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RELATIONS BETWEEN ACTIVATION ENERGIES FOR NUCLEATION AND OF GROWTH OF CRYSTALS

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The attempt to consider the influence of particle solvation of dissolved substances on the nucleation and growth of crystals during crystallization from solutions in classical thermodynamic theory of nucleation has been undertaken. A number of interesting relations between the activation energies of nucleation and of crystal growth are obtained. Comparison to the published literature data is carried out.

Keywords: activation energy, solvation, nucleation, growth of crystals, solution, dissolved substance, hydration.

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According to classical thermodynamic theory, the rate of nucleation of new phase in the volume of metastable (mother) phase is a fluctuating process and is directly proportional to concentration of critical nuclei of the appearing new phase [1–8]:

$$J = Z \cdot \omega \cdot n_c^*, \tag{1}$$

$$n_c^* = n^* \exp\left(-\frac{A_c}{k_B T}\right), \tag{2}$$

$$A_c = \frac{4}{3}\pi R_c^2 \sigma, \tag{3}$$

where J is the rate of nucleation in the volume of vapor, of gas, of melt or of solution, $\mathrm{s}^{-1}\cdot\mathrm{m}^{-3}$; Z is the nonequilibrium factor of Zeldovich; ω is the frequency of addition of particles of crystallizing substance to critical nuclei (after that, the nuclei transform into stable crystallization growth centers), s^{-1}; n_c^* is the concentration of critical nuclei of new phase, m^{-3}; n^* is the concentration of particles of crystallizing substance in supersaturated mother phase, m^{-3}; k_B – is Boltzmann constant, J/K; T is the temperature, K; A_c is the work of formation of critical nucleus of new phase, J; R_c is the radius of critical nucleus of new phase, m; σ is the specific surface energy (the surface tension), $\mathrm{J/m}^2$.

Equations (1)–(3) are correct for crystallization from vapor and gas phases. There is great interest present on the question of changing these equations of classical thermodynamic theory and applying them to crystallization from solution, if in the first approximation one takes into account hydration (for nonaqueous solution – solvation) of particles of crystallizing substance in solution. From first principles, for more clear detection of differences in crystallization processes for various condensed media, we will consider process of nucleation in molecular melts. It should be noted that usually the equations of classical nucleation theory describing nucleation from vapor and gas phases automatically, almost without changing, with little limitation, translate to crystallization in condensed media. It is clear, this is not completely right. Moreover, in the explicit form, the direct registration of nucleation differences in condensed media from nucleation in vapor and gas phases has not still been done. Below, we make an attempt to bridge this gap (in the first very rough approximation).

So, in the formation of a new phase in molecular melts (i.e. solidification of such melt), as opposed to crystallization from the vapor and gas phase, it is necessary to take into account the additional energy barrier that is specified with overcoming by particles of crystallizing substance of intermolecular forces connecting them with a melt. In other words, it is necessary to take into account the diffusion of particles of crystallizing substance in a melt. Therefore, Eq. (2) must be transformed into the form:

$$n_c^* = n^* \exp\left(-\frac{A_c}{k_B T}\right) \exp\left(-\frac{E_D}{RT}\right), \tag{4}$$

where E_D is the activation energy of diffusion of crystallizing substance in the volume of condensed medium, J/mol; R is the universal gas constant, J/(K·mol).

If the nucleus of new phase has form of a sphere with radius R_c, then for crystallization in a molecular melt, factor ω in Eq. (1) is defined by the equation [2,5]:

$$\omega = 4\pi R_c^2 K_n n^* a f_0 \exp\left(-\frac{E_D}{RT}\right), \tag{5}$$

where K_n is the coefficient of proportionality involving steric factor (the probability of suitable particle orientation) and others unaccounted factors; a is the length of diffusion jump of the particle of crystallizing substance, m; f_0 is the frequency of thermal vibrations of the particle of crystallizing substance, s^{-1}.

