A method is proposed for obtaining true transference numbers from moving boundary experiments through the aid of a non-electrolyte which does not migrate with the current.

BOSTON. MASS, April 16, 1910.

THE PHOSPHATES OF CALCIUM. IV.[1]

BY FRANK K. CAMERON AND JAMES M. BELL.

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Owing to the increasing importance of the phosphates of calcium in the fertilizer industry, a knowledge of their behavior in water and in solutions becomes increasingly important. Some years ago two papers[2] were published from this laboratory, in which it was shown that at 25° the solutions, resulting from the mixture of the phosphates of calcium with water, always contain a greater ratio of P_2O_5/CaO than does the original solid. Thus the effects observed are not merely solubility effects but there is also an hydrolysis. So, each of the phosphates of calcium may exist in equilibrium with a series of solutions, in which the ratios of P_2O_5/H_2O and CaO/H_2O vary between rather wide limits.

It was found that at 25° solid monocalcium phosphate could exist in equilibrium with solutions containing over 320 grams phosphoric anhydride per liter. Below this concentration the stable solid was dicalcium phosphate. In the former analyses of these solids, only the ratio P_2O_5/CaO was determined, no estimation having been made of the amount of water of crystallization. The solids analyzed were always contaminated with the adhering mother liquor. In the determination of the above ratio this contamination is not a very serious source of error, as the mother liquor was present in small quantity compared with the crystals, and as the mother liquor was always much poorer both in phosphoric anhydride and in calcium oxide than were the crystals. Further, any determination of the amount of water would have been subject to an enormous error, as the percentage of water in the crystals is small, and that in the adhering liquid was very large. Consequently, the composition of the solid phase was taken as $CaHPO_4.2H_2O$, the ordinary dihydrate of dicalcium phosphate.

That this assumption seemed to be confirmed was indicated in a paper published subsequently by Bassett.[3] In this paper it was announced that above 30° the solid dicalcium phosphate dihydrate changed into the anhydrous salt. At 30° there is an invariant point, the five phases being the two forms of dicalcium phosphate (anhydrous and dihydrate), monocalcium phosphate monohydrate, solution and vapor. Also it was

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[1] Published by permission of the Secretary of Agriculture.

[2] Cameron, Seidell and Bell, THIS JOURNAL, **27**, 1503, 1512 (1905).

[3] *Z. anorg. Chem.*, **53**, 34 (1907).

announced that 80° was the maximum temperature at which the dihydrate could exist, the five phases being the two hydrates of dicalcium phosphate, tricalcium phosphate, solution and vapor. Under these conditions there is a transition interval for the reaction

$$CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + \text{solution}$$

between 30° and 80°. Thus according to this publication the stable hydrate of dicalcium phosphate below 30° was the dihydrate, or possibly some higher hydrate.

Later Bassett[1] corrected his early temperature measurements, this transition interval being given as from 21° to 36°. This work would indicate that at 25° the anhydrous salt would be the stable form in equilibrium with the more concentrated solutions. And, as the temperature 25° is nearer 21° than 36°, it would be supposed that the dihydrate would exist over a much greater range of concentration than does the anhydrous salt. This supposition is, however, not confirmed by Bassett's results at 25°, for he finds that $CaHPO_4.2H_2O$ exists in equilibrium with solutions *below* 0.5 per cent. phosphoric anhydride. Above this value up to 23 per cent. phosphoric anhydride in solution, the solid phase is $CaHPO_4$. Thus the transformation at 25°

$$CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + 2H_2O$$

has the same vapor pressure as an aqueous solution containing approximately 0.5 per cent. phosphoric anhydride and 0.2 per cent. lime. It is obvious that this vapor pressure cannot be much below that of pure water. This result does not appear to be in accord with the following statement of Bassett.[2] "Ein solcher Versuch wurde begonnen, gab aber kein Resultat *wegen des ausserordentlich geringen Wasserdampfdruckes von* $CaHPO_4.2H_2O$."[3]

Owing to the confusion regarding the relative stability of the hydrated and the anhydrous dicalcium phosphate, the following experiments were made at 25°. Solutions of phosphoric acid of varying concentration were prepared, the total volume of these solutions being 180 cc. To each mixture weighed quantities of potassium chloride (about 5 grams) were added and Kahlbaum's tricalcium phosphate in sufficient quantity to give a permanent precipitate. The reasons for the addition of potassium chloride should be further explained. As has been stated above, an analysis of the solid phase with the adhering mother liquor is useless to determine the water present in a solid. Also, the residue method of Schreinemakers[4] and Bancroft[5] fails, because the line joining

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[1] *Z. anorg. Chem.*, 59, 1 (1908).

