

Rate of Crystallization of Calcium Fluoride

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Jensen¹ has presented very complete data on the rate of crystallization of calcium fluoride, but unfortunately has not analysed his data from the point of view of reaction kinetics. Though it is apparent that Jensen's primary concern was not the determination of the order of this reaction, it was thought desirable to analyse his data kinetically, in keeping with Mellor's plea² that chemists be not deterred from considering the simplifying kinetics of reaction because of casual mathematical difficulties.

Upon applying the various tests for order of reaction to Jensen's data, there is no question that the crystallization of CaF₂ is bimolecular, in terms of the supersaturation, in the later stages. This region corresponds to the period of growth of the crystal nuclei. The formation of these nuclei in unseeded solutions is reflected as an induction period in the rate curves, and it has been found that a first order equation accounts best for this portion of the curve.

On this basis the rate of desupersaturation due to seed formation will be

$$\frac{-ds_1}{dt} = k_1s$$

and concurrently these seeds grow to further deplete the concentration according to

$$\frac{-ds_2}{dt} = k_2nS^2.$$

The total rate of adjustment is:

$$\frac{dS}{dt} = \frac{ds_1}{dt} + \frac{ds_2}{dt} = k_1S + k_2nS^2.$$

The number of seeds formed (n) is larger, the greater the degree of supersaturation above a certain concentra-

tion, corresponding to Ostwald's supersolubility; and we can set (n) approximately proportional to S ; whence:

$$\frac{dS}{dt} = k_1S + k_2(k_3 + k_4S)S^2 = (a + bS + cS^2)S$$

The solution of this differential equation has the form:

$$A \ln \frac{S^2}{a + bS + cS^2} - B \ln \frac{d + eS}{f + eS} = t + \text{const.};$$

which cumbersome form robs it of further utility in the analysis. It does not exhibit directly any convenient inflection point and therefore is not useful in calculating the induction period. This can be approximated by solving the first and second order equations simultaneously for their point of intersection. The result is:

$$\ln(Si + \text{const.}) = -bt_i + \text{const.}^1$$

This expression is as good as Jensen's empirical equation to describe the induction period in terms of the pK of the solution. Better agreement is obtained by throwing the original solution into polar form and rotating to display a maximum corresponding to the terminus of the induction period.

This complexity and cumbersome manipulation will not be given in detail in this place. The conclusion confirmed is, that the precipitation of CaF₂ from supersaturated solutions is a simple combination of unimolecular and bimolecular reactions; corresponding to nuclei generation and growth respectively.

LITERATURE

- ¹ T. V. Jensen—Z. Phys. Chem. **A180** 93 (1937).
- ² J. W. Mellor—Higher Mathematics. Longmans-Green, 1926.