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Solvent effect on the kinetics of crystal growth

E B Treivus
St. Petersburg University

ABSTRACT. Experimental data for the solvent effect on the kinetics of crystal growth are summarised. The common analytical method based on the concept that crystallisation in solutions occurs essentially through random addition of particles to the crystal surface (normal growth mechanism) and the means for estimating the contribution of this mechanism are critically examined. The conclusion is made that the role of such a mechanism is overstated. A theory is formulated that enables the solvent effects pertaining to layered facial crystal growth to be estimated.

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I. Introduction

Solvent effects on crystallisation are interesting for a number of reasons. Solvent exchange is a useful method of studying mechanisms of chemical reactions in solutions, in particular, the growth of crystals. Finding the principles underlying this area is also worthwhile for applications since the current trend is toward expanding the number of solvents (organic liquids, metal melts, inorganic salts and oxides) used to grow crystals from solutions. The choice of solvent is important to various sectors of the chemical industry (processing crude petroleum, production of mineral fertilisers, reagents, pharmaceuticals, etc.) owing to the need to promote crystallisation and the desire to gain a greater yield and to change the shape of the crystallites in the required direction. In particular, the caking of a substance, the effectiveness of its separation from the mother liquor, its pharmaceutical efficacy, etc., depend on this shape. A review of studies in this area was published abroad more than 10 years ago.[1] Analogous publications have not appeared in the domestic literature.

II. Treatment of experimental data within the framework of the normal growth mechanism

The solvent was known to affect crystal shapes, i.e., the ratio of growth rates of their various faces, even at the start of the present century. Thus, the solvent affected the habit of crystals of urea, sulphur, etc.[2] According to Orlov,[3] these facts were related to the change of surface tension of the various faces since shortly before this the well-known Gibbs–Curie principle about the minimum surface energy of an equilibrium crystal had been formulated. It is now evident that this principle is inapplicable to nonequilibrium crystal shapes. How the concept of the role of surface energy in the kinetics of crystal growth has up to now been transformed will be clear from the following exposition.

Orlov[3] discovered that the facetting of NaOH crystals becomes complicated on going from aqueous solution to formamide and also on going to a mixture of water with certain hydroxy-acids. According to his viewpoint, the shape of crystals changes if the dissolved substance reacts chemically with the solvent. He saw signs of this in the high dielectric constant of formamide and in the structural features of the solvents used. A specific interaction with different crystal faces of complexes of the crystallising species and solvent species that have a variable structure in different solutions can change the crystal habit.[3] Apparently, this study was the first in which the possible role during crystallisation of a change in solution structure owing to a solvent change was pointed out.

Wells[4] pointed out the significance of a specific solvent interaction with different crystal faces. He illustrated this using resorcinol as an example. Certain opposing faces of resorcinol crystals have different structures. According to Wells, the faces terminating in hydroxyl groups are blocked by water molecules. This leads to preferential development of these faces during formation of resorcinol crystals. The nonpolar solvent benzene does not affect this selective adsorption. The crystal grows symmetrically in opposite directions.

Both these ideas are expanded upon or confirmed in subsequent studies. Kleber and Raidt[5] discovered that salol crystals in nonpolar solvents (CCl_4, C_6H_6) and in acetone have a shape corresponding to their symmetry type $2/mm$. The external symmetry is reduced to 22 if polar solvents (CH_3OH, C_2H_5OH, C_3H_7OH) are used. This phenomenon was related[5] to the solution structures. In nonpolar solvents, salol molecules are associated; in polar, they are not associated. However, it is not clear how this is related to the external crystal facetting. The concept of specific solvent adsorption has been developed.[6] The formation of a new face on $Hg(CN)_2$ crystals in CH_3OH solution was explained by epitaxy on this face of the complex $Hg(CN)_2.CH_3OH$. The similarity of the atomic distributions in planes of the growing faces of $Hg(CN)_2$ and $Hg(CN)_2.CH_3OH$ crystals confirms that epitaxy occurs.

Thus, the position was in essence taken[6] that solvent is specifically adsorbed if there are epitaxial relationships between faces of the crystallising substance and the solvent (a compound with it is a particular instance). The scale of the dimensional fit is an important condition and significant sign of the extent of specific solvent adsorption. It is noteworthy that, apparently, Petrov[7] first expounded the idea of selective epitaxial solvent adsorption on different faces of a single crystal and its role in their growth features.

Then, this idea was directly confirmed[8] by results of ice crystal formation on different faces of sodium bromate crystals.

