however, the solubility of gypsum decreases regularly as the amount of lime in solution increases.

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THE PHOSPHATES OF CALCIUM, III; SUPERPHOSPHATE.[1]

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IN former papers[2] from this laboratory, the three-component system—lime, phosphoric acid, water—has been investigated at 25°. It was found that there are three solubility curves, one representing solutions in equilibrium with monocalcium phosphate, ($CaH_4(PO_4)_2.H_2O$), one representing solutions in equilibrium with dicalcium phosphate, ($CaHPO_4.2H_2O$), and the third representing solutions in equilibrium with a series of solid solutions. The compositions of these solid solutions extend from pure lime to a solution of nearly the same composition as dicalcium phosphate. Another three-component system—lime, sulphuric acid, water—has been studied in this laboratory.[3] The composition of solutions which are acid, *i. e.*, those in which sulphuric acid is in excess of lime, has been published in the former paper, while the composition of solutions which are alkaline has been investigated in the second paper. Only one solid phase was found in this first investigation, *viz.*, gypsum ($CaSO_4.2H_2O$). Had that investigation extended to more concentrated solutions of sulphuric acid, another solid phase, anhydrite ($CaSO_4$), would undoubtedly have been found. In the case of the alkaline solutions, two solid phases were found, calcium hydroxide and gypsum. In solutions containing less than 1.22 grams of free lime per liter the solid phase was found to be calcium hydroxide.

This present investigation deals with the four-component system—lime, phosphoric acid, sulphuric acid, water—the essential constituents of the so-called "superphosphates."

A complete representation of the conditions obtaining in any four-component system can be attained only by the use of a space

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[2] Cameron and Seidell: This Journal; 27, 1503 (1905); Cameron and Bell: Ibid., 27, 1512 (1905).

[3] Cameron and Breazeale: J. Physic. Chem. 7, 571 (1903); Cameron and Bell: This Journal, 28, 1220 (1906).

model. Such a space model for this four-component system, would have as axes, the amounts of lime, sulphuric anhydride, and phosphoric anhydride per liter of solution. With the densities known, the amount of water in these solutions can be computed. However, this representation is cumbrous and so we have represented the results on one of the projections of this space model, *viz.*, on the coordinate plane bounded by the SO_3-axis and by the P_2O_5-axis. In other words, we have used a plane diagram representing all the conditions, with the exception of the lime content of the solutions. These conditions are described in the accompanying diagram (Fig. 1), in which some of the fields are so narrow as to necessitate their distortion in order to show plainly the regions involved.

In (Fig. 1) O represents a saturated solution of lime in water. On the OX axis, A represents the solution in equilibrium with dicalcium phosphate and the limiting solid solution; B represents the solution saturated with respect to both dicalcium phosphate and monocalcium phosphate. On the other axis, C represents the solution saturated with both calcium hydroxide and gypsum, and D the solution in equilibrium with both gypsum and anhydrite. The positions of the points A, B, C have been found by direct experiment, while the position of the point D has been determined in an indirect way. This method was adopted, since the change of gypsum to anhydrite, or *vice versa*, has been shown to be very slow. In his work on the various forms of calcium sulphate, van't Hoff[1] has shown that at vapor-pressures lower than 17.5 mm. at 25°, gypsum is transformed to natural anhydrite, and above that pressure the reverse change takes place. Applying this result to the present problem, we have determined the strength of sulphuric acid which has a vapor-pressure of 17.5 mm. when saturated with gypsum. The sulphuric acid solution having this vapor-pressure has been found, from the results of Richards,[2] to have a density of 1.235. This solution contains 25.71 per cent. SO_3,[3] or 317.5 grams SO_3 per liter. In this consideration no correction is made for the effect of the calcium sulphate in solution on the vapor-pressure, a correction which would be very small because of the low solubility of gypsum in sulphuric acid

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[1] Sitzungsber. Akad. Wiss. Berlin, 1901, 1140.

[2] Pr. Am. Acad. 33, 23 (1897-98).

[3] Fresenius "Quantitative Analysis," 1899, p. 676.

Fig.1 25°C.

