the constraints, and the temperature. In the case of hydrogen sulfide the heat capacity increases with decreasing temperature, due to the heat of polymerization and to other causes.

The writer wishes to express his thanks to Professor G. N. Lewis for suggesting the problem and the method of its attack.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

AN ELECTROMETRIC STUDY OF THE NEUTRALIZATION OF PHOSPHORIC ACID BY CALCIUM HYDROXIDE

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The difficulties incident to the indicator titrations of phosphoric acid and acid phosphates are well known. They are due chiefly to the instability and rearrangements of the phosphates produced in the course of the titration, and are magnified in practice both by the erroneous use of phenolphthalein as indicator, and by the use of sodium hydroxide in titration, a stronger base than is used in the commercial reactions with acid phosphates.[1] The instability of the various calcium phosphates has been indicated by numerous investigators but its application to analysis has not been clear. The electrometric method of titration is, however, uniquely adapted to the study of changes taking place during titration, and the following investigation was, therefore, undertaken to elucidate these changes. The complications produced by the instability of dicalcium phosphate are strikingly shown, and methods for their avoidance are indicated.

Several forms of exact electrotitration apparatus,[2] which were commercially available, are capable of determining the Sörensen (P_H) value within 0.01. Such accuracy, however, is unnecessary in ordinary chemical titrations and the instruments were therefore unnecessarily expensive. The apparatus used[3] was developed for the purpose, and can easily be assembled in any laboratory. It is independent of an exact potentiometer, a constant source of current, a calibrated rheostat, a standard cell, or any form of electrometer. It is based on the recommendations of J. H. Hildebrand.[4]

Phosphoric Acid with Calcium Hydroxide.—The curves shown herewith are plotted from the titrations, in the usual way, with abscissas representing cubic centimeters of alkaline or acid solution which is added, and ordinates representing the P_H value. The titration of phosphoric acid

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[1] Wadman, *J. Ind. Eng. Chem.*, **13**, 1146 (1921).

[2] Leeds and Northrup Co., Catalog 75. Arthur H. Thomas Co., Supplement 63.

[3] Bulletin 86, Central Scientific Company.

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

with sodium hydroxide gives the usual curve.[5] The neutralization by calcium hydroxide, however, involves more factors, as is shown by the curves in Figs. 1 and 2. Curve *a* follows the usual course up to the formation of monocalcium phosphate, but a precipitate, presumably of dicalcium phosphate, forms soon after. The voltage continues to rise normally somewhat beyond this point, but soon begins to fluctuate, and with further addition of lime water the solution actually grows distinctly more acid, as shown by the voltage drop. The addition of 2 cc. of saturated lime water increases the acidity by more than 50 times. Thereupon the voltage rises slowly, that is, the solution becomes more alkaline, until a sharp rise occurs at 30.0 cc. This obviously corresponds to the formation of pure tricalcium phosphate, since the quantity added is thrice that needed to produce the monocalcium salt. No rise corresponding to the dicalcium salt is apparent, though the increased acidity is obviously concerned with that salt. While no definite P_H value can thus be assigned to the dicalcium salt, the values of the mono- and tricalcium salts are, respectively, 4 and 8.5.

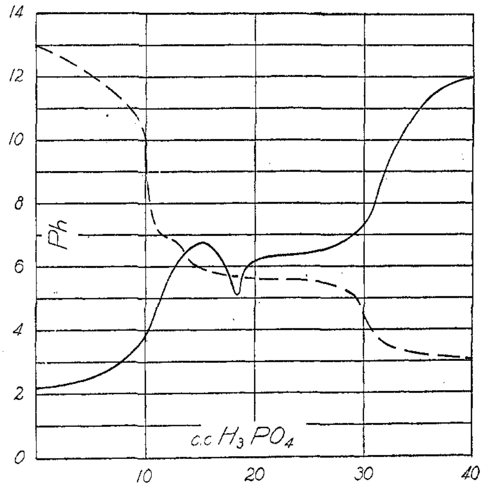

Fig. 1.

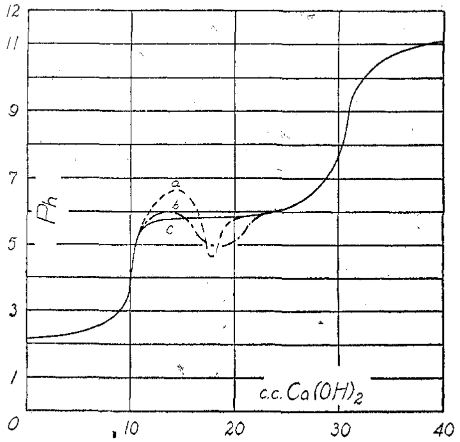

Fig. 2.

