tration range while the larger figure comes from an extended Debye–Hückel equation which fits at only one point, 0.05 *m*, and deviates widely at all other concentrations. The value of 7.93 is somewhat larger than the numbers derived for rare earth perchlorates by Spedding and Jaffe,[14] but the difference is probably not significant since different methods of calculation for different concentration ranges were used in the two cases. In any case, the $\mathring{a}$ is large and approaches the size of Bjerrum's q, which has a value of 10.5 Å. for 3-1 electrolytes.[15] Comparing the relative sizes of $\mathring{a}$ and q for gallium perchlorate with those of 2-1 electrolytes,[16] it is seen that ion-pair formation is negligible for this salt. Gallium perchlorate is, thus, a very strong, highly hydrated electrolyte.

[14] F. H. Spedding and S. Jaffe, This Journal, **76**, 884 (1954).

[15] Ref. 11, pp. 42–45.

[16] Ref. 11, pp. 422–423.

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The Preparation of Dicalcium Phosphate Dihydrate and Calcium Pyrophosphate

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Received November 15, 1954

In a high temperature phase equilibrium investigation of the system $Ca_3(PO_4)_2$–Al_2O_3–SiO_2,[1] a source of phosphorus pentoxide was required whose composition and purity was clearly established. It was found that commercial C.P. tricalcium phosphate was normally hydroxyapatite. Further to this the salts tested contained notable quantities of sodium and iron. The combination of non-stoichiometric composition and the presence of impurities had a notable effect on certain properties. For instance the melting point was depressed by approximately 330°, from 1730 to 1400°.

Barrett and McCaughey[2] met with the same difficulty in their investigation of the system CaO–P_2O_5–SiO_2, but found that calcium pyrophosphate obtained by calcining dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$) was a good source of phosphorus pentoxide for their mixtures. Contrary to Barrett and McCaughey's experience, tests made during the present investigation showed that the C.P. dicalcium phosphate obtained commercially was just as liable to compositional variation and alkali contamination as the tricalcium salt. The powerful fluxing action of alkalies renders salts containing them useless for phase studies.

Attempts to synthesize tricalcium phosphate by MacIntyre's method[3] met with no success. In this method $Ca_3(PO_4)_2 \cdot nH_2O$ is precipitated from chilled calcium sucrate solution by the addition of concentrated phosphoric acid in very slight excess. Although instructions were carefully followed, a gelatinous precipitate was obtained each time. Melting point and refractive index determinations indicated that the material produced was a hydroxyapatite.

It was noted that if MacIntyre's procedure was reversed, and chilled calcium sucrate added to dilute phosphoric acid, neutralization proceeded only to the displacement of the second hydrogen atom from the acid molecule. Further investigation indicated that this was an ideal method for the preparation of pure dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) of stoichiometric composition. This salt is easily converted into calcium pyrophosphate ($Ca_2P_2O_7$) by ignition at 900° and if combined with the stoichiometric proportions of pure calcium carbonate may be converted to tricalcium phosphate on high temperature ignition. Tricalcium phosphate in the low temperature form (β) is obtained from such mixtures by prolonged heating (12 hours) at approximately 1000°. If the mixture is heated at 1500° or above, the reaction is rapid and the high temperature form (α) obtained.

The preparation of these two compounds ($CaHPO_4 \cdot 2H_2O$ and $Ca_2P_2O_7$) was carefully studied and the optimum conditions for their formation determined.

Experimental

All the preliminary experiments indicated that provided the calcium sucrate was added to chilled dilute phosphoric acid, neutralization always stopped at the second stage of hydrogen replacement even when a large excess of calcium sucrate was present. Thus, provided the additions were made correctly, and the solutions kept chilled (10°) a good product was obtained without any special attention being paid to the quantities mixed. However, it is recommended that the quantity of reactants be carefully measured and only a slight excess of calcium sucrate used.

The stock of dicalcium phosphate was prepared as follows: 322.5 g. of C.P. calcium carbonate was calcined at 1000° for one hour and the lime so obtained dissolved in 5 liters of 22.5% CO_2-free aqueous sugar solution. Freshly ignited lime dissolved easily and completely in the sugar solution. The sucrate solution was chilled to 10° and added to 190 cc. of concentrated phosphoric acid (1.05 g. P_2O_5 per cc.) diluted to 3 liters with water. The phosphoric acid had previously been assayed by titration with standard sodium hydroxide solution, using phenolphthalein as indicator and a little sodium chloride to sharpen the end-point.

