Summary

The dielectric constants of hydrogen chloride, hydrogen bromide and hydrogen iodide have been measured from the liquid state near the freezing points down to −189° at frequencies from 300 to 60,000 cycles with special attention to the regions of transition. The transition temperatures shown by heat capacity measurements in the literature are closely checked by those shown by the dielectric constant curves. For some distance below the melting points the molecules in the crystalline solids orient in the externally applied field to almost the same extent as in the liquid, the polarizations usually varying between the transitions inversely as the absolute temperature. Change in molecular rotation at the transitions may result in an increase or a decrease in the dipole orientation in an externally applied field.

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Indicator Studies of Acids and Bases in Benzene[1,2]

BY VICTOR K. LA MER AND HAROLD C. DOWNES

1. Introduction

Although the quantitative study of acidity has been investigated exhaustively for the amphiprotic solvent water, and at present is being actively investigated for various acid and basic solvents, the subject has been virtually neglected for aprotic solvents like benzene. This has been due in no small part to the persistent view that the concept of acidity is without meaning in non-dissociating solvents. In a recent paper,[3] we have demonstrated that this view is erroneous since electrometric titrations of acids by bases can be carried out in benzene. In this present paper we shall give a quantitative measure of the acidity for a series of weak acids in benzene, by the use of indicator methods.

According to Brönsted[4] an acid HA is a substance which can dissociate a proton, leaving a conjugate base A, according to the scheme

$$\underset{\text{acid}}{\mathrm{HA}} = \underset{\text{proton}}{\mathrm{H}^+} + \underset{\text{base}}{\mathrm{A}} \tag{1}$$

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[1] This paper is from a dissertation presented by Harold C. Downes to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] A part of the material was presented at the Syracuse (June, 1932) meeting of the American Association for the Advancement of Science.

[3] La Mer and Downes, THIS JOURNAL, **53**, 888 (1931).

[4] Brönsted, (a) *Z. physik. Chem.*, **108**, 217 (1924), with Kai Pederson; (b) *Rec. trav. chim.*, **42**, 718 (1923), (definition of acid and base); (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 potential); (g) *Chem. Rev.*, **5**, 284 (1928), (review of subject); (h) THIS JOURNAL, **53**, 2478 (1931), with Bell (reaction velocity in benzene); (i) Meeting of British Association 39, 1932 (medium effect).

The dissociation of an acid cannot proceed perceptibly unless another base B

$$\begin{array}{ccccc} B & + & H^+ & = & BH \\ (\text{base} & + & \text{proton} & = & \text{acid}) \end{array} \qquad (2)$$

is present to accept the proton, yielding the typical reaction

$$\begin{array}{ccccccc} HA & + & B & = & HB & + & A \\ \text{acid}_1 & + & \text{base}_2 & = & \text{acid}_2 & + & \text{base}_1 \end{array} \qquad (3)$$

with the obvious restriction that the electric charge of the acid decrease by one and the charge of the base increase by one in forming the new base and the new acid, respectively. This definition is a satisfactory and useful one because, while explaining in a logical way the characteristic relationship of acids and bases, it assigns these characteristics as properties of the molecules themselves independently of the solvent.

Ordinarily the solvent by virtue of its own acid (or basic) character operates as the second acid–base system and facilitates ionization, a property most highly developed in water because of the ease with which it can act as an acid or a base (amphiprotic character) to meet the characteristics of the solute. Benzene on the other hand stands in sharp contrast to water; because of its aprotic nature it can act only as an inert diluent, consequently a second acid–base system must always be added to define equilibrium (3). By the same token the range of acidity possible should be greater and depend only upon the intrinsic character of the acids and bases added and not be limited as in the case of water by the acid strength of H_3O^+ and the basic strength of OH^-. At the same time, the low dielectric constant (D = 2.28) hinders the separation of particles of opposite electric charge and thus produces a state of affairs which bears no obvious relation to experience based largely upon aqueous solutions.

Investigations in benzene may be divided into two classes: (a) attempts by Hantzsch[5] to compare the acidity of a particular acid with the acidity of the same acid in another solvent, by studies on reaction velocity and extent of dilution necessary to decompose a salt; and (b) two preliminary investigations by Brönsted[4h] and by the authors,[3] to determine the acidity relations in benzene without reference to any other solvent. Hantzsch's method is open to the criticism[4h] that the kinetic influences of different media are specific and not predictable for any particular reaction.

Were it possible to refer the hydrogen electrode potentials measured in different media to a common scale, new definitions of acidity would be unnecessary. Since this is not possible at present, the strength of any acid may best be defined by the extent to which it reacts with any one base chosen as standard for the solvent in question.[4c,6] Thus the extent of

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(5) Hantzsch and co-workers, (a) *Z. Elektrochem.*, **29**, 221 (1923); (b) **30**, 194 (1924); (c) **31**, 167 (1925); (d) *Ber.*, **58**, 612 (1925); (e) **58**, 941 (1925); (f) **59**, 793 (1926); (g) **59**, 1096 (1926); (h) **60**, 1933 (1927); (i) *Z. physik. Chem.*, **125**, 251 (1927); (j) *Ber.*, **62**, 975 (1929); (k) **63**, 1180 (1930).

(6) Brönsted, Ref. 4g, pp. 288 and 291–295.

reaction of an acid HA with a base B may be measured experimentally by the relation

$$\frac{(\mathrm{HB})}{(\mathrm{B})}\,\frac{(\mathrm{A})}{(\mathrm{HA})}\cdot = \frac{K_{\mathrm{HA}}}{K_{\mathrm{HB}}} = K \tag{4}$$

which is a direct consequence of (3) for ideal solutions, where the parentheses designate the concentrations of the components. K is then one measure of the acidity and may be considered as due mutually to the strength of HA as an acid with strength constant K_{HA} and to the strength of HB as an acid with strength constant K_{HB}. Accordingly, we may write (4) as

$$a_{\mathrm{H}^+} = K_{\mathrm{HA}}\frac{(\mathrm{HA})}{(\mathrm{A})} = K_{\mathrm{HB}}\frac{(\mathrm{HB})}{(\mathrm{B})} \tag{5}$$

and define the proton activity a_{H^+} of the solution in terms of the concentrations[6] of whichever acid–base system (HA:A or HB:B) is most conveniently measured.[7] Equation (5) then yields a general expression for the relative proton activity which requires that for every solvent, one acid–base system be defined as standard. For this system, K_{HA} may be given any convenient value, and this value determines the number used to describe the acidity of any other acid–base system.

By the aid of equation (4), Brönsted has arranged twenty-four acid–base systems in the order of decreasing acid strengths in benzene. No numerical

TABLE I

Acids	Solubility, *M*	Solubility of salts	Remarks
Trichloroacetic	>1.0	Good	
Dichloroacetic	>1.0	Good	
Monochloroacetic	>1.0	Good	
Salicylic	0.04	Good	
Benzoic	.10	Good	
Formic	.10	Good	
Acetic	>1.0	Good	
Hydrochloric	>1.0	Practically zero	Salts too insoluble
Picric	0.3	Very small	Salts too insoluble
Monochlorophenols	*ca* .1	......	Too weak to standardize in water
1,3,5-Dinitrobenzoic	Very small	......	Too insoluble (interfering color phenomena)
2,4-Dinitrophenol	*ca* 0.25	......	
o-Nitrophenol	.1	......	(Interfering color phenomena)
o-Nitrobenzoic	.01	......	Too insoluble
Bases			
Piperidine	>1.0	Good	
Dimethylamine	>1.0		
Guanidine	Very small	......	Too insoluble

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(7) We will use the convention throughout that HA indicates any acid with a corresponding base A, while HB indicates any other acid with a corresponding base B, where all signs indicating the charge type to which the particular acid or base belongs have been intentionally omitted so that the equilibrium may be applied to any charge type.

data are presented and he emphasizes that the results are entirely provisional.[8]

La Mer and Downes have shown that it is possible to carry out electrometric titrations in benzene using the quinhydrone electrode. Their results prove that neutralization of an acid (trichloroacetic acid) by a base (diethylamine) actually occurs in benzene since a typical curve is obtained. The present work was undertaken with a view to improving the technique of the electrometric titrations for a more exact interpretation in conjunction with indicator studies.

In Table I is shown the list of acids and bases which have been tried, with comments upon their utility.

Similarly in Table II is shown a list of the indicators tested, arranged in order of preference.

TABLE II

CRITERIA OF INDICATORS IN BENZENE

1, Solubility; 2, constancy of strength as an acid; 3, stability of color; 4, precision of color match possible.