This short synopsis is necessary, in particular, because the domestic studies are not mentioned in the previous review.[1]

According to Berkovitch-Yellin,[9] polar faces preferentially adsorb polar solvent molecules. Nonpolar ones are solvated by nonpolar solvents. The solvent effect should be especially distinctly evident for crystals of those substances for which the different faces have considerably different polarities. By the polarity of a face is meant the degree of contrast in its electrostatic relief that is quantitatively characterised by the difference of the positive and negative peaks in the map of the electrostatic potential of this face. Such maps have been presented[9] for different crystal faces of benzamide, benzoic acid, α-glycine, E-cinnamide and succinic acid. The maxima of the positive and negative potentials are given. Within the framework of his hypothesis, Berkovitch-Yellin qualitatively explains the crystal shape of these compounds obtained from different solutions. Certainly this hypothesis helps the problem to be understood and possesses a certain predictive capability. However, the importance of dimensional fits is ignored in it.

According to Chan et al.,[10] hexamethylmelamine (an anti-tumour drug) crystals become most anisometric with increasing supersaturation on crystallisation from polar media. Crystals formed in polar media are less sensitive to a change of supersaturation. The spectroscopic features of solutions of this compound in both types of solvents are the same. The crystallisation of two organic compounds was used[10] to demonstrate that relatively well formed isometric crystals are formed from solutions that differ in ideal solubility. Needle-like crystals grow in other solutions. These studies are attempts to find common features of the solvent effect on crystal growth.

The solvation of different faces was quantitatively estimated for saccharose crystals in aqueous solution from the change of surface tension.[12]

For all studies up to the middle of the 1960s, and for many earlier ones including those mentioned above, a qualitative approach and the lack of control of the supersaturation and temperature was characteristic. It was noted in the best instances at what supersaturation, high or low, the experiments were conducted. The temperature was approximately indicated. The results of similar studies are dubious since they may be due not to a solvent effect but to the factors mentioned above. Furthermore, these data are not always reproducible. The first quantitative measurements of the growth rates in different solutions with accurately controlled conditions were described in 1967.[13] It was found that the growth rate of glyceryltripalmitate and glyceryltristearate (measured for one crystal direction) crystals is much higher in CCl_4 solution than in glyceryltrioleate solution. This is consistent with the noticeably higher solubility of these tristearides in the first solvent than in the second. This feature was not noted.[13] However, it then turned out that it is fundamental.

It has been discovered[14] that the growth rate of urotropine crystals from aqueous, ethanol and aqueous-acetone solutions directly depends on its solubility in these media. The solubility of biphenyl in toluene is almost 20 times greater than in CH_3OH (in mole fractions). The growth rate of biphenyl crystals from toluene solution is also almost 20 times greater than from CH_3OH.[15] The kinetics of KNO_3 crystal growth from a series of five solvents and four of their binary mixtures obey the same rules.[16] The growth rate of succinic acid crystals[17] with solubility expressed in molality or molarity also directly depends on its solubility in water and isopropanol although an inverse dependence is obtained if the solubility is expressed in mole fractions. The growth rates of separate faces of hexatriacontane crystals are directly proportional to the solubility of this paraffin in heptane, decane, pentane and petroleum ether.[18]

Table 1. Growth rate of *para*-xylene crystals V at various relative supersaturations σ (0 °C, 30 mass% solvent).[20]

Solvent	m_0	σ	10^4V, cm sec^{-1}	$10^2\beta$, cm sec^{-1}
Ortho-xylene	21.7	0.014	1.0	0.71
Toluene	21.7	0.012	0.7	0.58
Meta-xylene	21.8	0.009	0.6	0.67
Benzene	21.8	0.006	0.8	1.3
Ethylbenzene	21.9	0.002	2.2	11.0

Note. The concentration of the saturated solution m_0 in molality was calculated by us.

Table 2. Thermodynamic and kinetic parameters for growth of urea crystals (25 °C).[21]

Solvent	m_0	ΔH_{cr}, kJ mol^{-1}	α_2	α_3		$10^6\beta_2$, mol cm^{-2} sec^{-1}	
				(100)	(011)	[100]	[001]
Propanol	0.52	27	7.9	3.3	5.0	0.43	1.3
Ethanol	1.04	20	5.9	3.2	4.7	0.26	3.6
Ethyleneglycol	7.45	12	3.6	2.4	3.5	0.38	0.89
N-Methylformamide	7.45	11	2.9	2.4	3.6	1.5	3.5
Formamide	8.79	10	3.2	2.4	3.6	0.70	8.2
Water	20.0	12	3.2	2.4	3.7	43	140

