

THE CITRIC SOLUBILITY OF MINERAL PHOSPHATES

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(With 8 Diagrams.)

I. INTRODUCTORY.

THE Fertilisers and Feeding Stuffs Act 1906, Section 10, defines the expressions "soluble" and "insoluble" to mean that the fertilising constituent is soluble or insoluble in water, or, if specified in the invoice, to mean that the fertilising constituent is soluble to the extent guaranteed in a solution of citric acid, or other solvent, of the prescribed strength. In particular the section defines the percentage of soluble phosphate and the percentage of insoluble phosphate to mean respectively the percentage of tribasic phosphate of lime equivalent which has been, or that which has not been, rendered soluble. "Citric solubility" under the Act is further and more definitely defined in the Fertilisers and Feeding Stuffs General Regulations 1906 as follows:

"When, in an invoice relating to *basic slag* or *basic superphosphate*, it is specified that a certain percentage of the phosphate contained in the basic slag or superphosphate is soluble in citric acid, this shall be taken to mean that it is capable of being dissolved to the extent of such percentage when 5 grams of the fertiliser and 500 cubic centimetres of water, containing 10 grams of citric acid, are continuously agitated in a flask or bottle of about 1 litre capacity for the period of half an hour at the ordinary temperature."

It is clear from these regulations that "citric solubility" refers to basic slags and "basic superphosphates"¹ and that the citric solubilities of basic slags and of basic superphosphates have to be determined at "room" temperature by means of a 2 per cent. solution of citric acid, the duration of contact being limited to half an hour in a quantity of

¹ The seller need not, unless he chooses to do so, give any guarantee of citric solubility.

the fertiliser exactly one half in amount of citric acid present. The basis of this test is evidently the work of Wagner and appears to be of a wholly empirical character. Since Wagner's method has been adopted as an official test, citric solubility has been studied by a number of different workers. Stead¹ found that for normal basic slags the solubility increased with the amount of silica present. He also showed that citric solubility was associated with the degree of fineness of the powder. Robertson² studied the degree of solubility of mineral phosphates in citric acid using the official test. He shows that mineral phosphates are completely soluble in 2 per cent. citric acid solution if a sufficient number of extracts are made by successive half hour contacts. Robertson in his conclusions states that "Even a small amount of free lime or calcium carbonate decreases substantially the solubility of mineral phosphates as judged by the citric acid test. When a large amount of calcium carbonate or free lime is present, the citric acid test as commonly practised, is a test for lime and not for phosphates. It is important in this respect to distinguish between free lime and calcium carbonate, and lime actually entering into the composition of the phosphate. The higher the percentage of lime actually entering into the phosphate compound, the higher the citric solubility of the phosphate." He has also shown that fluor-spar greatly decreases citric solubility in slag and concludes that the official test gives no true idea of the solubility of the phosphate in slag. He states that "one of the effects of fluor-spar is to cause the formation of a phosphate which does not contain silica in combination as is the case with high citric soluble slags." The effect of fusing with fluorides apparently is that a compound of silicon and fluorine is formed leaving lime and phosphorus in combination. Dixon³ made a study of the citric solubility of various bone phosphates. In his case he varied the citric acid concentrations and with a constant weight of fertiliser he found that in every case the stronger the citric acid solution the greater was the amount of phosphate dissolved. Ramsay⁴ prepared pure tricalcium phosphate by mixing three equivalents of CaO with one equivalent of P₂O₅ and showed that 91 per cent. of the total phosphoric acid content of the pure tricalcium phosphate was soluble in the prescribed 2 per cent. citric acid solution in 30 minutes. He also showed that the simple addition of calcium carbonate reduced citric solubility. Russell and Prescott⁵ studied the citric solubility of the phosphates of the soil. They

¹ *Trans. Faraday Soc.* **16**, Part 2.

² *Soc. Chem. Ind.* No. 4, **35**.

³ *Journ. of Agric. Sci.* 1906, Part 4.

⁴ *Ibid.* June, 1917.

⁵ *Ibid.* Sept. 1916.

found a greater solubility for short periods of contact when compared with long periods and established the fact that adsorption of phosphate took place during long periods of contact.

II. CITRIC SOLUBILITY—OFFICIAL AND OTHERWISE.

The writer was attracted to this subject by the fact that the citric solubility of certain commercial phosphates was determined in a dilute citric acid solution (0.2 per cent.) and not by means of the 2 per cent. solution prescribed by the official test for slags.

Samples of ground mineral phosphate are occasionally guaranteed to contain as much as 50 per cent. "citric soluble" phosphate. To the unwary this might be taken to mean that the sample contained 50 per cent. "citric soluble" phosphate as determined by the official test for slags and "basic superphosphates" prescribed in the Regulations. As a matter of fact, however, the citric solubility in this case was determined for the sellers by agricultural analysts by agitating for half an hour 5000 parts of a solution of citric acid (0.2 per cent. strength) with 1 part of the sample. That is to say the amount of the citric acid employed was one-tenth of the amount officially prescribed while the proportion of fertiliser was 50 times less than the proportion prescribed as may be seen from the following table (Table I).

Table I.

Test	Citric acid	Fertiliser	Total volume
Official quantities	10 grams	5.0 grams	500 c.c.
Quantities for private test ...	1 gram	0.1 gram	500 "
i.e.	10 grams	1.0 "	5000 "

The following results (Table II) were obtained on using the official citric solubility test on samples of ground mineral phosphate and basic slag:

Table II.

