

INDUCTION PERIOD OF NUCLEATION AND METASTABLE ZONE WIDTH

Jaroslav NÝVLT

*Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6*

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Induction periods of nucleation and metastable zone width were measured for the system $\text{KCl}-\text{H}_2\text{O}$ at 40°C . The data for the induction period measured at constant undercooling produced at a finite rate were treated using relationships allowing for the time period of lower supersaturation. The relation $\dot{N}_N = 1/t_N$ has been found to apply to the system studied. The treatment of literature data for metastable zone width and induction period of nucleation in the systems $\text{KAl}(\text{SO}_4)_2-\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2-\text{H}_2\text{O}$ showed satisfactory agreement between values of nucleation exponent obtained by the two methods.

According to the way in which supersaturation is produced in solution, we distinguish two types of method for studying the metastable behaviour of supersaturated solutions, one based on following the metastable zone width at varying supersaturation (undercooling), and the other on measuring the induction period of nucleation at constant supersaturation. Apart from some sporadic attempts, the relationship between the two methods has not been described in the literature. The aim of this work was to check the consistency of the values of nucleation exponent obtained by the two methods.

THEORETICAL

The induction period of nucleation, t_N , is the time that elapses between the instant when the supersaturated state is generated and the point of time at which solid phase particles become detectable. This includes the time required for the birth of critical nuclei in supersaturated solution, and the time it takes for the nuclei to grow up to detectable size. Thus, we may write^{1,2}

$$t_N = t_i + t_n + t_g, \quad (1)$$

where t_i is the time required for an appropriate distribution of embryos to be established, t_n the time in which critical nuclei are generated, and t_g the time the critical nuclei take to grow up to detectable size. According to some theoretical papers³⁻⁵

t_i is negligible compared with t_N , so that

$$t_N \approx t_n + t_g \quad (2)$$

and the relative magnitudes of t_n and t_g determine which of the processes will control the induction period of nucleation. In the case of nucleation in solution, it may be expected⁶ that in the region of small supersaturations $t_n \gg t_g$. Assuming that when the induction period has elapsed a single critical nucleus has been generated in unit volume of solution, we can write

$$\dot{N}_N = 1/t_N \quad (3)$$

The relationship between the nucleation rate and the induction period has been expressed in the more general form⁷

$$\dot{N}_N = N_c/t_N \quad (4)$$

holding for homogeneous nucleation followed by diffusion or polynuclear growth, or⁸

$$\dot{N}_N = K/t_N, \quad (5)$$

where N_c represents the number of crystals formed in unit volume of solution, and K is an adjustable constant of unspecified physical significance.

When $t_n \sim t_g$ or $t_n \ll t_g$, the mechanism of particle growth up to detectable size becomes a significant factor determining the value of t_N ; for a survey of the relevant relations for t_N see, for example, the paper of Söhnel and Mullin⁹.

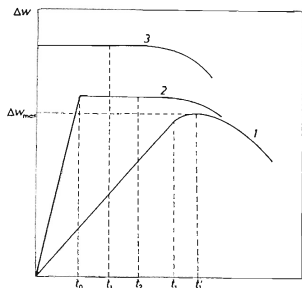


FIG. 1
Three modes of producing supersaturation in solution. (Curve numbers correspond to the numbering in the text)

Supersaturation in solution can be produced essentially in two ways (Fig. 1):

1) Supersaturation is formed at a constant rate $(-\dot{T})$ until time t'_1 when first crystals are detected. Theoretical analysis of this case⁶, which forms the basis of the metastable zone width measurement¹⁰, led to the relation

$$\log \Delta T_{\max} = A + 1/m \log(-\dot{T}), \quad (6)$$

where

$$A = -1/m \log k_N + (1 - m)/m \log(dw_{cq}/dT) \quad (7)$$

$$m = n \quad [t_g \rightarrow 0] \quad (7a)$$

or

$$m = (n + 3g + 4)/4 \quad [t_g \sim t_n] \quad (8)$$

2) The solution is supersaturated (*e.g.* by cooling) at a high rate until a required supersaturation is reached at time t_0 ; this supersaturation, ΔT_2 , is then maintained until first crystals appear at time t_2 (Fig. 1). The time t_0 is not negligible compared to t_2 . If in the first period supersaturation was produced at rate $(-\dot{T})$, it holds that

