

## EVALUATION OF EXPERIMENTAL DATA ON WIDTH OF METASTABLE ZONE IN AQUEOUS SOLUTIONS

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Data on width of the metastable zone in aqueous solutions of electrolytes published earlier<sup>1,2</sup> have been used for calculation of nucleation parameters according to the classical nucleation theories. While the size of clusters so obtained is in agreement with literature data, values of the interfacial surface energy are somewhat low. A close correlation was determined between the surface energy and cluster dimensions as well as between the cluster dimensions and supersaturation function. The unsteady state problem is discussed.

A semiempirical equation was derived, according to which the width of metastable zone  $\Delta c$  is a function of the cooling rate  $b$

$$(dc_s/dT) b = k_n \Delta c^m \cdot [\Delta c_{\max}] \quad (1)$$

This equation was used for correlation of our experimental data published earlier<sup>1,2</sup> on width of the metastable zone in various aqueous solutions of electrolytes. It is demonstrated that it is possible to find a number of general rules governing the value of the empirical nucleation parameters  $k_n$  and  $m$ , evaluated from Eq. (1). Here, an effort is made to find a relation between these coefficients and the nucleation parameters which are frequently used in classical nucleation theories.

### THEORETICAL

#### *Evaluation of the Nucleation Order*

Becker and Döring<sup>3</sup> derived for the "classical" nucleation rate the relation

$$J = K \exp(-\Delta G^*/kT), \quad \text{where} \quad (2)$$

$$\Delta G^* = 4/27 (\beta^3/\alpha^2) (M^2/\rho_c^2) \sigma_{12}^3 (\mu_1 - \mu_2)^{-2} = 1/3 \beta \sigma_{12} (r^*)^2 \quad (3)$$

and where the radius of a spherical critical nucleus  $r^*$  is given by relation

$$r^* = 2\beta M \sigma_{12} [3\alpha \rho_c (\mu_1 - \mu_2) N]^{-1}. \quad (4)$$

The difference of chemical potentials may be substituted by

$$\mu_1 - \mu_2 = kT \ln S. \quad (5)$$

Nielsen<sup>4</sup> has shown that

$$\partial \ln J / \partial \ln S = (\alpha \varrho_c N / M) (r^*)^3 = n^*, \quad (6)$$

where  $n^*$  represents the number of particles forming the critical nucleus. In the previous papers<sup>1,2</sup> we used Eq. (1) for evaluation of experimental data on the width of the metastable zone. This equation is based on the assumption that for a short period of time after reaching the boundaries of the metastable zone, the nucleation and the supersaturation rates are equal, which has recently been verified experimentally<sup>5</sup>. By plotting the logarithms of maximum undercooling,  $\Delta T_{\max}$  in dependence on the logarithm of corresponding cooling rates,  $b$ , straight lines with the slope  $m$  have been obtained. Starting with the Becker-Döring equation it is easy to show that this slope is given by equation

$$m = \partial \ln J / \partial \ln c = n^* \Delta c / c. \quad (7)$$

For sparingly soluble substances *e.g.*  $\text{BaSO}_4$ ,  $c_s \rightarrow 0$  and  $\Delta c \rightarrow c$ , so that  $m \rightarrow n^*$  and we have Eq. (6) derived by Nielsen. For other substances we must consider the more general form *i.e.* Eq. (7) because the plot according to Eq. (6) is not linear in this case. Eq. (7) together with the relation

$$\sigma_{12} = \frac{3}{2} \frac{kT}{\beta} \left( \frac{\alpha \varrho_c N}{M} \right)^{2/3} (n^*)^{1/3} \ln \left( \frac{\Delta c}{c_s} + 1 \right) = \frac{3}{2} \frac{\alpha \varrho_c N}{M} \frac{kT}{\beta} r^* \ln \left( \frac{\Delta c}{c_s} + 1 \right) \quad (8)$$

allows evaluation of fundamental nucleation parameters from the experimental value of nucleation order,  $m$ .