Basic slags				Mineral phosphate			
Citric sol. phos.	Total phos.	Fineness	Percent. of total phos. dissolved	Citric sol. phos.	Total phos.	Fineness	Percent. of total phos. dissolved
27.94	30.59	84.8	91.3	21.92	64.86	64.7	33.8
28.21	31.00	79.0	91.0	18.26	55.86	85.1	32.7
4.82	19.35	76.0	24.9	20.39	57.84	84.5	35.3
6.36	25.55	74.1	24.5	19.72	57.98	82.9	34.0
22.68	23.60	93.6	96.1	21.53	58.51	98.0	36.8
28.54	39.10	85.4	73.0	19.36	61.92	88.0	31.3

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The results of this table show that when mineral phosphate is as finely ground as basic slag a fair amount of phosphate is rendered "citric soluble" by the official method but the "citric solubility" of mineral phosphates appears generally to be much less than the citric solubility of slags, when this test is applied.

III. THE SCHEME OF EXPERIMENTAL WORK.

The citric solubility of mineral phosphates was accordingly studied at "room" temperature over a period of 30 minutes agitation:

(1) In varying dilution, the quantities of acid and mineral phosphate being constant.

(2) In varying concentrations of acid, the volume of fluid and the weight of mineral phosphate being constant.

(3) With varying amounts of the phosphatic fertiliser, the volume of the fluid and the concentration of acid being both constant.

In order to compare the citric solubility of mineral phosphates under the above conditions, with the citric solubility of a pure phosphatic compound, a fourth series of experiments was conducted, namely,

(4) the solubility of dicalcium phosphate in dilute hydrochloric acid.

It is evident that whatever be the value of determining the proportion of citric soluble phosphate in a phosphatic fertiliser, it is necessary, for comparative purposes, if other conditions are similar, that the test should be applied in the same way and with the same proportions of citric acid or of other acid and of fertiliser as prescribed officially, for basic slags and basic superphosphates.

Other conditions are, of course, open to study. For example we could have two of the above factors varying differently with a series of constant values for the third factor. The citric solubility of tricalcium phosphate and other pure phosphatic compounds could be studied and the results compared with the results from the above four series. The writer has not been able to carry out these latter experiments. He therefore submits the results of experimental work under the above four heads¹.

¹ The writer has to acknowledge his indebtedness to Mr John E. Ritchie, M.A., B.Sc., A.I.C., who has performed the necessary analytical determinations in the experiments on mineral phosphates, and has also given valuable assistance in preparing the memoir. He has also to thank Mr W. T. H. Williamson, B.Sc., A.I.C., for the determinations in the case of dicalcium phosphate.

IV. EXPERIMENTS WHERE THE QUANTITIES OF MINERAL PHOSPHATE AND CITRIC ACID USED WERE CONSTANT AND THE DILUTION WAS VARIED.

In order to determine the variability in citric solubility of mineral phosphate with varying dilutions of citric acid, a series of experiments was conducted with different dilutions shaking for half an hour, the time prescribed in the official test. The quantities of citric acid and of mineral phosphate used are indicated in the following table (Table III). Let m_1 = amount of citric acid used, m_2 = amount of mineral phosphate used, and m_3 = volume of fluid used. In this series the ratio m_1/m_2 was made constant (and equal to 2) in order to secure that the effect of the presence of $\text{Ca}(\text{OH})_2$ and of CaCO_3 and other hydrates and carbonates, on the citric acid concentration was of a constant character. Throughout this series of experiments 10 grams citric acid and 5 grams mineral phosphate were used, the volume being varied as shown in Table III.

Table III. *Quantities of mineral phosphate and citric acid used are constant—dilution, i.e. degree of concentration, varies.*

{ 5 grams mineral phosphate
10 grams citric acid

1 Exp.	2 Vol. of sol.	3 4 Wt. of Phosphate dissolved. Grams per volume stated		5 Phosphate dissolved per cent. of sample as $\text{Ca}_3(\text{PO}_4)_2$	6 7 Percentage dissolved of total phosphate content		8 9 Molecular concentration of phosphate at end of 30 minutes. Gram-mols. per litre	
		Observed as $\text{Ca}_3(\text{PO}_4)_2$	Theory as $\text{Ca}_3(\text{PO}_4)_2$		Observed	Theory	Observed	Theory
1	500	0.9620	0.9697	19.24	29.8	30.1	0.006206	0.006256
2	625	1.0210	1.0215	20.42	31.7	31.7	0.005270	0.005272
3	833	1.0875	1.0907	21.75	33.7	33.8	0.004210	0.004222
4	1250	1.2080	1.1990	24.16	37.5	37.2	0.003117	0.003094
5	2500	1.4070	1.4030	28.14	43.6	43.5	0.001815	0.001810

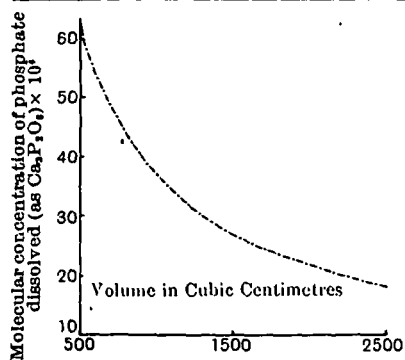


Diagram 1. See columns 8 and 9, Table III.

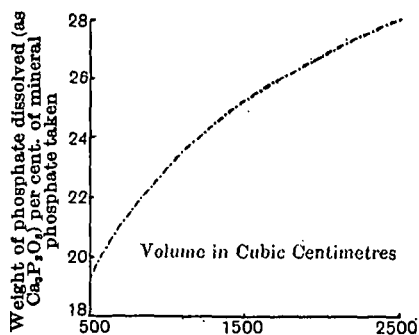
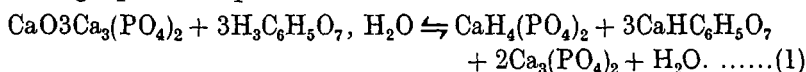


Diagram 2. See column 5, Table III.