The Attainment of Equilibrium Conditions.—The irregularities in the titration of the acid with lime water indicate that a rearrangement is going on such that the dicalcium phosphate produced perhaps undergoes decomposition into a more basic form which remains insoluble while a more acid form goes into solution. For instance, the dicalcium salt may give insoluble tricalcium phosphate and the much more soluble monocalcium salt, which latter shows the high acidity. If this is

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[5] Davis, Oakes and Salisbury, *J. Ind. Eng. Chem.*, **15**, 182 (1923).

the case, it is important that time be allowed for equilibrium to be reached. In the titration already plotted, readings were made rapidly, and immediately after the addition of the lime water. The allowance of about 3 minutes was thus certainly inadequate for such an equilibrium to be reached.

In order to allow time for the solution to come to equilibrium after each addition of calcium hydroxide, the following slow titration experiment was carried out.

Fifteen cc. of the solution of phosphoric acid was introduced into each of 75 small Erlenmeyer flasks. Various amounts of the saturated lime water were then added to each of the flasks except the first. Two cc. was added to the second, 4 to the third, and an increase of 2 cc. to each succeeding flask until the sixth, which received 10 cc. From this point to 35 cc. the calcium hydroxide solution added to each succeeding flask was increased by 0.5 cc. From that point on, 2cc. portions were again added. Enough distilled water was added to each flask to bring the total volume up to 60 cc.

The voltage reading was made first after 2 hours' standing. The result is shown in Curve *b* of Fig. 2. (Curve *a* is a repetition of Curve *a* of Fig. 1.) The flasks were thoroughly shaken each day, and after 10 days their Sörensen values were again measured, the results being shown in Curve *c* of Fig. 2. Daily shaking produced no further change, as shown by measurements made on the twentieth and on the thirtieth days. Curves *b* and *c* of Fig. 2 show that on standing there is an elimination of the original deficiency of hydrogen ions in the first portion of the curve beyond the monocalcium phosphate point and, as well, an elimination of the excess of hydrogen ions that immediately follows, on the rapid titration curve. In the final curve, representing equilibrium conditions, all irregularities have disappeared, and there is a true buffer solution. No indication of the formation of dicalcium phosphate remains.

Calcium Hydroxide with Phosphoric Acid.—Although the hydrogen electrode operates better when the potential is increasing, that is, when alkali is being added, the first titration was now reversed, the phosphoric acid solution being added to the lime water. The titration is shown in *b*, Fig. 1. Again, the P_H value of tricalcium phosphate is shown to be 8.5; again, there is no distinct drop to correspond to the dicalcium salt, while the monocalcium salt is well defined with a P_H of about 4. That the two vertical drops correspond to the tri- and the monocalcium salts, respectively, is shown by the fact that the volumes of acid solution added to produce them are 10 and 30 cc. While there is no such reversing effect as shown in Curve *a*, a slight irregularity due to the dicalcium salt may be observed, beginning at P_H 6.5. The reaction of the dicalcium phosphate is, therefore, slightly on the acid side of neutral, as would be expected, for the disodium salt is but very slightly alkaline. The drop, however, does not persist until 20 cc. is added, but soon gives an excellent buffer, the curve being practically a mirror image of *c*, Fig. 2.

The Phosphate Rearrangements.—Curves *b* of Fig. 1 and *c* of Fig. 2 indicate that when equilibrium is permitted there is no evidence of the permanent existence in any form, soluble or insoluble, of dicalcium phosphate, $CaHPO_4$. The extended horizontal line in each case indicates that the acid or alkali added is being used up completely, in accordance with the equations

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 = 3\ CaH_4(PO_4)_2 \qquad (1)$$

and

$$CaH_4(PO_4)_2 + 2\ Ca(OH)_2 = Ca_3(PO_4)_2 + 4H_2O \qquad (2)$$

In both cases, however, the reactions are slow, and there is evidence for the transitory existence of the dicalcium salt. These abnormalities and their automatic disappearance require interpretation.

