TITRATIONS IN ETHYL ALCOHOL AS SOLVENT.

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The use of alcohol as a solvent in acid-base titrations may be advantageous for two reasons. The first is its solvent power for certain substances, such as the fatty acids, which are not soluble in water. The second is the somewhat greater sharpness of the end-points obtainable.[2] This is due to the fact that the dissociation of alcohol is much less than that of water[3] so that there is a greater range of hydrogen-ion concentration between an acid and an alkaline solution. For the same reason the degree of alcoholysis of salts of weak acids and bases is less than the degree of hydrolysis, so that the change in hydrogen-ion concentration through the end-point is more rapid in alcohol than in water. The alkalies in the alcohol system are the ethylates, so that the neutralization of a weak acid by sodium ethylate would be represented in the ionic form by the equation, $HA + C_2H_5O^- = A^- + C_2H_5OH$. While the dissociation of the acid, HA, is doubtless smaller in alcohol than in water, the dissociation of the alcohol is so much less than that of water as to account for the small degree of alcoholysis just mentioned. The alcoholysis of the salt is, of course, represented by the reverse equation.

For the titration of weak acids and bases it is necessary to select an indicator which changes color at the hydrogen-ion concentration existing at the true end-point, when the acid and base are present in equivalent quantities.[4] The purpose of this investigation has been to prepare an indicator scale for alcoholic solutions similar to those in common use for aqueous solutions.[5]

Apparatus and Procedure.—The hydrogen-ion concentration was measured by means of a hydrogen electrode[6] against a standard mercurous bromide electrode. The hydrogen electrode, instead of being of the foil type previously described by one of us, was a gauze cylinder similar to that originally used by Cottrell in this laboratory.[7]

[1] The preliminary work of this investigation was described in 1919 in the Master's Thesis by Esther B. Kittredge. The major portion of the data herein presented is taken from the Master's Thesis by Edna R. Bishop, 1921.

[2] Folin and Flanders, THIS JOURNAL, **34**, 774 (1912).

[3] An accurate determination of this constant is being made in this laboratory, and will shortly be published.

[4] Hildebrand, THIS JOURNAL, **35**, 847 (1913).

[5] E. g., Salm, Z. physik. Chem., **57**, 471 (1907).

[6] The hydrogen electrode has been used previously, in alcoholic solutions by Hardman and Lapworth, J. Chem. Soc., **99**, 2242 (1911); **101**, 2249 (1912); to determine the transport number of HCl and the effect of water upon it.

[7] Schmidt and Finger, J. Phys. Chem., **12**, 406 (1908).

The standard electrode was made as described by Lewis, Brighton and Sebastian[8] substituting as electrode materials mercury, mercurous bromide and sodium bromide, 0.1 N in alcohol. Sodium bromide was substituted for the usual potassium chloride in order to get a more concentrated and hence better conducting electrolyte. The mercury used had been washed with nitric acid and distilled. The mercurous bromide was precipitated from c. p. sodium bromide and mercurous nitrate in the presence of mercury. It was then thoroughly washed with alcohol and 0.1 N sodium bromide in alcohol. The sodium bromide electrodes were reproducible within the limits of accuracy of the galvanometer.

The titrations were performed in a cell consisting of a beaker provided with a tight stopper through which were thrust the hydrogen electrode, the tip of the buret, an exit tube for hydrogen provided with a mercury seal, and the tube connecting with the standard electrode. The temperature was controlled to $25 \pm 1°$ by means of a hand-regulated thermostat. The rest of the apparatus was set up as described in previous papers from this laboratory.

The electromotive force of such a combination at $25°$ is given approximately by the familiar equation

$$E = E_o - 0.059 \ \log \ c$$

where c is the hydrogen-ion concentration and E_o the electromotive force of the mercurous bromide electrode against a normal hydrogen electrode. The value of E_o has not yet been determined so that values will be given in terms of electromotive force instead of hydrogen-ion concentration.