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It is seen from these results that the higher the dilution of citric acid, with m_1/m_2 kept constant, the greater is the proportion of citric solubility of the phosphate expressed as a percentage of the weight of the sample (column 5, Table III). Bassett¹ considers that the compound usually present in mineral phosphates is hydroxyapatite which may be written $[\text{Ca}_3(\text{PO}_4)_2]_3\text{Ca}(\text{OH})_2$. He also thinks it probable that hydroxyapatite is the only calcium phosphate that can permanently exist under normal soil conditions. It forms the stable solid phase over a range of acidity of great practical importance, as it can exist in contact with faintly acid, neutral or alkaline solutions. An attempt has been made to fit a theoretical curve to this series of experiments on the assumptions that there is equilibrium at the end of the experiment and that the following equation represents the reaction:



Of course other equilibrium equations including dicalcium phosphate can be written from which the same mass action equation can be deduced. The above equation is merely given as a suggestion.

The sample of mineral phosphate contained a proportion of CO_2 equivalent to 0.65 gram of calcium carbonate in 5 grams of the sample. Hence 1.36 grams of citric acid would be used up in the formation of citrates, leaving 8.64 grams of acid available to attack the phosphatic compound. If the original acid concentration is taken to be proportional² to the concentration at equilibrium, a constant should be obtained on applying the law of mass action. A good agreement between theory and observation is obtained on this hypothesis. If w = molecular concentration of acid after alkaline lime has been neutralised; u = molecular concentration of phosphate (expressed as tricalcium phosphate) at the end of 30 minutes agitation then we should have $u^4/w^3 = k$. The last two columns (columns 8 and 9, Table III) show the observed molecular concentrations and the theoretical values on the basis of above equation. A good fit is also obtained using the equation $u^4/(w - u)^2(w - 2u)$ when the theoretical values are found by Horner's method. Diagrams 1 and 2 show in graphical form the results of Table III.

¹ *Trans. Chem. Soc.* 1917, 111.

² The values of u from the equation $u^4/(w - 3u)^3$ show greater divergences from observational values than the values obtained from either of the equations given in the text. The ratio $\frac{(w - 3u)}{w}$ varies from .72 to .80, showing that the original concentration is nearly proportional to concentration at the end of 30 minutes shaking. Whatever the reason, the formula u^4/w^3 gives by far the best fit to the results.

A second set of experiments was carried out in which the ratio $m_1/m_2 = 10$ instead of 2, that is, in each case 10 times more citric acid than phosphate was used in each separate experiment. The undernoted table (Table IV) shows the quantities used and the results obtained. This set of experiments when plotted against the theoretical curve expressed in equation (1) was found to be a very bad fit. In order to determine the best fitting equation the ratio of the exponent x to the exponent z in the general equation $C = \frac{k_1 u^x}{k_2 w^z}$ was determined where C , k_1 and k_2 are constants. The ratio $\frac{\text{mean } x}{\text{mean } z}$ was found to be equal to $1.0669 = 16/15$.

The following table (Table IV) and accompanying diagrams (Diagrams 3 and 4) show the observed results and those reached from the equation,

$$C = \frac{u^{16}}{w^{15}}, \text{ or } \log C = 16 \log u - 15 \log w.$$

Table IV. *Quantities of mineral phosphate and citric acid constant—dilution varied.*

<div style="text-align: center;"> { 10 grams citric acid { 1 gram mineral phosphate </div>							
1 Exp.	2 Vol. of solution	3 Weight of phosphate dissolved as $\text{Ca}_3\text{P}_2\text{O}_8$		5 Percent. dissolved of total $\text{Ca}_3\text{P}_2\text{O}_8$ content	6 Phosphate dissolved per cent. of weight of sample	7 Molecular concentration at end of 30 minutes	
		Observed	Theory			Observed	Theory
1	500	0.5376	0.5388	83.3	53.76	0.003468	0.003476
2	625	0.5472	0.5464	84.8	54.72	0.002824	0.002820
3	833	0.5610	0.5565	87.0	56.10	0.002172	0.002154
4	1250	0.5708	0.5705	88.5	57.08	0.001472	0.001473
5	2500	0.5955	0.5960	92.3	59.55	0.000768	0.000769
6	5000	0.6180	0.6220	95.8	61.80	0.000399	0.000401

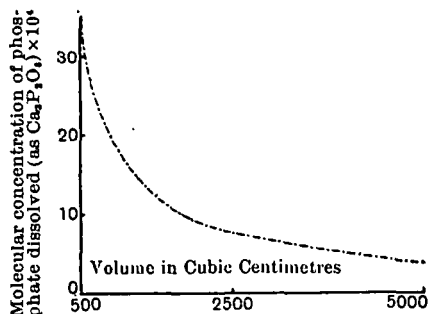


Diagram 3. See columns 7 and 8, Table IV.

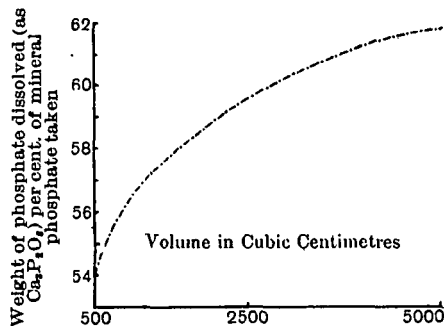


Diagram 4. See column 6, Table IV.

