefficients of quinone and hydroquinone are assumed to be constant during the titration and included in E'_0 . The presence of the tetra isoamyl ammonium iodide instead of complicating actually simplifies the theoretical interpretation of the cell since its presence stabilizes the activity coefficients during the progress of the titration by maintaining a more nearly constant environment, and by eliminating junction potential. Abundant proof¹³ now exists that the addition of an excess of a foreign neutral salt is the simplest way of eliminating these difficulties in aqueous solution, and the same principle should obtain in benzene. Owing to the much greater interionic effects in benzene it is important to reduce these disturbances as far as possible.

When trichloroacetic acid is in excess, the hydrogen-ion activity is most conveniently formulated in terms of its dissociation, hence¹⁴

$$a_{\text{H}^+} = K a_{\text{HA}} / a_{\text{A}^-} \quad (3)$$

or

$$E = E_0 + RT/NF \ln a_{\text{HA}} / a_{\text{A}^-} \quad (4)$$

where

$$E_0 = E'_0 + RT/NF \ln K \quad (5)$$

Since we have no means of determining the absolute value of E'_0 we have arbitrarily taken the potential of the reference electrode (2 trichloroacetic acid : 1 diethylamine) as zero, and plot only the differences in electromotive force as the titration proceeds. The further addition of base (diethylamine) by definition reduces the escaping tendency of protons (hydrogen

¹² Although the product is written in ionic form, the number of free ions in benzene solution is extremely small owing to the low dielectric constant.

¹³ La Mer and Sandved, THIS JOURNAL, 50, 2656 (1928). References to earlier work are given on page 2658.

¹⁴ Regarding formulation see W. Mansfield Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland, Chap. XXVII, particularly p. 529. Also Brönsted, Ref. 2 g, pp. 238, 289.

electrode potential) by the process represented by (1). As Fig. 2 shows, the proton potential curve on changing the relative amounts of acids and bases shows a close analogy to the neutralization curves of these acids and bases as ordinarily formulated for aqueous solution. When an amount of diethylamine greater than the stoichiometric equivalent, which is represented by the upturned arrow in Figs. 2 and 3, has been added, we pass to a new level of acidity which is determined by the ratio of $R_2NH_2^+$ to R_2NH° . The potential is then given by

$$E = E_0'' + RT/NF \ln (R_2NH_2^+)/ (R_2NH^\circ)$$

The most convenient means of characterizing the relative acidities (proton escaping tendencies) of the two conjugated systems (HAc°/Ac^-)

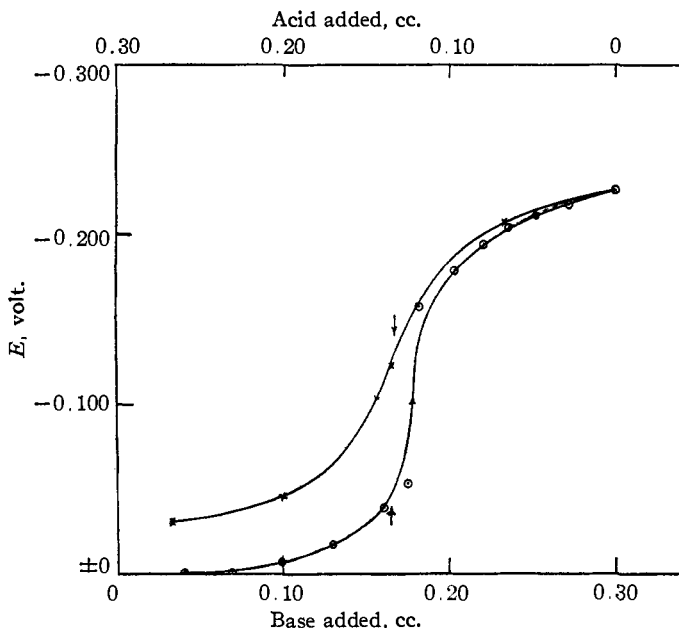


Fig. 2.—Electrometric titration of diethylamine-trichloroacetic acid.

and $(R_2NH_2^+)/ (R_2NH^\circ)$ are by the values of E_0' and E_0'' , respectively, which are equal to the respective values of E when the ratio is unity or the systems are at the half neutralization points. Our data are hardly sufficiently accurate or extensive to test the shape of the curves by plotting E against $\log (R_2NH_2^+)/ (R_2NH^\circ)$ or $\log (HA^\circ/A^-)$, but there can be little doubt but that the proton potential of the system diethyl ammonium \rightleftharpoons diethylamine is 0.40 volt less than for the system trichloroacetic acid \rightleftharpoons trichloroacetate.