#### Evaluation of Data on the Induction Period

On basis of the relation between the nucleation rate  $J$  and the induction period

$$J = 1/t_k \quad (9)$$

it follows

$$\log \frac{t_{k1}}{t_{k2}} = \frac{4}{27 \cdot 2 \cdot 3} \frac{\beta^3}{\alpha^2} \left( \frac{M}{\varrho_c N} \right)^2 \left( \frac{\sigma_{12}}{kT} \right)^3 c_s^2 (\Delta c_1^{-2} - \Delta c_2^{-2}). \quad (10)$$

The problem is how to determine the induction period  $t_k$  from measurements on the width of metastable zone carried out with constant cooling rate  $b$ . Knowing the total cooling time  $t_c$ , *i.e.*

$$t_c = \Delta T_{\max}/b \quad (11)$$

Eq. (9) can be written as

$$t_k \Delta c^m = 1/k_n \quad \text{or} \quad \int_0^{t_c} \Delta c^m dt = 1/k_n. \quad (12), (13)$$

This equation describes the time lag period due to the supersaturation changes at cooling. As

$$\Delta c = bt \, dc_c/dT, \quad (14)$$

the following equation may be derived

$$t_k = t_c/(m+1) \quad (15)$$

and therefore holds

$$\log(t_{k1}/t_{k2}) = \log(t_{c1}/t_{c2}). \quad (16)$$

By substituting equation

$$dc_s/dT = k_0 \quad (17)$$

and Eqs (16) and (14) into Eq. (10) we have

$$\sigma_{12}^3 = \frac{2.3 \times 27}{4} \frac{\alpha^2}{\beta^3} \frac{\varrho_c^2 N^2}{M^2} k^3 T^3 \frac{k_0^2}{c_s^2} \cdot \frac{\Delta T_1^2 \Delta T_2^2}{\Delta T_2^2 - \Delta T_1^2} \log \frac{\Delta T_1 b_2}{\Delta T_2 b_1} \quad (18)$$

and further

$$r^* = \frac{2}{3} \frac{\beta}{\alpha \varrho_c N} \frac{M}{kT} \sigma_{12} \frac{c_s}{k_0 \Delta T_{\max}}, \quad (19)$$

$$n^* = \alpha \varrho_c N (r^*)^3 / M \quad \text{and} \quad (20)$$

$$m = n^* k_0 \Delta T_{\max} / (c_s + k_0 \Delta T_{\max}). \quad (21)$$

Results calculated from Eqs (18) to (21) are within experimental errors identical with those calculated from equations given in the first part of this paper; e.g. for KCl, the value of  $m$  calculated from Eq. (21) is 5.2 as compared with the experimental value 6.0.

## RESULTS AND DISCUSSION

The data used for further evaluation have been published earlier<sup>2</sup>. Using known values of  $T$ ,  $M$ ,  $\varrho_c$ ,  $\varrho_1$ ,  $k_0$ ,  $p$ ,  $\Delta T_{\max}$ , and  $m$ , Eqs (7), (8) and (6) are transformed into relations

TABLE I  
Nucleation Parameters of Different Systems Calculated from Eqs (22) to (27)