The phosphoric acid was contained in a large stoneware vessel maintained at 10° by an ice-bath. The acid was vigorously stirred and the sucrate added slowly, in eleven stages. Samples for *p*H determinations were taken two minutes after each sucrate addition. Figure 1 shows how the *p*H changes as the acid is gradually neutralized. After stirring for one hour following neutralization the *p*H dropped to 8.2.

It will be noted that there is a slight inflexion in the neutralization curve at 2.5 liters calcium sucrate, the point of formation of monocalcium phosphate. The completion of the reaction, however, is clearly shown by the rapid rise in *p*H once the second hydrogen atom has been displaced from the phosphoric acid.

The dicalcium phosphate prepared by this method settles readily and may be filtered very easily. After filtration the precipitate was washed with 10 liters of cool distilled water. The excess calcium sucrate was washed out easily since it is a very soluble compound. The precipitate was dried at 50° for several days and stored ready for conversion to calcium pyrophosphate.

Since the ultimate aim was to produce tricalcium phosphate in mixtures used in the phase study, it was found convenient to calcine the dicalcium salt at 900° to obtain calcium pyrophosphate. Thus when tricalcium phosphate was required, calcium pyrophosphate and calcium carbonate were mixed in the proportions shown by the equation

$$Ca_2P_2O_7 + CaCO_3 \longrightarrow Ca_3(PO_4)_2 + CO_2$$

and the required tricalcium salt formed *in situ* when the mixture was heated to 1600–1700°.

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[1] P. D. S. St. Pierre, *J. Am. Ceram. Soc.*, **37** [6] 243 (1954).

[2] R. L. Barrett and W. J. McCaughey, *Am. Mineralogist*, **27**, 680 (1942).

[3] W. H. MacIntyre, G. Palmer and H. L. Marshall, *Ind. Eng. Chem.*, **37**, 164 (1945).

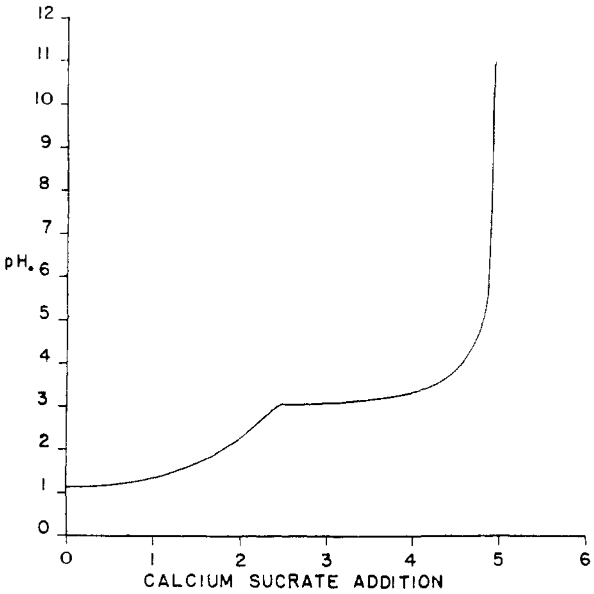

Fig. 1.—*p*H *vs.* neutralization of phosphoric acid by calcium sucrate, liters at 10°.

Prior to converting all the dicalcium phosphate to pyrophosphate, samples were taken for loss-on-ignition determinations at 900°. All samples were found to have a loss-on-ignition of 26.4%, and this is very close to the theoretical 26.2% for the reaction

$$2(CaHPO_4 \cdot 2H_2O) \longrightarrow Ca_2P_2O_7 + 5H_2O$$

It was concluded therefore that the dihydrate of dicalcium phosphate had been made by the reaction between the phosphoric acid and calcium sucrate.

Since pyrophosphate was used as the source of P_2O_5 in the preparation of mixtures for the phase study, chemical analyses were made of this compound rather than of the initial precipitate. Lime was determined by precipitating as calcium oxalate at *p*H 3 and titrating the precipitate dissolved in dilute sulfuric acid against permanganate. The filtrate and washings from the oxalate separation were used to determine the phosphorus. This determination involved a double precipitation of magnesium ammonium phosphate and finally weighing an ignited precipitate as magnesium pyrophosphate.