[2] *Loc. cit.*, p. 40.

[3] The italics are ours.

[4] *Z. physik. Chem.*, 11, 81 (1893).

[5] *J. Physic. Chem.*, 6, 178 (1902).

the two points (representing $CaHPO_4.2H_2O$ and $CaHPO_4$) is almost parallel with the tie lines, and consequently very slight errors of analysis of the solution or of the solid residue might give erroneous results regarding the composition of the solid phase. A modification of this method, the "tell-tale" method,[1] was employed. This differs from the method of residues in this way. By the method of residues lines joining the points representing solution and residue are joined and produced. Where three or more such lines pass through a point, the point represents the composition of the solid phase. By the "tell-tale" method, it becomes possible to calculate the quantity of liquid adhering to the crystals, and consequently to calculate how far to produce this tie line. Where the different tie lines met at a large angle, the first method has been used generally, but where tie lines meet at a very small angle, the second method is to be preferred. One condition to be fulfilled in this latter case, is that the "tell-tale" substance must be present only in the liquid phase. That the condition was satisfied here was indicated by the analysis of the liquid phase, for almost exactly the calculated quantity of chloride was found per unit of solution. Consequently this quantity is a measure of the quantity of solution adhering to the solid. Also from an analysis of the liquid the quantity of all the components present in the adhering liquid may be estimated. By subtracting these from the quantities found by analysis in the total residue, the composition of the solid may be found. In every case the quantity of water was determined by difference and so all the errors of experiment are heaped on these values. In spite of the fact that a slight error in the chloride determinations is multiplied many times in the corresponding quantities of water and that the water in the solid is the difference between two large values, the results by this method give fairly concordant values for the composition of the solid phases. The following table gives the results of the analyses:

TABLE.

	Solution.					Residue.				
No.	Total.	CaO.	P_2O_5.	KCl.	H_2O	Total.	CaO.	P_2O_5.	KCl.	H_2O.
112	25.014	0.052	0.152	0.685	24.125	9.162	1.934	2.336	0.099	4.793
115	24.528	0.103	0.290	0.659	23.476	10.531	2.439	3.033	0.091	4.968
119	26.196	0.249	0.685	0.703	24.559	8.463	1.609	2.054	0.102	4.698
122	15.701	0.252	0.741	0.409	14.299	7.278	1.774	2.271	0.053	3.180
126	5.469	0.161	0.500	0.134	4.674	11.627	2.719	3.561	0.094	5.253
127	3.656	0.158	0.585	0.090	2.823	21.495	5.745	8.134	0.189	7.427
130	5.254	0.287	1.355	0.106	3.506	14.797	2.095	6.051	0.157	6.494

The calculations of the compositions of the solid phase for one mixture (No. 126) follow. The ratios of the components in the residue, the solution and the solid are as follows:

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[1] Bancroft, *J. Physic. Chem.*, **9**, 558 (1905); later called the "tell-tale" method by Kenrick, *J. Physic. Chem.*, **12**, 693 (1908).

	KCl.	CaO.	P_2O_5.	H_2O.
Residue	1	28.93	37.87	55.88
Solution	1	1.20	3.73	34.88
Solid	.	27.73	34.14	21.00

The values for the solid are the differences between the corresponding values for the solution and residue. In molecular ratios the values for the solid are