	1	2	3	4	Color change[a]
Dimethyl Yellow	Good	Good	Good	Good on alkaline side	R-Y
Propyl Red	Good	Good	Good	Good on alkaline side	R-Y
Methyl Red	Good	Good	Good		R-Y
Neutral Red	Good	Poor	Poor	Fair	R-Y
Brom Phenol Blue	Fair	Good	Fair	Fair	Y-R
Brom Cresol Purple	Fair	Good	Fair	Fair	Y-R
Brom Cresol Green	Poor	Poor	Fair	Fair	Y-R
Brom Thymol Blue	Fair	Too far in alkaline range to test			
Malachite Green	Good		Very poor	Poor	
Trinitrobenzene (*sym*)	Good	Too far in alkaline range to test			
Chlor Phenol Red	Slight				
Thymol Blue	Slight				
Phenol Red	Insoluble				
Alizarine Yellow R	Insoluble				
Alizarine Red S	Very slight				
Meta Cresol Purple	Insoluble				
Methyl Orange	Insoluble				
Methyl Violet	Insoluble				
Phenolphthalein	Insoluble				
Thymolphthalein	Insoluble				
Tropaeolin O	Insoluble				

[a] Indicates color abbreviations: Red and Yellow

2. Electrometric Titrations

Except for a considerable improvement in the construction of the cell, the apparatus and methods were identical with those described previously.[3]

The cell consisted of two Pyrex parts (Fig. 1) which were cemented together on either side of a piece of filter paper. The paper was impregnated with a 5% gelatin

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[8] The series with the corresponding pK values in water is quoted by N. F. Hall, *Chem. Rev.*, **8**, 196 (1931), and need not be repeated.

solution and allowed to dry in the air. When dry it is practically impermeable to benzene solutions but will allow an electric current to pass. Platinum electrodes (2.54 cm. square welded to platinum wire) were placed in parts 1 and 2 with the wires brought out through the capillary tubes C and D. The electrodes were so arranged that they would lie flat against either side of the filter paper. With the electrodes in place, the filter paper was cemented to part 1, taking particular care that it was well fastened to the ends of the capillary tube A. A small hole was punched in the filter paper over the opening in capillary A so that it would connect directly with part 2 when the entire cell was assembled. Then part 2 was cemented to the lower side of the filter paper and, after drying, the cell was ready for use. Duco Household Cement proved satisfactory for short periods of time (*e. g.*, several days). Those parts of the glass which were cemented to the paper were ground smooth. When in use, the platinum wires were bent to dip into mercury cups through which connection was made to the potentiometer and ballistic galvanometer.

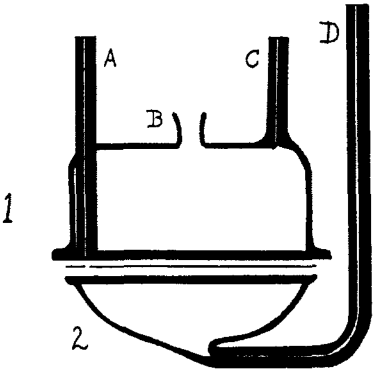

Fig. 1.—Cell for electrometric titration in benzene.

The solution for this cell was prepared by measuring into a 50-cc. graduated flask 10 ml. of 1.0 *M* acid, 5 ml. of 1.0 *M* base, filling nearly to the mark and saturating with tetraisoamylammonium iodide. A small amount (0.015 g.) of quinhydrone was added, and the solution adjusted to exactly 50 cc. This was poured into 2 through D until all of the air was removed from the lower part. Then 10 cc. was pipetted into 1 and the first measurement of potential taken, which differed from zero by only a few tenths of a millivolt. A 1.0 *M* solution of base was next added through the opening B in increments of 0.10 cc.. the solution being stirred by moving the electrodes. At the beginning of the titration the potential reached a steady value in a few minutes, but as the stoichiometric point was approached, three or four hours were necessary.

This cell eliminates the two largest sources of error in the earlier work; thus, (a) the capillary tube D and the gelatin impregnated filter paper reduce diffusion to an imperceptible amount, and (b) the evaporation of benzene and the absorption of moisture were very much lessened by reducing exposure to the air through the small opening B.

The results for trichloroacetic acid titrated with piperidine and for monochloroacetic acid, titrated with diethylamine, are shown in Fig. 2 (a, c) where the potential is plotted against the fraction of acid neutralized. When the acid is in excess, the proton activity is expressed by equation (5) yielding

$$E = E^\circ_A + \frac{RT}{nF} \ln \frac{(A)}{(HA)} \qquad (6)$$

and similarly when the base is in excess, yielding

$$E = E^\circ_B + \frac{RT}{nF} \ln \frac{(B)}{(HB)} \qquad (7)$$

where E°_A and E°_B represent normal potentials of the systems HA:A and HB:B, respectively, referred to a common arbitrary standard. For the reaction

$$\mathrm{HA} + \mathrm{B} = \mathrm{HB} + \mathrm{A}$$

$$E^\circ_{\mathrm{B}} - E^\circ_{\mathrm{A}} = \frac{RT}{nF}\ln K \tag{8}$$

where

$$K = \frac{(\mathrm{HB})}{(\mathrm{B})}\frac{(\mathrm{A})}{(\mathrm{HA})} \tag{9}$$

In order to determine the applicability of the above equations, the values of 0.059 log (A)/(HA) have been calculated and plotted against the observed potential (Fig. 2, b, d). It has been assumed that in each different titration, $E^{\circ}_{\mathrm{A}} = 0$.

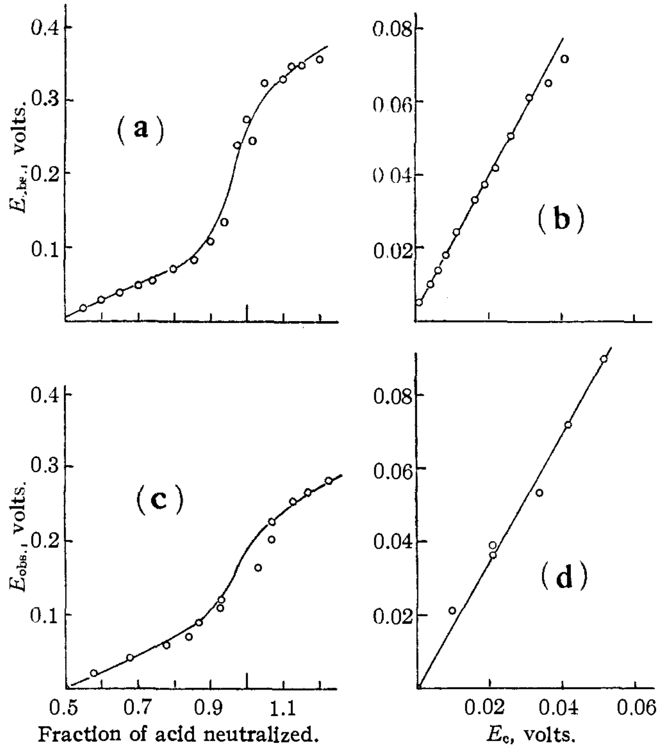

Fig. 2.

The data conform very well to straight lines but to our surprise the slopes proved to have almost twice the expected values. In other words, the measured values of E follow an empirical law

$$E = 2n_a E_c + E^\circ_{\mathrm{A}} \tag{10}$$

or

$$E = (2n_a)\ 0.059 \log \frac{(\mathrm{A})}{(\mathrm{HA})} + E^\circ_{\mathrm{A}} \tag{11}$$

when the acid is in excess, where n_a is a numerical factor varying from 0.87 to 0.96, and

$$E = E^\circ_B - (2n_a)\, 0.059 \log \frac{(B)}{(HB)} \qquad (12)$$

when the base is in excess. We have used the symbol n_a since this discrepancy may arise from transference of the anion. In adding tetraisoamylammonium iodide to increase the conductance we had hoped that it would at the same time obliterate transference effects. Unfortunately nothing is known about the magnitude of transference numbers in benzene, so that this possibility cannot be discussed with profit at the present time.

In any case, the factor of two remains unexplained. Nevertheless we feel it has a real significance in the light of Brönsted and Bell's surprising and inexplicable finding[4h] that in benzene the velocity constant for the decomposition of diazoacetic ethyl ester when catalyzed by carboxylic acids is proportional to the square of the acid concentration.

In Table III, values of E°_B are given for each system, calculated from equation (12). Owing to the instability of quinhydrone, particularly in the presence of excess base, these values are of only qualitative significance. Further attempts to determine relative strengths of acids in benzene by electrometric methods were consequently abandoned in favor of the indicator method.

