

The energy-volume coefficients are approximately independent of concentration in the range of pressure and temperature we have studied. The apparent volumes of sodium bromide in glycol are independent of temperature at constant volume of the solution, and are compared with the corresponding quantities in aqueous solution.

The thermal expansibilities of ethylene glycol both in the pure state and in solution at different pressures and temperatures are representable by a single linear function of $1/(B + P)$, a quantity which is obtained directly from the compressibilities of the solutions.

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[CONTRIBUTION FROM THE CLEVELAND CLINIC AND WESTERN RESERVE UNIVERSITY]

Electrometric and Conductometric Studies of the Neutralization Reactions of Phosphoric Acid. The Neutralization of Very Dilute Solutions of Phosphoric Acid with Sodium Hydroxide

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The first conductometric study of the titration reaction between phosphoric acid and sodium hydroxide was made by Daniel Berthelot,^{1c} who recorded data obtained by constant volume titrations of 0.5, 0.1 and 0.01 molar phosphoric acid solutions. His method involved the addition of the desired amount of titer to a given volume of acid and the dilution of the resulting solution to a standard volume. The conductivity of the diluted solution was then measured.

In discussing his results, it is convenient arbitrarily to divide the titration curve into four parts. The portion of the curve which lies between the abscissa values of 0 and 1.0 equivalent of base added will be referred to as the first branch of the curve; the portion between 1.0 and 2.0 equivalents of base added, as the second portion of the curve; the section between 2.0 and 3.0 equivalents of base added, as the third branch of the curve; and the portion of the curve beyond this point, as the fourth branch of the curve.

Using this notation, we found that in the most concentrated solution which Berthelot used, the first branch of the curve was not investigated, the second was reported as being straight, the third as being curved and blending into the fourth. On increasing the dilution to 0.1 molar, Berthelot found that the third end-point could just be detected. On going to 0.01 molar he reported that both the first and the second branches were

straight and that the third end-point had disappeared.

Further investigations by Kusters, Grütters and Geible,² by Schmidt,³ by Thiele and Roemer,⁴ and by Kolthoff,⁵ clearly indicate the existence of a tendency of the various branches of the curve to approach linearity with increasing degrees of dilution.

More recently the literature has been reviewed by Lanzing and van der Wolk,⁶ who at the same time presented data obtained from a series of eight titrations in an attempt to evaluate the results obtained by previous workers. By the use of their data, they confirmed the fact that neither the second nor the third stoichiometric point could be determined accurately by conductometric methods.

The first electrometric investigation of this neutralization reaction was carried out by Bovie⁷ and hence involved the use of the direct reading potentiometer of his own design. Although it was indicated by this work that the first and second inflection points corresponded exactly to the first and second stoichiometric points, respectively, a later investigation by Davis, Oakes and Salisbury⁸ showed that this was not quantitatively true when they titrated 0.0771 *M* phosphoric acid with 0.2 normal sodium hydroxide. However, they did show that in the titration of

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(1c) D. Berthelot, *Compt. rend.*, **113**, 851 (1891).

(2) Kusters, Grütters and Geible, *Z. anorg. Chem.*, **42**, 225 (1904).

(3) M. R. Schmidt, *Am. Chem. J.*, **40**, 305 (1908).

(4) A. Thiele and H. Roemer, *Z. physik. Chem.*, **63**, 711 (1908).

(5) I. M. Kolthoff, *Z. anorg. Chem.*, **112**, 165 (1920).

(6) J. C. Lanzing and L. J. van der Wolk, *Rec. trav. chim.*, **46**, 83 (1929).

(7) W. T. Bovie, *J. Med. Research*, **23**, 295 (1915).

(8) C. E. Davis, E. T. Oakes and H. M. Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923).

approximately 0.1 molar phosphoric acid the second stoichiometric point could be determined more accurately by the use of phenolphthalein than by the use of the second inflection in the electrometric curve. This, of course, does not prove that this would be the case over a wide range of concentrations.

Further work by Hoffman and Gortner,⁹ Wright and Gibson,¹⁰ Holt, LaMer and Chown,¹¹ Malaprade,¹² and Britton¹³ failed to show that the shape of the electrometric curve obtained in the titration of phosphoric acid with sodium hydroxide was independent of the concentration used or that the second inflection point in this curve quantitatively agreed with the second stoichiometric point.

