2. That colloidal manganese dioxide is especially easily obtained by incompletely oxidizing glucose (as well as fructose and galactose) in alkaline solution with potassium permanganate.
3. That the colloidal manganese dioxide is formed under these conditions first passes into a viscous or gel stage which subsequently changes into a limpid colloidal solution.
4. That the properties of the first stage agree well with those of a typical emulsoid, while the later stage seems more characteristically a suspensoid.
5. That the transformations of the emulsoid are typical and would be normal in every way if it were not for a slower but simultaneous transformation of the emulsoid into a suspensoid, owing to the effect of the alkali in accordance with the generalizations of Mayer, *et al.*
6. That both transformations are readily affected by variations in temperature, concentration of the reacting mixture and concentration of the alkali (KOH or NaOH).
7. That low temperatures are more favorable to the formation of the colloid.
8. That the concentrated colloid described here is readily coagulated by warming.
9. Suggestions are made indicating possible relationships between the remarkable properties of manganese in biochemical reactions and the properties of colloidal manganese dioxide as described above.

CHICAGO, ILL.

A CONDUCTIVITY STUDY OF THE REACTION BETWEEN CALCIUM NITRATE AND DIPOTASSIUM PHOSPHATE IN DILUTE SOLUTION.[1]

BY W. A. WITHERS AND ALEX. L. FEILD.

Received January 7, 1915.

It is generally agreed that a soluble calcium salt reacts with dipotassium phosphate in the presence of an excess of ammonia to form an amorphous precipitate of tricalcium phosphate with no tendency to become crystalline on standing. When, on the other hand, ammonia is not added, there occurs a reaction in regard to which there is a great difference of opinion. The present investigation was made in order to determine the nature of the latter reaction.

Introductory.

It has been known for some time that tricalcium phosphate, when precipitated in neutral solution, has a composition which only approximates to the theoretical, due to the hydrolytic action of the solvent. This

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[1] Read at the meeting of the North Carolina Section of the American Chemical Society, Raleigh, N. C., May 2, 1914.

hydrolysis has been studied by Warington[1], Georgievics,[2] and recently by Cameron and Hurst,[3] and Cameron and Seidell.[4] In these researches the solid tricalcium phosphate was added to a certain volume of water. Analyses were made after equilibrium conditions were reached. From a consideration of the data available, Cameron and Hurst draw the following conclusions:[5]

> "From these facts it appears that no matter what compound, or mixture of compounds, containing only calcium and phosphoric acid ($Ca_n(PO_4)_m$), be placed in water there will result free phosphoric acid in the solution with separation of calcium hydroxide. The calcium hydroxide may then react to form a more basic and less soluble phosphate, or simply form a mixture with the phosphate, the solubility of which is decreased by its presence."

Furthermore, it was shown by Warington[6] and verified by Cameron and Seidell[6] that the decomposing action of water upon tricalcium phosphate depends upon the relative masses of the phosphate and water that are brought together.

An extensive study of equilibrium conditions in the system, lime (CaO)–phosphoric acid (P_2O_5)– water, has been made by Cameron and Seidell,[7] and yet more fully by Cameron and Bell.[8] The last-mentioned investigators conclude that in dilute solution, giving a neutral or nearly neutral reaction to phenolphthalein, the solid phase will be tricalcium phosphate or a solid solution of nearly the same composition; and, furthermore, that if there is a range of solution in equilibrium with tricalcium phosphate such a range would be very small.

It will now be understood that a reaction involving the formation of tricalcium phosphate will not in general be a simple one, due to the partial hydrolysis of the tricalcium phosphate to a more basic phosphate or a solid solution, containing lime as one constituent. For the sake of convenience, however, we shall consider that the tricalcium phosphate formed corresponds in composition to the theoretical, whenever equations are given for the reaction between calcium nitrate and dipotassium phosphate. Any hydrolysis which takes place can be considered subsequently and independently.

There is much disagreement among the text-books in regard to the reaction under consideration. Some give equations for the reaction which are so obviously incorrect that they will not be considered here—

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[1] *J. Chem. Soc.*, 26, 983 (1873).

[2] *Monatsh.*, 12, 566 (1891).

[3] This Journal, 26, 885 (1904).

[4] *Ibid.*, 26, 1454 (1904).

[5] *Loc. cit.*, p. 905.

[6] *Loc. cit.*

[7] This Journal, 27, 1503 (1905).

[8] *Ibid.*, 27, 1512; 28, 1222 (1906).

such as the immediate formation of dicalcium phosphate. The various reactions which deserve our consideration are represented by the following equations:

Equation 1. (*a*) $4K_2HPO_4 + 4Ca(NO_3)_2 = Ca(H_2PO_4)_2 + Ca_3(PO_4)_2 + 8KNO_3$.