TABLE III

	E°_B	$E^\circ_A = 0$
Trichloroacetic acid–piperidine	0.495	
Trichloroacetic acid–diethylamine	.429	
Monochloroacetic acid–diethylamine	.347	

3. Formulation of Indicator Results

(a) Ideal Case.[9]—Consider an acid HA, a very much weaker acid HB, and an indicator whose acid form is HI dissociating to their conjugate bases A, B and I as follows[9]

$$HA = H^+ + A \qquad (13)$$
$$HB = H^+ + B \qquad (14)$$
$$HI = H^+ + I \qquad (15)$$

If the components behave as ideal solutes, then the mass law in terms of concentrations is valid and the extent to which the above acids dissociate a

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[9] The electrometric titrations indicate that the mixture of an acid with a base in benzene results in salt formation in the customary sense. Although benzene is an associating solvent, this process of salt formation can be formulated as an ionization, *viz.*, a proton exchange between two neutral molecules, resulting in two oppositely charged molecules. The problem of defining the state of association or dissociation of the salt formed is beyond the scope of this work.

Clark ["The Determination of Hydrogen Ions," Williams and Wilkins Co., 1928, pp. 398–403] has emphasized that the logical interpretation of many galvanic cell reactions in water requires the assumption that a metallic ion exerts its characteristic potential against a metal by a mechanism which necessitates that the ion exists in the form of a very stable complex.

In spite of that fact, the equations for these cells are still written in simple ionic form in aqueous chemistry although the numerical results are patently absurd. Since this method of formulation is accepted for the aqueous case, no apology will be offered for its use in benzene where our knowledge is more limited, even though it is recognized that the dissociation of salts in benzene is extremely minute.

proton may be expressed by the relative values of the constants in the expressions

$$\frac{(\mathrm{H^+})(\mathrm{A})}{(\mathrm{HA})} = K_{\mathrm{HA}} \tag{16}$$

$$\frac{(\mathrm{H^+})(\mathrm{B})}{(\mathrm{HB})} = K_{\mathrm{HB}} \tag{17}$$

$$\frac{(\mathrm{H^+})(\mathrm{I})}{(\mathrm{HI})} = K_{\mathrm{HI}} \tag{18}$$

Consider a solution of an acid HA with a negligible concentration of an indicator I present. The reactions which occur as base B is added may be expressed by subtracting equations (17) and (18), respectively, from (16). Thus

$$\mathrm{HA} + \mathrm{B} \rightleftharpoons \mathrm{HB} + \mathrm{A} \tag{19}$$

$$\mathrm{HA} + \mathrm{I} \rightleftharpoons \mathrm{HI} + \mathrm{A} \tag{20}$$

Corresponding to the mass law relations

$$\frac{(\mathrm{HB})(\mathrm{A})}{(\mathrm{B})(\mathrm{HA})} = \frac{K_{\mathrm{HA}}}{K_{\mathrm{HB}}} = K_{\mathrm{B}} \tag{21}$$

$$\frac{(\mathrm{HI})(\mathrm{A})}{(\mathrm{I})(\mathrm{HA})} = \frac{K_{\mathrm{HA}}}{K_{\mathrm{HI}}} = K_{\mathrm{I}} \tag{22}$$

Since the actual concentration of indicator is negligible with respect to the concentration of acid and base present, the presence of the indicator equilibrium (20) exerts no appreciable displacement on the equilibrium (19) and the extent to which (20) takes places is a measure of the proton escaping tendency of the buffer system formed. That is, proton activity is defined for equations (16), (17) and (18), as

$$a_{\mathrm{H^+}} = K_{\mathrm{HA}}\frac{(\mathrm{HA})}{(\mathrm{A})} = K_{\mathrm{HB}}\frac{(\mathrm{HB})}{(\mathrm{B})} = K_{\mathrm{HI}}\frac{(\mathrm{HI})}{(\mathrm{I})} \tag{23}$$

which can be put in the form

$$p\mathrm{H} = \log\frac{\mathrm{A}}{\mathrm{HA}} + pK_{\mathrm{HA}} \tag{24a}$$

$$= \log\frac{\mathrm{B}}{\mathrm{HB}} + pK_{\mathrm{HB}} \tag{24b}$$

$$= \log\frac{\mathrm{I}}{\mathrm{HI}} + pK_{\mathrm{HI}} \tag{24c}$$

where the symbol p is the customary abbreviation for the negative logarithm.

Thus, if the relative values of pK_{HA}, pK_{HB} and pK_{HI} are known, and an arbitrary value assigned to one of them, one scale of acidity is numerically fixed.

Experimentally I/HI is measured by assuming Beers law, so that

$$\frac{\mathrm{I}}{\mathrm{HI}} = \frac{\text{fraction of total color in alkaline form}}{\text{fraction of total color in acid form}} \tag{25}$$

If the total depth of solution used in the colorimeter is 15 mm. and on the comparison color side R mm. is acid color then 15–R mm. will be base color, then

$$\log \frac{\mathrm{I}}{\mathrm{HI}} = \log \frac{15 - R}{R}$$

In measuring A/HA (or B/HB) it is assumed that equation (7) goes practically to completion ($\mathrm{K_B} \gg 1$). Thus

(A) = concentration of base added or fraction of acid neutralized
(HA) = total acid minus base added, or 1 − fraction neutralized

In logarithmic form, equation (22) becomes

$$\log \frac{\mathrm{A}}{\mathrm{HA}} = \log \frac{\mathrm{I}}{\mathrm{HI}} - pK_{\mathrm{I}} \qquad (26)$$

By plotting log A/HA against log I/HI as in Fig. 3, a family of parallel lines with unit slope results, three members of which have been selected to cut the log (I)/(HI) axis at the points +1, 0, −1, corresponding to the condition that the strength of the acid HA is respectively less than, equal to, or greater than, the strength of the indicator acid HI by one logarithmic unit (or to a factor of ten-fold in the strength constants K_{HA}). Consequently the intercept on either axis is a measure of the strength of the acid relative to the strength of the indicator.

(b) Indicator or Acid Associated.—The mechanisms, postulated in (13) and (14), however, are not the only ones possible. As in the previous case, our attention can be focused on the reaction of the acid with the indicator.

Consider the case where the indicator is associated and consequently may act as a polybasic acid with no measurable distinction between the individual steps by which neutralization occurs. Thus

$$n\mathrm{HA} = n\mathrm{H}^+ + n\mathrm{A} \qquad (27)$$
$$= n\mathrm{H}^+ + \mathrm{I} = \mathrm{H}_n\mathrm{I} \qquad (28)$$
$$= n\mathrm{HA} + \mathrm{I} = \mathrm{H}_n\mathrm{I}^+ + n\mathrm{A} \qquad (29)$$

with corresponding mass action relations

$$\frac{(\mathrm{H}^+)^n\,(\mathrm{A})^n}{(\mathrm{HA})^n} = K^n_{\mathrm{HA}} \qquad (30)$$

$$\frac{(\mathrm{H}^+)^n\,(\mathrm{I})}{(\mathrm{H}_n\mathrm{I})} = K_{\mathrm{H}n\mathrm{I}} \qquad (31)$$

and

$$\frac{(\mathrm{H}_n\mathrm{I})\,(\mathrm{A})^n}{(\mathrm{I})\,(\mathrm{HA})^n} = \frac{K^n_{\mathrm{HA}}}{K_{\mathrm{H}_n\mathrm{I}}} = K'_{\mathrm{I}} \qquad (32)$$

which in logarithmic form becomes

$$n \log \frac{\mathrm{A}}{\mathrm{HA}} = \log \frac{\mathrm{I}}{(\mathrm{H}_n\mathrm{I})} - npK_{\mathrm{HA}} + pK_{\mathrm{H}_n\mathrm{I}} \qquad (33)$$

It is to be noted that the K_{HA} in equation (30) is a dissociation constant as well as a measure of the acid strength relative to a second system, and obviously the same constant as in equation (5). However, $K_{\mathrm{H}_n\mathrm{I}}$ is a dissociation constant but *not* a measure of the acid strength under the same conditions as in section (a) although $\sqrt[n]{K_{\mathrm{H}_n\mathrm{I}}}$ *is* a measure of the acid strength of the indicator. Obviously, since in benzene the hydrogen-ion concentration is meaningless, it must be replaced by the proton activity. Thus from (31), we have

$$a^n_{\mathrm{H}^+} = K_{\mathrm{H}_n\mathrm{I}} \frac{\mathrm{H}_n\mathrm{I}}{\mathrm{I}} \tag{34}$$

Since the present interest is in comparative proton activities, it is obvious that the nth root must be used

$$a_{\mathrm{H}^+} = \sqrt[n]{K_{\mathrm{H}_n\mathrm{I}}} \sqrt[n]{\frac{\mathrm{H}_n\mathrm{I}}{\mathrm{I}}} \tag{35}$$

Consequently the proton activities of the indicators which behave as polybasic acids are proportional to the nth root of the total dissociation constant.

