Investigations on the Solubility of Calcium Phosphates

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Paper read at the *Nordic (19th Scandinavian) Scientist Meeting* in Helsingfors 11th August, 1936.
Translated from the report of the meeting, pp. 344–48

For some time past, together with P. Damsgaard-Sørensen and A. Tovborg Jensen, I have been studying the solubility of calcium phosphates, a very complicated problem. Our investigations are not yet terminated, but certain facts have been proved, and it is of these I shall speak in the following.

The difficulties of the work were considerable. The *concentrations* of phosphate and calcium to be measured were *small*. The solutions have the tendency to remain *supersaturated* and *saturation equilibria are but slowly established*, even in the presence of the solid calcium phosphates. Great difficulties arose because, as shown by A. Rindell, *solid calcium phosphates decompose in the presence of water*. We have finally succeeded in overcoming all these difficulties by using X-ray analysis (Debye-Scherrer diagrams) in a constant control of the nature of the precipitates.

Theoretically, a troublesome complication arises, because in calcium phosphate solutions, to a certain degree, complexes are formed between calcium and phosphate. This plainly manifests itself in the fact that calcium phosphate solutions show a more acid reaction than corresponding sodium phosphate solutions with the same degree of neutralization with respect to phosphoric acid. A complex, such as $Ca(HPO_4^-)_2$ seems to have nearly the same acid strength as the ion $H_2PO_4^-$ and is consequently much more acid than the ion HPO_4^{--}. The strength with which the hydrogen ions are bound is determined more by the free electric charge of the PO_4-group, than by the number of hydrogen atoms tied up to it. We have not yet succeeded in determining the composition and amount of the complexes. Fortunately the degree of complex formation is usually less than 10 per cent, and since it is impossible to determine the composition of the dilute solutions of calcium phosphates with great accuracy, this complex formation is not taken into account in the following calculations of solubility products.

Besides the *primary calcium phosphate* $Ca(H_2PO_4)_2,H_2O$, with degree of neutralization 1 and 1 molecule of water of crystallization (we shall call it (1,1)-phosphate) we have until now studied the two *secondary calcium phosphates*, the di-hydrate (2,2) and the "anhydrous" salt, which, however, always contains about $^1/_6$ H_2O, and which is therefore designated the $(2,{}^1/_6)$-phosphate. According to Trömel's excellent investigations, with which we perfectly agree, tertiary calcium phosphates are never precipitated from aqueous solutions. Precipitates of that composition are always mixtures of the *hydroxyl apatite* $Ca_5(PO_4)_3OH$, with a degree of neutralization $3^1/_3$ and calcium phosphates with a degree of neutralization below 3. We have studied especially the solubility of the hydroxyl apatite, which is precipitated from boiling aqueous solutions showing incipient red colour with phenolphthalein. In air-dry condition this contains a little water, about 1 H_2O when the formula is written as above. I shall call it $(3^1/_3,1)$-phosphate. Its particles are so small that the substance has colloidal properties, yet it shows the same Debye-Scherrer lines as ignited hydroxyl apatite.

Finally we determined the solubility of a *new crystalline calcium phosphate*, which we encountered by chance. It has the formula $Ca_4(PO_4)_3\,H,3H_2O$, that is to say, with a degree of neutralization $2^2/_3$, and 3 molecules crystal water, $(2^2/_3,3)$-phosphate.

For the calcium phosphates mentioned we use as "solubility products" in saturated solutions the following expressions:

$$pL_{1,1} = -\log([Ca]\cdot[H_2PO_4]^2) = p[Ca] + 2p[H_2PO_4],$$

$$pL_{2,{}^1/_6} = -\log([Ca]\cdot[HPO_4]) = p[Ca] + p[HPO_4],$$

$$pL_{2,2} = -\log([Ca]\cdot[HPO_4]) = p[Ca] + p[HPO_4],$$

$$pL_{2^2/_3,3} = -\log\left(\frac{[Ca]^4\cdot[HPO_4]^3}{A_H{}^2}\right) = 4p[Ca] + 3p[HPO_4] - 2pA_H,$$

$$pL_{3^1/_3,1} = -\log\left(\frac{[Ca]^5\cdot[HPO_4]^3}{A_H{}^4}\right) = 5p[Ca] + 3p[HPO_4] - 4pA_H.$$

[Ca], $[H_2PO_4]$ and $[HPO_4]$ designate the molar concentrations of the calcium and hydrogen-phosphate ions, A_H the hydrogen ion activity, and pL the negative logarithm of L.

In the following table the values of these solubility products at 18° C and 37° C are collected.

$$\begin{array}{lll}
pL_{1,1} & & < -1^{\star} \\
pL_{2,2} & (18^\circ) = & 6.57 - 3.99\sqrt{\mu} \\
pL_{2,2} & (37^\circ) = & 6.62 - 4.12\sqrt{\mu} \\
pL_{2,{}^1/_6} & (18^\circ) = & 6.81 - 3.99\sqrt{\mu} \\
pL_{2,{}^1/_6} & (37^\circ) = & 7.01 - 4.12\sqrt{\mu} \\
pL^{\text{diss.}}_{2^2/_3,\ 3} & (18^\circ) = & 11.8 - 14.0\sqrt{\mu} \\
pL^{\text{prec.}}_{2^2/_3,\ 3} & (18^\circ) = & 9.3 - 14.0\sqrt{\mu} \\
pL^{\text{diss.}}_{2^2/_3,\ 3} & (37^\circ) = & 12.1 - 14.4\sqrt{\mu} \\
pL^{\text{prec.}}_{2^2/_3,\ 3} & (37^\circ) = & 10.7 - 14.4\sqrt{\mu} \\
pL^{\text{diss.}}_{3^1/_3,\ 1} & (37^\circ) = & 7.5 - 16.5\sqrt{\mu} \\
pL^{\text{prec.}}_{3^1/_3,\ 1} & (37^\circ) = & 6.5 - 16.5\sqrt{\mu}
\end{array}$$

In the formulae μ indicates the ionic strength.