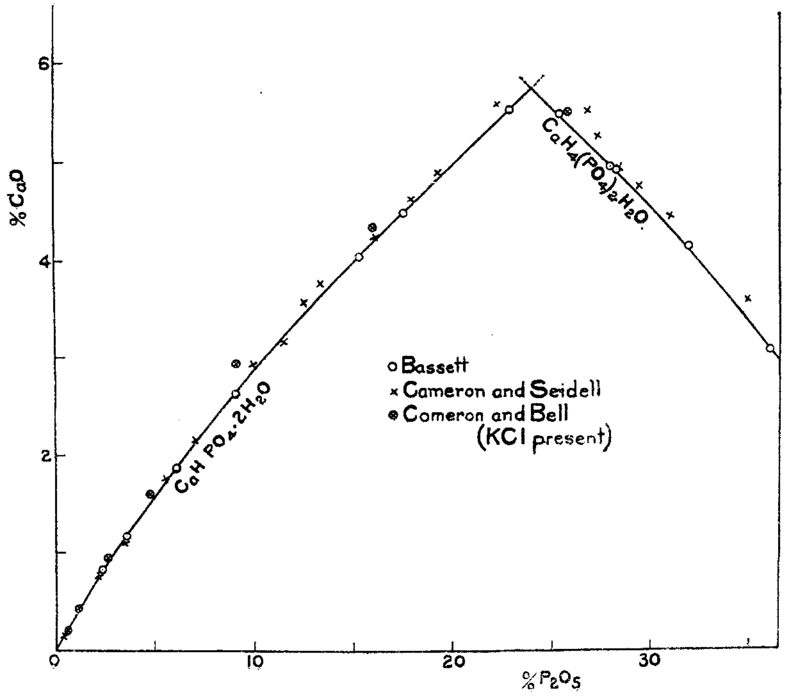
$$2.06\ CaO : 1.00\ P_2O_5 : 4.86\ H_2O.$$

The following table gives the molecular ratios calculated similarly for the solids in each of the other mixtures:

TABLE.

No.	CaO.	P_2O_5.	H_2O.	Composition of solids.
112	2.11	1	4.39	
115	1.94	1	4.51	$2CaO.P_2O_5.5H_2O$
119	2.03	1	4.66	or
122	2.02	1	4.78	$CaHPO_4.2H_2O$
126	2.06	1	4.86	
127	1.99	1	1.72	
130	1.04	1	2.55	$CaO.P_2O_5.3H_2O$ or $CaH_4(PO_4)_2.H_2O$

It is evident from these results that the stable solid phase up to a concentration of about 15 per cent. P_2O_5 is $CaHPO_4.2H_2O$. One result



(No. 127) indicates that there is a lower hydrate of $CaHPO_4$. It is probable that this is the anhydrous salt and that the single point (No. 127) gives the conditions at 25° for the transition

$$CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + 2H_2O.$$

As the KCl present in solution influences the vapor pressure of the solution, concentrations of calcium oxide and phosphoric anhydride in each case are somewhat lower than for the corresponding solution where no potassium chloride is present.

These results also show the effect of potassium chloride in concentrations of about 25–30 grams per liter upon the system $CaO–P_2O_5–H_2O$. In the accompanying diagram are given the results of Bassett, of Cameron and Seidell, and of the present paper where potassium chloride is present. These last results lie above the curves drawn through the former points. Thus the effect of the potassium chloride is to increase the lime in solution.

In this paper it has been shown that:

1. The presence of potassium chloride in solution containing calcium oxide and phosphoric anhydride increases slightly the lime content of solutions in equilibrium with dicalcium phosphate and monocalcium phosphate.

2. By the "tell-tale" method the composition of the solid phases was found to be $CaHPO_4.2H_2O$ and $CaH_4(PO_4)_2.H_2O$ with a region between, which was not explored, where the composition of the solid was probably $CaHPO_4$.

3. This result is in accord with Bassett's last determination of the transition interval of $CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + 2H_2O$ but is not in accord with his direct determination of the compositions of the solid phases.

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BASIC NITRATE OF YTTRIUM.

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Of all the methods that have been published for the separation of yttrium and erbium, the classic procedure of Bahr and Bunsen[1] still serves best. It was therefore considered that a study of the system Y_2O_3, N_2O_5, H_2O would be highly interesting.

The only basic nitrate mentioned by Bahr and Bunsen was given the formula (recalculated) $2Y_2O_3.3N_2O_5.9H_2O$, which was derived from the analysis of the air-dried salt. It is highly probable that their compound was contaminated with normal nitrate from adherent mother liquor.

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[1] *Ann.*, **137**, 1 (1866).