Substance	T, K	Solid phase absent			Solid phase present								
		$b = 2 \text{ K/h}$		$\sigma_{12}$	$b = 2 \text{ K/h}$		$\sigma_{12}$						
		$n^*$	$r^* \cdot 10^8$		$n^*$	$r^* \cdot 10^8$							
KCl	303	646	17.1	0.54	455	15.2	0.68	473	15.4	0.67	334	13.8	0.84
KBr	303	299	13.9	0.35	124	10.3	0.45	200	12.1	0.46	84	9.1	0.59
KI	303	1116	23.1	0.17	589	18.7	0.26	726	20.0	0.23	384	16.2	0.35
NH <sub>4</sub> Cl	303	508	15.4	0.51	346	13.6	0.61	325	13.3	0.69	222	11.7	0.82
KNO <sub>2</sub>	303	1722	25.1	0.04	920	20.3	0.11	1336	23.1	0.05	714	18.7	0.13
KNO <sub>3</sub>	303	48	7.8	1.33	32	6.8	1.47	11	4.5	4.06	8	3.9	4.49
NaNO <sub>2</sub>	303	325	12.9	0.57	178	10.6	0.86	238	11.6	0.70	131	9.5	1.06
NaNO <sub>3</sub>	303	365	14.1	0.49	207	11.8	0.51	271	12.8	0.60	154	10.7	0.62
NH <sub>4</sub> NO <sub>3</sub>	303	557	17.5	0.32	300	14.2	0.36	511	17.0	0.34	275	13.8	0.38
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	303	587	20.8	0.30	385	18.1	0.34	338	17.3	0.44	222	15.1	0.49
H <sub>3</sub> BO <sub>3</sub>	303	53	7.8	1.09	24	6.0	1.93	40	7.1	1.34	18	5.4	2.37
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (COOK) <sub>2</sub>	303	—	—	—	—	—	—	111	15.1	0.11	22	8.8	0.32
K <sub>2</sub> SO <sub>4</sub>	303	69	9.8	2.57	59	9.3	2.93	58	9.2	2.93	50	8.7	3.34
NaBr	303	76	10.0	0.58	34	7.7	0.67	17	5.9	1.67	9	4.5	1.93
NaI	303	469	19.5	0.22	260	16.0	0.33	241	15.6	0.34	134	12.8	0.52
Na <sub>2</sub> SO <sub>4</sub>	298	—	—	—	—	—	—	280	23.4	0.12	137	18.4	0.16
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	303	—	—	—	—	—	—	348	21.8	0.21	176	17.3	0.23
Na <sub>2</sub> CO <sub>3</sub>	301	98	15.8	0.90	77	14.7	1.08	39	11.1	1.85	31	10.2	2.22
Na <sub>2</sub> CrO <sub>4</sub>	303	60	14.3	0.48	41	12.6	0.64	13	7.9	1.55	10	7.0	2.06
Na <sub>2</sub> HPO <sub>4</sub>	293	16	9.2	1.30	12	8.3	1.61	5	4.9	4.72	5	4.4	5.84
FeSO <sub>4</sub>	303	—	—	—	—	—	—	130	15.8	0.26	66	12.6	0.31
CuSO <sub>4</sub>	303	44	10.0	0.85	20	7.7	1.26	17	7.0	1.72	9	5.4	2.56
Ca(NO <sub>3</sub> ) <sub>2</sub>	293	—	—	—	—	—	—	414	22.3	0.11	167	16.5	0.14
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	303	9	7.5	2.62	6	6.5	4.20	5	4.9	6.18	4	4.3	9.91
(NH <sub>2</sub> ) <sub>2</sub> CO	303	492	16.6	0.73	346	14.8	0.81	392	15.3	0.85	276	13.7	0.94

TABLE II  
Comparison of  $\sigma_{12}$  Values (erg/cm<sup>2</sup>) of Different Authors

Substance	Ref. <sup>6</sup>	Ref. <sup>7</sup>	Ref. <sup>8</sup>	Ref. <sup>9</sup>	This paper
NaCl	77—210	—	3.53	—	—
NaBr	69.3—174	—	—	—	0.58—1.93
NaI	50.7—107	—	—	—	0.22—0.52
KCl	56—121	151	2.49—2.68	27	0.54—0.84
KBr	54—118	139	1.44—1.56	23	0.35—0.59
KI	58—113	—	0.83—0.93	—	0.17—0.35
K <sub>2</sub> SO <sub>4</sub>	—	—	—	23	2.57—3.34
NH <sub>4</sub> Cl	—	—	—	30	0.51—0.82

TABLE III  
Values of the Supersaturation Ratio  $S$  Given by Different Authors

Substance	Ref. <sup>10,11</sup>	Ref. <sup>8</sup>	This paper ( $b = 20$ )
KCl	1.095	1.06	1.013
KBr	1.056	1.05	1.021
KI	1.029	—	1.006
NaNO <sub>2</sub>	1.36—2.08	—	1.021
NaNO <sub>3</sub>	1.36—2.52	—	1.018
NH <sub>4</sub> NO <sub>3</sub>	1.064—1.10	—	1.012
K <sub>2</sub> SO <sub>4</sub>	1.37	—	1.164
CuSO <sub>4</sub>	2.50	—	1.175

$$n^* = m(1 + 10p\varrho_1/k_0 \Delta T_{\max}), \quad (22)$$

$$r^* = (0.208n^*M/\varrho_c)^{1/3} \cdot 10^{-8}, \quad (23)$$

$$\sigma_{12} = 0.416 \varrho_c \frac{T}{M} \frac{k_0 \Delta T_{\max}}{10p \varrho_1} (r^* \cdot 10^8). \quad (24)$$