Experiment 6 of Table IV is an experiment identical in character with the private test already mentioned (see Table I). The results of experiments parallel to this experiment were used by certain sellers to describe the citric solubility of the mineral phosphate put on the market. It will be seen that Exp. 6 falls naturally into its place among the experiments given in Table IV. The amount of phosphate dissolved amounts to 62.2 per cent. of the weight of mineral phosphate tested while the same phosphate, analysed in accordance with the official test (Table III, Exp. 1) shows a citric solubility of 19.24 per cent. If we consider the proportion dissolved in relation to the total amount of phosphate present expressed as tricalcic phosphate it is found that, by the official method 29.83 per cent. of the total $\text{Ca}_3\text{P}_2\text{O}_8$ content is dissolved, while by the private test (at great dilutions, see Table IV) 95.8 per cent. of the total $\text{Ca}_3\text{P}_2\text{O}_8$ content was dissolved. These results show what might naturally be expected, namely, a much higher solubility of mineral phosphate in the experiments where the constant ratio $m_1/m_2 = 10$ (Table IV) was used than where $m_1/m_2 = 2$ (Table III) was used. In other words if m_1/m_2 is made large enough we should reach the limit of 100 per cent. citric solubility for all very high dilutions.

The results in Table II show that, using the official test on both slags and mineral phosphates, slags generally show a higher citric solubility than mineral phosphates. If the unofficial test (Exp. 6, Table IV) was universally applied to slags we should have similar high solubility figures, in other words the citric solubility at high dilution would be practically 100 per cent. and the only item of information which would be valuable to the purchaser would be the actual proportion of phosphate, expressed as tricalcium phosphate, present in the fertiliser. In some slags the citric solubility in terms of total phosphate content is as much as 90 per cent. (see Table I) and therefore the actual increase on dilution must be necessarily small compared with the increase in citric solubility on dilution of any mineral phosphate.

The undernoted table (Table V) shows the average composition of five commercial mineral phosphates¹. The sixth (Egyptian) was analysed in my laboratory.

Since calcium carbonate is present in varying proportions in commercial mineral phosphate it is clear that with a constant initial molecular concentration of citric acid, varying quantities of citric acid will be available to attack the insoluble phosphate. For example, suppose we selected two different varieties of mineral phosphate, ground to the same

¹ Robertson, *J.S.C.I.*, 35, p. 218.

degree of fineness, and containing the same proportions of hydroxyapatite but quite different proportions of calcium carbonate. The sample which contained the smaller quantity of calcium carbonate would show a higher citric solubility than the second sample which contained a higher proportion of calcium carbonate, due to the presence of a relatively large proportion of free citric acid in the former.

Table V. *Composition of Mineral Phosphates.*

		Makatea Island	Florida Pebble	Algerian	Gafsa	Tunisian	Egyptian
Calcium oxide	52.38	47.10	46.13	43.30	48.40	46.81
Phosphoric acid	38.24	31.50	27.27	25.35	26.13	29.52
Carbon dioxide	1.69	3.04	6.70	5.50	9.03	9.42
Moisture	1.46	1.00	0.72	3.26	0.98	—
Combined moisture and organic matter ...	{	3.39	2.41	3.28	4.39	3.21	2.06
Ferric and aluminium oxides ...		1.01	1.60	2.59	4.98	4.25	2.78
Magnesium oxide	1.35	1.90	2.02	1.72	0.90	0.77
Sand	0.28	7.03	8.12	7.56	4.65	7.73
Undetermined	0.20	4.42	3.17	3.94	2.45	0.91

Citric solubility is not necessarily a test of the availability of the phosphate to the plant in the soil. If the sample is finely ground and has a low citric solubility, the lowness of the citric solubility in the case of mineral phosphate would mainly be due (1) to the presence of alkaline material which would neutralise a large proportion of the citric acid, leaving the residue to act on the phosphate and (2) to the chemical constitution of the phosphatic mineral. In the case of slags the citric solubility would be mainly dependent on (1) the compounds of fluorine as shown by Robertson, (2) the presence of alkaline lime as shown by Ramsay, and (3) the chemical constitution of the phosphatic compound in the slag. It has yet to be shown that the phosphate in mineral phosphate is not utilised by the plant as readily and as efficiently as the phosphate from slags. In other words the exact chemical composition of the phosphatic compounds in the various mineral phosphates and slags has, in each case, to be demonstrated. It appears to be necessary to test the citric solubility of phosphates of *known composition* against their availability in the soil as shown by yield of crop. The results would then show how far, if at all, citric solubility is a measure of availability in the soil. Since the commercial fertilisers tested contain varying quantities of alkaline lime, fluorides and other interfering substances, and since the chemical constitution of the fertilisers is incompletely known, the writer can see no scientific validity in the use of citric solubility as a measure of availability. The three practical tests appear to be:

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- (1) Total phosphatic content.
- (2) Degree of fineness of the powder.
- (3) Presence or absence of substances capable of inhibiting growth.

A fourth test of scientific, as well as practical, value would be a test demonstrating the constitution of the phosphatic compounds in the fertiliser.

If citric solubility cannot be regarded as a useful and practical test for mineral phosphate it is still less valid as a comparative test for slags and mineral phosphates alike owing to the varying composition of slags and to their widely different chemical composition and constitution when compared with mineral phosphates.