The same was observed for growth rates of individual faces of stearic acid crystals in hexane, decane, dodecane and octane.[18,19] The crystallisation of *para*-xylene (Table 1), which was studied in connection with the problem of separating the precipitate from the mother liquor, and urea (Table 2) can also be used as examples. The kinetic coefficient β appears in both tables as a parameter characterising the growth rate. In the first instance, it is calculated by us from original data presented in Table 1 using the equation $\beta = V/\sigma$. In other words, it is assumed that the growth rate is linearly dependent on the supersaturation. In fact, this function is nonlinear and β is therefore somewhat high. In the second instance, β was determined using the equation $\beta = V/(\sigma - \sigma_{cr})$, where σ is the total supersaturation of the solution and σ_{cr} is the critical supersaturation within which the face does not grow. The quantity σ_{cr} is unique for different solutions. It is zero for aqueous and formamide solutions of urea. The quantity α (Table 2) is discussed below.

In general, the correlation between the crystal growth rate and the solubility is considered to be firmly established although there are exceptions. For example, an inverse dependence is observed for the growth rate of stearic acid crystals from butanone and octane-2-one solutions (Table 3). It is noteworthy that the described feature contradicts the old Van't Hoff rule,[25,26] according to which the rate constant is inversely proportional to the solubility of the reagents.

Table 3. Data for growth of *B*- and *C*-modifications of stearic acid crystals.[22–24]

Solvent	m_0 (25 °C)	ΔH_{cy}, kJ mol^{-1} (25 °C)		V, rel. units		$E^{\neq}$, kJ mol^{-1}	
		B	*C*	*B*	*C*	*B*	*C*
Butanone	0.16	78	74	2.4	2.9	180	105
Octane-2-one	0.37	72	67	1	1	110	73

Note. The activation energy $E^{\neq}$ for growth in butanone solution is found for the (110) face at 13–25 °C; from octane-2-one solution, 16–29 °C. The solubility in molality is calculated by us using previous data.[22,24]

The features of crystal growth from various solvents were analysed using the so-called "entropy factor" (α-factor, Jackson–Temkin factor, roughness factor or parameter),[1,27–30] which was first introduced to analyse growth of crystals from the melt. Small α-factors indicate small differences between the bond energy of species in the crystal and that of the same species with solvent or similar entropies for the crystal and dissolved substance. In other words, these α-factors reflect the strong solvation of the crystal faces, characterised by a low interfacial surface tension. Hence, atomic species should add randomly at small α to the crystal surface at any point (so-called "normal" or "continuous" crystal growth). As a result, the face should be "atomically rough". It is noteworthy that the term "atomically rough" has two meanings. These are the morphological one, as here, and the energetic one. In the second instance, the atomic roughness is the source of normal growth and not its consequence.

For certain intermediate α values, where the surface tension of a face and, consequently, the end of an atomic layer on it, is comparatively small, layered growth of an ideal (defect-free) face is possible owing to formation on it of two-dimensional nuclei even at low supersaturations. Further increasing α should indicate the necessity of large supersaturations for two-dimensional nucleation. At low supersaturations at these α values, the ideal face should not grow at all. At relatively high α values (large surface tension), layered growth is possible that is caused only by dislocations in the crystals. Dislocational growth becomes more significant as α increases. In other words, higher α values indicate that the face is atomically smooth.

The difference between an atomically rough surface and an atomically smooth (singular) one is illustrated in Fig. 1, in which free-energy activation barriers to transfer of an atomic species from solution onto the crystal and its migration along the face are presented for both instances. The barrier (solid line) to direct transfer into the crystal, characterised by the quantity of $\Delta\overleftarrow{G}_0^{\neq}$, is also shown in Fig. 1. This barrier is higher than the previous one since it is accompanied by more extensive desolvation. All points on an atomically rough surface are equivalent for adding atoms to it. They have identical energies for adding atoms to kinks in a step on the crystal surface. The dashed line in Fig. 1*b* outlines the barrier to diffusion along an atomically rough surface, which is also rather high compared with an atomically smooth surface. There should be intermediate instances since it is assumed that the contribution from the normal growth mechanism can vary.

