A STUDY OF THE SOLUBILITY OF TRICALCIUM PHOSPHATE IN NEUTRAL AND AMMONIACAL SOLUTIONS OF VARIOUS SALTS.

by

Robert Jeptha Seay

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CHAPTER I

Introduction

Mr. Dean of the Knoxville Fertilizer Company in a talk to a class of the University of Tennessee in the autumn of 1933 said that no revolutionary advance had been made in the phosphate industry since the discovery of the process of making acid phosphate from rock phosphate and sulfuric acid. Heretofore, the greatest amount of experiment has been made on the reactions of the rock phosphate with acids, particularly sulfuric and phosphoric. Less attention has been given to the possibility of reactions in neutral and alkaline solutions. F. K. Cameron[1] and his co-workers have been the most extensive experimenters on the solubility of tricalcium phosphate in water and neutral salt solutions. In the historical division of this thesis all this information is presented. In the experimental work ammoniacal solutions of ammonium salts were used as solvents. Most of the experiments recorded in the literature use a prepared compound corresponding to the formula $Ca_3(PO_4)_2$ as a basis for their experiments. It would be of interest to know to what degree these results are applicable to phosphate rock in which the principal constituent is apatite $\overline{Ca_3(PO_4)_2CaF_2}$. In general the

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(1) Cameron and Hurst, J. Am. Chem. Soc., 26, 885 (1904);
Cameron and Seidell, ibid. 26, 1454 (1904);
Cameron and Bell, ibid. 27, 1503 (1905); 27, 1512 (1905); 28, 1222 (1906).

rock phosphate is less soluble than is pure tricalcium phosphate. It is known to be much less available as plant food. Finely ground rock phosphate, which was obtained from the Knoxville Fertilizer Company, was used in this research. It analizes approximately 48-49% P_2O_5.

CHAPTER II

Historical

Solubility of Tricalcium Phosphate in Water[2]

In every case in speaking of the solubility of tricalcium phosphate in water, it is correct to speak of the solubility of the products of hydrolysis, CaO and P_2O_5, rather than the solubility of tricalcium phosphate which may be present in minute amounts only. In this case as in every case of determining solubilities, the state of the tricalcium phosphate is important whether freshly precipitated, dried, ignited, of a natural product as apatite, a phosphate rock, bone, etc.

Table I

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Water After Varying Periods of Contact.

Temperature 25°C. 1 gm. solid per 40cc. solvent. Constant Shaking

Number of Days of Contact	Grams of PO_4 per Liter
1	0.1989
3	0.2060
8	0.2163
20	0.2288
37	0.2302
81	0.2339

(2) Cameron and Hurst, J. Am. Chem. Soc., 26, 885 (1904).

This table shows that very long periods are required to establish true equilibrum. It can be seen that the phosphate hydrolized at aconstantly diminishing rate. Equilibrum was practically reached in about thirty five days. It is improbable that true equilibrum was reached even after eighty one days.

Table II[3]

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Water which was Free from Carbon Dioxide.
Temperature 25°C. Time of Contact: twelve days, frequent shaking.

cc. of Water per gram of Solid.	Grams PO_4 per liter of solution.
2.5	1.2293
5.0	0.9049
10.0	0.6805
20.0	0.3825
40.0	0.2156
80.0	0.1315
100.0	0.1131
200.0	0.0679
400.0	0.0427

(3) Ibid.

It will be observed here that while the actual amount of phosphoric acid increases as the proportion of water to solute increases, the relative concentration of the solution decreases.

Table III[4]

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Water.

	Grams of $Ca_3(PO_4)_2$ per Liter
H_2O (CO_2 free)	0.01 to 0.10
H_2O (CO_2 saturated)	0.15 to 0.30

It will be seen from these figures and the statements made by Cameron and Hurst that the results of the solubility of calcium phosphate in water vary considerably with different investigators. Some of the factors influencing these variations are: (1) The method of preparing the calcium phosphate; (2) The time allowed for equilibrum to occur; (3) The method of measuring the dissolved compound, whether the calcium or the phosphate in solution is determined.

(4) Seidell, "Solubilities of Inorganic and Organic Compounds." p. 212, 1919.

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Table IV

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Solutions of Calcium Chloride when in the proportion of one gram Calcium Phosphate to 40cc. solution.
Temperature 25°C. Time of contact: Five days, continuous shaking, one day settling.