In regard to the chemical constitution of phosphatic fertilisers it has already been noted that hydroxyapatite is considered by Bassett as the chemical compound probably present in mineral phosphate. Morison states¹ that the molecular ratio of phosphoric anhydride to calcium oxide P_2O_5/CaO is $1/5$ in slags and supports Stead's conclusions that the phosphatic content in basic slags consists of a chemical union of tetracalcium phosphate and monocalcium silicate $(CaO)_4P_2O_5CaOSiO_2$. On the other hand the ratio of phosphoric anhydride to calcium oxide in Bassett's hydroxyapatite is $3/10 = 1/3\frac{1}{3}$. Morison also deals with the effect of free lime on the citric solubility of slags and shows that the greater the amount of free lime in a slag the greater is the total solubility after three extractions. On the other hand Ramsay² shows that about 91 per cent. of the total phosphoric acid in pure tricalcium phosphate is soluble in the prescribed 2 per cent. citric acid solution. This degree of solubility is very similar to the degree of solubility of the best grades of slags (see Table I). He also shows that by the simple addition of calcium carbonate to pure tricalcium phosphate the citric solubility is reduced from 91 to 84 per cent. This is naturally to be expected and the apparent greater solubility of phosphate with increase of lime content found by Morison must be due to other causes. It should be noted that the quantities of free lime present in Morison's samples are relatively small. The increase in solubility with an increase of silica and the decrease in solubility in the presence of fluorides have already been mentioned. Robertson finds that calcium carbonate decreases substantially the solubility of phosphates as judged by the 2 per cent. citric acid test. The exact effect of the presence of calcium carbonate or calcium hydroxide on the solubility of phosphate of a known composition can of course be found

¹ *Journ. Agri. Sci.* 1909.

² *Ibid.* 8, p. 277.

a priori. The difficulty arises when the composition of the phosphates is unknown and when other interfering substances are present. Since the nature of the substances present are unknown, equations expressing the law of mass action cannot be written down in these cases.*

The following table (Table VI) shows the average composition of some commercial slags as given by Collins (*Chemical Fertilisers*, p. 122).

Table VI. *Composition of Slags.*

			1	2	3	4	5
Total P_2O_5	12.60	20.49	9.09	17.57	19.35
Silica	17.69	10.12	13.49	7.77	12.12
Lime	38.02	46.81	40.43	52.22	44.75
Magnesia	4.24	2.92	5.01	1.94	0.11
Manganese oxide	7.39	4.38	5.41	9.37	4.68
Iron	12.89	9.98	13.83	8.13	9.10

These latter tables (Tables V and VI) show in a general way the differences between slags and mineral phosphates. These two classes of fertilisers contain non-phosphatic residues differing in chemical composition, and residues which are common to both in different proportions. The results of this section show that citric solubility is merely a special case of the law which has been proved to hold for the solubility of a definite chemical substance in dilute acids and it can always be stated *a priori* when the conditions are known for a definite substance in a definite dilution. When, however, we pass from a single substance to mixtures of varying composition citric solubility cannot be descriptive of available phosphate of definite composition. The reason for this lies (1) in the unknown changes which take place in the initial molecular concentration of the citric acid, due to the formation of calcium and other citrates from the carbonates and hydrates present in the fertiliser, (2) in the unknown changes which take place on agitating phosphatic fertilisers of varying composition and (3) in the known effects produced by the presence of fluorides and of silica.

V. EXPERIMENTS IN WHICH THE VOLUME OF FLUID AND THE WEIGHT OF MINERAL PHOSPHATE ARE BOTH CONSTANT, THE VARYING FACTOR BEING ACID CONCENTRATION.

We shall now consider condition (2) namely, where the amount of mineral phosphate (m_2) and the volume of fluid (m_3) are both constant, i.e. $m_3/m_2 = \text{constant}$, while the amount of citric acid is varied.

The following series of experiments was carried out with a constant weight of mineral phosphate (5 grams) in varying concentrations of citric acid in a constant volume of 500 c.c. The undernoted results (Table VII)

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show that if the acidity is expressed as the molecular concentration of citric acid at the end of 30 minutes shaking, $K = u^4/w^3$ fairly accurately describes the solubility of the phosphates at the acid concentrations named.

Table VII. *Amount of mineral phosphate present and volume constant—acidity varies.*

$m_3/m_2 = 100$; vol. = 500 c.c. = m_3 ; m_2 = mineral phosphate = 5 grams

1 Exp.	2 Wt. citric acid in 500 c.c.	3 Acidity as citric acid at end of 30 minutes	4 5 Wt. of phosphate dissolved as $\text{Ca}_3\text{P}_2\text{O}_8$ in 500 c.c.		6 Per-centage dissolved of total $\text{Ca}_3\text{P}_2\text{O}_8$ content	7 $\text{Ca}_3\text{P}_2\text{O}_8$ found per cent. of phosphate taken	8 9 Molecular concentration of phosphate at end of 30 minutes	
			Observed	Theory			Observed	Theory
1	10 grms.	8.87 grms.	0.9675	0.9492	30.0	19.35	.006242	.006124
2	8 "	7.02 "	0.8119	0.7958	25.2	16.24	.005238	.005134
3	6 "	5.11 "	0.6743	0.6250	20.9	13.48	.004350	.004032
4	4 "	3.25 "	0.4495	0.4470	13.9	8.99	.002900	.002884
5	2 "	1.34 "	0.2176	0.2300	6.7	4.35	.001404	.001484
6	1 "	0.49 "	0.1020	0.1082	3.2	2.04	.000658	.000698

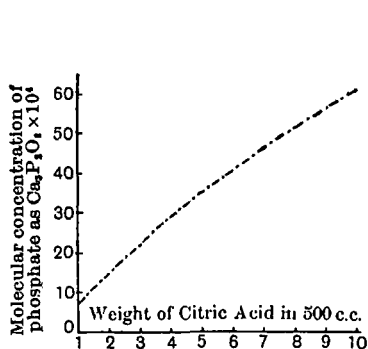


Diagram 5. See columns 8 and 9, Table VII.