As a test upon the reversibility of the process we added trichloroacetic acid to the solution containing excess base, as shown by the upper curve in

Fig. 1. The curve for this back titration does not correspond exactly to the forward curve. This may be due to possible diffusion through the porous glass membrane or to changing environmental effects during the titration. More work must be undertaken before this point can be regarded as settled. The fact that the equivalence point (downward arrow of Fig. 2) coincides as closely as it does with the point of inflection is strong evidence that acid-base relations in benzene are quite analogous to those in water as far as potential is concerned.

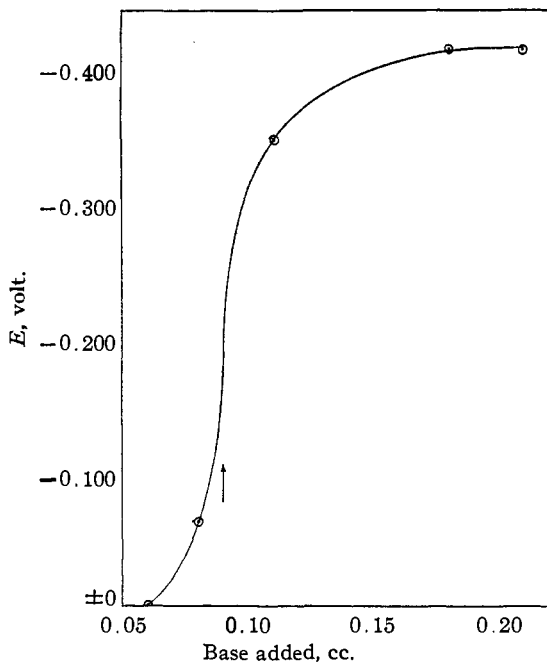


Fig. 3.—Titration of 3 cc. of (0.0266 M) trichloroacetic acid in benzene by diethylamine (1 M) in benzene. Equivalent point, 0.08 cc.

The question arises, would these curves be obtained in absolutely dry benzene?¹⁵ The saturation value for water in benzene is given as 0.57 part per thousand at 20°. It hardly seems likely that the still smaller amount of water in equilibrium with the atmosphere could be entirely responsible for the conductivity and electrometric titration curves. However, we must point out that although indicator changes are immediate and reproducible in moist benzene, one of us (V. K. L.) has observed that this does not always hold true when benzene is dried over sodium. We prefer to leave open the question of the effect of traces of water until a more refined technique has been developed.

¹⁵ E. Juanita Greer, *THIS JOURNAL*, **52**, 4191 (1930).

We wish to thank Dr. George Walden for placing his electrical instruments at our disposal.

III. Summary and Conclusions

1. An electrometric method is described for titrating acids and bases in benzene using quinhydrone electrodes.

2. The curve obtained when trichloroacetic acid is titrated electrometrically with diethylamine has the same characteristics that are observed in aqueous solution on titrating a strong acid with a strong base.

3. The difference in hydrogen electrode potential (proton escaping tendency) between the trichloroacetic acid system and the diethylammonium acid system is of the order of 400 millivolts.

4. Conductivity titrations of acids and bases in benzene exhibit the anomalous behavior similar to that reported by Paul Walden for salts in benzene. The equivalence points correspond to minima regions in the conductance titration curves.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION.

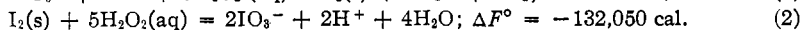
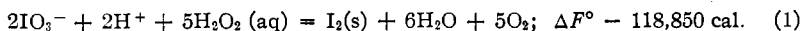
III. THE REDUCTION OF IODATE ION BY HYDROGEN PEROXIDE¹

BY HERMAN A. LIEBHAFSKY

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The equations and the free energy data² for the reactions



make it evident that the $\text{I}_2\text{-IO}_3^-$ couple is capable of catalytically decomposing hydrogen peroxide. The present investigation was begun with an extensive series of experiments on the iodine-iodate catalysis, but the results obtained proved to be so complex that no definite conclusions concerning the mechanism of the catalysis could be drawn from them alone. These data showed, however, that the catalysis was the result of several compensating reactions, of which two—the oxidation of iodine by hydrogen peroxide and the reduction of iodate ion by that same substance—gave hope of being suitable for separate study. In the second paper of this series there have been presented some experimental results on the former

¹ The preceding papers of this series are Part I, Bray and Liebhafsky, *THIS JOURNAL*, **53**, 38 (1931), and Part II, Bray and Caulkins, *ibid.*, **53**, 44 (1931).

² Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 607-608.