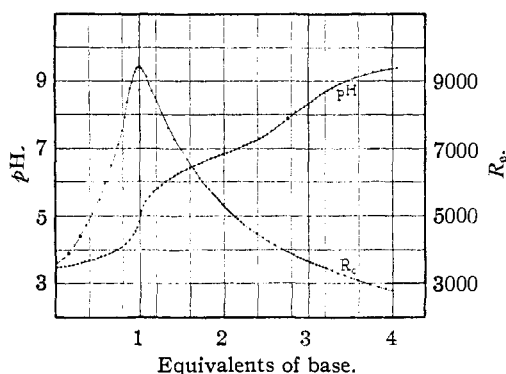


Fig. 1.—Titration of 0.000275 *M* phosphoric acid with 0.0205 *M* sodium hydroxide.

Experimental

The solutions of phosphoric acid to be titrated were prepared by dilution from a stock solution which had been carefully standardized against potassium acid phthalate. The sodium hydroxide used in the preparation of titer was purified according to the method of Clark.¹⁴ The procedure suggested by Pregl¹⁵ was especially helpful in preparing solutions approximating the desired normality. The exact normality of this titer was then determined by titration against a standard hydrochloric acid solution. Conductivity water prepared by a method similar to that suggested by Kendall¹⁶ was used in the preparation of all solutions.

The *pH* of the solutions was determined by means of a glass electrode and calomel half-cell, the potential of the

(9) W. F. Hoffman and R. A. Gortner, *J. Phys. Chem.*, **29**, 769 (1925).

(10) A. H. Wright and F. H. Gibson, *Ind. Eng. Chem.*, **19**, 749 (1927).

(11) L. E. Holt, V. K. LaMer and H. B. Chown, *J. Biol. Chem.*, **114**, 509 (1925).

(12) M. L. Malaprade, *Ann. chim.*, **11**, 104 (1927).

(13) H. T. S. Britton, *J. Chem. Soc.*, 614 (1927).

(14) W. M. Clark, "Determination of Hydrogen Ions," first edition, Williams and Wilkins Company, Baltimore, Md., 1920, p. 71.

(15) F. Pregl, *Z. anal. Chem.*, **67**, 23 (1925).

(16) J. Kendall, *THIS JOURNAL*, **38**, 2461 (1916).

complete cell being measured by means of a direct reading Beckman *pH* meter. The conductometric curve was determined by measuring the resistance offered by the solutions to a 1000-cycle current across two platinized platinum electrodes. The alternating current bridge used for this purpose was a modification of that designed by Jones and Josephs.¹⁷ The bridge was balanced by means of a cathode ray tube null point detector similar in design to one previously suggested for this purpose by Hovorka and Mendenhall.¹⁸

A series of four electrometric and conductometric curves representing the titration reaction of varying concentrations of phosphoric acid in water with sodium hydroxide solutions serving as titer are presented in an attempt to determine the effect of the initial concentration of the acid on the shape of the curve. Only this one factor has been changed throughout the entire series.

Discussion

The first titration, the curve for which is given in Fig. 1, involves the reaction between 0.000275 molar phosphoric acid and 0.0205 normal sodium hydroxide. Electrometrically, it has been found that the phosphoric acid solution of this normality has a *pH* of approximately 3.4, and that this value increases rather rapidly and almost linearly until about seven-tenths of an equivalent of base has been added. On continuing the titration, it is found that the rate at which the *pH* changes increases until a point of inflection is reached with the addition of one equivalent of base.

Having passed the first stoichiometric end-point, it is observed that the *pH* continues to increase but that the rate at which this change occurs is continually decreasing. It is interesting to note that between the limits of 0.7 and 1.3 equivalents of base added, the curve is symmetrical with respect to the ordinate value of *pH* 5.0 and equivalents of base added. After passing the abscissa value of 1.3, the symmetry with respect to the previously mentioned coordinates is destroyed by the increasing rate at which the *pH* increases. As the second stoichiometric point is reached, the electrometric curve continues without the appearance of an inflection. Even when $d(pH)/dE$ is plotted against the number of equivalents of sodium hydroxide added there appears no inflection point either at or near the second stoichiometric point. This also applies to data reported in Figs. 2, 3, and 4. However, a point of deflection does occur with the addition of approximately 2.5 equivalents of titer.

The failure of the second inflection point to

(17) G. Jones and R. C. Josephs, *ibid.*, **50**, 1049 (1928).