Grams $CaCl_2$ per liter	Grams PO_4 dissolved per 1.
0	0.2185
1	0.1383
5	00.1150
10	0.1050
25	0.0979
50	0.0905
100	0.0797
200	0.0626

The increasing concentration of the calcium chloride seems to decrease the solubility of the phosphate. This may be due to the formation of a common ion (Ca^{++}) which forces back the solubility of the calcium phosphate or the hydrolized calcium hydroxide and consequently lessens the solubility of the phosphoric acid.

(5) Cameron and Hurst, J. Am. Chem. Soc., 26, 885 (1904).

Table V[6]

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Solutions of Calcium Nitrate.

Temperature 25°C. Time of contact: Sixteen days, constant shaking.

Grams of $Ca(NO_3)_2$ per liter.	Grams of PO_4 per liter
0.0	0.2136
1.0	0.1907
5.0	0.1110
10.0	0.1053
25.0	0.1064
50.0	0.1098
100.0	0.1132
200.0	0.1093

The pressure of a common ion (Ca^{++}) probably explains the above results as in the case of calcium chloride.

(6) Cameron and Hurst, J. Am. Chem. Soc., 26, 885 (1904).

Table VI[7]

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Solutions of Potassium Chloride.

Temperature 25°C. Time of contact: Thirty days, frequent shaking. One gram solid to forty cc. solution.

Grams KCl per liter	Grams PO_4 per liter	Grams of Ca per l.
5	0.2265	0.0392
25	0.2224	0.0614
75	0.2157	0.0672
150	0.2151	0.0757
300	0.2137	0.0800

The increase in the solubility of the phosphate may be due to the increase in the solubility of the calcium hydroxide which is caused by the potassium chloride.

(7) Ibid.

Table VII[8]

Solubility of Calcium Phosphate, $Ca_3(PO_4)_2$, in Solutions of Sodium Nitrate.

Temperature 25°C. Time of contact: Thirty days, with frequent shaking. One gram of solid to 40cc. of solution.

Gms. of $NaNO_3$ per liter.	Gms. of PO_4 per liter.	Gms. of Ca per liter.
5	0.1189	0.0329
25	0.2291	0.0757
75	0.2372	0.1057
150	0.2425	0.1343
3000	0.2077	0.1315

These results are not very satisfactory. The sodium nitrate apparently had little effect on the amount of phosphate entering solution but the amount of calcium was markedly increased.

W. O. de Coninck[9] heated tricalcium phosphate, $Ca_3(PO_4)_2$, in a concentrated solution of normal sodium carbonate on a steam bath for eighty seven hours at a temperature of 97-8°C. There was no reaction between these substances.

(8) Ibid.

(9) de Coninck, Chem. Abstracts, 5, 2042 (1911).

A. Terreil[10] found that when one hundred grams of the acid was neutralized with ammonia, the following amounts of normal calcium phosphate were dissolved.

Table VIII.
Solubility of Calcium Phosphate in Solutions of Ammonium Salts.

Salt	Grams $Ca_3(PO_4)_2$ dissolved
Ammonium Chloride	0.655
Ammonium Nitrate	0.309
Ammonium Sulfate	1.050
Ammonium Acetate	0.255
Ammonium Tartrate	4.560
Ammonium Citrate	6.010
Ammonium Malate	1.120

K. K. Gedroits[11] found that the phosphorous of the soil and that of the phosphates became more readily available in the presence of ammonium sulfate and ammonium nitrate.

Warington[12] showed that tricalcium phosphate, which contains slightly more lime than the formula requires,

(10) Seidell, "Solubilities of Inorganic and Organic Compounds", p. 876, 1911.

(11) Gedroits, Chem. Abstracts, 5, 2294 (1911).

(12) Warington, J. Chem. Soc., 26, 983 (1873).

was decomposed by boiling water, giving a ratio of phosphoric acid to lime of approximately three to one. The decomposing action is possessed to a lesser extent by cold water.

Cameron and Hurst concluded that an increase in the temperature increased the decomposition of the solid phosphate whether in water or salt solution. They decided that attempts to apply the mass law were not satisfactory because of the complexity of the reactions between the hydrolized products and the solutes and also because of indefinate equilibrum conditions.

