On the Mechanism of Precipitation of Sparingly Soluble Salts, Preliminary note

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The kinetic laws which seem to govern the formation of crystal germs in supersaturated solutions of different sparingly soluble salts leads to the assumption of a mechanism which can be described as follows:

Let us take as an example the precipitation of silverchromate. We shall denote by A a silver ion and by B a chromate ion.

By mere chance it may happen that two such ions form what we shall call a cluster of the second order, this meaning that the two particles are in the same volume-element of molecular dimensions ($\sim 10^{-27}$ liter). This may be illustrated by means of the reaction equation

$$A + B \rightleftharpoons X_2$$

where X_2 is the cluster of the second order.

Now such a cluster may capture a third particle according to the equation

$$A + X_2 \rightleftharpoons X_3$$

and so on until at last by the capture of a sixth particle a germ (Q_6) of the sixth order is formed according to the equation

$$A + X_5 \rightarrow Q_6$$

To understand the experimentally determined kinetics we must assume that a "germ" is different from a "cluster" in so far as it is much more probable, that it will capture a particle than it will loose one. The whole sequence of reactions thus becomes

$$\begin{array}{ll} A + B \rightleftharpoons X_2 & (\pm 1) \\ A + X_2 \rightleftharpoons X_3 & (\pm 2) \\ A + X_3 \rightleftharpoons X_4 & (\pm 3) \\ B + X_4 \rightleftharpoons X_5 & (\pm 4) \\ A + X_5 \rightarrow Q_6 & (\pm 5) \end{array}$$

As now the clusters must be assumed to be very short living we may calculate the velocity s of the formation of germs by using the conditions of stationarity of the concentrations of the clusters. When b is the instantaneous concentration of B-particles, w_1 the probability per unit time for a B-particle to react according to the scheme (+ 1), w_{-1} the probability (p.u.t.) for X_2 to react according to the scheme (−1), w_2 the probability (p.u.t.) for X_2 to react according to (+ 2) a.s.o. we get [1]

$$b/s = 1/w_1 + w_{-1}/w_1w_2 + w_{-1}w_{-2}/w_1w_2w_3 + w_{-1}w_{-2}w_{-3}/w_1w_2w_3w_4 + w_{-1}w_{-2}w_{-3}w_{-4}/w_1w_2w_3w_4w_5$$

From elementary considerations it turns out that $bw_1 = x_2^0 w_{-1}$; $bw_1w_2 = x_3^0 w_{-1}w_{-2}$ and so on, where x_i^0 means the (virtual) thermodynamical equilibrium concentration of X_i (not the actual steady state concentration of X_i). We may therefore write $1/s$ in the form

$$1/s = 1/bw_1 + 1/x_2^0w_2 + 1/x_3^0w_3 + 1/x_4^0w_4 + 1/x_5^0w_5$$

A rough estimate taking into account the effect of electrostatic attractions shows that the denominators of the members in the sum decrease from the left to the right by large factors (100 − 1 000) when the concentrations of A and B are not too large. We may therefore neglect all the members except the last one and we get thus

$$s = x_5^0 w_5$$

as the velocity of germ-formation.

In this calculation we have neglected reactions between clusters. The reason is that the concentration of clusters even of low orders (*e. g.* two) is small as compared to the concentration of single particles. Furthermore we have neglected the possibility that the germ $\overset{\bullet}{Q}_6$ may loose a particle, or rather we have assumed that a sixth member in the sum derived from the fifth by multiplication with w_{-5}/w_6 is small against the fifth. This again means that we have assumed that a germ has a much greater probability of capturing a particle than of loosing one. In contrast to this we estimated above that a cluster has a much greater probability for loss than for capture. As now the assumption of this contrast is necessary to explain the kinetics we arrive at the conclusion, that a "germ" is qualitatively different from a "cluster". It is as if by capturing its last particle the germ falls into a potential well, which it only with difficulty can leave. By closer consideration of the circumstances one gets the impression that electrostatic forces are not sufficient to explain the formation of germs, but that other not so evident forces must come into play.

The further fate of the germs, when once they have been "born" is of course to grow by capturing new particles, until eventually the ionproduct of the solution has reached the saturation value.

Returning finally to the velocity expression it is seen that the product $x_5^0 w_5$ must be of the form $k_6\ a^4b^2$ or if we define c as the third root of the ionproduct a^2b:

$$s = k_6 c^6$$

It is this formula which by integration yields an expression of the form

$$t_a\ c_0^5 = k_a$$

which was discussed in a previous note.

It must be added that both the experiments and the calculations hitherto applied are very crude, so crude that even changes in the orders of the different germs are not quite excluded, but such changes would not affect the general results which are that the size (order) of crystal germs can be determined by kinetical experiments and that the germs are far less than hitherto has been assumed.

Experimental and theoretical work on the problem is being continued.

1. Christiansen, J. A. *e. g. Z. physik. Chem.* **B 33** (1936) 145.

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A Preliminary Report on the Synthesis of Taurine and Cystamine labelled with Radioactive Sulfur

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Taurine, free and in combination with the cholic acids, has been demonstrated to exert a series of physiological, pathological and pharmacological actions. In order to investigate its metabolism and some of the above functions by means of isotopic methods, a synthesis for the labelling of this compound with radioactive sulfur has been worked out. The labelled taurine will then be combined with the cholic acids by chemical or biological synthesis.

The formation of taurine from L(+)-cysteine through L(−)-cysteic acid has been demonstrated to take place in the animal organism [1, 2]. Certain findings,

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