(*b*) $Ca(H_2PO_4)_2 + Ca_3(PO_4)_2 = 4CaHPO_4$.

Equation 2. (*a*) $2K_2HPO_4 + 3Ca(NO_3)_2 = Ca_3(PO_4)_2 + 2HNO_3 + 4KNO_3$.

(*b*) $2HNO_3 + Ca_3(PO_4)_2 = 2CaHPO_4 + Ca(NO_3)_2$.

Equation 3. $4K_2HPO_4 + 3Ca(NO_3)_2 = Ca_3(PO_4)_2 + 2KH_2PO_4 + 6KNO_3$.

The second step in Equation 1 is usually considered to take place very slowly, but more quickly upon acidifying.[1]

Equation 1 is given by Remsen.[2]

Similarly the second step in Equation 2 would occur only after long standing. Lang and Kaufman[3] give an equation analogous to (2) as being that generally accepted by texts as representing the reaction between silver nitrate and disodium orthophosphate.

The present investigation makes use of conductivity measurements to determine what reaction, or reactions, actually take place when calcium nitrate is added in increasing quantities to a given quantity of dipotassium phosphate. The volume is kept constant. The concentration employed throughout the investigation is 1 g. of K_2HPO_4 per liter, to which calcium nitrate is added in quantities up to 500 mg. nitrogen, as calcium nitrate, per liter. Whenever solutions of phosphoric acid or monopotassium phosphate are used, their concentration is equivalent to 0.5455 g. PO_4 per liter, which is the amount of PO_4 present in 1 g. of dipotassium phosphate.

After deciding which equation correctly expresses the reaction, this conclusion is verified by determinations of the composition of the liquid phase at various stages of the reaction. The method of conductivity titrations is employed for these determinations.

Method and Apparatus.

The solutions of calcium nitrate used were standardized by precipitating as calcium oxalate and titrating the precipitate with $0.1N$ permanganate, standardized by means of pure ferrous ammonium sulfate. The phosphoric acid and phosphate solutions were analyzed by precipitating with magnesia mixture, igniting, and weighing as magnesium pyrophosphate. Duplicate analyses agreed very closely.

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[1] Ostwald, "Principles of Inorganic Chemistry" (1902), p. 522.

[2] Remsen, "Chemistry" (1890), p. 538.

[3] THIS JOURNAL, 27, 1515 (1905).

The solution of potassium hydroxide contained a small quantity of carbonate, and was carefully protected from the atmosphere. It was standardized by a conductivity titration with hydrochloric acid, which, in turn, had been analyzed by weighing as silver chloride. The nitric acid solution was similarly standardized by the conductivity method against the standardized potassium hydroxide solution. Both of these solutions had a normality of 0.0574. 10 cc. of either acid or base reacted with 100 cc. of the phosphate solutions, according to equations which will be given later.

The same cell was used in all measurements of conductivity, and was of the "dipping electrode" type for dilute solutions as furnished by Eimer and Amend. It was standardized by means of 0.005 *N* potassium chloride solution, and showed a cell constant of 0.1222. Corrections were made in all cases for the conductivity of the distilled water from which the solutions were made up. Measurements were made according to the usual method of Kohlrausch. The slide-wire, furnished by Fritz Kohler, was carefully calibrated, and the resistances used had a guaranteed accuracy of a few tenths of one per cent. The electrically heated thermostat was operated throughout the investigation at 30°, and was controlled by a vapor-pressure thermoregulator, previously described by one of us,[1] which kept the bath constant within 0.01°.

When a single conductivity measurement was to be made upon a solution, a portion of the solution was removed and placed in a thin-walled test tube immersed in the bath. The conductivity cell was then dipped into the test tube, and, after temperature equilibrium was reached, the bridge reading was taken.

When a conductivity titration involving a number of measurements was made, 100 cc. of the unknown solution, diluted with distilled water to 200 cc., was placed in a spherical short-necked flask supplied with a three-hole stopper. Through this passed a stirring rod, the conductivity cell, and the tip of a buret containing the reagent which was added in the desired amount. After each addition of reagent from the buret the contents of the flask were stirred and allowed to attain the temperature of the bath before bridge readings were taken. In addition the cell was raised and lowered several times during this interval so as to allow the solution between the electrodes to mix with the surrounding solution.

The general principles underlying this and similar methods of physico-chemical volumetry have been discussed in detail by P. Dutoit.[2] The apparatus used by him is essentially the same as the one herein described, except that we use a different form of cell, which cannot be affected by such operations as stirring, and addition of reagent.

[1] THIS JOURNAL, **36**, 72 (1914).