(18) F. Hovorka and E. E. Mendenhall, *J. Chem. Education*, **16**, 239 (1939).

appear at the exact second stoichiometric point is best understood in view of the equations developed by Eastman¹⁹ and Roller.²⁰ From these equations it is agreed that no inflection point should be anticipated if $C_a K_a$ is less than (2.7×10^{-13}) and that the point of inflection in the electrometric curve will agree exactly with the stoichiometric point only when the ionization constant of the acid, K_a , becomes infinite.

Applying this generalization to the titration of a phosphoric acid solution where C_a , the concentration of the acid, is equal to (2.75×10^{-4}) and where the third ionization constant is equal to (3.6×10^{-13}) , no inflection should be expected at the third stoichiometric point since the value of $K_{a3} C_a$ is approximately equal to (1×10^{-16}) .

In this same titration, an inflection should be expected as a result of the second stage of neutralization since K_{a2} is equal to (2×10^{-7}) , thus giving the term $K_{a2} C_a$ the value of (5.5×10^{-11}) . It will be noted that the numerical value of this term has closely approached the limit at which an inflection possibly could be produced and it is, therefore, not surprising that the deviation of the inflection point from the stoichiometric point is relatively large.

Figures 2, 3 and 4 illustrate the effect of increasing concentrations on the position of the point of inflection. Figure 2 involves the reaction between 0.000561 molar phosphoric acid and 0.0205 molar sodium hydroxide. Figure 3 represents 0.000856 molar phosphoric acid and Fig. 4, 0.000967 molar phosphoric acid. In each case 0.0205 molar sodium hydroxide solution is used. The feature which is most outstanding from the viewpoint of analytical chemistry is that the clarity of the first inflection point increases markedly as the concentrations are increased. It is also important that in these extremely dilute solutions the second stoichiometric point cannot be ascertained from the second inflection point, due to its large deviation from the latter.

The conductometric curves which are presented are particularly significant since they represent the neutralization of phosphoric acid in a reaction which is not complicated by the formation of a precipitate. The explanation of these curves is relatively simple. As the hydrogen ions are replaced by the less mobile sodium ions, the resistance of the conductivity cell increases rapidly until

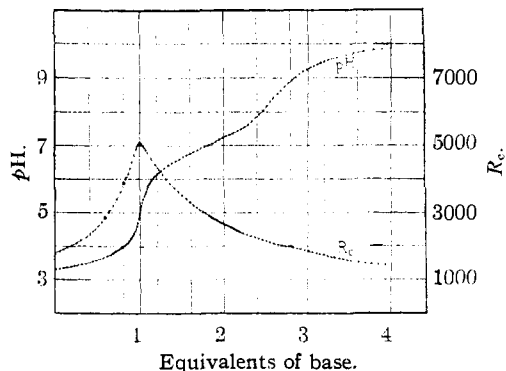


Fig. 2.—Titration of 0.000561 *M* phosphoric acid with 0.0205 *M* sodium hydroxide.

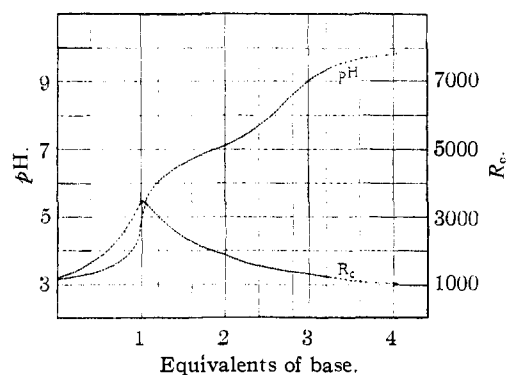


Fig. 3.—Titration of 0.000856 *M* phosphoric acid with 0.0205 *M* sodium hydroxide.

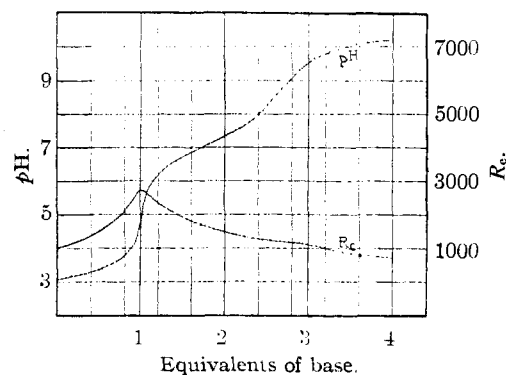


Fig. 4.—Titration of 0.000967 *M* phosphoric acid with 0.0205 *M* sodium hydroxide.

the first stoichiometric point has been reached. At this stage of the titration the concentration of hydrogen ions has been reduced until it is small as compared to the other ion concentrations and is, therefore, no longer the factor mainly responsible for the conductivity of the solution.