If to an acid solution in the cell, sodium ethylate solution be added from the buret, and the e.m.f. plotted against the cubic centimeters of sodium ethylate added, a curve·will be obtained in which the point of inflection represents the end-point of the titration. The shape of the curve will depend on the strength of the acid used.

The proper indicator for a given titration is one which changes color near the point of inflection of the e.m.f. curve. However, in order to determine where a given indicator changes color, an acid-base curve should be selected which is as flat as possible in the region of the color change, so that the e.m.f. may easily be controlled within narrow limits. It is necessary, therefore, to find acids and bases of various strengths so that the entire range from acid to base may be covered by flat portions of curves.

Materials Used.—It was found necessary to use chemicals free from oxidizing agents, in order that there should be no other reaction taking place at the electrode and that the e.m.f. obtained should be a true measure of the hydrogen-ion concentration. The alcohol was purified by distilling from conc. sulfuric acid (10–15 cc. of acid per liter of alcohol) to remove the amines and most of the water, distilling from silver nitrate

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[8] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

(5 g. per liter) and a small amount of potassium hydroxide to remove the aldehydes and similar oxidizing bodies, and finally removing the last trace of water by shaking with calcium oxide for 2 days and distilling.

Sodium ethylate was prepared by dissolving metallic sodium in alcohol cooled in an ice-bath (at 0°). When the alcohol is not kept cold during the reaction resinous bodies are formed which seriously interfere with the constancy of the hydrogen electrode. As a simple means of obtaining the desired amount of sodium, it was sucked up while molten into glass tubes so that any desired length could be measured off and dissolved. The concentration of the solution could thus be determined by weighing the tubes before and after dissolving the sodium or by titrating with a standard acid solution.

The phenol was purified by distillation and kept in the dark, as the colored variety seemed to contain an oxidizing substance which affected the electrode.

Hydrochloric acid solution was prepared by dropping conc. sulfuric acid on sodium chloride, and passing the gas through calcium chloride into alcohol. Ammonium ethylate solution was prepared by dropping water on sodium hydroxide and ammonium chloride and passing the gas through soda lime into alcohol.

Aniline was purified as described by Gattermann,[9] omitting the ether extraction.

Titration Curves.—Fig. 1 gives titration curves of various acids with sodium ethylate and of bases with hydrochloric acid. Table I gives data concerning concentrations and end-points.

TABLE I

Substance titrated (15 cc. of solution)	N	Titrating solution	End-point Cc.
Acetic acid	0.068	NaOEt	14.2
Ammonia	0.2	HCl	9.2
Aniline	0.2	HCl	15.5
Chlorophenol	0.068	NaOEt	11.0
Maleic acid	0.0515	NaOEt	18.0
Palmitic acid	0.074	NaOEt	11.2
Phenol	0.2	NaOEt	8.5
Sulfuric acid	0.074	NaOEt	12.7

It required about 45 minutes for the solutions to become saturated with hydrogen and the electrode to come to equilibrium. After additions of
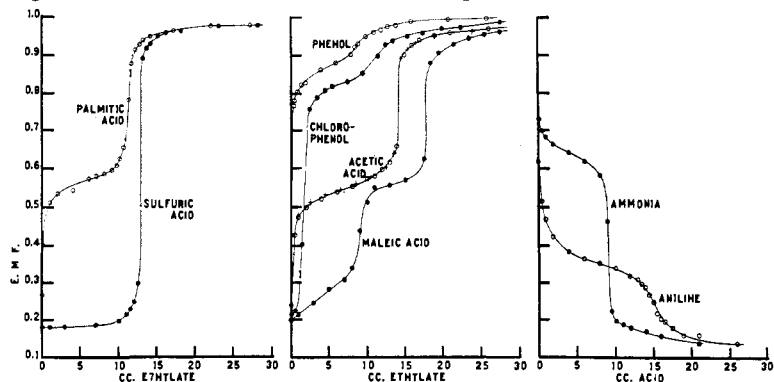

Fig. 1.—Titrations in ethyl alcohol solutions.