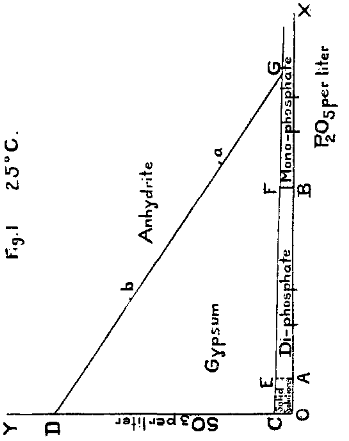


Fig. 2.

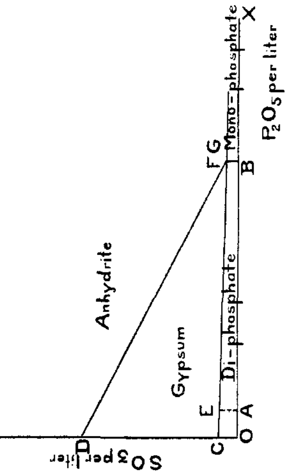


Fig. 3.

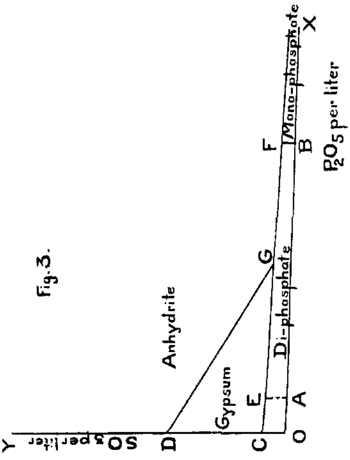
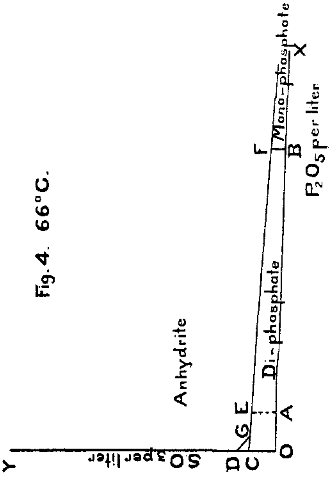


Fig. 4. 66°C.



of that strength. This solubility has been estimated by extrapolation from the results of Cameron and Breazeale[1] to be approximately 1 gram of calcium sulphate per liter of solution.

The determination of the possible fields has been investigated by adding small quantities of sulphuric acid to various solutions epresented on the diagram by points on the line OX. In all cases the addition of a little sulphuric acid causes a white precipitate which upon microscopic analysis proved to be gypsum.

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[1] Loc. cit.

This indicates that the fields over which the phosphates of calcium can exist are very narrow indeed. An analysis for sulphates was made of three of these solutions, one about midway between A and B in the diagram, one very near B, and the third on BX. The sulphuric acid content of these three solutions was found to be 0.9, 0.6 and 0.3 gram SO_3 per liter respectively, and hence the line C E F G lies very close to OX, the two lines converging as we pass to the right. Analyses of some of these solutions have been made by Cameron and Seidell,[1] their lime content and phosphoric acid content being practically the same when no gypsum is present as it is when the solution is saturated with respect to gypsum. These solutions lie on the line E F, near the point E. Thus it is evident that the presence of gypsum has no appreciable effect on either the lime content or the phosphoric acid content of the solutions, and as the amount of the sulphate in solution is greater in this region than it is farther to the right, it is apparent that the solutions near F and to the right of F have the same lime content and phosphoric acid content as those on the axis OX. The positions of the points E and F have therefore been taken as almost identical with the positions of A and B.

Finally, the position of the line forming the boundary between the gypsum and anhydrite fields has been found. From the work of van't Hoff, which has been cited above, the vapor-pressure at which gypsum and anhydrite remain in equilibrium at 25°, is 17.5 mm. Consequently, the solutions on the diagram which have that vapor-pressure are on the boundary line between the two fields. In these determinations we have not attempted to obtain equilibrium conditions but we have found whether various solutions had vapor-pressures above or below this value. This has been accomplished by placing a weighed solution (25 grams of solution in a weighing-bottle) known to have this vapor-pressure in a bottle containing the unknown solution. After a time the former solution was again weighed, and from the loss or gain it has been found whether the vapor-pressure of the unknown solution was above or below 17.5 mm. In this way the position of the point G has been determined, at which point gypsum, anhydrite and monocalcium phosphate co-exist as solids in equilibrium with a solution. Also we have found the position of two points,

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[1] This Journal, 26, 1461 (1904).

a and *b*, along the line D G which separates the gypsum field from the anhydrite field.