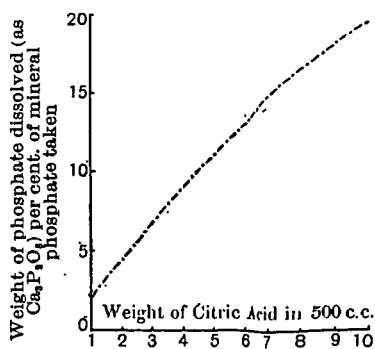


Diagram 6. See column 7, Table VII.

The accompanying diagrams (Diagrams 5 and 6) show the results of Table VII. These results show clearly increasing citric solubility with increasing acid concentration but with constant weight of mineral phosphate in a constant volume. In a citric solubility test, used as a measure of availability, it seems necessary therefore to show that a two per cent. solution is the concentration of citric acid best suited for the utilisation of phosphate by the plant. Would it not be more in accordance with scientific practice firstly, to ascertain the constitution of the phosphatic fertilisers, and secondly, to determine what rôle concentration has in the life history of the plant?

VI. EXPERIMENTS WITH CONSTANT VOLUME AND CONSTANT CONCENTRATION OF ACID BUT WITH VARYING QUANTITIES OF MINERAL PHOSPHATES.

In the first set of experiments fairly high constant values of m_1/m_2 were used. We shall now consider the effect of making m_1/m_2 small, m_1 and m_3 being in this case constant and m_2 the variable. If m_1/m_2 is made small enough we should have a citric solubility practically zero for all dilutions. An example indicating the approach to the latter condition is given in the following table (Table VIII) where the third set of conditions is observed. (See also Diagrams 7 and 8.)

Table VIII. *Amount of citric acid and volume constant—amount of mineral phosphate (m_2) used varied.*

		$\frac{m_3}{m_1} = 50$		{ 10 grams citric acid = m_1 500 c.c. volume = m_3		
Exp.	Wt. of mineral phosphate taken — m_2	Ratio m_1/m_2	Acidity expressed as citric acid at end of 30 minutes	Amount of phosphate dissolved as $\text{Ca}_3\text{P}_2\text{O}_8$	Mol. conc. of phosphate dissolved at end of 30 minutes	Citric solubility expressed as $\text{Ca}_3\text{P}_2\text{O}_8$ per cent. of phosphate taken
1	5 grams	2	8.87	0.9705	.006261	19.41
2	10 „	1	8.50	0.8660	.005587	8.66
3	20 „	0.5	7.65	0.6070	.003916	3.04
4	40 „	0.25	5.98	0.4110	.002652	1.03

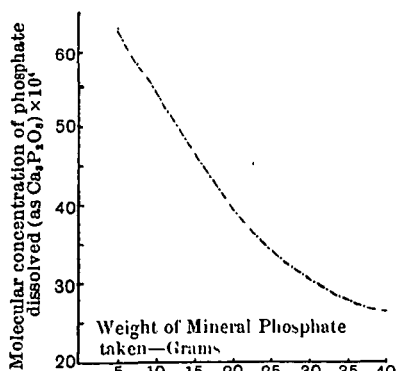


Diagram 7. See Table VIII.

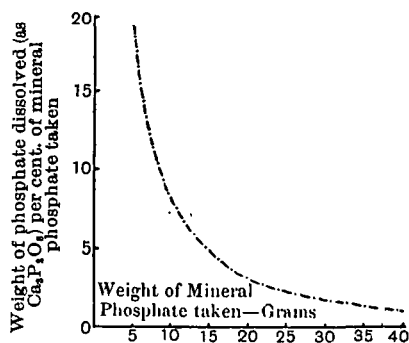


Diagram 8. See Table VIII.

If the mineral phosphate contained merely tri- or di-calcium phosphate and was quite free from $\text{Ca}(\text{OH})_2$, CaO or CaCO_3 and also was in excess, mere variations in the quantity taken would have had little or no effect on the amount of citric acid present at the end of the period of shaking. The presence of $\text{Ca}(\text{OH})_2$ naturally reduces the acid concentration with the result that, while 19.41 per cent. of the 5 grams mineral phosphate was dissolved only 1.03 per cent. mineral phosphate was dis-

solved when 40 grams of the fertiliser were taken. It is thus shown, which is also apparent *a priori*, that citric solubility depends on the quantity of mineral phosphate or slag used. With quantities like 50 grams or 100 grams of mineral phosphate the citric solubility would be extremely small. On what theoretical grounds are quantities like 5 grams (official test) in the case of slag and 1 gram (private test) in the case of mineral phosphate used to determine the availability of phosphate in the soil?

VII. THE INCOMPLETENESS OF THE REACTIONS.

All the foregoing results have been considered from the standpoint of the amount of phosphate dissolved per cent. of the weight of mineral phosphate taken. It is desirable, however, to consider the amount of phosphate dissolved in relation to the amount theoretically obtainable if the reaction were complete. We cannot say definitely what the reaction is but we know that the equation in Section IV gives a suitable prediction formula. Suppose we put the question: What proportion of the amount indicated by this equation is obtained in each separate experiment? We know from theory that the hydrogen ion concentration of an acid is increased by dilution and we should therefore expect *greater proportions of the possible total amounts* at higher dilutions than at lower dilutions. Let us consider the first series of experiments from this standpoint. If the citric acid concentration at the beginning of the reaction was $3w$ gram-molecules and the reaction went completely, according to the equation given in Section IV we should have w gram-molecules of monocalcium phosphate formed, equivalent to w gram-molecules of tricalcium phosphate. Hence for the completed reaction we should have w gram-molecules of citric acid giving $1/3 w$ gram-molecules of tricalcium phosphate. Suppose we find only y gram-molecules of tricalcium phosphate then $\frac{3y \times 100}{w}$ is the percentage of the theoretical amount which has been found. The following table (Table IX) shows the concentration of the citric acid, the theoretical amount of phosphate obtainable in a complete reaction according to the equation, the actual amount of phosphate obtained, as gram-molecules of tricalcium phosphate per litre, and the percentage of the theoretical amount of phosphate obtainable.

