Radius of Critical Nucleus - Revisited

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Introduction

Classical [1] or new [2, 3] literature presents the Gibbs-Thompson formula for the critical radius of nucleus. However, there are doubts, why some substances got this parameter rather in the range of *nm* but others in *μm*. Here is a critical review of the main reasons of these discrepancies.

Theory

The radius of spherical critical nucleus at some supersaturation level can be written as:

$$r_c = \frac{2\sigma V_m}{RT\ln(S)} \quad . \qquad (1)$$

The dominant effect of the supersaturation ratio on the radius can easily be proved. However, influence of the surface tension and molar volume cannot be overlooked. We could rewrite equation (1) in the next form:

$$\ln\left(\frac{c(r)}{c^*}\right) = \ln(S) = \frac{2\sigma V_m}{RTr} \quad . \qquad (2)$$

Essentially all the data needed to apply these formulae are accessible. Molar volume is just a quotient of molar mass and solid (crystal) density.

Calculations and results

Calculations were performed for several substances, i.e. NaCl, KCl, $NaNO_3$, CuO, Fe_3O_4, Ag, CdSe, sugar and $BaSO_4$ for the range of supersaturation levels from 1.001 till 10.00. Results are plotted in Fig. 1.

For most of these substances rc (S=1.001) is in the range of μm besides CuO and Ag for which is about 0.1 μm however for sugar 14 μm and the tendency is kept with increasing supersaturation getting r_c(S=10.0) below 1nm for CuO, Ag and Fe_3O_4. Fig. 2 shows the influence of particle radii on the relative supersaturation S-1 as compared to the equilibrium.

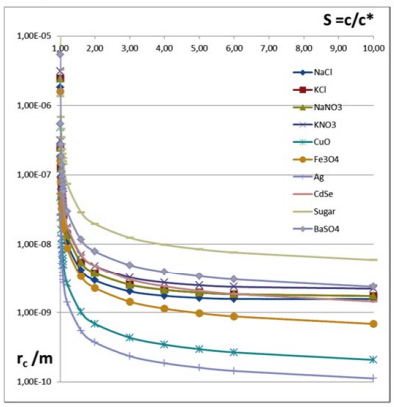

FIG.1 Radius of critical nucleus vs supersaturation for the chosen substances

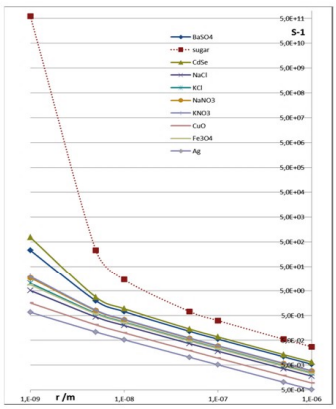

FIG. 2 of relative supersaturation S-1 as a function of particle size for selected substances

Most of these substances, with small crystal sizes in the range of nanometers, show large driving force for dissolution of such particles. However, CuO and Ag crystals in the range of 10 nm seem to be stable enough not to be dissolved. Number of molecules inside the critical nucleus could be calculated from:

$$n = \frac{k_v r_c^3}{v} \quad . \qquad (3)$$

Figure 3 presents this dependence for the chosen substances. The above values are related to the crystal structure and it is worth to note that the smallest are calculated for Ag and CuO and the highest for sugar. An important parameter for real precipitation is the induction time, which depends also on the number of molecules within the critical nucleus:

$$\tau = \frac{6d^2 n}{D\ln(S)} \quad . \qquad (4)$$

For low supersaturations it could have large values (Fig.4). However, for high ones, is in range of μs or even ns. Both Figures (3 and 4) shows a similar behavior. The quickest precipitation is for Ag and CuO and the longest for sugar, at the same supersaturation.

In addition to the critical nucleus diameter, for manufacturing small crystals, homogeneous primary nucleation rate [9] is of a profound importance:

$$J = \Omega \exp\left(-\frac{\Delta G_c^{hom}}{kT}\right) \quad , \qquad (5)$$

where:

$$\Omega = \frac{D}{d^5 n}\left(\frac{4\Delta G_c^{hom}}{3\pi kT}\right) \quad . \qquad (6)$$

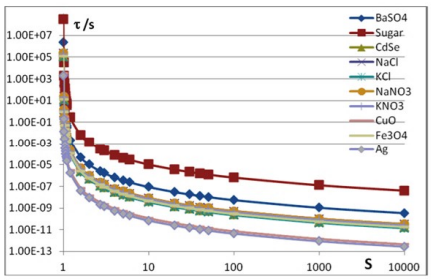

FIG. 4 Dependence of induction time on supersaturation

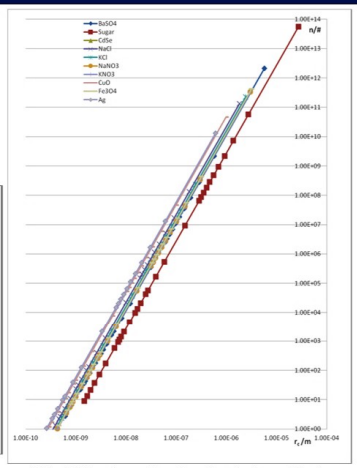

FIG. 3 Number of molecules in the critical nucleus

Table 1 Critical supersaturations S_c for selected substances

	Ag	*CuO*	*NaCl*	*Fe_3O_4*	*KCl*	*KNO_3*	*$NaNO_3$*	*CdSe*	*$BaSO_4$*	*sugar*
S_c	1.49	1.81	3.1	5.65	5.87	9.2	9.9	21	600	$0.75\cdot10^8$

Figure 5 presents calculated values of primary nucleation rates for chosen substances vs supersaturation. Again, Ag and CuO have the highest nucleation rate and sugar the smallest. Critical supersaturation levels could be obtained from the plots or calculated numerically for J=10^6[#/s/m^3] = (1[#/s/cm^3]), see Table 1. An obvious conclusion is that primary nucleation in real cases, is not the prevailing mechanism, especially for ionic salts and sugar.

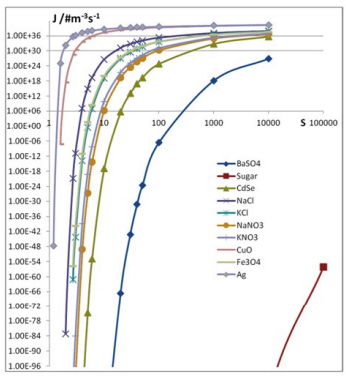

FIG. 5 Dependence of induction time on supersaturation

Conclusions

Some substances such Ag and CuO from their physicochemical properties are predestined to have stable nanocrystals in proper conditions. However, this is possible for other substances only by a special preparation technique [4].

Acknowledgments

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Symbols:

$c(r)$	equilibrium concentration for crystal of radius r	[mol/m^3]
c^*	equilibrium concentration	[mol/m^3]
d	interplanar distance in the cristal lattice	[m]
D	diffusion coefficient	[m^2/s]
ΔG_c^{hom}	Gibbs energy difference for critical nucleus	[J]
J	primary nucleation rate	[#/s/m^3]
k_V	volumetric shape factor	[-]
n	number of molecules in nucleus	[-]
R	universal gas constant R=8.314 J/mol/K	[J/mol/K]
S	supersaturation	[-]
T	absolute temperature	[K]
v	volume of the molecule	[m^3]
V_m	molar volume	[m^3/mol]
σ	surface tension	[J/m^2]
τ	induction time	[s]
Ω	pre-exponential term eq. (6)	[#/s/m^3]

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