$$t_0 = \Delta T_2 / (-\dot{T}). \quad (9)$$

Combining the power law¹⁰ and Eq. (5), we can write

$$\dot{N}_N = k_N \Delta T_2^m (dw_{cq}/dT)^m = K/t_N. \quad (10)$$

It should be remembered, however, that in the first period the supersaturation varied and consequently, the corresponding nucleation rate was lower. Eq. (10) may be rewritten in the form

$$K = t_N k_N \Delta T_2^m (dw_{cq}/dT)^m. \quad (11)$$

Over a narrow temperature range the rate constant k_N can be considered constant, and the induction period of nucleation may be divided into two parts:

$$\begin{aligned} K &= (dw_{cq}/dT)^m \left[\int_0^{t_0} k_N (-\dot{T}t)^m dt + \int_{t_0}^{t_2} k_N \Delta T_2^m dt \right] = \\ &= (k_N \Delta T_2^m) [t_0/(m+1) + (t_2 - t_0)] (dw_{cq}/dT)^m. \end{aligned} \quad (12)$$

Thus, the induction period comprises a certain fraction of the time of cooling t_0 and the time period of constant undercooling ΔT_2 . Comparing Eqs (11) and (12),

we find

$$t_N = t_0/(m + 1) + (t_2 - t_0). \quad (13)$$

3) The supersaturation is produced instantaneously (*e.g.* on mixing solutions in precipitation), see Fig. 1; in this case

$$t_N = t_3. \quad (14)$$

EXPERIMENTAL

The metastable zone width was measured on the system KCl-H₂O saturated at 40°C, using an apparatus described earlier¹⁰ and equipped with a temperature-programmed digital controller¹¹. The solution was made up from KCl of analytical grade (Lachema Brno) and distilled water, closed in a 100-cm³ Erlenmeyer flask and slowly stirred with a magnetic stirrer (60 r.p.m.). The temperature was monitored by means of a Pt resistance thermometer, and controlled by a proportional controller activating in turn an infralamp and a fan. The solution was cooled at two preset cooling rates, 2 and 20 K/h, and the temperatures were recorded at which first crystals became visible. Ten measurements were carried out at each cooling rate. The average values of maximum undercooling, ΔT_{\max} , were, respectively, 1.28 ± 0.08 K and 2.43 ± 0.10 K.

The induction periods of nucleation were measured in the same solution, using the same apparatus. The solution was heated 0.5°C above the saturation temperature, kept at that temperature for 15 min and then cooled at a rate of 60 K/h until a required undercooling was reached. The time interval of cooling and the onset of crystal separation were recorded. The results (50 runs for each supercooling, 1, 1.5 and 2 K) are shown in Fig. 2.

DISCUSSION AND CONCLUSIONS

The results obtained for the metastable zone width of KCl demonstrate that the measurements were very well reproducible. A least-squares fit to Eq. (6) yielded $A =$

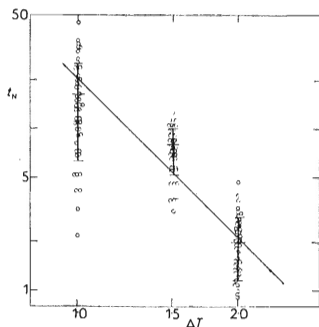


FIG. 2
Induction period for KCl as a function of undercooling

$= 7.75 \cdot 10^{-3}$ and $m = 3.56$. Smoothed values of undercooling calculated back from Eq. (6) are 1.27 (2 K/h), 1.65 (5 K/h) and 2.43 (20 K/h). The value of m obtained for KCl in the present study is substantially lower compared with the value quoted previously¹² ($m = 6.01$); considering the great sensitivity to the measured values of undercooling, we can ascribe this difference, at least partly, to refined temperature measurement.

