# Homogeneous Nucleation in Barium Sulfate Precipitation

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From experiments reported previously we deduced [1] that the barium sulfate particles formed in 0.001 M aqueous solution start their growth on foreign nuclei (impurity particles). In the present work we have used much higher concentrations (up to 0.04 M) and we found that when the initial concentration is above 0.01 M most of the crystals originate from homogeneously formed nuclei.

The experiments were performed by mixing equivalent amounts of solutions of barium chloride and sodium sulfate. Analytical grade chemicals were dissolved in ordinary distilled water. The induction period was measured as the time between the mixing and the appearence of visible turbidity. At low concentrations, where the induction period was longer than about 1 second the solutions (usually 100 ml of each) were poured from 250 ml beakers into a 600 ml beaker; a stop watch was started in advance of the experiment and the solutions poured together at 5 seconds. When the first turbidity was observed in diffuse daylight near the window the watch was stopped and 5 seconds substracted from the reading. The times were reproducible within about 30 %. No special precautions were taken to avoid nucleating impurities, except that the 600 ml beaker was rinsed in concentrated sulfuric acid which dissolves the barium sulfate formed on the walls.

At the highest concentrations the solutions were mixed in a Roughton T tube [2] and the induction period $t$ calculated from the rate of flow and the distance between the place where the solutions meet and the site of just visible turbidity. This was observed in diffuse daylight. The reproducibility is fair, but the precipitation zone is rather unsharp, corresponding to about 50 % of uncertainty. Because so wide a range of times is covered (almost seven decades) this uncertainty does not hide the phenomena to be studied. The solutions were sucked from two 200 ml measuring cylinders by opening a stopcock between the stem of the T tube and an evacuated 2 liter separating funnel acting as a recipient for the mixture.

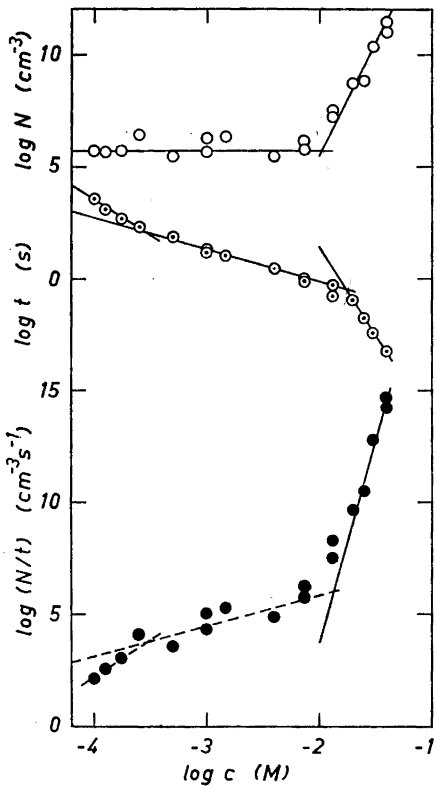


*Fig. 1.* The following quantities are shown as functions of the initial concentration $c$ of barium sulfate. From above: 1, number concentration of crystals formed. 2, induction period. 3, quotient of the former two; for $c > 0.01$ M ($\log c > -2$) this is assumed to equal the rate of homogeneous nucleation.

In the end of each experiment the number of crystals formed per unit volume was determined by counting under the microscope. At the highest concentrations a peptizing agent had to be added to the sample to be put under the microscope, in order to prevent the coagulation of the particles. Gelatine, carboxymethylcellulose and sodiumpyrophosphate all were able to redisperse the precipitate when it had coagulated.

The same upper limit of the concentrations that can be used seems to arise from

the difficulty of observing the time in the T tube and by the impossibility of redispersing the precipitate by gentle means.

In Fig. 1 we see from the upper curve that within the reproducibility the number of crystals is independent of the initial concentration $c$ when the latter is less than 0.01 M and proportional to $c^{10}$ (the tenth power of the concentration) at $c > 0.01$ M. We do not know any other mechanism than homogeneous nucleation that can explain this phenomenon.

The second curve in Fig. 1 consists of three straight lines, corresponding to three different types of precipitation reaction. A similar curve (drawn from a compilation of different authors' data) has been published before [3], but without interpretation. Now we know that at $c < 0.0004$ M (log $c < -3.4$) the crystals grow by a fourth-order surface reaction, and at $c > 0.0004$ M the rate determining step is diffusion through the liquid [4]. The change of growth-controlling mechanism is the cause of the change of slope of the curve.

The other elbow is situated very close to the concentration where, as deduced from the upper curve, the precipitation process changes from being induced by foreign nuclei into development from spontaneously formed nuclei.

The bottom curve has been calculated as the number of crystals formed per unit volume, divided by the induction period. In case of homogeneous nucleation the induction period is supposed to be of the same order of magnitude as the effective nucleation period, and therefore we conclude that for $c > 0.01$ M the points of the curve show the rate of nucleation. This rate turns out to be proportional to $c^{18}$ so that, in the language of chemical kinetics, the nucleation is an eighteenth order reaction.

A more detailed analysis of these results based on the Volmer-Becker-Döring theory of nucleation [5] will be published later. It leads to the conclusion that the interface tension between barium sulfate and aqueous solution is $90 \pm 10$ ergs/cm$^2$, both when it is calculated from the slope and from the position of the curve.

The surface tension of barium sulfate has never been measured before. Enüstün and Turkewich [7] recently found $\gamma = 84 \pm 8$ ergs/cm$^2$ for strontium sulfate against aqueous solution, and discovered the reason why all previous attemps to measure the surface tension of barium sulfate had failed. Enüstün and Turkewich calculate the surface tension of barium sulfate from the two assumptions, (1), the nucleus contains $3 \times 3 \times 3$ unit cells, and (2), the critical supersaturation ratio is 21.5. From the present work the most probable values are (1) 18 ions or 9 molecules of $BaSO_4$ = 775 Å$^3$, and (2) extrapolating the tangent to the right hand end of the bottom curve on Fig. 1 until log $(N/t) = 0$ we get the critical concentration for spontaneous nucleation, $c = 10^{-2.2}$ M. Thus $c/s = 10^{2.8} = 630$ when $s$ = solubility of $BaSO_4 = 10^{-5}$ M. From these data, and eqn. (15) of Enüstün and Turkewich' paper, about 90 ergs/cm$^2$ is found for the surface tension, the exact value depending on the geometry assumed for the nucleus.


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Received January 31, 1961.

## Does Insulin Bind Hexokinase to Liver Mitochondria?

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During the last years excellent progress has been made about the rôle of insulin in conjunction with the transport of sugars through cell membranes. There are, however, still a lot of effects of insulin on the cell metabolism which cannot be easily explained by an altered permeability only. This is especially evident in liver tissue, where insulin has no significant effect on the transport of glucose. The metabolism of glucose in liver is nevertheless strongly dependent on the presence of insulin.