It has recently come to my notice that this problem has also been independently studied at Statens Farmaceutiska Laboratorium, Stockholm, Sweden, by A. Brunzell and H. Seidlitz; by a coincidence it was established that both investigations have led to fundamentally the same result.

On the Kinetics of Formation of Precipitates of Sparingly Soluble Salts *

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To get information regarding the mechanism of precipitation we have made preliminary experiments on the systems bariumchloride + sulphuric acid and silver nitrate + potassium chromate.

For the more concentrated solutions (0.01 molar) we used a flow method according to Roughton's principle [1]. Three glass tubes, two for inflow of the two component solutions and one for outflow of the mixture were cemented into a "crosshead" from perspex, containing the mixing chamber and adjacent channels for inflow and outflow. The outflow tubing had a bore of about 2 mm.

In the outflow tube the place and thus the time of occurrence of visible precipitation could be observed. In that way precipitations occuring in times after the mixing from 10^{-3} seconds to about 10^{-1} seconds could be observed. By stopping the flow and noting the time of appearance of visible precipitation observations could be
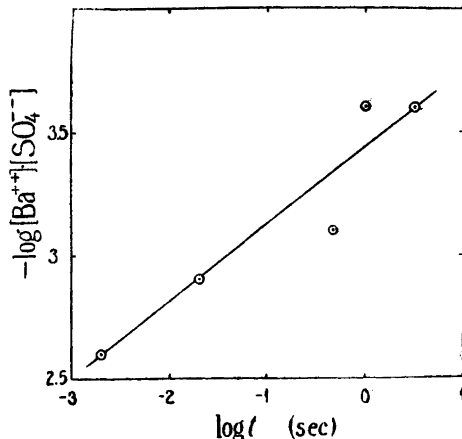
Fig. 1. The diagram represents the relation between the product of the concentration of barium ions and sulphate ions and the time of visible precipitation. Dekadic logarithms, time in seconds, concentration in moles/liter.

taken in times from about 1 to about 10 seconds, while longer times than that could be observed simply by mixing of the two solutions in a beaker.

The scale of times thus extends over an interval of 4 to 6 powers of ten.

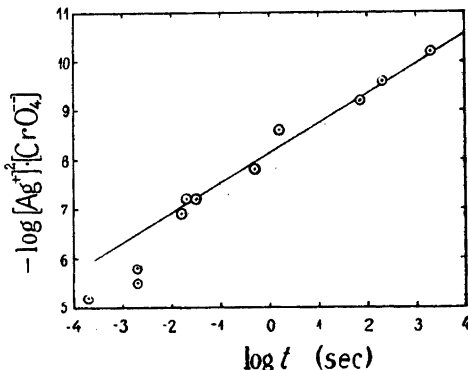The times for visible precipitation could only be determined to within a factor of

Fig. 2. The diagram represents the relation between the product of the concentration of silverions (squared) and of chromate ions and the time of visible precipitation.

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 calciumfluoride A. Tovborg Jensen [2] 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

$$\text{or by} \quad \begin{cases} tc_0^7 = 10^{-14.31} \\ tc_0^8 = 10^{-16.81} \end{cases} 18° \text{ C; time in seconds}$$

If the precipitation time is assumed to mean the time t_a when the reaction has taken place to a constant fraction α 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

$$t_a \ c_0^{p-1} = k_a$$

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.

1. Roughton, F. J. W. e. g. Proc. Roy. Soc. (London) A 155 (1936) 258.
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-