Results calculated from these equations are summarized in Table I. Other calculations for the same substance but under different conditions can be made by using simple relations

$$n_2^* = n_1^* \frac{(\Delta T_{\max})_1}{(\Delta T_{\max})_2} + m \left[ 1 - \frac{(\Delta T_{\max})_1}{(\Delta T_{\max})_2} \right], \quad (25)$$

$$r_2^* = r_1^* \left[ \frac{(\Delta T_{\max})_1}{(\Delta T_{\max})_2} \right]^{1/3}, \quad (26)$$

$$(\sigma_{12})_2 = (\sigma_{12})_1 \left[ \frac{(\Delta T_{\max})_2}{(\Delta T_{\max})_1} \right]^{2/3}. \quad (27)$$

The calculated values of  $n^*$  and  $r^*$  seem to be quite reasonable and in good agreement with the data given by other authors<sup>4</sup>. The values of  $\sigma_{12}$  are very low, in many cases  $\sigma_{12} < 1$  erg/cm<sup>2</sup>. But even if we could ascribe a physical meaning to this quantity (it is difficult to discuss the meaning of surface energy of a cluster comprising some tens of particles only, and to use the thermodynamic description of such a small system) we must expect the interfacial tension between a crystal face and a supersaturated solution containing sublattices to be very low. In Table II, there are compared some values of  $\sigma_{12}$  published by other authors with those calculated. The

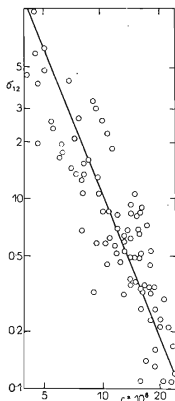


FIG. 1

Correlation of  $\sigma_{12}$  with  $r^*$

The given points are taken from Table I, the line represents Eq. (29).

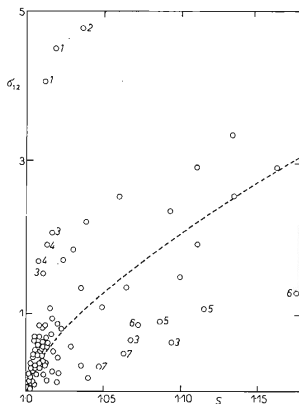


FIG. 2

Correlation of  $\sigma_{12}$  with  $S$

The numbers of some points are in accordance with Fig. 3.

immense spread of these values suggests that  $\sigma_{12}$  has perhaps no physical meaning and thus that it is only an adjustable parameter in the equations. This concerns the nucleation in condensed phases only, since the classical model is perhaps for nucleation in vapours more realistic.

There is another possible explanation of extremely low values of  $\sigma_{12}$  resulting from our data: It is obvious from Table I, that the value of  $\sigma_{12}$  depends on supersaturation; with its increase (*e.g.* with higher cooling rate  $b$ ) the  $\sigma_{12}$  is higher, too. Nevertheless, our measurements were carried out with very low supersaturation. In Table III there are compared values of supersaturation ratio  $S$

$$S = c/c_s \quad (28)$$

TABLE IV  
Time Lag  $t_k$  in Comparison with the Cooling Time  $t_c$  (s)