CHAPTER III

Theoretical

Cameron and Hurst[13] make the statement that the system of $Ca_3(PO_4)_2$ in a salt solution is too intricate to apply the mass law. The law would be still less applicable to solutions of greater complexity, such as those proposed in the present investigation.

Ionization of tricalcium phosphate in water:

$Ca_3(PO_4)_2$ plus aq. $\rightleftharpoons$ 3 $Ca(OH)_2$ plus 2 $H_3(PO_4)_2$ $\rightleftharpoons$

3 Ca^{++} plus 2 PO_4^{---}.

The action of the calcium ion depresses the solubility of the tricalcium phosphate.

The effect of increasing the solubility of the tricalcium phosphate by the addition of a salt having no common ions is due to changing the nature of the solvent.

In the ammoniacal salt solutions used in the present experimental investigation, the ionization is as follows: This example shows ammonium chloride.

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(13) Cameron and Hurst, J. Am. Chem. Soc., 26, 885 (1904).

$NH_4(OH) \rightleftharpoons NH_4^+ + OH^-$

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

$(NH_4)_2CO_3 \rightleftharpoons 2\ NH_4^+ + CO_3^{--}$

$MgCO_3 \rightleftharpoons Mg^{++} + CO_3^{--}$

$Ca_3(PO_4)_2 \rightleftharpoons 3\ Ca^{++} + 2\ (PO_4)^{---}$

The reaction which is desired is as follows:

$$Ca_3(PO_4)_2 + 2\ MgCO_3.CaCO_3 + (NH_4)_2CO_3 \longrightarrow$$

$$2\ MgNH_4PO_4 + 5\ CaCO_3.$$

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Table IX

Equilibrum in the System Magnesium Carbonate, Ammonium Carbonate, and Water at 30°C. (Lafoulaine 1925)

	Mols per 100 mols of H_2O	
MgO	CO_2	NH_3
0.160	1.487	1.193
0.075	2.427	2.233
0.008	3.745	3.837
0.006	1.593	10.386
0.008	0.095	11.029
0.001	0.010	10.981
0.007	0.102	15.710

(14) Seidell, "Solubilities of Inorganic and Organic Compounds", p. 163, 1928.

The preceding table gives a portion of the figures of the equilibrum of magnesium carbonate, ammonium carbonate, and water. This gives the relative amounts of dissolved substances under conditions similar to the present investigation. The addition of an ammonium salt would merely increase the concentration of ammonia and add another ion to the system.

Table X[15]

Solubility of Ammonium Magnesium Phosphate in Several Solvents.

Grams of NH_4MgPO_4 per 100 grams Solvent in:

t°	Water	Aq. 5% NH_4NO_3	Aq. 5% NH_4Cl	1 pt.NH_3 (d. .96) 4pts.H_2O	Aq. 5% NH_4Cl 4pts. NH_3/100	Aq. 10% NH_4Cl 4 pts. NH_3 /100
20	0.052	0.046	0.105	0.0098	0.0165	0.0541
40	0.036	0.064	0.071	0.0136		
60	0.040	0.085	0.173	0.0174	0.0274	0.0731
80	0.019	0.101	0.191	0.0145		

The Ammonium Magnesium Phosphate is slightly more soluble in solutions of ammonium nitrate and ammonium chloride than it is in water. In a solution of ammonia, however, the solubility is greatly decreased. When the ammonium chloride and ammonia are both present the effect of the ammonia in

(15) Seidell, "Solubility of Inorganic and Organic Compounds", p. 61, 1919.

depressing the solubility of the ammonium magnesium phosphate far overbalances the action of the ammonium chloride in increasing its solubility.

The compound formed, $MgNH_4PO_4$, is rendered very insoluble by the great excess of ammonium ions produced by the ammonium hydroxide, ammonium chloride, and ammonium carbonate. The magnesium ions produced by the magnesium carbonate have the same effect on the magnesium ammonium phosphate. The calcium ions formed from the tricalcium phosphate unite with the carbonate ions produced by the magnesium and the ammonium carbonates to form calcium carbonate. The compound is rendered very insoluble by the excess carbonate ions. As the calcium and phosphate ions are removed from the solution more calcium phosphate ionizes.

The results looked for here cannot be predicted quantitatively on the basis of the mass law. The extent to which the predictions based on the mass law may hold can be determined only by experiment. After the system has approached equilibrum it is proposed to determine the per cent of water-soluble phosphate and the citrate-soluble phosphate in the solid material. This will give an indication of the value of the material as fertilizer.