The explanation of the rapid titration curve (*a*, Fig. 2) offers no insuperable difficulty. The following reactions, which would account for the phenomena, are suggested. On the addition of calcium hydroxide to the monocalcium phosphate, dicalcium phosphate is formed, and part of this precipitates.

$$CaH_4(PO_4)_2 + Ca(OH)_2 = 2CaHPO_4 + 2H_2O \qquad (3)$$

The voltage attained is that of a mixture of mono- and dicalcium phosphates. When about half the total possible quantity of the dicalcium salt has been formed and a considerable quantity of it has already precipitated, then either through automatic rearrangement in accord with Equation 5 below, or by the direct reaction

$$2CaHPO_4 + Ca(OH)_2 = Ca_3(PO_4)_2 + 2H_2O \qquad (4)$$

a small quantity of tricalcium phosphate is formed. This, however, is much less soluble than the dicalcium salt, and immediately precipitates; but the inoculation with these crystals causes a rapid decomposition of the dicalcium phosphate into the insoluble tricalcium salt and the soluble monocalcium salt.

$$4CaHPO_4 = Ca_3(PO_4)_2 + CaH_4(PO_4)_2 \qquad (5)$$

If we can assume such an instability of the dicalcium phosphate it will be rapidly removed from solution, and the predominating constituent of the solution is again the monocalcium phosphate. The continued addition of alkali then neutralizes the latter with the formation of tricalcium phosphate. The curve is approximately horizontal, therefore, until the point corresponding to a solution of pure tricalcium phosphate is reached.

The only assumption involved, to this point, is that dicalcium phosphate is unstable and rearranges to give the tri- and monocalcium salts. For this there is abundant evidence in past work. Rindell[6] showed that both monocalcium and dicalcium phosphates in water solution give a solution which is more acid and a solid phase which is more alkaline than that of

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[6] Rindell, *Compt. rend.*, **134**, 112 (1902); "The Solubility of Several Calcium Phosphates," Helsingfors, **1899**.

the original salt. Cameron and his co-workers[7] conclude that no matter what compound containing only calcium and phosphoric acid be placed in water solution, there will result free phosphoric acid and the separation of calcium hydroxide with the solid; but their work, with fairly high concentrations of phosphate, indicates that the most stable of the 3 common phosphates is the dicalcium salt. Buch's detailed study of this salt,[8] however, shows a very marked increase in the acidity of the solution soon after its preparation, such that the soluble portion existed to about 90% of the monocalcium salt. Cameron and Bell[7d] showed that at concentrations as low as those used here (0.05 *N*) the solid phase approaches the composition of tricalcium phosphate. Jolibois[9] has recently shown that through wide variations in the ratio of calcium to phosphate in the original solution, a relatively basic precipitate forms and the supernatant liquid is in all cases largely monocalcium phosphate. The dicalcium salt is found in solution only in the presence of a considerable excess of calcium. There is a variation in the composition of the precipitate, with numerous intermediate compounds probable, good crystals of the compound P_2O_5-$2CaO.P_2O_5 3CaO.10H_2O$ being certainly obtained. The growth of acidity in a dicalcium phosphate solution is thus well recognized. Cameron and Seidell[7b,7c] relate that when a neutral calcium chloride solution is added to a solution of disodium phosphate, which is of course alkaline, the consequent solution is distinctly acid, as shown by indicator tests. This is the same phenomenon that is recorded in the above electrotitrations. The drop in voltage as alkali is added is, therefore, satisfactorily explained on the basis here suggested, though the titrations themselves can give no definite evidence on the composition of the solid phase.

The recovery of the voltage on standing, however, that is, the disappearance of this acid if time for the attainment of equilibrium is allowed, is not so easy to interpret. Here is the exact opposite of the previous reaction. Both the immediate development of acid and its subsequent elimination are entirely automatic, and occur under exactly the same conditions, with the exception that the first process takes place in a medium whose hydrogen-ion concentration is less than 10^{-6}, while that of the second is 10^{-5}. Since the first process, however, continues until an acidity of 10^{-5} is reached, this acidity cannot itself be the agent which causes the apparent reversal of the reaction. The other possible difference in conditions under which the two changes take place is that in the first rapid rearrangement, when acidity is produced, solid dicalcium phosphate is still present, while later this may be absent because entirely decomposed,

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[7] Cameron and others, THIS JOURNAL, **26**, (a) 885, (b) 1454 (1904); **27**, (c) 1503, (d) 1512 (1905).

[8] Buch., *Z. Anorg. Chem.*, **52**, 325 (1907).