In regard to the physical interpretation, equation (29) means that the indicator or the acid may be capable of combining with one or more protons. If the value of n is greater than unity, then one molecule of indicator can combine with more protons than does one molecule of the acid. If n is less than unity the acid can combine with more protons than the indicator. If log (A)/(HA) is plotted against log (I)/($\mathrm{H}_n\mathrm{I}$) as in (Fig. 3), then according to (33) the slope of the line obtained will be equal to $1/n$.

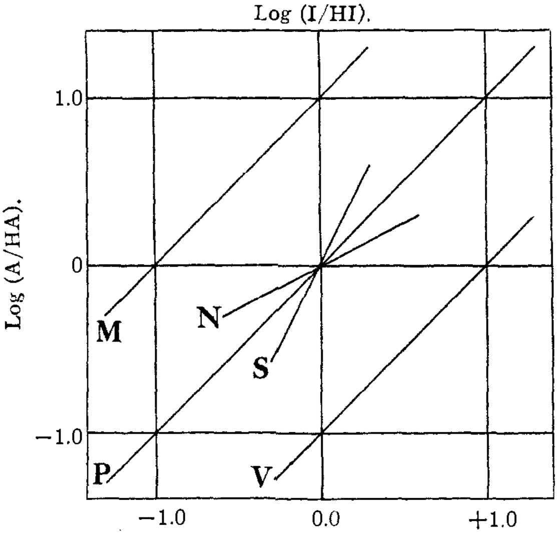

Fig. 3.—Indicator formulation: M, $K_{\mathrm{HA}} = 10\ K_{\mathrm{HI}}$, $n = 1$; P, $K_{\mathrm{HA}} = K_{\mathrm{HI}}$, $n = 1$; N, $n = 2$; S, $n = 1/2$; V, $K_{\mathrm{HA}} = 0.1\ K_{\mathrm{HI}}$, $n = 1$.

Values of n different from unity may be accounted for by assuming either HA or HI to be polybasic acids. The conventional picture would be the association of either HI or HA. Regarded in this sense, n is a measure of the degree of association of HI relative to the association of HA, where

$$n = a/b \tag{36}$$

a = number of molecules in the HI aggregate

b = number of molecules in the HA aggregate

If $n > 1$, then HI is associated more than HA. If $n < 1$, HA is associated more than HI. This means that we cannot distinguish, if $n = 2$, between the case where HA exists in the form of single molecules and HI as double molecules, and the case where HA exists as double and HI as quadruple molecules.

(c) **Formulation for Bases.**—The situation with respect to the titration of a base with an acid is entirely analogous, except that the indicator is initially an acid.

$$n\mathrm{B} + \mathrm{H}_n\mathrm{I} = n\mathrm{HB} + \mathrm{I} \tag{37}$$

$$\frac{(\mathrm{B})^n}{(\mathrm{HB})^n}\,\frac{(\mathrm{HI})}{(\mathrm{I})} = K_\mathrm{I} \tag{38}$$

$$n \log \frac{(\mathrm{B})}{(\mathrm{HB})} = \log \frac{(\mathrm{I})}{(\mathrm{HI})} - pK_\mathrm{I} \tag{39}$$

But here

(B) = concentration of free base = 1 − fraction neutralized = $1 - f$

(HB) = concentration of salt = fraction neutralized = f

Hence

$$\log \frac{(\mathrm{B})}{(\mathrm{HB})} = -\log \frac{f}{1-f}$$

while the quantity log (I)/(HI) retains the same meaning which it had for the titration of an acid with a base. In making the calculation in this manner, the strength is evaluated in terms of the conjugate acid HB rather than in terms of the free base B.

4. Experimental Procedure

(a) **Preparation of Benzene Solutions.**—The solutions in benzene were made up of approximately the strength desired and standardized against an aqueous solution of sodium hydroxide, by extraction with a constant quantity of water.

The burets were of 2-cc. capacity, with a small reservoir, and graduated in 0.01 cc.

The benzene was thiophene free (Merck, Eimer and Amend, and Kahlbaum). In some cases it was dried with sodium and in other cases not. No difference was observed as a result of this treatment.[10,11]

The sulfonphthalein indicators were from La Motte, and the others from the Eastman Kodak Company. They were employed without further purification. See Sec. 9 on Neutral Red. The acids, trichloroacetic, dichloroacetic, and monochloroacetic, were from the Eastman Kodak Company; formic, benzoic, and salicylic acids from Columbia University laboratory supplies.

(b) **Titration.**—The titration in benzene solution was performed in one of the cups of the colorimeter. In principle, the colorimeter[11] consists of two columns of liquid, the total depth of which was always 15 mm. One side contained two small reservoirs, one with the acid form of the indicator solution in benzene, the other with the basic form.

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[10] Menzies and Wright, *J. Phys. Chem.*, **35**, 1655 (1931), for efficacy of drying over sodium. For the detection and elimination of traces of water see Rosenbaum and Walton, THIS JOURNAL, **52**, 3568 (1930); J. Greer, *ibid.*, **52**, 4191 (1930).

[11] Bausch and Lomb hydrogen ion colorimeter, employing Hasting's and Sendroy's modification of Gillespie's principle. See Clark, Ref. 9, pp. 168 *et seq.*

These were so arranged that the total depth of 15 mm. might consist of either all of the acid color, all of the basic color, or any mixture of the two.

The light from a 75-watt bulb placed at a distance of 75 cm. was passed through the fixed depth of solutions.

Solutions of the acid and basic color were made up and each placed in the proper reservoir. On the test side was placed an acid solution (0.10 to 0.01 *m*) having an indicator concentration of about 0.00001 *m*.

The largest single source of error in the titrations was the visual one in matching colors. The uncertainty in any one reading may be as large as 0.5 mm. This may cause an uncertainty in log (A)/(HA) of ±0.14 for any stage of the titration where log (I)/(HI) and log (A)/(HA) lie between +0.8 and −0.8. The results for duplicate titrations agreed to about ±0.10 logarithmic units.

5. Presentation and Discussion of Data

The numerical results of a typical titration are shown in Table IV. These and other titrations are plotted in Figs. 4 and 5. In the same manner separate diagrams are obtained for every indicator. The complete results are summarized in Table V where the slopes and the intercepts on the log (I)/(HI) axis are given. Each value in this summary is the average result of at least two separate experiments. It is observed that the relation between log (A)/(HA) and log (I)/(HI) is linear, and the slope is equal to $^1/_2$ for the 0.01 M acids and $^1/_3$ for the 0.10 M acids with the exception of

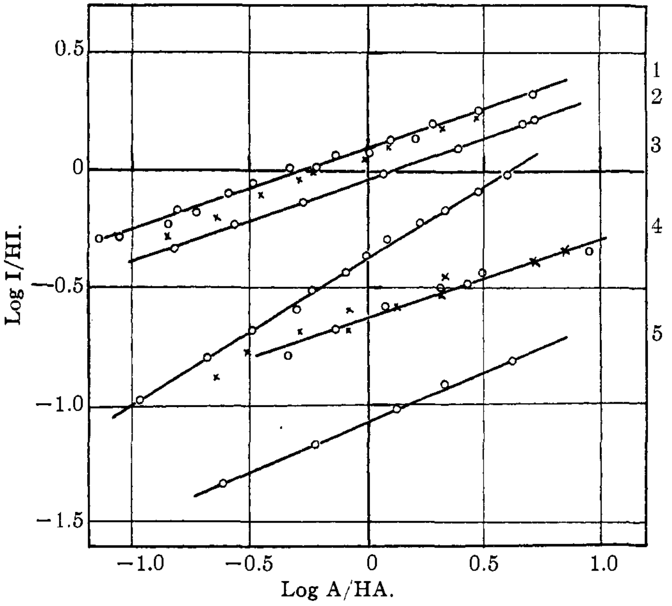

Fig. 4.—Dimethyl yellow: 1, trichloroacetic acid, 0.10 *M*; 2, trichloroacetic acid, 0.05 *M*; 3, trichloroacetic acid, 0.01 *M*; 4, dichloroacetic acid, 0.10 *M*; 5, dichloroacetic acid, 0.05 *M*; ○ = piperidine used as base; × = diethylamine used as base in (1) and (4).

acetic acid corresponding to n equal to either 2 or 3 or some intermediate value. No values outside of this range have been substantiated. As a consequence of the different values of n, lines representing different concentrations of one acid may cross each other. For example, in Fig. (5), 0.10 M monochloroacetic acid behaves like a weaker acid than 0.01 M monochloroacetic acid.