The calcium pyrophosphate stock used for making the phase study mixtures was found to be of exact stoichiometric composition, that is, 44.1% CaO, 55.9% P_2O_5. No sodium or alkali salts could be detected on a Beckman flame photometer (sensitive to 0.002% Na).

Experiments were carried out to check the effect of (a) temperature and (b) great excess calcium sucrate in the preparation of the dicalcium salt. To study these factors several runs were made in the manner described for the stock material, but varying appropriately the temperature or sucrate excess. Analyses were also made on the resulting products. The experimental results may be summarized as follows.

1. At temperatures up to 20° the neutralization of phosphoric acid proceeds to the second stage of hydrogen displacement only.
2. Above 20° neutralization begins to carry on to the third and final stage.
3. Dicalcium phosphate settles readily and is easily filtered. As soon as the third stage neutralization commences the mixed precipitate becomes gelatinous and difficult to filter.
4. Below 20° excess calcium sucrate does not appear to react appreciably with the precipitated dicalcium phosphate, even after two hours stirring.

In view of the purity of the calcium pyrophosphate obtained by the sucrate method it was considered worthwhile to investigate quantitatively some of its physical properties in order to evaluate data given in the literature.

The melting point determined by the Geophysical Laboratory quench method was found to be 1356 ± 2°. This figure is in excellent agreement with the 1353° given by Hill, *et al.*,[4] but is considerably higher than the figure of 1300° given by Trömel, *et al.*,[5] and Barrett and McCaughey.[3]

Hill, *et al.*,[4] state that calcium pyrophosphate transforms from the β- to α-form (*i.e.*, low to high temperature form) at 1140°, but Bale, *et al.*,[6] report a figure of 1270° for this inversion point. The experience of this investigation was that the transformation is extremely sluggish and that the β-form will not transform rapidly to the α until 1250°. Thus, whatever the true transformation temperature is, it would appear that temperatures in the region of 1250° are needed to bring about the transformation in a short period of, say, one hour. It was also noted that molten pyrophosphate had a tendency to supercool and then freeze rapidly to form the low temperature or β-modification.

The refractive indices of the α- and β-forms of pyrophosphate were determined under the petrographic microscope by immersing samples in various oils of known index. The data obtained are as follows and are in agreement with those given by Hill, *et al.*[4]

α-$Ca_2P_2O_7$: biaxial negative, $\alpha = 1.584$, $\gamma = 1.605$

β-$Ca_2P_2O_7$: uniaxial positive, $\omega = 1.630$, $\epsilon = 1.638$

The densities of the two forms were determined on a Berman torsion balance. The α-modification has a density of 2.88 g. per cc., and the β a density of 3.09 g. per cc., both taken at 25°.

(4) W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sc.*, **242**, 457, 542 (1944).

(5) G. Trömel, H. J. Harkort and W. Hotop, *Z. anorg. Chem.*, **256**, [6] 253 (1948).

(6) W. F. Bale, J. Bonner, H. C. Hodge, H. Adler, A. R. Wreath and R. Bell, *Ind. Eng. Chem., Anal. Ed.*, **17**, 491 (1945).

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Copolymer Composition Distribution[1]

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RECEIVED DECEMBER 13, 1954

The differential composition distribution function for an ideal copolymer has been given by Wall.[2] The general case has been treated by Skeist using graphical methods which do not require that the instantaneous compositions be given by the copolymer equation 1.[3]

$$\frac{dm_1}{dm_2} = \frac{M_1}{M_2} \cdot \frac{r_1M_1 + M_2}{M_1 + r_2M_2} \qquad (1)$$

where

m_1 and m_2 are instantaneous polymer mole fractions for species 1 and 2
M_1 and M_2 are instantaneous monomer mole fractions for species 1 and 2
r_1 and r_2 are the reactivity ratios for the more reactive and the less reactive monomers, respectively

The differential composition distribution function has not been given in explicit form for the general case.

For those cases in which the copolymer equation 1 is a valid description of instantaneous composition relationships this equation may be combined with the equation of Rayleigh 2[4] to give an explicit dif-

(1) Financial assistance was received through the School of Engineering Research of the University of Toronto.

(2) F. T. Wall, THIS JOURNAL, **63**, 1862 (1941).

(3) I. Skeist, *ibid.*, **68**, 1781 (1946).

(4) Lord Rayleigh, *Phil. Mag.*, **8**, 534 (1902).