The radius of critical nucleus can be found using Gibbs-Thomson relationship [3–8]:

$$R_c = \frac{2\sigma \cdot \Omega}{k_B N_A T \ln\left(\frac{n^*}{n_0^*}\right)}, \tag{6}$$

where Ω is the volume of one mole of the nucleus substance, m^3/mol; n_0^* is the equilibrium concentration of particles of crystallizing substance in mother phase at given temperature, m^{-3}; N_A is the Avogadro's number, mol^{-1}.

Taking into account Eqs. (1)–(6), one can find the equation for nucleation rate in molecular melts:

$$J = \frac{16 Z \pi a f_0 K_n \sigma^2 \Omega^2 \cdot (n^*)^2}{(RT)^2 \ln^2\left(\frac{n^*}{n_0^*}\right)} \exp\left(-\frac{E_1}{RT}\right) \exp\left(-\frac{16\pi N_A \sigma^3 \Omega^2}{3(RT)^3 \ln^2\left(\frac{n^*}{n_0^*}\right)}\right), \tag{7}$$

where $R = k_B N_A$; E_1 is the activation energy of nucleation process in the volume of condensed phases, J/mol, as is seen, for molecular melts $E_1 = 2E_D$.

For the transition from molecular melts to the aqueous (and non-aqueous) solutions of inorganic salts it is necessary to take into account that in such solutions the crystallizing (dissolved) substance is in the form of hydrated (solvated) molecules and ions. Hence, an attachment of molecule or ion to the critical nucleus (and also formation of the critical nucleus) will be apparently connected with overcoming an additional potential barrier that is specified by hydration (solvation) of molecules and ions of dissolved substance in solution.

It is known that dissolution of solid substances in liquids and, particularly, of inorganic salts, is caused by interaction of molecules of solvent with molecules and ions of soluble substance. This brings a reduction of intermolecular interactions and links between ions in solid substance. As a result, molecules and ions of solid substance begin to pass into solution, and the solid substance dissolves. Under such conditions, the molecules and ions of dissolved substance in solution are hydrated and solvated, i.e. are surrounded by shell of solvent molecules. Therefore, for reverse transfer from the liquid phase into the solid one they must drop this shell. Last is connected with overcoming corresponding potential barrier. Hence, the attachment of molecules and of ions of dissolved substance to a critical nucleus (and also formation of the critical nucleus) will be possible only after their partial (or full) dehydration (desolvation). Thus, new additional factors it is necessary to introduce into Eqs. (4) and (5):

$$n_c^* = n^* \exp\left(-\frac{A_c}{k_B T}\right) \exp\left(-\frac{E_D}{RT}\right) \exp\left(-\frac{E_{ds}}{RT}\right), \tag{8}$$

$$\omega = 4\pi R_c^2 K_n n^* a f_0 \exp\left(-\frac{E_D}{RT}\right) \exp\left(-\frac{E_{ds}}{RT}\right), \tag{9}$$

where E_{ds} is the energy of dehydration (desolvation) of particles of dissolved substance at their transition from the volume of liquid phase into solid one, J/mol.

If one considers that $n^* = [C] \cdot 10^3 \cdot N_A$, where $[C]$ is the molar concentration (mol/l) of a supersaturated solution of crystallizing substance then one can find the equation for the rate of nucleation in a salt solution:

$$J = \frac{16 \cdot 10^6 Z \pi a f_0 K_n \sigma^2 \Omega^2 N_A^2 [C]^2}{(RT)^2 \ln^2\left(\frac{[C]}{[C_0]}\right)} \exp\left(-\frac{E_1}{RT}\right) \exp\left(-\frac{16\pi N_A \sigma^3 \Omega^2}{3(RT)^3 \ln^2\left(\frac{[C]}{[C_0]}\right)}\right), \tag{10}$$

where $E_1 = 2(E_D + E_{ds})$.