The induction period of nucleation was difficult to measure by the method employed; as seen from Fig. 2, the reproducibility of measurement was very poor. The induction periods at 1 K, 1.5 K and 2 K of undercooling were found to be 15.7 ± 9.5 min, 8.0 ± 2.4 min and 2.01 ± 0.85 min, respectively. Thus, the scatter in the measured data was reduced from the initial 60% to 30% as the undercooling was increased. It should be pointed out that we worked with very low supersaturations, from $S = 1.007$ ($\Delta T = 1$ K), to $S = 1.015$ ($\Delta T = 2$ K). The substantially greater reproducibility of measurement quoted in the literature relates to high supersaturations of 2 and over. Eq. (10) can be rewritten as

$$\log \Delta T = 1/m \log (K/k_N) - 1/m \log t_N - \log (dw_{\text{eq}}/dT), \quad (15)$$

so that the data for the induction period as a function of undercooling may be treated in a manner analogous to that used for the data on the metastable zone width (Eq. 6). Since, however, the calculation of the actual values of t_N according to Eq. (13) requires the knowledge of the value of m , we solve Eqs (13) and (15) using an iterative procedure. For experimental data on the system KCl-H₂O, this procedure yields $m = 3.0$. In view of the considerable scatter in the experimental values of t_N , this result is in satisfactory agreement with the value obtained from the metastable zone width measurement.

In order to elucidate the relationship between the nucleation rate and the induction period (conf. Eqs (3), (4), and (5)), the proportionality constant K has been evaluated from the measured data. Substituting $k_N = 2.87 \cdot 10^6$, obtained from Eq. (7) for $dw_{\text{eq}}/dT = 0.00293$ kg/K kg of solvent, into Eq. (11) yields $K = 1.13$, a value very close to unity. On these grounds we can accept the validity of Eq. (3) for the given system.

Another system for which comparison of the two methods can be made is KAl.(SO₄)₂-H₂O. The data on the metastable zone width¹³ provided the value $m = 1.90$. Induction periods of nucleation in this system were studied¹⁴ on mixing solutions of the components K₂SO₄ and Al₂(SO₄)₃. The authors worked with far higher supersaturations (up to $S = 2.68$ at 15°C, and $S = 1.57$ at 35°C). Evaluation of the data in like manner to that used in this work, according to

$$\log (S - 1) = 1/m \log (K/k_N) - 1/m \log t_N, \quad (16)$$

results in $m = 1.56$, again in satisfactory agreement with the value calculated on the basis of the metastable zone width measurement. For $k_N = 0.035$, the value of K is found to be 2 to 3, thus within the same order of magnitude as above.

For ammonium nickel sulphate the measurements of metastable zone width provided the values $m = 2.0$ (ref.⁸) and $m = 3.18$ to 4.95 (ref.¹⁵), while the respective values obtained by measuring the induction periods were $m = 2.0$ (for $S < 1.3$) and $m = 3.2$ (for $S > 1.8$). The difference found has been ascribed⁸ to different mechanisms of nucleation, but even so the agreement between the two kinds of data is remarkable.

It may be concluded that measurements of the metastable zone width provide values of the nucleation kinetic exponent which compare well with those obtained by measuring the induction periods of nucleation under various conditions. In the region of small supersaturations, the reproducibility has proved to be better for data on the metastable zone width. For induction period measurements the reproducibility has been found to improve with increasing supersaturation. Finally, it has been verified that the induction period of nucleation is the reciprocal of the nucleation rate (Eq. 3).

LIST OF SYMBOLS

A	constant in Eq. (6)
g	kinetic exponent of crystal growth
K	constant in Eq. (5)
k_N	nucleation rate constant
m	apparent order of nucleation
N_c	number of crystals in unit volume of suspension
\dot{N}_N	numerical nucleation rate
n	true order of nucleation
S	relative supersaturation
T	temperature
ΔT	undercooling
ΔT_{\max}	maximum undercooling
$-\dot{T}$	cooling rate
t	time
t_g	time required for crystals to grow up to detectable size
t_i	time required for a cluster size distribution to be established
t_N	induction period
t_n	time required for birth of critical nucleus
w_{eq}	solubility

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