[2] *Bull. soc. chim.*, **7** (1910).

Part 1. Experimental.

Conductivity Measurements.—Varying quantities of a solution of calcium nitrate were added to a solution of dipotassium phosphate of constant composition (1 g. per liter). Three series of measurements were made on these mixtures, as follows: 1. Immediately after mixing; 2. At the end of 24 hrs.; 3. At the end of 48 hrs. During the entire time the solutions were kept in stoppered bottles at a temperature of 30°, and were repeatedly shaken, especially before conductivity measurements were made.

The results are given in Table I. Values are expressed in $\text{ohms}^{-1}\ \text{cm}^3$.

Table I.

1 g. K_2HPO_4 per liter.

Solution number.	Mg. N as $Ca(NO_3)_2$ per liter.	Specific conductivity. 1. t = 0 hrs.	2. t = 24 hrs.	3. t = 48 hrs.
1	0	0.001425	0.001425	0.001425
2	2.5	0.001437	0.001435	......
3	5.0	0.001447	0.001448	0.001450
4	7.5	0.001471	0.001435	......
5	8.75	0.001451	0.001426	......
6	10.0	0.001464	0.001435	0.001435
7	25.0	0.001496	0.001446	0.001446
8	50.0	0.001574	0.001472	0.001468
9	100.0	0.001750	0.001563	0.001551
10	120.0	0.001806	0.001620	......
11	150.0	0.002019	0.001856	0.001856
12	200.0	0.002261	0.002247	0.002251
13	300.0	0.003032	0.003022	0.003026
14	350.0	0.003402	0.003396	0.003404
15	500.0	0.004517	0.004521	0.004521

Equilibrium conditions seem to have been practically reached at the end of 24 hrs., but the values for the 48 hr. period will be considered as representing more nearly such a condition. There is, however, very little difference between the two sets of values—less than 1% in all cases. As a matter of fact both of these sets of values are approximately attained after the lapse of several hours.

Fig. 1 shows graphically the conductivity values for the varying additions of calcium nitrate—the dotted curve representing initial conditions (immediately after mixing), while the continuous curve represents values at the end of 48 hrs. In Fig. 2 is represented, on a larger scale, the first portion of the two curves.

The Conductivity Curve—Time 48 hrs.—We will first confine our attention to the continuous curve representing conditions at the end of 48 hrs. It will be observed (Fig. 1) that there is a decided break in the curve at a point corresponding to the addition of about 120 mg. N as calcium nitrate. In accordance with the well-known principle discussed by Dutoit[1] and by Miolatti and Pizzighelli,[2] such a break undoubtedly represents the completion of some reaction. Now of the equations given above for the reaction between calcium nitrate and dipotassium phosphate, the only one which requires these particular proportions (120 mg. N to 1 g. of K_2HPO_4) is Equation 3. Both Equations 1 and 2 require 160 mg. N as calcium nitrate for complete reaction with 1 g. of K_2HPO_4.

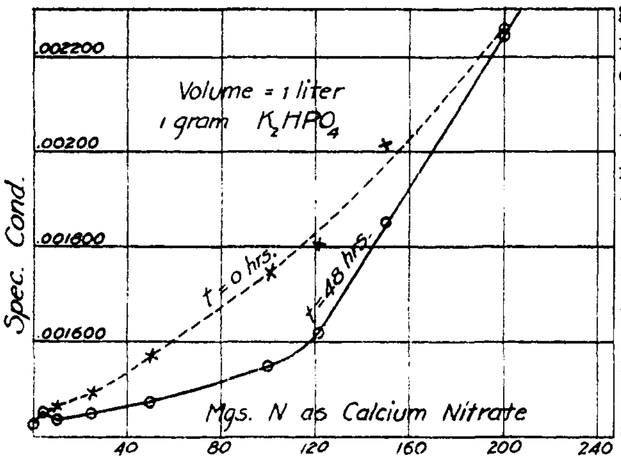

Fig. 1.

All evidence to be presented later in this article appears to strengthen this conclusion. Although several of the leading texts state that dicalcium phosphate is a final product of the reaction, we have not observed any formation of this salt in solutions which have stood several months. If such a formation occurs, it progresses with extreme slowness.