To determine the point G various solutions along BX, whose vapor-pressure are not different from those along F G, have been investigated with the following results: The solution containing 485 grams P_2O_5 per liter caused an increase in weight of 0.080 gram in two days; the solution containing 563 grams P_2O_5 per liter caused a decrease in weight of 0.026 gram in two days. As these experiments were carried on under identical conditions, we have interpolated to find that solution which should show no change in weight. This has been found to contain 545 grams P_2O_5 per liter, and therefore G is determined. The positions of the points *a* and *b* have been found by similar pairs of determinations. The composition of the solution at *a* is 350 grams P_2O_5 per liter and 120 grams SO_3 per liter, and the composition at *b* is 150 grams P_2O_5 per liter and 275 grams SO_3 per liter.

The following table gives the data concerning the invariant or "constant" solutions at 25°.

Point.	P_2O_5 per liter. Grams.	SO_3 per liter. Grams.	CaO per liter. Grams.	Solid phases present.
O	0	0	1.17	$Ca(OH)_2$.
A	3	0	1.5	Solid solution; $CaHPO_4.2H_2O$.
B	317	0	77.	$CaH_4(PO_4)_2.H_2O$; $CaHPO_4.2H_2O$.
C	0	0.9	1.9	$Ca(OH)_2$; $CaSO_4.2H_2O$.
D	0	317.5	1.	$CaSO_4.2H_2O$; $CaSO_4$.
E	3	0.9	1.5	Solid solution; $CaSO_4.2H_2O$; $CaHPO_4.2H_2O$.
F	317	0.6	77.	$CaSO_4.2H_2O$; $CaHPO_4.2H_2O$; $CaH_4(PO_4)_2.H_2O$.
G	545	0.2	38.	$CaSO_4.2H_2O$; $CaSO_4$; $CaH_4(PO_4)_2.H_2O$.

To describe the conditions which obtain at any other temperature than 25° it is necessary to determine how the various points on the diagram are affected by changes of temperature, and also to determine whether any new solid phases appear. In the present case a microscopic examination of the crystals formed at the higher temperature has revealed no new types and it is therefore probable that there are no new solid phases. Above the temperature 66° the solid gypsum, stable at all lower temperatures, becomes unstable and therefore does not appear on the diagram representing the conditions at 66°. It has been found by experiment that the points B and F move to the right with rising temperature. In other words the two phosphates of calcium co-exist in solutions which become richer in phosphoric acid as the temperature increases. The points E and A have not been investigated at any temperature other than 25°, but it is certain from qualitative experiments that at higher temperatures there is a field for solid solutions just as there is at 25°. This has been indicated in Figs. 2, 3 and 4 by the dotted line E A. The direction in which the point D moves with change of temperature can be predicted from the results of van't Hoff[1] upon the vapor-pressure at which gypsum and anhydrite exist in equilibrium. The composition of sulphuric acid solutions which have the same vapor-pressures at 10°, 25° and 35° have been computed from the data upon the vapor-pressures of these solutions,[2] with the following results. It is apparent that the point D approaches C with rise of temperature.

Temperature, ° C.	Vapor pressure at which gypsum and anhydrite co-exist.	Composition of H_2SO_4 with same vapor-pressures in per cent. H_2SO_4.
10	5.79	37.6
25	17.5	31.5
35	32.2	28.5
66	150.	0.

At 66° gypsum and anhydrite co-exist in contact with their own solution in water. The presence of lime, whose solubility in water at this temperature is less than 1 gram per liter, will lower this temperature very slightly. Similarly along the line C E G F, the point G is continually moving towards the point C. Consequently, it is evident that the field for gypsum disappears at a temperature of 66° and anhydrite becomes the stable solid over a very great range of solutions.