Substance	$b = 2 \text{ K/h}$			$b = 20 \text{ K/h}$		
	$t_K$	$t_c$	$t_c/t_K$	$t_K$	$t_c$	$t_c/t_K$
KCl	561	2 970	5.3	67	423	6.3
KBr	335	2 952	8.8	35	720	20.6
KI	181	1 800	9.9	21	342	16.3
NH <sub>4</sub> Cl	413	2 196	5.3	69	324	4.7
KNO <sub>2</sub>	188	2 160	11.5	32	405	12.7
KNO <sub>3</sub>	12	4 050	337.5	3	630	210.0
NaNO <sub>2</sub>	261	3 420	13.1	29	630	21.7
NaNO <sub>3</sub>	216	3 150	14.6	26	558	21.5
NH <sub>4</sub> NO <sub>3</sub>	54	1 350	25.0	5	252	50.4
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	41	5 400	131.7	5	828	165.6
H <sub>3</sub> BO <sub>3</sub>	995	3 204	3.2	126	756	6.0
(NH <sub>2</sub> ) <sub>2</sub> CO	143	3 204	22.4	9	459	51.0
<i>p</i> -C <sub>4</sub> H <sub>6</sub> (COOK) <sub>2</sub>	1 569	5 580	3.6	293	2 988	10.2
K <sub>2</sub> SO <sub>4</sub>	16	18 720	1 170.0	6	2 250	375.0
NaBr <sup>a</sup>	89	8 820	99.1	14	2 034	145.3
NaI <sup>a</sup>	65	3 960	60.9	10	720	72.0
Na <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	38	522	13.7	6	108	18.0
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>a</sup>	65	1 800	27.7	5	360	72.0
Na <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	10 790	2 970	0.3	1 299	387	0.3
Na <sub>2</sub> CrO <sub>4</sub> <sup>a</sup>	55	17 820	324.0	13	2 700	207.7
Na <sub>2</sub> HPO <sub>4</sub> <sup>a</sup>	56	5 220	93.2	15	774	51.6
FeSO <sub>4</sub> <sup>a</sup>	95	1 674	17.6	19	333	17.5
CuSO <sub>4</sub> <sup>a</sup>	215	8 100	37.7	16	1 926	120.4
Ca(NO <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	45	1 080	24.0	6	270	45.0
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> <sup>a</sup>	10	20 700	2 070	1	3 960	3 960

<sup>a</sup> Hydrated substances.

given by different authors with our experimental values which are much lower. This difference can be explained so that other authors formed the supersaturation by a sudden lowering of temperature, whereas in our measurements this change was very slow. Gindt<sup>8</sup> has calculated the values of  $\sigma_{12}$  from the heats of dissolution and states that these results may be compared with the experimental values of  $\sigma_{12}$  which are of the same order as ours. On the contrary, Kahlweit<sup>9</sup> found higher values. The similarity of values obtained in the absence and in the presence of added crystals proves that in both cases the nucleation was not homogeneous but heterogeneous (secondary) one. The value of  $\sigma_{12}$  calculated from such experimental data must be of course lower than in the case of homogeneous nucleation.

From Table I it strikes that the value of  $\sigma_{12}$  decreases with increasing  $r^*$ . This dependence is shown in Fig. 1 and a line given by

$$\sigma_{12} = 316(r^* \cdot 10^8)^{-2.5} \quad (29)$$

has been drawn through the field of points.

This dependence of  $\sigma_{12}$  on  $r^*$  may, however, be only apparent and a result of two other dependences: of  $\sigma_{12}$  on the supersaturation ratio  $S$  and of  $r^*$  on  $S$ . These dependences are plotted in Figs 2 and 3. It is clear that these two correlations are not as good as that one shown in Fig. 1 which holds especially for correlation of  $\sigma_{12}$  with  $S$ . Nevertheless, the positive deviations of certain points in Fig. 2 are compensated by negative deviations of these points in Fig. 3 and so the correlation of  $\sigma_{12}$  with  $r^*$  (Fig. 1) seems to be a better one. By combining Eq. (29) with Eq. (24) we obtain a much better correlation of  $r^*$  with  $S$ , which can be written in a simple form