It is seen that this percentage is practically identical with the percentage in col. 5 of Table III. Indeed the numbers in col. 5 of that table multiplied by 1.016 give the percentage in col. 4 of Table IX. This arises from the following considerations. If a_1 be the weight of phosphate

dissolved and a_2 = weight of mineral phosphate taken for the particular dilution v then $100 \frac{a_1}{a_2} = p_1$ = amount of phosphate dissolved as a percentage of amount of mineral phosphate taken. The number of gram-molecules of citric acid per litre in each case may be written $\frac{10}{210} \times \frac{1000}{v} = w$ where v is the dilution. The amount of phosphate theoretically obtainable expressed as tricalcium phosphate is therefore $w/3 = x$ gram-molecules per litre. The amount of phosphate found also expressed as tricalcium phosphate in gram-molecules per litre is $\frac{a_1}{310} \times \frac{1000}{v} = y$.

Table IX. *Table showing amount of phosphate found per cent. of amount theoretically obtainable, at various dilutions on basis of equation, Section IV.*

Exp.	Gram-molecules per litre			Phosphate found per cent. of amount theoretically obtainable
	Concentration of citric acid	Phosphate theoretically obtainable in complete reactions	Phosphate actually obtained	
1	·0952	·0317	·0186	19·55
2	·0762	·0254	·0158	20·75
3	·0572	·0191	·0126	22·10
4	·0381	·0127	·0094	24·55
5	·0190	·0063	·0054	28·59

Now the number of gram-molecules dissolved expressed as a percentage of the number of gram-molecules theoretically obtainable is clearly

$$\frac{y}{x} \times 100 = p_1 \times \frac{63a_2}{310} = p_2.$$

In the series under consideration $a_2 = 5$ and thus we have

$$p_2 = p_1 \times \frac{63}{62} = 1.016 p_1.$$

With increasing values of a_2 it is known that a smaller series of values of p_1 would be obtained (see Table VIII). For example, if 40 grams of mineral phosphate were taken then $p_2 = 8p_1$ (approximately). The results in Table IX merely illustrate the well-known fact that solubility depends on the hydrogen ion concentration. They further show that it is misleading to adopt a particular set of weights to test citric solubility and to express the solubility in terms of the weight of mineral phosphate taken for the experiment, if it is intended to judge the quality of a phosphatic fertiliser by the result so obtained.

VIII. DICALCIUM PHOSPHATE EXPERIMENTS.

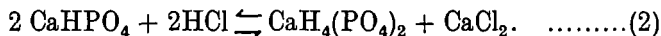
The observed amount of phosphate dissolved by citric acid per cent. of the theoretical amount for a completed reaction found in these experiments may be contrasted with corresponding figures obtained from the interaction between a pure substance like dicalcium phosphate and hydrochloric acid. A series of experiments was conducted with this end in view. In each experiment a constant quantity (25 grams) of precipitated dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was shaken for half an hour in a constant volume (500 c.c.) of water. The proportion of hydrochloric acid was varied as shown in Table X. The following results were obtained :

Table X.

Volume constant = 500 c.c.; dicalcium phosphate = 25 grams

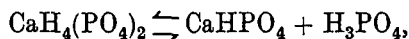
Exp.	I	II	III	IV		V
	Original concentration of HCl. Gram mols. per litre = w	Concentration of phosphate after shaking. (gram-mols. $\text{CaH}_4(\text{PO}_4)_2$ per litre) = u	Theoretical concentration of phosphate of phosphate k $u = \frac{k}{1+2k} \times w$	Grams of dicalcium phosphate dissolved per litre		
				Observed	Theory	
1	·2856	·1299	·1325	44·69	45·58	
2	·2285	·1058	·1060	36·40	36·46	
3	·1713	·0792	·0795	27·24	27·35	
4	·1142	·0547	·0530	18·82	18·23	
5	·0571	·0265	·0265	9·12	9·12	
6	·0286	·0124	·0133	4·27	4·58	

These results show the decreasing percentage of phosphate dissolved with decreasing acid concentration as usually obtained in such experiments. The result, however, to be contrasted with the corresponding previous results, is the relative completeness of the reaction as seen in cols. I and II of the above table (Table X). Since there is excess of dicalcium phosphate the undernoted equation may be taken to represent the reaction namely,



In this equation two molecules of hydrochloric acid are used up to produce one molecule of monocalcium phosphate and one molecule of calcium chloride. Hence if we start with w gram-molecules of hydrochloric acid we shall have, for a completed reaction, $\frac{1}{2}w$ gram-molecules of monocalcium phosphate, the substance determined. If w = molecular concentration of hydrochloric acid per litre at the beginning of the experiment and u = molecular concentration of phosphate expressed as $\text{Ca}_3(\text{PO}_4)_2$ per litre at the end of 30 minutes shaking when equilibrium may be presumed in this case to be established, then according to the

law of mass action we should expect $k = u/w - 2u$ to describe the experimental results. An inspection of col. III (Table X) will show that the formula reasonably fits the data. No account has been taken of the degree of ionisation in the above equilibrium equation. The extent of the reverse action,



has also been neglected.