It will be noticed that the first portion of the curve shows rather striking irregularities. The maximum which occurs at a point corresponding to the addition of 5 mg. N evidently represents the beginning of the formation of a precipitate. The solutions containing quantities of calcium nitrate up to this amount remained perfectly clear on standing. That small part of the curve representing the addition of from 5 to 10 mg. N shows the occurrence of some reaction whose exact nature is rather doubtful. We can say

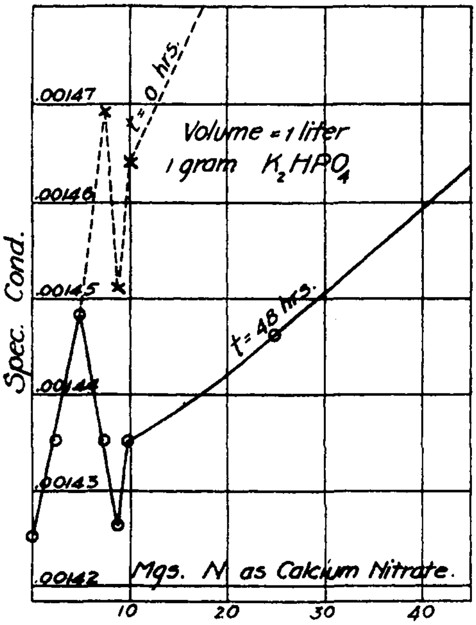

Fig. 2.

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[1] *Loc. cit.*

[2] *J. prakt. chem.*, 77, 417; *C. A.*, 2, 2346.

with certainty, however, that the portion between 10 and 120 mg. N represents a reaction which, neglecting any hydrolysis of the tricalcium phosphate, can be represented by Equation 3. Further addition of calcium nitrate gives a curve which is practically a straight line, showing that this excess of calcium nitrate gives rise to no definite reaction with precipitate or solution. The results given later in this article indicate that an excess of calcium nitrate decreases slightly the amount of PO_4 present in solution, which effect may be looked upon as a further precipitation of tricalcium phosphate, or a lowering of the solubility of the same. Moreover, under the conditions of our experiment, tricalcium phosphate appears to dissolve as the dicalcium salt.

Conductivity Curve—Time 0 hrs.—In making conductivity measurements upon freshly mixed solutions it was noticed from the values obtained that the solutions were undergoing, in many cases, a comparatively rapid change. This change in conductivity occurred only for a short while after mixing, and was always toward a lower value.

An attempt was made, therefore, to make a series of measurements as soon as possible after mixing in order to obtain the maximum value. The results are those given in Table I, Column 1, and are represented graphically by the dotted curve in Figs. 1 and 2. Both solutions were brought to the temperature of the bath independently, and then mixed rapidly so as to avoid heat loss. In this way bridge readings could be taken within one or two minutes after mixing. Nevertheless, this set of readings can not be considered as accurate as those obtained later upon the same mixed solutions. The points as plotted lie on a fairly smooth curve. It intersects the curve representing conditions at the end of 48 hrs. at a point corresponding to about 200 mg. N as calcium nitrate, and from that point onward practically coincides with it. On account of the difficulty in obtaining the readings, it is impossible to say whether there is any break along this portion of the dotted curve. There is, however, a well defined maximum at a point corresponding to 7.5 mg. N, which is probably analogous in its significance to that present in the lower curve, and marks the point at which the precipitation reaction begins.

A special study of one solution mixture was made in order to determine, if possible, something concerning the rapidity and progress of the change in conductivity mentioned above, which is doubtless due to some chemical reaction. A solution containing the usual quantity of dipotassium phosphate (1 g. per liter), to which 80 mg. N as calcium nitrate had been added, was selected for this experiment. The change seemed to be particularly noticeable at such a concentration of the latter salt.

Conductivity values, determined at various intervals, are given in Table II.

TABLE II.

80 mg. N as calcium nitrate to 1 g. K_2HPO_4. Volume, 1 liter.

Time. Min.	Specific conductivity.	Time. Min.	Specific conductivity.
0	0.001667	11	0.001623
1	0.001667	13	0.001555
3	0.001662	15	0.001552
5	0.001662	17	0.001546
7	0.001662	19	0.001546
9	0.001653	23	0.001546

This experiment was repeated several times. The initial and final values were identical in each case; and, after the major change in conductivity began, the change was completed in practically the same time. In some cases, however, a longer time elapsed than that shown in Table II before the drop in conductivity began; in no case did this occur before the lapse of seven minutes after mixing. It seems then that there is some unstable compound present which changes over into another form comparatively rapidly when once started. All these solutions were stirred vigorously and continuously, so that temperature conditions and concentration was constant throughout the solution under observation.

Since an appreciable time elapsed before this drop in conductivity occurred, an attempt was made to separate the liquid phase from the precipitate before the change occurred. Such was accomplished by filtering by suction through a hardened filter on a Buchner funnel. The filtrate was perfectly clear. After standing for about thirty minutes this filtrate became cloudy from the formation of a precipitate, probably of tricalcium phosphate. This shows that the observed change in conductivity is at least partly caused by a precipitation reaction, and not entirely by the action of the supernatant solution upon the precipitated tricalcium phosphate, such as would accompany the formation of dicalcium phosphate either by hydrolysis or by a reaction similar to that indicated by Equation 1*b*.