⁹ Gattermann, "Practical Methods of Organic Chemistry," Macmillan and Co., 1903, p. 189.

titrating solution equilibrium was attained in about 10 minutes. The titrations are therefore much slower than when aqueous solutions are used.

It will be seen that the curves, as was expected, are very similar to those obtained for aqueous solutions, but that the difference in e.m.f. between acid and alkaline solutions is greater on account of the smaller dissociation constant of alcohol, as previously explained. The curves are quite reproducible, as illustrated by the two sets of points upon the curve for acetic acid.

Table of Indicators.—Examination of the curves obtained shows that the aniline and hydrochloric acid curve is flat enough for the determination

TABLE II

COLOR CHANGES OF INDICATORS IN ETHYL ALCOHOL

Indicator	Conc. G. per 1	No. of drops	Titrating solution	E.m.f. of color changes
Bitter almond oil green	1.5	5	HAc-NaOEt	Green 0.69 colorless
Bromophenol blue	1	5	HCl-aniline	Yellow 0.34 green 0.47 blue
Cresol red	1	5	HCl-aniline	Pink 0.20, orange 0.30
Curcumin	Sat.	2	HAc-NaOEt	Greenish-yellow 0.66 red 0.85 orange 0.91 golden
Cyanine	1	8	HCl-aniline	Colorless 0.24 blue
Gallein	1	5	HAc-NaOEt	Rose 0.68 violet-blue
Iodeosin	Sat.	5	HCl-aniline	Golden-brown 0.20 pink
Methyl green	Sat.	8	HAc-NaOEt	Blue 0.66 lavender
Methyl orange	1	5	HCl-aniline	Pink 0.20 orange 0.23 yellow
Methyl violet	1	5	HAc-NaOEt	Violet 0.95 colorless
Methyl red	Sat.	9	HAc-NaOEt	Red 0.54 orange 0.62 yellow
Naphtholbenzoin	1	10	HAc-NaOEt	Light brown 0.70 blue
p-Nitrophenol	1	5	HAc-NaOEt	Colorless 0.61 yellow-green
Phenolphthalein	10	5	Phenol-NaOEt	Colorless 0.68 red
Resorcin blue	1	5	HAc-NaOEt	Red 0.39 blue
Rosalic acid	1	5	HAc-NaOEt	Golden 0.58 orange 0.65 pink
Sodium alizarin sulfonate	Sat.	10	HAc-NaOEt	Greenish-yellow 0.50 orange 0.57 rose 0.82 violet
Thymol blue	1	10	HCl-aniline	Red 0.30 golden
Thymolphthalein	10	5	Phenol-NaOEt	Colorless 0.82 blue
Trinitrobenzene	Sat.	5	HAc-NaOEt	Colorless 0.68 golden-orange
Tropaeolin	Sat.	5	HCl-aniline	Salmon-pink 0.20 orange 0.23 golden
Tropaeolin OO	Sat.	5	HCl-aniline	Pink 0.15 orange 0.20 yellow

of the color changes of indicators from about 0.14 to 0.45 volts, acetic acid and sodium ethylate from 0.45 to 0.70 volts and from 0.90 to 0.97 volts, p-chlorophenol and sodium ethylate from 0.75 to 0.98 volts. These three pairs practically cover the range.

After the titration curves were obtained it was unnecessary to repeat the titration with the hydrogen electrode with each indicator investigated. Time was saved in most instances by determining the amounts of acid and base required to produce a certain color change and then finding the corresponding e.m.f. from the original hydrogen-electrode curve. This indirect method was indeed necessary with such indicators as trinitrobenzene which oxidized the hydrogen electrode, thus giving values for the e.m.f. which were not true measures of the hydrogen-ion concentration.