If the degree of ionisation of hydrochloric acid is taken into account together with the fact that a minute quantity of calcium hydroxide was found to be present in the dicalcium phosphate used it is found that $2u$ is slightly greater than w as may be seen on inspection of Table XI (col. IV). The value of $2u/w$ varies from 1.008 to 1.039, the average value being 1.0228 and theory requires this ratio to be equal to unity for a completed reaction.

Table XI.

I	II	III	IV
Concentration of dissociated HCl (gram-mols. per litre) $=w$	Gram-mols. $\text{CaH}_4(\text{PO}_4)_2$ $=u$	$2u$	$\frac{2u}{w}$
.2576	.1299	.2598	1.0085
.2087	.1058	.2116	1.0139
.1573	.0792	.1584	1.0070
.1053	.0547	.1094	1.0389
.0514	.0265	.0530	1.0311
.0239	.0124	.0248	1.0377

The work in this section is intended merely to illustrate the approximation to a completed reaction in the case of a known phosphate. More detailed work is necessary and a fuller consideration of the theory is also necessary in order to give a complete physico-chemical explanation of the phenomena.

IX. CONCLUSIONS.

(1) If constant weights of sample and of citric acid are used in a series of experiments, the only quantity varied being the volume, the quantity of phosphate dissolved per cent. of weight of sample taken increases with increasing volumes. With 5 grams of sample and 10 grams of citric acid, the citric solubility varied from 19.24 to 28.14 per cent. of weight of sample. With 1 gram of sample and 10 grams of citric acid, the citric solubility varied with increasing dilution from 53.8 to 61.8 per cent. of weight of sample. The effect of the presence of alkaline lime was eliminated by maintaining m_1/m_2 at a constant value and with increasing dissociation as a result of increasing dilution increasing percentages of

phosphate were dissolved (i.e., percentages of mineral phosphate taken). The molecular concentration on the other hand (i.e. number of gram-molecules per litre) decreased with increasing dilution. It is not held that the equations describing the results are valid for concentrations or dilutions outside those used in these experiments.

(2) If a constant weight of sample and a constant volume are used in a series of experiments, the concentration of citric acid being varied from 1 gram to 10 grams, the citric solubilities varied from 4.4 to 19.4 per cent. of weight of sample taken. That is to say, citric solubility increased, as we should expect, with increased acid concentration at constant volume and with a constant weight of hydroxyapatite.

(3) If a constant weight of citric acid and a constant volume are used in a series of experiments, the quantities of sample being varied from experiment to experiment, the citric solubilities decreased from 19 to 1 per cent. of weight of sample taken. These decreases are due (1) to the presence of Ca(OH)_2 in the molecule of hydroxyapatite, (2) to the presence of Ca(OH)_2 , CaO or CaCO_3 in the free condition and (3) to the fact that the results are expressed in terms of mineral phosphate taken for analysis.

(4) It is seen that, other conditions being constant, citric solubility depends upon an unlimited choice of constant values of any two factors, together with an unlimited number of values of the third varying factor. If, therefore, a citric solubility test has to be adopted, the theoretical condition determining the relative quantities of sample, acid and volume must be found, otherwise the test has no practical value. Wagner has not supplied any theoretical basis for selecting the specified constant quantities of the three factors. We can, therefore, at will select for slags suitable values of sample, acid and volume to secure high citric solubility values. We can, however, select at will quite different values of sample, acid and volume which will give equally high citric solubility values for mineral phosphates. Further, we could select for both slags and mineral phosphates suitable values of sample, acid and volume which would give, on the one hand, perfect citric solubility (100 per cent.) or, on the other hand, no citric solubility at all.

(5) The citric solubility of mineral phosphate has been contrasted with the solubility of a pure substance, dicalcium phosphate, in hydrochloric acid. It is shown that with the dilutions used and with an excess of dicalcium phosphate the reaction is practically complete. Since there is an excess of dicalcium phosphate it has been assumed that the main substance present at the end of the reaction is monocalcium phosphate.

(6) Citric solubility, if applied to fertilisers may in a certain degree

be a measure (1) of fineness of grinding as already pointed out by other workers, but it seems necessary also to postulate similarity of composition in comparing degrees of fineness in practice, (2) of the presence or absence of alkaline substances in fertilisers approximately of the same composition and ground to the same degree of fineness, (3) of the presence or absence of fluorides as well as alkaline substances in slags and (4) of the differences in the constitution of the phosphatic compounds in finely ground fertilisers containing approximately the same proportions of extraneous substances.

None of these conditions are realisable in practice because the proportions and the actions of extraneous substances are generally undetermined and because the nature of the phosphatic compound present is either unknown or is not given. Further we can with any phosphatic fertiliser irrespective of its composition and constitution, use concentrations or dilutions to get any value of citric solubility we please. Citric solubility is therefore an unreliable empirical test of the agricultural value of mineral phosphates and slags. It has yet to be shown that high citric solubility is a measure of the presence of phosphate in a readily available condition for plant growth, or is an indication of the presence of a highly citric soluble phosphatic compound of a known chemical constitution. We are driven, therefore, to the conclusion that the only practical tests of value of phosphatic fertilisers from the agricultural standpoint are:

- (1) Total phosphatic content.
- (2) Degree of fineness of grinding.
- (3) Freedom from injurious substances and of substances inhibiting plant growth.

The effect of using different kinds of phosphatic fertilisers on yield of turnip crop, where the same amount of fertilisers, expressed as tricalcium phosphate, is applied in each case forms the subject of a separate communication.

(Received December 23rd, 1921.)