While there is no direct evidence in support of the conclusion, it appears probable that the phenomenon described may be due to the temporary formation of monocalcium phosphate along with the tricalcium phosphate, in accordance with Equation 1*a* given above. This salt is, as shown by Cameron and Seidell,[1] unstable in dilute solution, being easily hydrolyzed. This monocalcium phosphate, temporarily formed, would be converted into tricalcium phosphate in accordance with the equation,

Equation 4. $3Ca(H_2PO_4)_2 + 4K_2HPO_4 = Ca_3(PO_4)_2 + 8KH_2PO_4$.

If we combine Equations 1*a* and 4 we obtain Equation 3, which, as has been shown, represents conditions after equilibrium is reached.

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[1] *Loc. cit.*

Discussion of Results.—All solutions of dipotassium phosphate to which calcium nitrate had been added with formation of a precipitate showed an acid reaction to phenolphthalein and to litmus, due to the presence of the monopotassium phosphate formed according to Equation 3. Congo red showed the presence of free acid in no case, nor did the conductivity titrations performed later give any indication of the presence of free acid, either nitric or phosphoric. It seems that the absence of free acid could have been predicted from purely chemical considerations. Free nitric acid acts upon dipotassium phosphate in dilute solution with the formation of monopotassium phosphate and potassium nitrate, while phosphoric acid gives only monopotassium phosphate. In either case, any acid formed by the progress of the imaginary reaction would finally convert all of the dipotassium phosphate into the more acid salt. Furthermore, monopotassium phosphate does not form a precipitate even with an excess of calcium nitrate.

Part 2. Experimental.

The liquid phase in contact with the phosphate precipitates in the various mixtures evidently contains varying quantities of dipotassium phosphate and monopotassium phosphate, together with potassium nitrate, and if added to the mixture in excess, calcium nitrate also. A knowledge of the relative proportions of mono- and dipotassium phosphate present in the various mixtures would, if obtained, lead to a confirmation of one of the several reactions given previously in this discussion. It might be mentioned at this point that the evidence obtained from such analytical results confirms the existence of the reaction expressed by Equation 3 as representing conditions at the end of 48 hrs. On account of the short duration and instability of the first step in the interaction of the two salts, for which we suggest Equation 1*a*, no analytical results could be obtained to prove its existence with certainty.

In order to investigate with the greatest possible accuracy the composition of the liquid phase, we have made use of some of the principles found in the work of Berthelot[1] on the basicity of phosphoric acid, and in the work of Thiel and Roemer[2] on the same subject.

Berthelot found that, when a solution of potassium or sodium hydroxide is added in increasing amounts to a given quantity of dilute phosphoric acid, the conductivity decreases regularly until sufficient alkali is added to form the primary salt. Here there is a sharp break in the curve, which proceeds regularly with increasing conductivity values until sufficient alkali is added to form the secondary salt. At this point there was a decided change in direction of the curve again, although not so sharply defined as the first break. There was no break observed corresponding

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[1] *Compt. rend.*, **113**, 851 (1891).

[2] *Z. physik. Chem.*, **63**, 711 (1908).

to the formation of the normal salt. Thiel and Roemer[1] observed that the position of these breaks in the curve depended to some extent on the concentrations employed, and that, for very dilute solutions approached most nearly to the theoretical value. We have found that this method may be used for quantitatively determining the amount of phosphoric acid and dihydrogen phosphate present in a dilute solution. Furthermore, we have originated a somewhat similar method for determining the amount of dipotassium phosphate present, *e. g.*, by the addition of increasing quantities of nitric acid to the phosphate solution. There is a very sharp break corresponding to the transformation of the dipotassium into the monopotassium salt. Dutoit[1] gives similar curves, obtained by adding to a phosphate solution uranyl nitrate according to the well-known analytical practice.

Conductivity Titration of Phosphoric Acid.—This proceeds according to the equation:

Equation 5. $H_3PO_4 + KOH = KH_2PO_4 + H_2O$

Fig. 3 shows the character of the curve obtained. At this dilution it is very similar to the ordinary neutralization curve of a strong acid. This is given merely for the sake of completeness, since no free acid was observed in the course of the analyses.