[9] Jolibois, *Compt. rend.*, **169**, 1161 (1919).

in accordance with Equation 5. In the absence of the solid dicalcium salt, another process then intervenes to remove the acid on further standing. Buch[8] has already reported the same phenomenon, and finds it dependent on the latter factor. Daily analyses of the solution above a solid phase which was originally pure dicalcium phosphate showed at first a marked rise in solubility and a simultaneous rise in the ratio of P_2O_5/CaO, that is, increase of acid, which continued until all the original dicalcium salt had rearranged. Thereupon there was a marked drop in solubility accompanied by a decrease in the ratio, such that the previous excess of acid completely disappeared. This latter action he attributed to the formation of intermediate phosphates. Some such process probably takes place. The acid may be removed by the slow formation of an insoluble intermediate phosphate which holds the acid in the solid phase. There are objections to this interpretation. The present research, however, throws no light on the real nature of this second process which acts to remove the acid in solution. The ultimate curve, obtained on equilibrium, completely omits the dicalcium phosphate stage, and gives an ideal picture of the neutralization passing from the mono- directly to the tricalcium phosphate stage, so that the long horizontal portion of the curve represents the equilibrium between these 2 phosphates.

Applications to Analysis.—It is the fluctuations shown by the rapid titration curve (*a*, Fig. 1) which lead to the uncertain results obtained in the usual indicator titrations of monocalcium phosphate. The use of sodium hydroxide in the titration of this salt increases the difficulty for two reasons. First, the presence of this stronger alkali undoubtedly acts to complicate further the rearrangements here noted by allowing more complicated intermediate compounds. Second, the alkalinity of the solution during titration is raised so that the fluctuations come more readily within the range of hydrogen-ion concentration of the color change of phenolphthalein. The use of calcium hydroxide in titration and an indicator changing at a higher P_H value, such as thymolphthalein is, therefore, beneficial.

Finally, it should be pointed out that with complicated reactions so dependent on the P_H value of the media, the study of the reactions occurring in the use of monocalcium phosphate in baking powders or of the value of this salt for such purposes can be reliably made only with the alkali used in the powder, that is, with sodium bicarbonate. The course of the reaction and the end products cannot be the same when other bases are used. In particular, it should be noted that the P_H value of sodium bicarbonate, while higher than that of monocalcium phosphate and thus capable of beginning the neutralization, is lower than that of tricalcium phosphate, and it is thus itself unable to form this latter salt without the aid of sodium carbonate produced by heating the mixture. Even sodium carbonate is but slightly more alkaline than tricalcium phosphate, and the titrations above recorded agree with other methods of analysis in indicating that the baking powder reaction stops somewhat short of the complete neutralization of the phosphate to the tricalcium salt stage.

Summary

Graphic representation of both the slow and the rapid electrotitration of phosphoric acid with calcium hydroxide shows that the existence of dicalcium phosphate is transitory so that under equilibrium conditions only the mono- and tricalcium salts are present. The rearrangements involved herein are responsible for part of the difficulty in titrating monocalcium phosphate for its "neutralizing value."

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[Contribution from the Laboratory of Physical Chemistry, Princeton University]

THE ADSORPTION OF GASES BY OXIDE CATALYSTS

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In the adsorption of gases by solid bodies, two more or less distinct phenomena have been observed. Adsorption by inert adsorbents, such as charcoal, mica and silica, has been described as "physical," to distinguish it from the "chemical" type shown by active adsorbents, such as metals. Langmuir,[2] however, considers the adsorption by inert substances due to secondary, and that by active adsorbents due to primary, valence forces. On this basis both types are chemical, and accordingly in the present paper adsorption by active adsorbents will be designated as "primary" and that by inactive adsorbents as "secondary."

The forces involved in primary adsorption are, in general, comparatively strong; "selective" and "irreversible" adsorption are necessarily cases of this type. Here adsorption is determined by chemical affinity in its usual sense. The residual valence forces to which secondary adsorption is due are weaker and less specific. The tendency of different gases to be held by secondary adsorption is measured by their relative boiling or melting points. The tendency of different adsorbents to hold a given gas by secondary adsorption may perhaps, in a similar way, be measured by the melting points, or related properties, of the adsorbents.

The two types of adsorption[3] may be further differentiated in respect to

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[1] National Research Fellow in Chemistry.

[2] Langmuir, (a) This Journal, **40**, 1400 (1918); (b) **38**, 2267 (1916).

[3] A third type, that in which actual liquid condensation occurs, will not be discussed in this paper.