$$(r^* \cdot 10^8)^{-3.5} = 0.00132 \rho_c T(S - 1)/M, \quad (30)$$

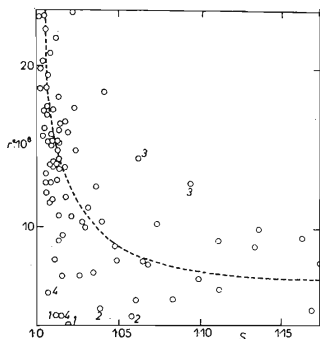


FIG. 3  
Correlation of  $r^*$  with  $S$   
1  $\text{KNO}_3$ ; 2  $\text{Na}_2\text{HPO}_4$ ; 3  $\text{Na}_2\text{CrO}_4$ ; 4  $\text{NaBr}$ ; 5  $\text{Na}_2\text{CO}_3$ ; 6  $\text{CuSO}_4$ ; 7 potassium terephthalate; 8  $\text{Na}_2\text{B}_4\text{O}_7$ .



which is plotted in Fig. 4. It is obvious that most substances comply with the line drawn through the experimental points with the exception of several points located on another line having the same slope.

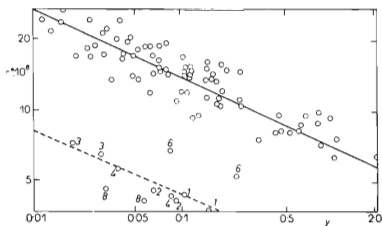


FIG. 4

Correlation According to Eq. (30),  $y = 0.00132 \cdot \rho_c T (s - 1) / M$

The numbers of some points are in accordance with Figs 2 and 3.

### The Unsteady State Problem

The relation (2) obtained by Becker and Döring<sup>3</sup> represents the steady state nucleation kinetics. Later studies considered nucleation as an unsteady state process and *e.g.* Zeldovich<sup>12</sup> obtained a partial differential equation describing this process. Its solution has been found by many authors<sup>13</sup> using different assumptions, but the evaluation of experimental data remains always somewhat uncertain. The question arises whether our measurements reflect the unsteady state behaviour or not. For a rough estimate we may compare the time lag calculated from Eq. (9) and the experimental cooling time. If this cooling time is much longer than the time lag calculated for the experimental conditions, the measurements may be taken like those for the steady state. The time lag  $t_k$  (in seconds) can be determined from Eq. (9)

$$t_k = 3600 / k_n \Delta c^m \quad (31)$$

The actual cooling time,  $t_c$ , is given by the undecooling,  $\Delta T_{\max}$ , and by the cooling rate,  $b$

$$t_c = 3600 \Delta T_{\max} / b \quad (32)$$

with the new results of calculation based on data published earlier<sup>2</sup> given in Table IV. It is evident from this Table that with the exception of  $\text{Na}_2\text{CO}_3$  in all other cases the total cooling time is much longer than the time lag, *i.e.* the cooling rate is sufficiently slow to enable the corresponding rearrangement of clusters of particles to take place and so the experimental conditions are close to those of the steady state.

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## LIST OF SYMBOLS

$b$	cooling rate ( $K/h^{-1}$ )
$c$	concentration ( $kg\ m^{-3}$ )
$c_s$	concentration of the saturated solution ( $kg\ m^{-3}$ )
$\Delta c$	supersaturation ( $kg\ m^{-3}$ )
$\Delta G^*$	molar free enthalpy of formation of a critical nucleus
$J$	nucleation rate
$k$	Planck's constant
$k_0$	temperature coefficient of the solubility ( $kg\ m^{-3}\ deg^{-1}$ )
$k_n$	nucleation constant ( $(c/l)^{1-m}\ h^{-1}$ )
$K$	constant
$M$	molecular weight
$m$	nucleation order
$N$	Avogadro's number
$n^*$	number of particles forming a critical nucleus
$p$	concentration (weight %)
$r^*$	radius of critical nucleus (m)
$S$	supersaturation ratio
$T$	temperature (K)
$\Delta T_{max}$	maximum undercooling (K)
$t$	time (h)
$t_K$	time lag (h)
$t_c$	cooling time (h)
$\alpha$	volume shape factor
$\beta$	surface shape factor
$\mu$	chemical potential
$\rho_c$	density of crystals ( $kg\ m^{-3}$ )
$\rho_l$	density of solution ( $kg\ m^{-3}$ )
$\sigma_{12}$	interfacial surface energy ( $erg/cm^2$ )

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