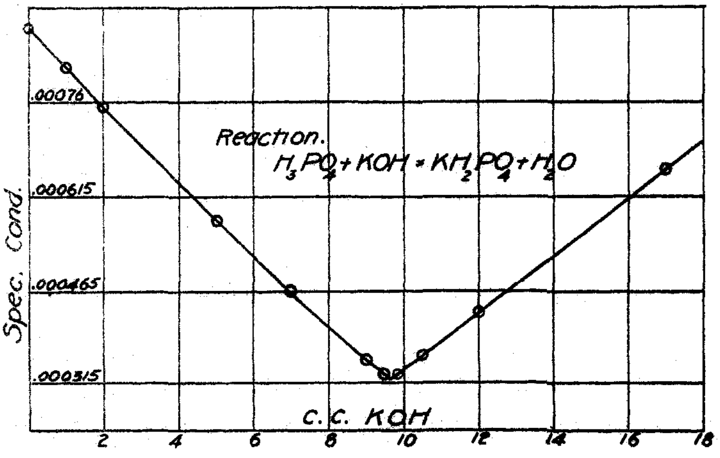

Fig. 3.

Conductivity Titration of Dihydrogen Phosphate.—This takes place according to the equation,

Equation 6. $KH_2PO_4 + KOH = K_2HPO_4 + H_2O$.

Fig. 4 shows the character of the conductivity curve obtained. While Berthelot[1] and Thiel and Roemer[1] did observe a more or less noticeable break at this point, they did not suggest that such was decided enough

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[1] *Loc. cit.*

for use in a quantitative determination of dihydrogen phosphate. Since the present investigation is concerned with concentrations which vary within comparatively narrow limits, it has been found practical to use this break for the accurate determination of this form of phosphoric acid when present in dilute solutions, such as heretofore described.

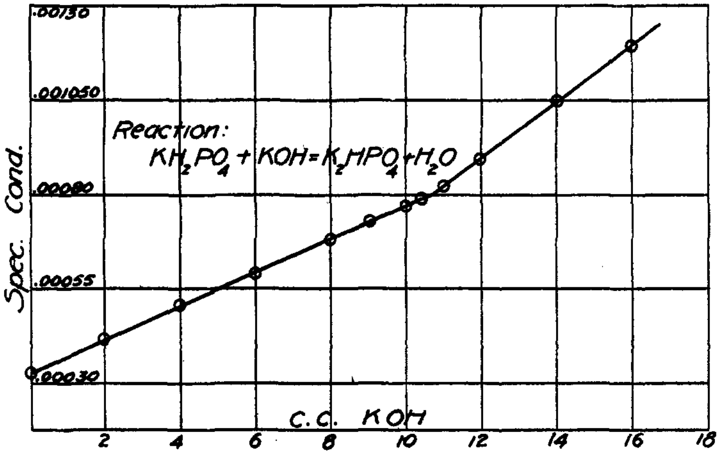

Fig. 4.

It was necessary, however, to apply corrections which were directly proportional to the total phosphate present in solution. The break was found to occur in all cases at a point beyond the theoretical addition of alkali. The excess of monopotassium phosphate, calculated from the curve, amounted to 11.8% of the total phosphate present in the solution, both being measured as grams of PO_4 per liter. In order to verify the existence of this break beyond the theoretical point indicating the completion of Equation 6, potassium hydroxide was added in varying amounts to a similar quantity of dipotassium phosphate. A break in the conductivity curve, identical in its nature, was observed when alkali corresponding to 11.8% of the total phosphate had been added. This proof was regarded as conclusive.

Conductivity Titration of Monohydrogen Phosphate.—This is possible on account of the fact that the equation,

Equation 7. $K_2HPO_4 + HNO_3 = KH_2PO_4 + KNO_3$.

goes to completion in dilute solution, or practically so. The conductivity curve is shown in Fig. 5. In contrast to the titration of dihydrogen phosphate, the present procedure requires a smaller amount of acid than the theoretical, the difference between the observed and calculated quantities being again proportional to the total amount of phosphate in the solution. This correction of the observed value for monohydrogen phosphate under our experimental conditions amounted to 5.0% of the total phosphate present.

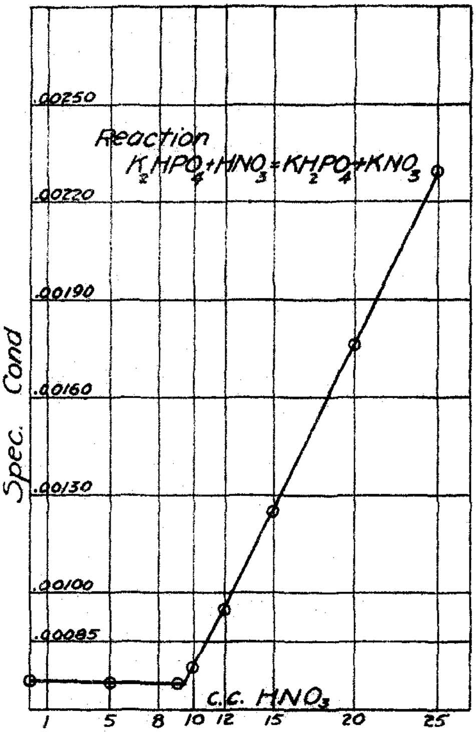

Fig. 5.