Now let's examine a process of heterogeneous nucleation on foreign and the crystallizing substrates. So, the rate of surface nucleation on a foreign substrate and the concentration of critical nuclei on the surface of the substrate, according to approved assumptions, are defined by expressions:

$$J_S = Z \cdot \omega_S \cdot n_{cs}^*, \tag{11}$$

$$n_{cs}^* = n_s^* \exp\left(-\frac{A_c}{k_B T}\right) \exp\left(-\frac{E_{DS}}{RT}\right) \exp\left(-\frac{E_{dsad}}{RT}\right), \tag{12}$$

where J_S is the rate of surface nucleation on a foreign substrate, $\mathrm{s}^{-1} \cdot \mathrm{m}^{-2}$; ω_S is the frequency of attachment of particles of crystallizing substance to critical nuclei on the surface of the substrate (after this the critical nuclei transform into stable growing centers of crystallization), s^{-1}; n_{cs}^* is the concentration of critical nuclei on the surface of the substrate, m^{-2}; n_s^* is the concentration of particles of dissolved substance adsorbed on the surface of the substrate, m^{-2}; E_{DS} is the activation energy of surface diffusion of particles of crystallizing substance along the surface of the substrate, J/mol; E_{dsad} is the energy of dehydration (desolvation) of particles of crystallizing substance at their attachment from adsorbed layer on the surface of the substance to critical nucleus, J/mol.

Note, that according to the classical theory of nucleation, [3,5] Eq. (11) supposes that critical nuclei arise from particles of crystallizing substance adsorbed onto the surface of a substrate.

With heterogeneous nucleation, as with nucleation in a volume, the formed nuclei of critical size will transform into centers of crystallization and maintain their strong growth only after attachment to at least of one particle (molecule or ion) of crystallizing substance. However, as opposed to homogeneous nucleation, in present case, this attachment can proceed in two ways [5]: (1) due to the connection of particles (molecules or ions) of the dissolved (crystallizing) substance from the volume of solution and (2) by means of addition of particles (molecules or ions) of the dissolved (crystallizing) substance adsorbed on the surface of the substrate and their subsequent surface diffusion to the formed nucleus of new phase.

If with nucleation on a foreign substrate, the critical nucleus has a ball segment form and its subsequent growth proceeds due to the attachment of particles (molecules or ions) of the dissolved (crystallizing) substance from the volume of solution, then, according to [5] and accepted assumptions, Eq. (9) becomes:

$$\omega_S = 2\pi R_c^2(1-\cos\theta)K_n n^* a f_0 \exp\left(-\frac{E_D}{RT}\right)\exp\left(-\frac{E_{ds}}{RT}\right). \tag{13}$$

If subsequent growth of the critical nucleus proceeds by means of attachment of particles (molecules or ions) of the dissolved (crystallizing) substance adsorbed on the surface of the substrate, then one can obtain by analogy the following:

$$\omega_S = 2\pi R_c \sin\theta \cdot K_n n_s^* a f_0 \exp\left(-\frac{E_{DS}}{RT}\right)\exp\left(-\frac{E_{dsad}}{RT}\right). \tag{14}$$

In the first approximation, one can also take that:

$$n_s^* = K_{na}\cdot n^* \cdot \exp\left(-\frac{E_D}{RT}\right)\exp\left(-\frac{E_{dsa}}{RT}\right), \tag{15}$$

where K_{na} is the coefficient of proportionality; E_{dsa} is the energy of dehydration (desolvation) of particles of crystallizing substance at their adsorption on the surface of the substrate (at transition from the volume of liquid phase on the surface of the substrate), J/mol. Obviously, $E_{ds} = E_{dsa} + E_{dsad}$.

Then, after corresponding substitutions, the equation describing the rate of heterogeneous nucleation on a foreign substrate in solution may be obtained:

$$J_S = \frac{8\cdot 10^6 Z\pi a f_0(1-\cos\theta)K_n K_{na}\sigma^2\Omega^2 N_A^2[C]^2}{(RT)^2\ln^2\left(\frac{[C]}{[C_0]}\right)}\exp\left(-\frac{E_2}{RT}\right)\exp\left(-\frac{16\pi N_A\sigma_{ef}^3\Omega^2}{3(RT)^3\ln^2\left(\frac{[C]}{[C_0]}\right)}\right), \tag{16}$$

$$J_S = \frac{4\cdot 10^6 Z\pi a f_0\sin\theta\cdot K_n K_{na}^2\sigma\Omega N_A^2[C]^2}{RT\ln\left(\frac{[C]}{[C_0]}\right)}\exp\left(-\frac{E_3}{RT}\right)\exp\left(-\frac{16\pi N_A\sigma_{ef}^3\Omega^2}{3(RT)^3\ln^2\left(\frac{[C]}{[C_0]}\right)}\right), \tag{17}$$