With $2^2/_3$- and $3^1/_3$-phosphates, it has been necessary to introduce two pL values, corresponding to dissolution ($pL^{\text{diss.}}$) and precipitation ($pL^{\text{prec.}}$), because in the times of rotation used, it was not possible from both sides to attain saturated solutions of the same compostion. As a rule, in the course of twenty-four hours, it is possible, from unsaturated and supersaturated sides, by rotation with the solid phase, to obtain solutions, whose composition will then remain unchanged for weeks, and which are yet quite far removed from each other.

The pL values, quoted above, permit a computation of the solubilities and transformations of the phosphates examined, under very different conditions. A graph gives the most perspicuous survey of these conditions. In fig. 1, curves are drawn for a series of round pA_H-values, which show the connection between $p\,[\text{Ca}]$ and $p[\text{P}]$ in saturated solutions. [P] the total concentration of phosphoric acid may, for pA_H-values between 4 and 10 be computed from $[\text{HPO}_4]$ according to the formula

$$[\text{P}] = [\text{HPO}_4] \cdot \frac{K'' + A_H}{K''}$$

in which K'' is the 2nd (incomplete) dissociation constant of the phosphoric acid.

It is our intention to study further the solubility of ignited, anhydrous, hydroxyl apatite, and eventually, other hydroxyl apatites. After that, the solubility of the important fluor apatite will be determined. For this, some preparatory work has

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[*] The primary calcium phosphate (1,1) is so soluble that it is misplaced to compute its solubility product. According to Bassett's solubility determinations, L at 25° C must be considerably larger than 15.

already been done. Finally, a series of typical, natural phosphates (raw phosphates, bone phosphates) will be studied, to determine whether their solubilities are in agreement with observations made in studying pure, artificially prepared phosphates.

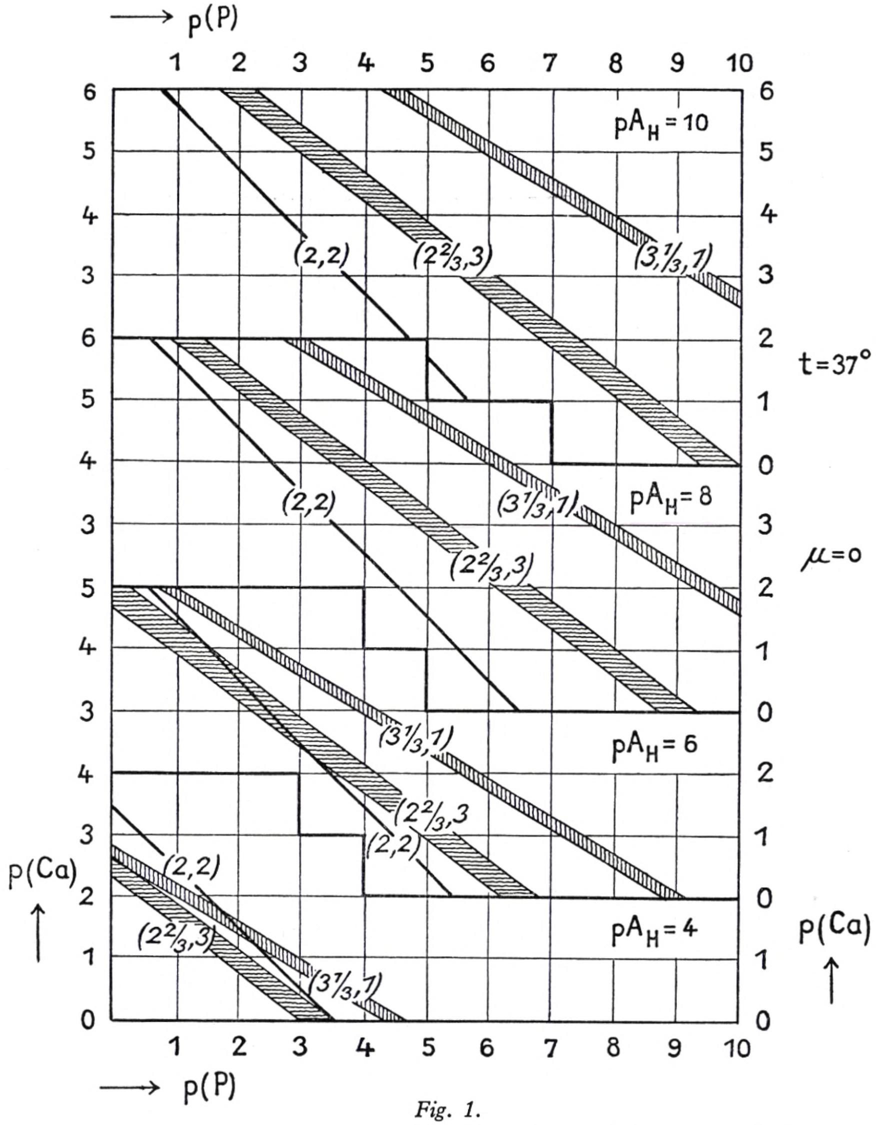

Fig. 1.