It is evident that at some temperature intermediate between 25° and 66° the point F, which is moving to the right with increasing temperature, will meet the point G which is moving to the left. At this point we have a sextuple point, or six phases, vapor, solution, and the four solids anhydrite, gypsum, mono- and dicalcium phosphates. This state of affairs can exist at only one temperature and one vapor-pressure. This is shown diagrammatically in Fig. 2. As the temperature increases still further, the points D and G approach C, and Fig. 3 illustrates the state of affairs at some temperature below 66°. At the temperature 66° the field for gypsum disappears altogether.

From the preceding results and diagram (Fig. 1) the effect of

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[1] Loc. cit.

[2] Landolt and Börnstein: Phys.-Chem. Tabellen (1905), pp. 166–167.

water upon a mixture of the salts may be deduced. We shall neglect in the following consideration the effect of substances other than gypsum and monocalcium phosphate, which substances are nearly always present in commercial superphosphates, *viz.*, ferric phosphate, aluminum phosphate, calcium chloride or fluoride, etc. All these substances will have some influence upon the positions of the various points and lines in the above diagram but if their amount is small we may neglect their influence. Let us leach a superphosphate composed of gypsum and monocalcium phosphate at 25°. The addition of water to monocalcium phosphate crystals causes a partial change to dicalcium phosphate and a solution saturated with respect to both phosphates. A small amount of gypsum will also pass into the solution. If water be added to this solution, or if the solution be drained away and fresh water added, more of the monocalcium phosphate will disappear and dicalcium phosphate will be formed. The net effect of this leaching is to wash out some free phosphoric acid, together with considerable quantities of calcium and a very small quantity of gypsum. If the addition of water is rapid, the time for this change may be very short indeed. During this change the composition of the solution is represented by the point F of Fig. 1, and if equilibrium conditions are obtained, the composition of the solution will remain constant until *all* the monocalcium phosphate disappears. It will be observed that the greater part of the original calcium phosphate has been removed. This may be partially represented by the equation

$$CaH_4(PO_4)_2 = CaHPO_4 + H_3PO_4,$$

all the phosphoric acid in excess of the compound $CaHPO_4$ being leached away, together with a considerable amount of the diphosphate, which is dissolved. Upon the removal of some of the solution and dilution of the residue by fresh water, the composition of the leachings will change rapidly until the point E is reached. Here another change takes place, the crystalline dicalcium phosphate giving up phosphoric acid, which carries some of the phosphate into solution. The solid changes to a solid solution of lime and phosphoric acid and upon continued leaching this solid solution changes gradually to that solid solution which in saturated gypsum solutions dissolves unchanged, *i. e.*, the ratio of lime and phosphoric acid which have gone into solution is the same as in the solid solution. Over this range of concentrations gypsum has a much higher solubility and it will probably disappear before the solid solutions have all disappeared.

We may therefore divide the process of leaching of superphosphate roughly into four stages: First, monocalcium phosphate disappears, and solid dicalcium phosphate and a solution of phosphoric acid containing much of the lime are formed. The weight of the resulting dicalcium phosphate is less than one-half of the original monocalcium phosphate. Very little gypsum has gone into solution at this stage. The second stage consists in the complete change of dicalcium phosphate into an amorphous solid solution, and very much more gypsum goes into solution. The third stage in the leaching process is the gradual change in the solid solution to one containing relatively less phosphoric acid and more lime. The liquid solutions are now quite dilute and consequently gypsum will dissolve freely, and it is certain that the gypsum will all be washed away before the calcium phosphate (as solid solution) has been all dissolved. The fourth stage consists in the slow solution in water of a relatively insoluble solid solution of lime in phosphoric acid, which contains relatively more lime than would be required by the formula $Ca_3(PO_4)_2$.

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THE COMPOSITION OF THE DRAINAGE WATERS OF SOME ALKALI TRACTS.[1]

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IN the reclamation of an alkali tract the analysis of the drainage water is the most ready method of following the changes taking place within the soil. That the nature of the drainage water and the changes which it may undergo are problems of great practical importance is obvious when it is considered that agricultural plants display such marked difference in their tolerance of different salts and salt mixtures in their nutrient media. It is also important to note that a study of drainage water not only furnishes a clue to the nature of the soil solution in the land from which it flows, but that it may have an important bearing on the management of neighboring lands upon which it may be desirable

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