Results of Conductivity Titrations.—It has been assumed that the breaks in the conductivity curves obtained by adding either potassium hydroxide or nitric acid are not sufficiently affected by the amounts of potassium nitrate, initially present in the mixtures, to appreciably alter the results obtained. In those cases where calcium nitrate had been added in excess, it was not possible to determine the amount of dihydrogen phosphate present without the formation of a precipitate of tricalcium phosphate at the point where enough potassium hydroxide had been added to render the solution alkaline. It is possible, however, that even in such cases there is a break corresponding to the amount of dihydrogen phosphate present.

Since in all solutions investigated the total phosphate was made up only of mono- and dihydrogen phosphate, the total phosphate was first approximately determined as being equal to the sum of the uncorrected values of the two latter forms. Using this value of total phosphate for calculating the magnitude of the corrections to be applied, as described above, new values were obtained for the amounts of mono- and dihydrogen phosphate. This furnished a more nearly correct value for total phosphate than the one first used. Three successive approximations were sufficient.

Determinations, by means of the methods and apparatus described, of H_2PO_4, HPO_4, and total PO_4 were made upon six solutions representing various points in the reaction between calcium nitrate and dipotassium phosphate. The results are given in Table III, together with the theoretical values which should obtain if we consider that Equation 3 represents the reaction which occurs. The results are represented graphically in Fig. 6. The dotted lines in this figure represent the theoretical values. All values in the table and figure represent percentage of original PO_4 (0.5455 g. per liter).

Table III.—Composition of Liquid Phase.

Volume, 1 liter; 1 g. of K_2HPO_4 initially.

Mg. N as $Ca(NO_3)_2$ added.	PO_4 as HPO_4.		PO_4 as H_2PO_4.		Total PO_4.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.
20	8.78	8.37	0.82	0.82	9.60	9.19
50	6.04	5.91	2.26	2.04	8.30	7.95
80	3.85	3.44	3.66	3.28	7.51	6.72
100	2.53	1.82	4.28	4.09	6.81	5.91
120	1.58	0.00	5.14	5.00	6.72	5.00
150	1.37	0.00	..	5.00	..	5.00

Discussion of Results.—The results of the conductivity titrations, given in Table III and shown graphically in Fig. 6, bring to light some interesting points. In the first place, there is close agreement between the observed and theoretical values for dihydrogen phosphate throughout the range of solution mixtures investigated. The observed values, however, for monohydrogen phosphate and total phosphate exceed the theoretical by amounts which increase with increasing quantities of calcium nitrate, up to a point corresponding to the completion of the reaction expressed by Equation 3. Beyond this point further addition of calcium nitrate diminishes slightly the amount of monohydrogen phosphate present.

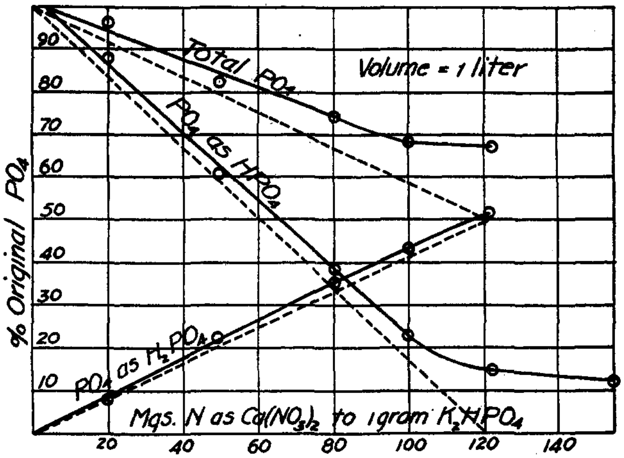

Fig. 6.

These data indicate that the principal reaction to be considered is, as has been proposed previously in this article, expressed by Equation 3. Furthermore, the tricalcium phosphate formed in accordance with this equation appears to be so hydrolyzed that a portion dissolves as monohydrogen phosphate, the resulting calcium oxide probably forming a solid solution with the remainder of the unhydrolyzed tricalcium phosphate. There are no indications to show that dihydrogen phosphate is formed by the hydrolysis of tricalcium phosphate under the conditions of these experiments. An examination of Table III will show that the extent of this hydrolysis, which is measured by the excess of the observed value of monohydrogen phosphate above the theoretical, increases with increasing amounts of calcium nitrate, and is approximately proportional to the amount of the latter. This may be considered as due to the progressive formation of dihydrogen phosphate in accordance with Equation 3, and the resulting increase in the hydrogen ion concentration.

