

about 2. We take them to mean the times of appearance of a certain constant and not quite small fraction of the maximum density of the precipitate.

The experiments were difficult to perform when the concentrations of the component solutions were not practically equivalent, and our results are therefore valid only for this case. The temperature was about 20° C.

The results are plotted in Figs. 1 and 2 in logarithmic diagrams. It is obvious that notwithstanding the inaccuracy of the single experiment the results can be fairly well expressed by relations of the form.

$$t \cdot c_0^{p-1} = k$$

where  $t$  is the time of precipitation,  $c_0$  the original molar concentration taken as the  $i$ 'th root of the ionic product, if one molecule dissociates into  $i$  ions,  $p$  a constant and  $k$  another constant.

For bariumsulphate we find

$$t \cdot c_0^7 = 10^{-11.8}$$

and for silverchromate

$$t \cdot c_0^5 = 10^{-13.5}$$

We remark that for bariumsulphate an exponent 6 would give about as good an agreement with the experiments as 7, while for silverchromate neither the exponents 4 nor 6 could very well agree with the experiments.

In a paper on precipitation of calcium-fluoride A. Tovborg Jensen<sup>2</sup> has found a similar relationship between what he calls the incubation time and the concentration but experimentally his incubation times are defined as the times of appearance of visible precipitation just as ours. His time range extends only over about 2 powers of ten but he has been able to show that his times are reproducible inside a

factor which is less than 1.5. Tovborg Jensens experiments from his table 3 p. 102 can be represented either by the expression

$$\text{or by } \left. \begin{array}{l} tc_0^7 = 10^{-14.31} \\ tc_0^8 = 10^{-16.81} \end{array} \right\} 18^\circ \text{ C; time in seconds}$$

If the precipitation time is assumed to mean the time  $t_\alpha$  when the reaction has taken place to a constant fraction  $\alpha$  of the maximum extent it can be shown that if the reaction velocity  $s$  is of the form

$$s = k_p \cdot c^p$$

where  $c$  is the instantaneous concentration, integration yields the expression

$$t_\alpha c_0^{p-1} = k_\alpha$$

We therefore conclude that the velocity of precipitation is proportional to the 7th or 8th power of the instantaneous concentration in the case of bariumsulphate, to the 8th or 9th power in the case of calciumfluoride and to the 6th power in the case of silverchromate.

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2. Tovborg Jensen, A. *Z. physik. Chem.* **A 180** (1937) 93.

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## Kinetic Determination of the Size of Crystal Germs

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According to well known assumptions the formation of visible crystals in a supersaturated solution takes place in at least two steps *viz.* the formation of in-

visible "germs" and their growth to visible dimensions. Now it follows from the theory of Smoluchowsky<sup>1</sup> which has lately been used and extended by La Mer<sup>2</sup> that the velocity of growth of germs in a supersaturated solution is proportional to the instantaneous concentration in a low power. In the above note it has been shown that the velocities of precipitation of some slightly soluble salts in sharp contrast to this are proportional to the concentrations in powers from 6 to 9. Therefore the rate-determining step in the experiments described in the note cannot be the growth but must be the formation of crystal germs.

Elementary kinetical considerations show that the power in which the instantaneous concentrations appear in the velocity expression is equal to the number of single particles (ions) in a germ, and it is therefore possible to determine this number by kinetic experiments.

However, the experiments are at the present stage not in all cases sufficiently accurate to decide with certainty which of two consecutive whole powers is the right one.

Stoichiometric arguments can however be used for the decision, if we assume that a germ is always electroneutral.

That this assumption is probably correct can be seen from the more detailed discussion of the mechanism of the formation of germs given in the note below. It is evident from this that it is an essential property of the germ that it has a low probability of losing a particle. Now from electrostatics it follows immediately that a charged complex particle containing several single particles has a much greater probability of losing an ion than a neutral one and our assumption is therefore probably correct.

If the stoichiometric composition of the precipitate shows that it contains  $i$  ions, the number of particles in the germ must thus be an integer times  $i$ .

For bariumsulphate we had for the exponent  $p$  the choice between 7 and 8. When we assume the germ to be electroneutral, we must choose  $8 = 4 \cdot 2$ , which means that the germs contain 4 bariumions and 4 sulphate ions.

For silverchromate we found the number  $6 = 2 \cdot 3$  meaning that a germ of this substance contains 4 silverions and 2 chromateions.

For calciumfluoride we calculated from Tovborg Jensens experiments<sup>3</sup> the number 8 or 9. The condition of neutrality decides for  $9 = 3 \cdot 3$  which means that germs of this substance contain 3 calciumions and 6 fluorions.

It is thus seen that by an experimental investigation of the kinetics of precipitation combined with stoichiometric considerations we can determine the number of single particles in a crystal germ or as we may say the size of the germ.

That some sort of "germs" are necessary to initiate the crystallization of a supersaturated solution is practically an empirical fact, but they have always been assumed to contain many single particles. To quote an example La Mer<sup>4</sup> who follows Frenkel<sup>5</sup> speaks of embryos, complex particles which contain hundreds of single particles and nuclei which are still greater.

In contrast to this we have found that the germs contain only rather few particles and it is to avoid confusion with Frenkel's and La Mer's nomenclature that we have chosen the name germ.

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2. La Mer, V. K., and Dinegar, R. H. *J. Am. Chem. Soc.* **72** (1950) 4847.
3. Tovborg Jensen, A. See the preceding note.
4. La Mer, V. K., and Dinegar, R. H. *J. Am. Chem. Soc.* **73** (1951) 380.
5. Frenkel, J. *Kinetic theory of liquids*. Oxford (1945) chapter 7.

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