The reason for using dolomite is economic only. The tricalcium phosphate is used in the form of rock phosphate. The phosphate is made a carrier for ammonia without utilizing any acid.

CHAPTER IV

Experimental

The compounds used were:

Magnesium carbonate, purified;

Ammonium carbonate, purified;

Finely ground Florida rock phosphate, 49% P_2O_5.

The following solutions were made up by saturating 250 cc. of ammonium hydroxide with the ammonium salt.

Table XI. Ammoniacal Solutions of Ammonium Salts.

Ammonium Acetate
Ammonium Chloride
Ammonium Nitrate
Ammonium Oxalate
Ammonium Sulfate

To 150 cc. of the solvent was added 5 grams of ammonium carbonate, 10 grams of magnesium carbonate, and 5 grams of rock phosphate. This mixture was placed in a closed flask and agitated continuously for fourty eight hours. It was allowed to settle for three days. The sample was then analized for citrate-soluble phosphate by the official method of the Association of Agricultural Chemists.

Table XII

Percentages of Citrate-Soluble Phosphates		
Solvent: Ammoniacal Solution of:	% rock phosphate converted to citrate soluble P_2O_5.	% total P_2O_5 converted to citrate sol. P_2O_5
Ammonium Acetate	3.35	6.84
Ammonium Chloride	8.43	17.20
Ammonium Nitrate	3.26	6.66
Ammonium Sulfate	6.83	13.90
Ammonium Oxalate	5.24	10.70
Ammonium Nitrate, Chloride, and Acetate in equal parts.	5.11	10.40

CHAPTER V

Discussion of Results

The average value of the percentages of citrate-soluble P_2O_5 in the ammonium chloride, ammonium acetate, and ammonium nitrate solutions is 5.01%. The value of the citrate-soluble P_2O_5 in the solution consisting of one part of ammonium chloride, one part of ammonium acetate, and one part of ammonium nitrate is 5.11%. The following conclusions can be drawn: First, the acid ion affects the extent of the reaction. Second, the acid ion has a selective action, not being affected by other acid ions but working independently.

The chloride ion has the best influence on the reaction, with the sulfate ion coming second. This is not in the same order as the solubility of the tricalcium phosphate in neutral solutions of ammonium salts.

This result may be explained by the statement of Balareff.[16] He says that when magnesium phosphate is precipitated from a solution containing a large excess of ammonium chloride, especially if there is also an excess of ammonia present, it is contaminated apparently with the compound $Mg(NH_4)_2PO_4)_2$. The formation of the above compound may in part explain the formation of more citrate-soluble compound when ammonium chloride is used than when ammonium sulfate is used.

The compound, ammonium magnesium phosphate, is very available as a fertilizer both in respect to the phosphate and

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(16) Balareff, Chem. Abstracts, 12, 2296 (1918).

the nitrogen. Mach and Lederle[17] found that both trimagnesium phosphate, $Mg_3(PO_4)_2$, and magnesium ammonium phosphate were relatively quite soluble in CO_2-free distilled water. The solubility of magnesium ammonium phosphate is shown in Table X (q. v.). The magnesium ammonium phosphate is more soluble in cold water than it is in hot water.

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(17) Mach and Lederle, Chem. Abstracts, 26, 4900 (1932).

CHAPTER VI

Conclusion

Because of the very slow solution and dissociation rate of tricalcium phosphate, especially when it is in the form of rock phosphate, any reaction involving its solubility would be necessarily slow. The reaction appears to go to completion but at a very slow rate. The limiting factor for the completion of the reaction is time. The rate of the reaction is influenced by the following factors:

1. Temperature
2. Ammonium salt used.
3. Concentration of the Ammonium salt.
4. Concentration of Ammonia.

The present investigation is not of sufficient scope to determine the effect that all of these variables have on the rate of solution. If the reaction could be made commercially practicable, it would have the following advantages:

1. No acid would be required.
2. The product would be alkaline in nature.
3. The phosphate would be a carrier of ammonia without requiring the use of additional acid.

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* Only the abstract was read.

APPROVAL

The foregoing thesis is hereby approved as a credible study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrent its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

Name Jedsan H. Robertson

Title Professor of Chemistry