where $E_2 = 2(E_D + E_{ds}) + E_{DS}$ is the activation energy of the surface nucleation at growth of critical nucleus due to the attachment of particles (molecules or ions) of the dissolved (crystallizing) substance from the volume of solution, J/mol; $E_3 = 2(E_D + E_{DS} + E_{ds})$ is the activation energy of surface nucleation at growth of critical nucleus by means of connection of particles (molecules or ions) of the dissolved (crystallizing) substance adsorbed on the surface of the substrate, J/mol; σ_{ef} is the efficient specific surface energy, J/m^2 [3–6].

As is seen, if our assumptions are true, then $E_3 = E_2 + E_{DS}$. From this, it follows that due to lower activation energy, heterogeneous nucleation in solutions must proceed predominantly by means particles (molecules or ions) attachment of the dissolved (crystallizing) substance from the volume of solution.

Heterogeneous nucleation on the crystallizing substrate, in contrast to heterogeneous nucleation on foreign substrate, proceeds due to the formation not three-dimensional but two-dimensional nuclei, not the analogous three-dimensional particles [3–8]. In the case, if the critical nucleus has the form of a disk, its radius (R_{cs}) and the work of formation (A_{cs}) are [3–8]:

$$R_{cs} = \frac{\sigma \cdot \Omega}{RT \ln\left(\frac{n^*}{n_0^*}\right)}, \tag{18}$$

$$A_{cs} = \frac{\pi \cdot \Omega\sigma^2 a_0}{RT \ln\left(\frac{n^*}{n_0^*}\right)}, \tag{19}$$

where a_0 is the parameter of crystal lattice of crystallizing substance, m.

Similarly, as before, one can propose that the surface nucleation on the crystallizing substrate may occur in two ways: (1) due to the attachment of particles of the crystallizing substance from the volume of solution and (2) by means of addition of adsorbed on the surface of the substrate particles of the crystallizing substance. Corresponding substitutions give equations for the rate of nucleation on the crystallizing substrate:

$$J_S^* = \frac{2 \cdot 10^6 Z\pi a f_0 (1-\cos\theta) K_n K_{na} \sigma^2 \Omega^2 N_A^2 [C]^2}{(RT)^2 \ln^2\left(\frac{[C]}{[C_0]}\right)} \exp\left(-\frac{E_2}{RT}\right) \exp\left(-\frac{a_0 \pi N_A \sigma^2 \Omega}{(RT)^2 \ln\left(\frac{[C]}{[C_0]}\right)}\right), \tag{20}$$

$$J_S^* = \frac{2 \cdot 10^6 Z\pi a f_0 \sin\theta \cdot K_n K_{na}^2 \sigma \Omega N_A^2 [C]^2}{RT \ln\left(\frac{[C]}{[C_0]}\right)} \exp\left(-\frac{E_3}{RT}\right) \exp\left(-\frac{a_0 \pi N_A \sigma^2 \Omega}{(RT)^2 \ln\left(\frac{[C]}{[C_0]}\right)}\right). \tag{21}$$

Now, we consider the growth of crystals (the kinetic mode, when diffusion is negligible). In the case of atomically roughened crystal faces and normal growth mechanism, the particles of the crystallizing substance can attach to the growing crystal at any point on its surface, and the crystal growth rate is described by the first order equation related to the supersaturation of a solution [5]:

$$V = k_1 \exp\left(-\frac{E_4}{RT}\right) ([C] - [C_0]), \tag{22}$$

where V is the linear growth rate of a face of a crystal, m/s; k_1 is the coefficient of proportionality; E_4 is the activation energy of the normal mechanism of crystal growth process, J/mol.