TABLE IV

TYPICAL TITRATION

0.1 M Trichloroacetic Acid–piperidine with Dimethyl Yellow

Log (A)/(HA)	−0.294	−0.229	−0.167	−0.049	0.010	0.070	0.128	0.189	0.252	0.315
Log (I)/(HI)	−1.16	−0.86	−0.73	−0.57	−0.33	−0.13	0.10	0.28	0.48	0.71

TABLE V

SUMMARY OF TITRATION DATA

Acid	Concentration	Slope	Intercept	Indicator
Trichloroacetic acid	0.10	0.31	−0.32	Dimethyl Yellow
	.05	.37	+ .14	Dimethyl Yellow
		.37	+ .10	Dimethyl Yellow
	.01	.54	+ .61	Dimethyl Yellow
		.50	+ .67	Dimethyl Yellow
	.10	.33	+ .08	Methyl Red
	.10	.33	± .00	Propyl Red
Dichloroacetic acid	.10	.33	−3.06	Brom Phenol Blue
	.10	.31	+1.94	Dimethyl Yellow
		.33	+1.90	Dimethyl Yellow
	.05	.35	+3.21	Dimethyl Yellow
Monochloroacetic acid	.10 wet	.31	−0.47	Brom Phenol Blue
	.10 dry	.33	− .67	Brom Phenol Blue
	.01	.48	− .78	Brom Phenol Blue
Salicylic acid	.01	.51	−1.35	Brom Phenol Blue
Formic acid	.01	.50	+0.91	Brom Phenol Blue
Acetic acid	.10	.50	+3.68	Brom Phenol Blue
		.50	−0.49	Brom Cresol Purple
Benzoic acid	.01	.50	+2.72	Brom Phenol Blue
Piperidinium Ion	.10	.47	+2.82	Brom Cresol Purple
Diethylammonium Ion	.10	.50	+0.30	Brom Cresol Purple
	Data for Neutral Red			
Dichloroacetic acid	.01	.46	−1.58	Feb. 12, 1932
Monochloroacetic acid	.01	.53	+0.00	Feb. 12, 1932
		.48	− .79	Apr. 18, 1932
Formic acid	.01	.50	+1.75	Feb. 12, 1932
Acetic acid	.10	.45	+1.19	Apr. 16, 1932
		.46	+1.00	Apr. 18, 1932
		.45	+1.10	Dec. 11, 1931

The formulation (33) cannot be expected to represent more than a first approximation. It assumes that as long as the ratio (A)/(HA) is constant, the absolute values of either (A) or (HA) are immaterial. We know this is approximately true for weak acids in water,[12] but not if the relative changes in ionic strength are large.

6. Special Considerations

(a) Theory of Indicator Measurements in Benzene.—That the colors of the indicator ion or ionogen are not affected by the concentration of neutral salt present, or in general by the concentration of the solution, is one of the fundamental assumptions made for indicator measurements in aqueous solutions. Halban and Ebert[13] have shown that this condition is not exactly fulfilled in aqueous solution, but it is an error which has been almost universally neglected. When the solvent is benzene, however, it is to be expected that this error may be greatly magnified.

It has been found that in addition to a rapid reversible acid–base equilibrium, there is a more gradual irreversible change in color, which is closely connected with the total concentrations of acid and base in the system. In a similar fashion, the effects of dichromatism which are so troublesome for indicators like Brom Cresol Purple in water, are intensified in benzene.[14] The color transformation in water is brought about by a change in the concentration or total depth of the indicator solution through which the light passes. In benzene the color transformation depends on the concentration of neutralized acid or base present. In studying indicators in concentrated sulfuric acid, Hammett and Deyrup[15] have found anomalies of this character to be quite marked.

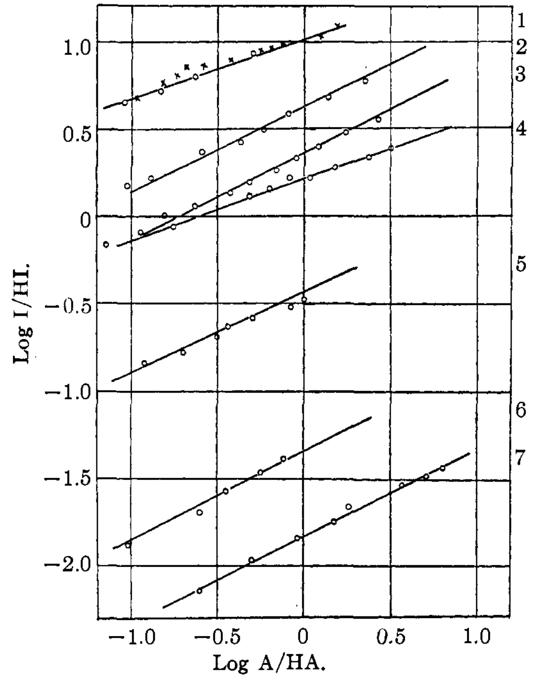

Fig. 5.—Brom phenol blue: 1, dichloroacetic acid, 0.10 *M*; 2, salicylic acid, 0.01 *M*; 3, monochloroacetic acid, 0.01 *M*; 4, monochloroacetic acid, 0.10 *M*; 5, formic acid, 0.01 *M*; 6, benzoic acid, 0.01 *M*; 7, acetic acid, 0.10 *M*.

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(12) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1928, p. 24.

(13) Halban and Ebert, *Z. physik. Chem.*, **112**, 321 (1924); *ibid.*, **112**, 359 (1924); Sidgwick, Worboys and Woodward, *Proc. Roy. Soc.* (London), **A129**, 537 (1930).

(14) Clark, Ref. 9, pp. 162–163.

(15) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

If Brom Phenol Blue is added to a benzene solution of pure acid, the solution remains colorless. As base is added, a yellow color appears which cannot be discharged by addition of acid. It becomes more intense the greater the amount of base added, until a reversible color change from yellow to red takes place, analogously to the color change in water from yellow to purple. If the acid is very dilute, the color will change progressively from yellow to a yellow–purple mixture, to a yellow–red mixture and finally to red without any yellow present on the addition of base.

On the other hand, if Brom Phenol Blue is added to a benzene solution of a pure base, a purple color is observed. If the base is moderately concentrated (greater than 0.01 M) the addition of acid changes the purple to a red color and finally when an excess of acid is added, changes the red to a yellow. The change from purple to red is an irreversible change, for no matter how great an excess of base is added to the red solution, the purple color will not be regenerated. If the base is extremely dilute, the addition of an excess of acid will change the purple color directly to yellow.

For indicators whose color change is from red in acid to yellow in alkaline form, the change is similar but less obvious. The change in acid color due to change in salt concentration is a change in intensity, and similarly the yellow color change in the basic form is a change in intensity.

For this reason if an attempt is made to titrate an acid using the color of the indicator in pure acid solution as a standard color, the intensity of color in the test solution will decrease slowly until the reversible acid–base color change takes place. After this point has been reached, the change will take place more rapidly with an equal rate of addition of base. If this deviation from ideal behavior is due to the choice of an incorrect color for an acid standard, it is possible to correct the data obtained by determining approximately the reading of the colorimeter at which the reversible color change starts. In one case the color changed slowly from a reading of the colorimeter of 15 mm. with no base added, to a reading of 7.8 mm. at which point $\log (A)/(HA) = -1.20$. Since the rapid color change did not start until the reading was about 8 mm., the value of $\log (I)/(HI)$ was calculated on the basis of 8 mm. ($\log (I)/(HI) = \log (8 - R)/R$) instead of the usual 15 mm. total depth. This assumes that the color obtained at 8 mm. is the acid color corresponding to the reversible acid–base color change of the system, which shall be designated as the true acid color. It is found that when this calculation is made, the relation between $\log (A)/(HA)$ and $\log (I)/(HI)$ is linear and has the expected slope.

In Fig. 6 (curves 2, 3, 4) we have three examples of this correction, where the lines are drawn from the original corrected data while the points represent a different titration, with the true acid color used as color standard. The two methods of correction are seen to agree within the limits of experimental error.

In a similar fashion it is possible to interpret a titration where the acid color has been partly transformed to the basic color. An example of this type of correction is shown in Fig. 6, line 1, where the line is drawn from corrected data and the points are the result of new titrations.

Since the effect of environment is continuous it is to be expected that for the titration of every acid, different color standards must be used for the true acid and the true basic colors for one indicator for each concentration employed.