Finally we can conclude that an excess of calcium nitrate diminishes slightly the hydrolysis of tricalcium phosphate.

Summary.

1. A conductivity study of the reactions between calcium nitrate and dipotassium phosphate in dilute solution has been made. A constant concentration of dipotassium phosphate (0.5455 g. PO_4 per liter) has been employed, with amounts of calcium nitrate varying from 0 to 500 mg. *N* as calcium nitrate per liter.

2. From the occurrence of a break in the conductivity curve representing the addition of 120 mg. *N* as calcium nitrate per liter, the conclusion is drawn that the reaction which obtains at the end of 48 hrs. (for practical purposes, at the end of one or two hours) can be represented by the equation

$$4K_2HPO_4 + 3Ca(NO_3)_2 = Ca_3(PO_4)_2 + 2KH_2PO_4 + 6KNO_3.$$

3. Evidence is presented to show that for a short while after mixing there occurs some reaction, probably

$$4K_2HPO_4 + 4Ca(NO_3)_2 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2 + 8KNO_3.$$

This is an unstable condition, however, and persists for a short while only (about seven minutes in the case investigated). After this short interval has elapsed, there occurs a reaction which is characterized by further precipitation of tricalcium phosphate and which results in a condition shown by the equation immediately preceding. This reaction establishes a stable condition. It proceeds very rapidly at first, more slowly finally. The unstable condition is never reached when an excess of calcium nitrate is added, or else persists for an exceedingly short time. In this case the stable condition is reached immediately.

4. In order to further verify the occurrence of the equation,

$$4K_2HPO_4 + 3Ca(NO_3)_2 = Ca_3(PO_4)_2 + 2KH_2PO_4 + 6KNO_3,$$

the liquid phase of a number of solution mixtures was analyzed at the end of 48 hrs. by means of a method of conductivity titration. These mixtures represented various steps in the progress of the reaction. A comparison of the observed values for mono- and dihydrogen phosphate and total phosphate with the theoretical values was then made.

5. The amount of dihydrogen phosphate in the liquid phase was determined by means of the break in the conductivity curve obtained on adding increasing amounts of dilute potassium hydroxide solution. While the occurrence of this break has been recorded by previous investigators, its location does not seem to have been hitherto utilized for a quantitative analysis of an unknown solution.

The amount of monohydrogen phosphate in the liquid phase was determined by means of a similar break obtained on adding increasing amounts of dilute nitric acid. In this case both the principle involved and its application to physico-chemical volumetry are given here for the first time.

6. The results of the conductivity titrations further verify the equation given in paragraph 2 above.

7. Furthermore, the deviation of the observed values of monohydrogen phosphate from the theoretical shows that the precipitated tricalcium phosphate undergoes partial hydrolysis, in such a way as to appear in the liquid phase as monohydrogen phosphate.

8. The extent of this hydrolysis is roughly proportional to the concentration of the dihydrogen phosphate present, and is slightly diminished by excess of calcium nitrate.

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THE BEHAVIOR OF CERTAIN HYDRAZINE SALTS ON DECOMPOSITION BY HEAT.[1]

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In 1899 Sebanejeff[2] described a method for the preparation of hydronitric acid depending upon the action of nitric acid on hydrazine sulfate. It was observed that when hydrazine mononitrate was treated with concentrated sulfuric acid at ordinary temperature, nitric oxide was evolved, a reaction which did not occur at —15°. On heating with dilute sulfuric acid, hydronitric acid was produced and was given off.

The hydrazine dinitrate, which proved to be much less stable than the corresponding monocompound, was decomposed under three sets of conditions and its decomposition products were studied—(1) at 80° to 85°; (2) on a water bath, with a limiting temperature of 100°; (3) at ordinary temperatures over sulfuric acid.

On warming this compound to 80 to 85°, this author found that the nitrate decomposed and yielded the volatile products, hydronitric acid, nitric acid, nitrogen and water, and the nonvolatile products, the neutral mononitrate and ammonium nitrate. Upon heating on the water bath, at 100°, the decomposition of the dinitrate occurred very much as it did at the temperature of 80–85°, except that the decomposition was more complete, yielding a residue containing only ammonium nitrate.

When the hydrazine dinitrate was allowed to stand at ordinary temperature in a desiccator over sulfuric acid, there occurred a continuous evolu-

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[1] A chapter from the thesis submitted by the author to the Faculty of Cornel University, May 1908, for the degree of Doctor of Philosophy.

[2] *Z. anorg. Chem.*, **20**, 21 (1899).