It is obvious, that if crystals have atomically roughened faces, then the particles of the crystallizing substance, before being incorporated into the crystal lattice of growing crystal, as for nucleus formation, in the beginning, must carry out a diffusion jump from the volume of a liquid phase to a kink in the surface of the crystal, and after that, to drop the surrounding shell of solvent molecules. Then, it should be expected that:

$$E_4 = E_D + E_{ds}. \tag{23}$$

With the dislocation growth mechanism of crystal faces and low supersaturation of solution [5]:

$$V = k_2 \exp\left(-\frac{E_5}{RT}\right)([C] - [C_0])^2, \tag{24}$$

where k_2 is the coefficient of proportionality; E_5 is the activation energy of the dislocation mechanism of crystal growth process, J/mol.

In the dislocation mechanism of crystal growth, similarly to the heterogeneous nucleation process, the incorporation of crystallizing substance particles into the lattice of the growing crystal can occur in two ways: (1) due to the direct attachment of the particles of crystallizing substance from the volume of solution and (2) by means of incorporation of particles of the crystallizing substance adsorbed on the crystal surface and their subsequent surface diffusion to the steps of growth. In the first way the activation energy of the crystal growth process must be also described by Eq. (23) (i.e. $E_5 = E_4$), in the second way, taking into account the process of the surface diffusion, one may obtain:

$$E_5 = E_D + E_{DS} + E_{dsad} + E_{dsa} = E_D + E_{DS} + E_{ds} = E_4 + E_{DS}. \tag{25}$$

If the assumptions we make are true, then it may be found the next relations among the activation energies of growth and nucleation processes of crystals:

$$E_1 = 2E_D + 2E_{ds} = 2E_4, \tag{26}$$

$$E_2 = 2(E_D + E_{ds}) + E_{DS} = 2E_4 + E_{DS} \approx 2E_4. \tag{27}$$

From the above expressions, it follows that the activation energy of homogeneous nucleation in molecular melts [please see Eq. (7)] must be equal to the doubled activation energy of diffusion of particles of crystallizing substance in the volume of the melt, and heterogeneous nucleation and growth of crystals in solution occur mainly by attachment of crystallizing substance particles directly from the volume of solution, since the activation energy of these processes are below the activation energy for the attachment of crystallizing substance particles from an adsorbed layer onto the surface of a crystal or substrate. Besides, processes of heterogeneous nucleation on foreign and similar substrates must have almost equal activation energies.

It is interesting to compare the obtained relations with published experimental data. Unfortunately, there are few published results allowing us to test this [9–13].

In two of our previous papers [9, 10], it was shown that the rates of heterogeneous nucleation of calcium sulphate on a foreign substrate (stainless steel) and on the same substrate are really best described by Eqs. (16) and (20), and their activation energies are almost identical. So, according to [9, 10], the activation energy of nucleation of calcium sulphate on the surface of stainless steel (a foreign substrate) is 100.9±15.6 kJ/mol, and on itself – 139.4±40.8 kJ/mol (the significance level is 0.05). As is seen, within the limits of experimental error, they coincide. Next, the activation energy for the process of dislocation growth (the quadratic dependence of the growth rate on supersaturation of solution) of the crystal face (120) of gypsum crystals was 59.1±7.8 kJ/mol (the significance level was 0.05) [10]. This also confirms the above-obtained relation (27): $E_2 = 139.4 \pm 40.8$ kJ/mol $\approx 2E_4 = 2 \times (59.1 \pm 7.8)$ kJ/mol $= 118.2 \pm 15.6$ kJ/mol.

In [11], the energies of hydration for KCl and NaCl were calculated by the method of thermodynamic cycle and are 60.8 – 61.5 kJ/mol and 47.4 – 47.8 kJ/mol, respectively. Experimental data on the activation energies for normal growth processes of KCl and NaCl crystals in spontaneous crystallization of these salts from aqueous solutions were found in works [12, 13]. They are 61.8 – 65.2 kJ/mol [12] and 49.1±5.9 kJ/mol respectively [13]. Meanwhile, according to Eq. (23) the activation energy of process of growth of crystals at normal mechanism must be approximately equal to the dehydration energy for the salt [the activation energy of diffusion in water solution has value about several kJ/mol, therefore, it may be omitted in Eq. (23)]. It is seen, from published data of works [11–13], the surprisingly precise realization of this relationship is observed.

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