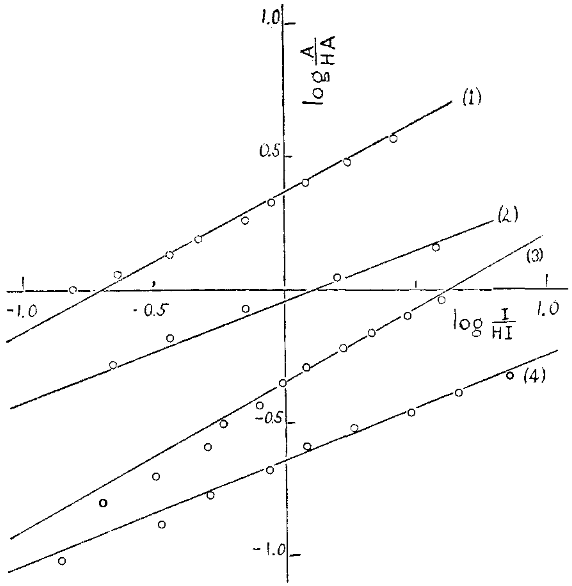

Fig. 6.—(1), Monochloroacetic acid, 0.01 *M*, indicator, brom phenol blue; (2), trichloroacetic acid, 0.05 *M*, indicator, dimethyl yellow; (3), trichloroacetic acid, 0.01 *M*, indicator, dimethyl yellow; (4), dichloroacetic acid, 0.10 *M*, indicator, dimethyl yellow.

Several investigators[13] have pointed out that the color and dissociation constant of an indicator depend on the concentration of all the dissolved substances, although the effect is usually a small one in water. Only those indicators which have proved to be relatively insensitive to salt errors have survived. It is necessary only to call attention to these cases to make it obvious that the situation in benzene is quite similar.

(b) **Proof of Non-Specificity of Bases Used.**—It has been assumed that the titration of an acid with a base is independent of the particular base used if a stoichiometrically smaller quantity of base is present than of acid. In order to determine in how far this assumption is justified, several titrations have been repeated, using first piperidine, then diethylamine. The data for some of these titrations are plotted in Fig. 4. The examples shown are representative of all the results. No case has been found where the differences between the two bases could be detected.

(c) **Change Due to Saturation of the System with Water.**—Using a solvent like benzene it is important to ascertain the effects of small concentrations of water. To this purpose, a titration was made of dry monochloroacetic acid with dry piperidine in dry benzene. The benzene and the piperidine were dried with sodium. The acid was dried over sulfuric acid and an indeterminate solution prepared rapidly. This solution was then transferred directly to a clean buret, standardized, and titrated in duplicate at once. The result is shown in Fig. 7, line 1. A second titration was made with the same materials, but in this case the benzene solution of the acid was saturated with water by blowing moist air over the top until cloudiness appeared in the solution. The second titrations are shown in Fig. 7, line 2.

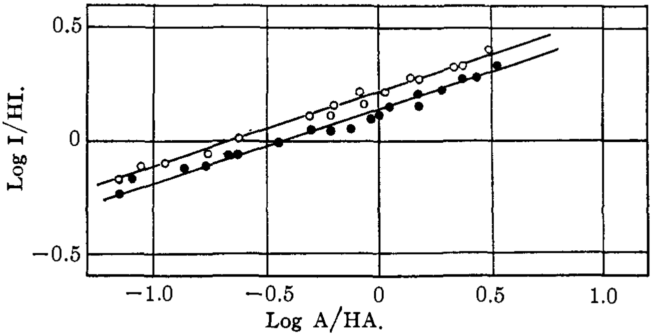

Fig. 7.—Monochloroacetic acid titrated in ○, dry benzene; ●, wet benzene; brom phenol blue as indicator.

We conclude that the presence of water sufficient to saturate the benzene solution, in the titration of an acid, functions in the same way as a small undetermined amount of base, lowering the entire curve about 0.10 logarithmic unit, the value of *n* remaining unchanged. No gross error will be made if the water present in ordinary benzene exposed to the air is neglected, at least in the case of acids of the strength of the chloroacetic acids, since the solution is not by any means saturated as was the second titration.

7. Method of Correlation

According to the mechanism postulated in equation (33), we can either compare the acidity of the two buffer systems HA_1:A_1 and HA_2:A_2 at equal concentration ratios $(A_1)/(HA)_1$ and $(A_2)/(HA)_2$ or compare the values of these ratios when the same indicator color has been produced. If *n* were unity in all cases, the two methods would give identical results, but since *n* varies the correct method must be chosen.

In order to compare the strengths of two acids HA_1 and HA_2 each titrated with any one indicator HI we may employ equation (33) for each acid and take the difference. Thus

$$n_1 \log \frac{\mathrm{A}_1}{\mathrm{HA}_1} - n_2 \log \frac{\mathrm{A}_2}{\mathrm{HA}_2} = \log \left[\frac{\mathrm{I}}{\mathrm{H}_n\mathrm{I}}\right]_1 - \log \left[\frac{\mathrm{I}}{\mathrm{H}_n\mathrm{I}}\right]_2 - n_1 pK_{\mathrm{HA}_1} + n_2 pK_{\mathrm{HA}_2} + pK_{\mathrm{H}_{n_1}\mathrm{I}} - pK_{\mathrm{H}_{n_2}\mathrm{I}} \quad (39)$$

When the comparison is made of the extent of neutralization of each acid necessary to produce half transformation of the indicator, then $\left[\frac{\mathrm{I}}{\mathrm{H}_n\mathrm{I}}\right]_1 = \left[\frac{\mathrm{I}}{\mathrm{H}_n\mathrm{I}}\right]_2 = 1$, and the method is designated as the *isochroic* or equal color comparison. In this case

$$n_1 \log \frac{\mathrm{A}_1}{\mathrm{HA}_1} - n_2 \log \frac{\mathrm{A}_2}{\mathrm{HA}_2} = n_2 pK_{\mathrm{HA}_2} - n_1 pK_{\mathrm{HA}_1} + pK_{\mathrm{H}_{n_1}\mathrm{I}} - pK_{\mathrm{H}_{n_2}\mathrm{I}} \quad (40)$$

The left-hand members of this equation (40) can be measured, but the right-hand members cannot be analyzed in terms of acidity unless either $n_1 = n_2$ or unless we restrict ourselves to one acid at two concentrations rather than to two acids. No simple comparison can be made along the log (A)/(HA) axis, when n_1 is not equal to n_2. When $n_1 = n_2$, then

$$\log \frac{\mathrm{A}_1}{\mathrm{HA}_1} - \log \frac{\mathrm{A}_2}{\mathrm{HA}_2} = pK_{\mathrm{HA}_2} - pK_{\mathrm{HA}_1} \quad (41)$$

and the differences in intercepts along the log (A)/(HA) axis give directly the relative logarithmic strength constants of one acid in terms of the other as defined by $a_{\mathrm{H}^+} = K_{\mathrm{HA}}$ (HA)/(A).

The strengths of all the acids may be obtained (relative to one acid chosen as a standard) by measuring along the log (A)/(HA) axis the distance from acid A to acid B for indicator 1, then the distance from acid B to acids C, D, E, and F for indicator 2 or what amounts to the same thing, by superimposing the two indicator diagrams so that the lines for acid B (which is common to both) coincide and the log (A)/(HA) axis is common to both diagrams. This allows a direct measure along the extended axis of the difference between the strengths of any two acids, provided $n_1 = n_2$.

If an attempt is made to measure the difference in strengths between two indicators, different results, equal in number to the different concentrations at which the acid is titrated in both indicator solutions will result, since n varies with concentration. This follows from equation (33) as may be seen from a simple calculation, similar to the one above for two indicators and one acid, when n is variable.

It is possible, however, to correlate the indicator diagrams in a second way. The diagrams for two indicators that have an acid in common, may be superimposed by making the log (I)/(H_nI) axes coincide, and varying the distance between the two origins until each line, for the acid in common is an extrapolation of the other. This may be done analytically by the use of equation (33) as in the previous case, yielding

$$\log \left[\frac{\mathrm{I}}{\mathrm{H}_n\mathrm{I}}\right]_1 - \log \left[\frac{\mathrm{I}}{\mathrm{H}_n\mathrm{I}}\right]_2 = n_1 pK_{\mathrm{HA}_1} - n_2 pK_{\mathrm{HA}_2} + pK_{\mathrm{H}_{n_2}\mathrm{I}} - pK_{\mathrm{H}_{n_1}\mathrm{I}} \quad (42)$$

This amounts to comparing the color ratios produced (for a single indicator H_nI) when each of two acids, HA_1 and HA_2 are half neutralized ($A_1/HA_1 = A_2/HA_2 = 1$) and will be designated as the *isohalsine* or equal salt comparison. Thus if $n_1 = n_2 = n$, the difference in strength constants of the two acids is measured by $1/n$th of the difference of the intercepts on the log $(I)/(H_nI)$ axis. Consider next two concentrations of the same acid which are found experimentally to have different values of n. Then equation (42) becomes

$$\log\left[\frac{I}{H_nI}\right]_1 - \log\left[\frac{I}{H_nI}\right]_2 = pK_{I_1} - pK_{I_2} \qquad (43)$$

where

$$pK_{I_1} = n_1pK_{HA_1} - pK_{H_{n_1}I}$$
$$pK_{I_2} = n_2pK_{HA_2} - pK_{H_{n_2}I}$$

Thus the difference in the intercepts along the log $(I)/(H_nI)$ axis for two concentrations of the same acid is a direct measure of the difference in extent to which the acids HA_1 and HA_2 react with the indicator H_nI, the value of n changing. In order to reduce this to an acidity difference, it must be divided by n. Since, however, n is not constant but varies from 2 to 3, the result is only approximately correct. In making this correlation, any concentration of acid may be used and the apparent strength of the indicator remains constant. All of the change in relative strength between the acid and indicator has been attributed to the acid.