The indicators investigated, concentration, number of drops used and e.m.f. of the color change are given in Table II. The positions of most of the indicators in alcohol are close to their positions in water but there are exceptions, $e.\ g.$, cyanine is considerably displaced toward the acid side, and some indicators which are useful in water cannot be used at all in alcohol. The e.m.f.'s of the color changes are accurate to approximately 0.03 volts. Of course the color does not change abruptly at the e.m.f. given, so that the figures should be considered as indicating a color intermediate between the two limiting colors.

Titration of Fatty Acid in Presence of Fat.—As an illustration of the use of the indicator table we will give results for the titration of a free fatty acid in the presence of its glyceride, a problem of some analytical importance. Palmitic acid and palmitin were selected for the purpose. By reference to Fig. 1, it will be seen that palmitic acid is neutralized by sodium ethylate at about 0.8 volt so that thymolphthalein should change color close to the true end-point. The following table gives the results of four titrations with 0.157 N sodium ethylate solution, tripalmitin being present in each case nearly to the point of saturation.

TABLE III

Solvent alcohol	Palmitic acid	
	Taken G.	Found G.
Absolute.............................	0.467	0.467
Absolute.............................	0.493	0.490
Commercial 95%.....................	0.513	0.512
Commercial 95%.....................	0.436	0.439

The results show that an accurate titration is possible by this means, and further that extreme dehydration of the alcohol is unnecessary. The chief effect of small amounts of water is to decrease the solubility of the fat and thus retard the titration.

It is obvious that suitable indicators can be selected by the aid of Table II for the other titrations represented by the curves in Fig. 1. For example,

the end-point for ammonia corresponds to about 0.38 volt, but the curve is steep between 0.25 volt and 0.53 volt. Evidently, therefore, bromophenol blue, changing at 0.34 volt, or resorcin blue, changing at 0.39 volt, should give a sharp end-point in the titration of ammonia.

Summary.

Hydrogen-electrode titration-curves are given for a number of reactions in the ethyl alcohol system, together with a table of indicators for use in such reactions. The possible applications of the data obtained are illustrated by the titration of a fatty acid in the presence of its glyceride.

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NOTE.

The Relation Between Entropy and Probability.[1] The Integration of the Entropy Equation.—The rate of increase of the specific heat with the entropy of a given element or compound depends upon the probability of the randomness of the individual particles. At the absolute zero, or at the point of zero kinetic energy we are quite certain that each particle will remain in a fixed position. The probability, therefore, will be unity. At relatively high temperatures the probability of that state prevailing is very nearly zero. Now, the mathematical expression of the above statements may be assumed to be proportional to the term, $\dfrac{C\infty - C}{C\infty}$,

which at the absolute zero is unity and at relatively high temperatures approaches zero, or,

$$\frac{dC}{dS} = K \left\{ \frac{C\infty - C}{C\infty} \right\} \tag{1}$$

Assuming that when C is zero S is also zero, Equation 1 on integration gives,

$$S = \frac{C\infty}{K} \log \frac{C\infty}{C\infty - C} \tag{2}$$

The value of K may be readily obtained by substituting in Equation 1 $C dT/T$ for its equal dS and integrating. Thus,

$$\frac{dC}{dT} = \frac{K(C\infty - C)C}{C\infty \ T}. \tag{3}$$

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[1] The specific heats of all solid substances decrease with the temperature and approach zero as the absolute temperature approaches zero. This experimental fact led to the assumption that at the absolute zero of temperature the specific heat of all substances is actually zero. Following this announcement many attempts were made, notably by Einstein, (*Ann. Physik*, [4] **22**, 180 (1907)), Nernst and Lindemann, (*Sitzt. Akad. Wiss. Berlin.*, 494, 1911), Debye, (*Ann. Physik*, [4] **39**, 789 (1912)), and by Planck, "Theorie der Wärmestrahlung," to express the specific heat as a simple function of the absolute temperature, but with no success.