The most important fact illustrated by these curves is the approach to linearity which accompanies decreasing concentrations. However, even in the most dilute solutions which were studied a

(19) E. D. Eastman, *THIS JOURNAL*, **47**, 332 (1925).

(20) P. S. Roller, *ibid.*, **50**, 1 (1928).

linear relation between the equivalents of titer added and the resistance offered to the conductivity cell had not been established.

Summary

1. Electrometric and conductometric curves for the titration of very dilute solutions of phosphoric acid with sodium hydroxide have been presented.

2. The first stoichiometric point of the reaction is analytically indicated by a maximum in the conductometric curve and by an inflection in the electrometric curve.

3. Within the limits of concentration studied, the second stoichiometric point cannot be ascertained from the second inflection point by either of the methods which were used.

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The Significance of X-Ray Diffraction Patterns Obtained from Starch Granules¹

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In contrast to the situation with cellulose, little information regarding the structure of starch has been gained from application of X-ray diffraction methods.² However, Katz and his co-workers³ have shown that starches offer a variety of types of diffraction pattern, and once these are interpreted much can be expected from study of the diffraction data.

X-Ray investigation of starches has been limited to powder patterns which, while indicating in many instances a surprising degree of crystalline organization, are relatively weak and diffuse and have offered no great wealth of information. It is impossible, even microscopically, to observe external crystal symmetries, and no one has yet succeeded in obtaining oriented fiber patterns.⁴ In the absence of knowledge concerning geometrical relationships between visible structure and diffraction pattern, and between separate diffractions, the problem is a difficult one indeed.

While it may be unnecessary to abandon hope of securing oriented diffractions eventually, in the present paper this limitation is accepted. In attempting to determine what progress can be made from powder patterns alone, one soon discovers that with starch the variety of patterns exhibited compensates somewhat for the limitations of individual ones. By obtaining accurate information for a number of related patterns, and by comparing line positions and intensities

in these, it is possible to draw conclusions regarding the structures responsible for them.

Experimental

Choice of Materials.—Native granular starches exhibit the most satisfactory degree of crystalline perfection while offering a variety of similar, yet recognizably different, patterns. Náray-Szabó⁵ and Katz and van Itallie⁶ indicate that granular starches yield patterns which are of two chief types, designated by the latter investigators as "A" (cereal starches) and "B" (tuber or potato starches). A "C" class represents intermediates which are usually fairly close to one or other of the extremes. It is of interest to make a detailed comparison of representatives of the A and B types, because of a feeling that similar molecular structures must underlie the observed essential similarities in gross structure and optical properties existing in all types of granule.

For this purpose the present paper describes experiments employing cornstarch as a source of A patterns and potato starch for the B type. Intermediates, chosen to bridge the gap between types partially, are waxy maize starch which yields almost an A pattern, and banana starch whose diffractions depart from the B variety.

Diffraction Methods.—Data required for interpretation of powder photographs must be accurate. In the case of starch, accuracy is difficult to achieve because of a certain amount of lack of definition in the patterns themselves, the low scattering ability of the atoms involved and possibly also the presence of amorphous material diluting the crystalline component. The points of experimental procedure listed below were found essential, and failures to observe one or more of them are responsible for the fact that all previously published data are inadequate for the present purpose.

(1).—Starches must be kept moistened during the photographing of their diffraction patterns. Katz and Derksen⁷ have shown that water is essential to the observation of a crystalline starch pattern. It is equally true that the pres-

(1) Journal Paper No. J-880 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 639. Supported in part by a grant from the Corn Industries Research Foundation.

(2) See H. Mark, *Chem. Rev.*, **26**, 184 (1940).

(3) J. R. Katz, *et al.*, series of papers in *Z. physik. Chem.*, Ser. A, 1930-1939. See particularly those cited below.

(4) See, for example, K. H. Meyer, H. Hopff and H. Mark, *Ber.*, **A62**, 1111 (1929).

(5) St. v. Náray-Szabó, *Ann.*, **465**, 299 (1928).

(6) J. R. Katz and Th. B. van Itallie, *Z. physik. Chem.*, **A150**, 90 (1930).

(7) J. R. Katz and J. C. Derksen, *ibid.*, **A150**, 100 (1930).