Thus since the isohalsine correlation provides not only a comparison of the apparent strengths of different acids but also a comparison of the apparent strength change of a single acid at two different concentrations, we will use it to represent the results. Since, in general, n approximates 2, the log $(I)/(H_nI)$ axis will be compressed to half its size, so that acidity is denoted as

$$P_H = {}^1/_2 \log \frac{(I)}{(H_nI)} \qquad (44)$$

Numerical values are assigned by assuming that trichloroacetic acid has the same strength in benzene that it has in water, *viz.*, $pK = 0.70$. The result is shown in Fig. 8.

8. General Discussion

Figure 8 provides a scale of acidity which is exact, within the limits of experimental error, for those acids which are now represented by lines with a slope of unity, and is approximately correct for those lines with slopes less than unity. It has the advantage of representing the experimental results directly. Our knowledge of benzene solutions is too incomplete at present to allow an exact interpretation of the effect of dilution.

Our numerical results agree with the order of strengths obtained by Brönsted[4c,16] in all but two cases. He finds that salicylic acid is weaker than monochloroacetic acid, which our measurements show cannot be true

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(16) Table I above.

when both acids are measured at the same concentration. In addition he places Neutral Red between Brom Phenol Blue and Brom Cresol Green, whereas it has been our experience that the acid strength of Neutral Red in benzene varies with conditions.

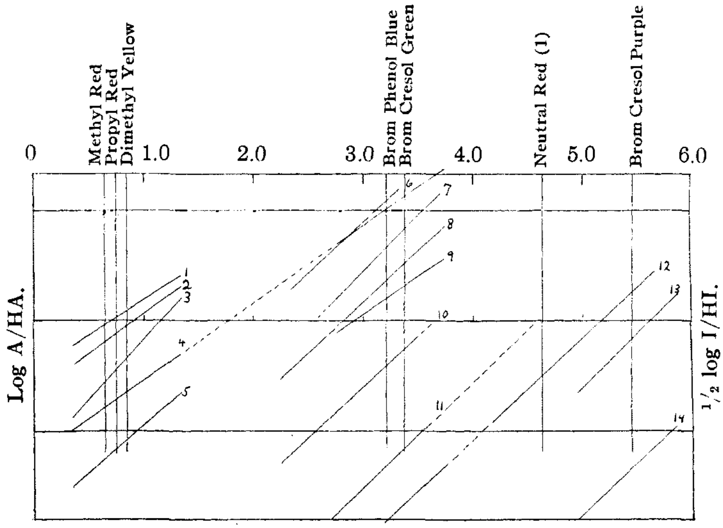

Fig. 8.

1.	Trichloroacetic acid	0.10 M	8.	Monochloroacetic acid	0.01 M
2.	Trichloroacetic acid	.05 M	9.	Monochloroacetic acid	.10 M
3.	Trichloroacetic acid	.01 M	10.	Formic acid	.01 M
4.	Dichloroacetic acid	.10 M	11.	Benzoic acid	.01 M
5.	Dichloroacetic acid	.05 M	12.	Acetic acid	.10 M
6.	Dichloroacetic acid	.01 M	13.	Diethylammonium ion	.10 M
7.	Salicylic acid	.01 M	14.	Piperidinium ion	.10 M

To compare acid strengths in benzene with those in water, we have plotted in Fig. 9 the values (shown in Table VI) of pK in water against the intercepts on the $^1/_2$ log $(\mathrm{I})/(\mathrm{H}_n\mathrm{I})$ axis in Fig. 9. The latter will be designated as pK_{benzene}. As would be expected, the uncharged acids are observed to retain the same differences in strength among themselves that exist in water. In addition, the strengths of the cationic acids have increased to a considerable extent over their strengths in water, relative to the uncharged acids. Since this effect has been predicted[17] a calculation was made to determine the extent to which piperidine reacts with a number of acids.

If an acid and a base are mixed in equivalent quantities at concentration c, then a concentration x of the new acid and base results. From Fig. 8, values of pK may be measured by the difference in intercepts between piperidine and the acid considered, then substituted into equation (4). Thus $x^2/(c - x)^2 = K$, or $x/c = \sqrt{K}/(1 + \sqrt{K})$ = fraction of com-

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(17) Ref. 4g, pp. 296, 298.

TABLE VI

RELATIVE STRENGTHS OF ACIDS IN WATER AND BENZENE

Acids	*pK* in water	*pK* in benzene
Trichloroacetic acid	0.7[a]	0.70
Dichloroacetic acid	1.3[a]	1.75
Monochloroacetic acid	2.86[c]	2.90 = 0.10 *M*
		2.80 = .01 *M*
Salicylic acid	3.0[a]	2.55
Formic acid	3.7[a]	3.64
Benzoic acid	4.2[a]	4.58
Acetic acid	4.7[a]	5.18
Methyl Red	5.1[b]	0.64
Propyl Red	5.4[b]	.74
Dimethyl Yellow	3.5[a]	.84
Brom Phenol Blue	3.98[b]	3.22
Brom Cresol Green	4.67[b]	3.38
Brom Cresol Purple	6.3[b]	5.46
Neutral Red	7.4[b]	4.64
		2.80
Diethylammonium Ion	11.0[b]	5.62
Piperidinium Ion	11.1[a]	6.80

[a] Hall, *Chem. Rev.*, **8**, 191 (1931). [b] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928. [c] Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

pletion at the stoichiometric point. The result of these calculations is shown in Table VII. However, in our titrations the reaction is more nearly complete than the figures indicate because the acid is in excess and forces the reaction (3) to the right.[18]

TABLE VII

EXTENT OF REACTION WITH PIPERIDINE WITH EQUIVALENT AMOUNTS OF ACIDS

Acid	Fraction of completion
Trichloroacetic	0.999
Dichloroacetic	.991
Monochloroacetic	.989
Acetic	.865

Since the acidity differences among the uncharged acids are the same in benzene as in water, it can be inferred that the indicators belong to several other different charge types. One can attribute a *zwitterion* structure to the sulfonphthalein indicators which would account for their displacement. An indicator like Dimethyl Yellow is probably of the charge type HB^+. This assumption fits in well with the anomalous behavior of Neutral Red as well as for the mechanisms proposed for Methyl Red and Propyl Red. However, on this basis, it is indicated that piperidine is an acid of charge type H_2B^{++}, with diethylamine of possibly an even higher charge type. This is not surprising since the benzene titrations contain a factor *n* which has been considered as due to association of the indicator.

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(18) Ref. 4e, p. 2061.

Although the actual acid–base reaction has been treated in a subsidiary manner, it is quite possible that the base as well as the indicator may be associated, so that in benzene an acid of charge type H_nB^{n+} is formed.

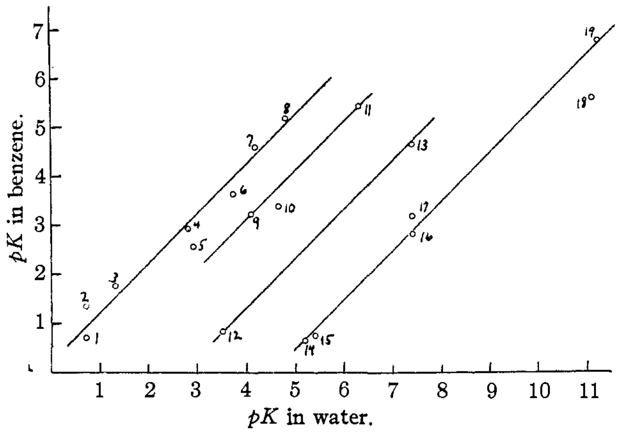


Fig. 9.

1. Trichloroacetic acid 0.10 M
2. Trichloroacetic acid 0.01 M
3. Dichloroacetic acid 0.10 M
4. Monochloroacetic acid 0.01 M
5. Salicylic acid 0.10 M
6. Formic acid 0.01 M
7. Benzoic acid 0.01 M
8. Acetic acid 0.10 M
9. Brom Phenol Blue
10. Brom Cresol Green
11. Brom Cresol Purple
12. Dimethyl Yellow
13. Neutral Red (1)
14. Methyl Red
15. Propyl Red
16. Neutral Red (2)
17. Neutral Red (3)
18. Diethylamine
19. Piperidine

9. Neutral Red

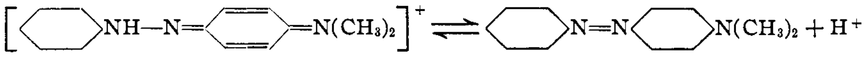
The titrations with various indicators fitted the above scheme of formulation with the exception of Neutral Red. The first sample of this indicator was obtained from the Eastman Kodak Laboratories and will be designated by the initials E. K. L. Titrations, made of 0.01 M dichloroacetic, monochloracetic and formic acids, showed Neutral Red to be a stronger acid than Brom Phenol Blue by 0.38 logarithmic units, while several titrations of 0.10 n acetic acid revealed that it might act as a weaker acid than Brom Phenol Blue by 1.40 units.

From these titrations it was evident that Neutral Red must really be acting as two different indicators in different acidity ranges. In a solution of a strong acid (0.01 M monochloroacetic acid), Neutral Red has a fairly deep red color, while in a weaker acid (0.10 M acetic acid), it is pink. When sufficient base has been added to either acid, however, the final color is yellow. In other words, if an attempt is made to measure the proton activity of a benzene solution with Neutral Red, a definite color will be obtained but it is not possible to tell with which color range the color is associated. Accordingly for an analytical indicator it is useless. For present purposes it will be as useful as any other indicator to determine the manner in which the acidity of a buffer system varies in the immediate acidity range in which the particular sample of indicator changes color.

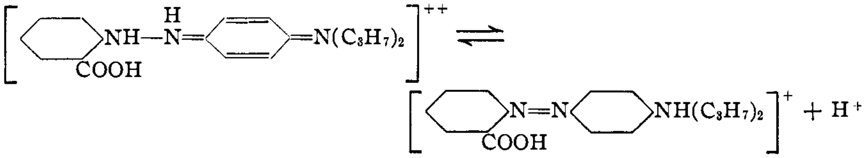
Later, through the kindness of W. Mansfield Clark, a specially purified sample of the free base of Neutral Red was obtained.[19] When this was titrated with acetic acid, the result was identical with that obtained from the first sample. When used in titrating monochloroacetic acid, however, it was found that Neutral Red (W. M. C.) had the same strength as Brom Phenol Blue. A second titration was made using Neutral Red (E. K. L.) with monochloroacetic acid. It showed Neutral Red (E. K. L.) to be of the same strength as Brom Phenol Blue also.

It is believed that the dual role of Neutral Red is due to successive reactions of the base with an acid, whereby one or two protons are exchanged, depending on the strength of the acid.

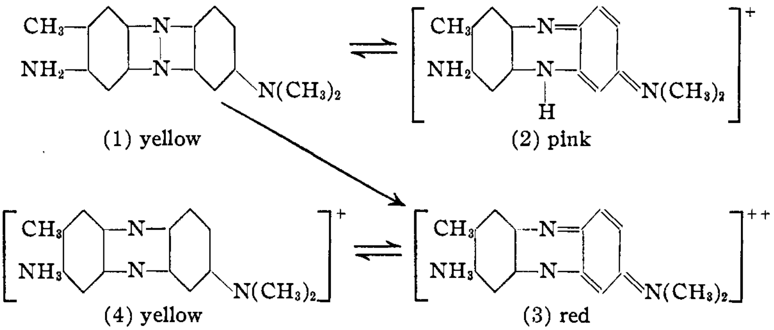
From the diagram of relative acid strength in benzene and water (Fig. 9), it can be seen that acids of the same charge type lie along lines with a slope of one. This would place Neutral Red as the same charge type as Dimethyl Yellow for the weaker acid (N. R. 1) and as Propyl Red (N. R. 2 and 3) for the stronger acid. W. M. Clark[20] writes the formula of Dimethyl Yellow salt as



and we suggest for Propyl Red



On this basis two reactions of Neutral Red are possible



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(19) Clark and Perkins, THIS JOURNAL, **54**, 1228 (1932).

(20) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1928, p. 112.

The type of reaction where the extra proton can attach itself more or less irreversibly to a nitrogen without involving quinoid formation is not predictable but is entirely possible.[21] The color obtained for the full basic color in titration of a strong acid (formula 4 for Neutral Red) is yellow, whereas if we were dealing with successive additions of a proton to 1, we should expect the color to go from yellow to pink to red, then in reverse order as protons are removed. In other words, if a base is added to monochloroacetic acid, we should expect a very slow change from the deepest red to a lighter shade, a rapid change to pink, a slow change in the pink and finally a rapid change from pink to yellow. However, no evidence of a slow change in the pink has been found, which would be indicated by the curve becoming parallel to the log (A)/(HA) axis. In fact, the experimental points become more nearly parallel to the log (I)/(HI) axis. This must mean that if the pink color is due to a definite compound, the change either from forms 1 to 3, or from 1 to 2 to 3, must be an irreversible one, and the yellow color at the end must be due to a different compound than the yellow obtained when Neutral Red is dissolved in benzene.

The fact that the more acid form of Neutral Red does not have the same strength at all times is not surprising, since the Schiff bases with which Moore and Gale[21] were dealing formed a red di-hydrochloride which was converted slowly to a yellow form without change in composition. In addition we have observed that if Neutral Red in benzene solution is allowed to stand in sunlight for some hours, it will transform irreversibly from yellow to a reddish form which will precipitate out, leaving a colorless solution. It is evident that no definite values can be ascribed to the strength of Neutral Red as an indicator.

Summary

1. A method based on the use of indicators has been developed for measuring quantitatively the relative strengths of acids and bases in benzene. The method has been applied to sixteen acid–base systems, seven of which are indicators.

2. Uncharged acids in benzene retain the same numerical differences in strength among themselves that exist in water, whereas indicators exhibit marked changes in strength on passing from water to benzene.

3. The results of La Mer and Downes for electrometric titration of acids and bases in benzene have been verified and extended by the use of an improved form of cell. The e. m. f. readings are almost twice those predicted by the Nernst equation; a similar behavior has been recorded for the velocity of reactions catalyzed by acids in benzene.

4. It has been shown by electromotive force and indicator methods that the addition of a base to an acid results in salt formation. The extent of this reaction has been determined.

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(21) Moore and Gale, THIS JOURNAL, **30**, 394 (1908); Moore and Woodbridge, *ibid.*, **30**, 1000 (1908)

5. It has been shown that the action of diethylamine and piperidine as bases in dilute solution is not specific when determining the strength of a given acid.

6. Neutral Red behaves anomalously as an indicator in benzene.

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The Structure of Electrodeposited Alloys. II. The Effect of Current Density and Temperature of Deposition on the Structure of Silver–Cadmium Deposits[1]

BY CHARLES W. STILLWELL AND HENRY I. FEINBERG

In a recent paper[2] the relation between the composition and crystal structure of electrodeposited silver–cadmium alloys was reported. It was found that the two metals are deposited either as solid solutions or compounds, corresponding in general to the solid solutions or compounds existing in thermal alloys of the same composition. A mixture of the two metals is never deposited.

The present investigation was undertaken to determine the effect of current density and temperature of deposition on the structure of the deposits. It is at least possible that under extreme conditions of deposition the two metals might be plated independently rather than as solid solutions or compounds.

Experimental

The baths from which the alloys were plated were made as described by Stout and Thummel.[3] Cadmium oxide was dissolved in sodium cyanide with specified quantities of sodium sulfate, nickel sulfate, sodium tartrate and turkey red oil. The solution contained 39 g. of cadmium per liter. The composition of the bath was varied by adding to this the desired quantities of a sodium argenticyanide solution containing 58 g. of silver per liter. The alloys were deposited on sheet copper, 10 × 2 cm. and 0.1 cm. in thickness. Two duriron anodes were used, the cathode being adjusted between them, 5.0 cm. from each. Three plates were prepared for each set of conditions. In each case the first and third were analyzed and the second was used to determine the diffraction data. The composition of the plates was determined by precipitating silver as silver chloride, removing the copper electrolytically from an acid solution and precipitating the cadmium electrolytically from a basic cyanide solution.[4]

The effect of current density upon the composition of the deposits is shown in Table I. All the specimens were deposited at room temperature (27°), and from a bath containing 11.6 g. of silver and 31.5 g. of cadmium per liter.

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(1) This paper was presented at the Denver meeting of the American Chemical Society.

(2) Stillwell and Stout, THIS JOURNAL, **54**, 2583 (1932).

(3) Stout and Thummel, *Trans. Electrochem. Soc.*, **59**, 337 (1931).

(4) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, pp. 197, 205.