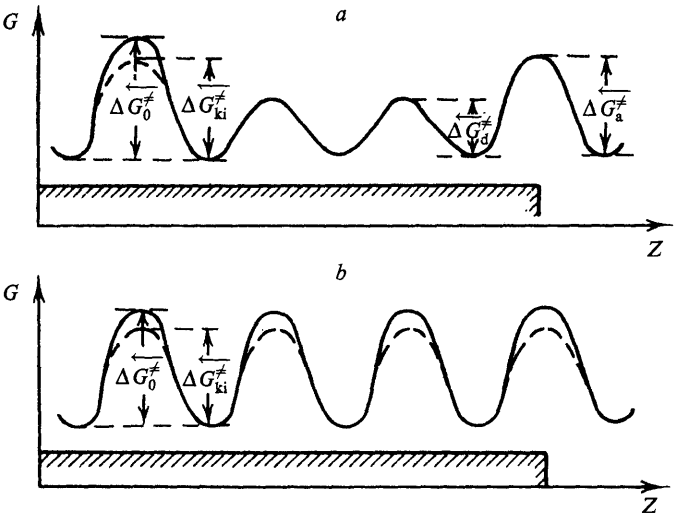


Figure 1. Free energy as a function of position of an atomic particle on a crystal surface (the crystal surface is hatched): an atomically smooth face (α ≳ 3) (*a*) and an atomically rough face (α ≲ 3) (*b*). The quantity *z* is the reaction coordinate, $\Delta\overleftarrow{G}_a^{\neq}$ is the free energy of activation for transferring particles from solution into the adsorbed layer on the face (this transfer is accompanied by incomplete desolvation of the crystallising particles), $\Delta\overleftarrow{G}_d^{\neq}$ is the activation energy for surface diffusion of adatoms, $\Delta\overleftarrow{G}_{ki}^{\neq}$ is the activation energy for transfer from the adsorbed layer on a face into a kink on a step accompanied by further partial desolvation (the corresponding barrier is shown as a dashed line).

Thus, a phase transition characterised by low α values should have a high growth rate with a linear dependence on supersaturation and poorly facetted, more or less isometric crystals. Increased growth rates for the normal mechanism are the result of a high density of growth sites on the crystal surface. Crystallisation at high α values should be accompanied by the nonlinear dependences of the growth rate on supersaturation that are typical of layered growth and formation of well formed crystals with a more distinct anisometry than for normal growth, according to the structure of a given crystal. The correlation between α and the crystal-growth features are well observed for melts.

Computer modelling demonstrated (see also previous theoretical estimates[31]) that surface roughness, normal growth and a linear dependence of rate on supersaturation occur for α less than a critical $\alpha_{cr} \approx 2.5$ (Ref. 1) or 3 (Ref. 28). For the range $2.5 \lesssim \alpha \simeq 4$ (Ref. 1) [according to other estimates from 3 to 5 (Ref. 28)], two-dimensional nuclei form comparatively easily and the dependence of growth rate on supersaturation begins to acquire a nonlinear nature. At larger α in a relatively broad range of supersaturations, growth is possible only if dislocations are present and the faces are atomically smooth. These results were obtained by modelling a Kossel crystal (a crystal consisting of closest packed cubes) and considering interactions only between nearest neighbours. For actual crystals differing in structure, types of chemical bonds and shapes of the species comprising them, α values indicating one crystallisation mechanism or another possibly will greatly vary.

The following equations are proposed for calculating α for solutions

$$\alpha_1 = \zeta \frac{\Delta H_{cy}}{RT_{cy}} = \zeta \frac{\Delta S_{cy}}{R}, \quad (1)$$

$$\alpha_2 = \frac{4\gamma_{1a}}{RT_{cy}}, \quad (2)$$

$$\alpha_3 = \zeta \left(\frac{\Delta H_f}{RT_f} - \ln x \right). \quad (3)$$

Here ζ is the crystallographic anisotropy factor that depends on the actual face (ratio of bond energy of the crystal building block within an atomic layer parallel to the given face to the total bond energy or, to a first approximation, the ratio of the number of nearest neighbours in an atomic layer to the coordination number), ΔH_{cy} is the heat of crystallisation, ΔS_{cy} is the entropy of crystallisation, γ_{1a} is the surface tension of an end of an atomic layer on the given crystal face, ΔH_f is the heat of fusion, T_{cy} is the crystallisation temperature, and T_f is the melting point (m.p.). The quantity x has been given different meanings in various studies.[15,17,28] At present, solubilities of substances in mole fractions are preferred for x.

Calculations of α using Eqn. (1) have been shown to be unreliable[1] although this expression is used with ΔH_f and ΔS_f for melts. It is well known that the heat and, therefore, the entropy of crystallisation sometimes have negative values. This makes calculation of α using Eqn. (1) meaningless. Unjustifiably small α are obtained for athermal solutions that have low ΔH_{cy} although they are far from ideal. Furthermore, Eqn. (1) does not consider the individual solvation of different faces. A calculation using Eqn. (1) and ΔS_{cr} for growth of urotropine crystals from aqueous solution (apparently ignoring the sign of ΔS_{cy} since the heat of crystallisation of urotropine from aqueous solution is negative) gave $\alpha = 0.9$.[27] This should indicate that poorly facetted crystals grow. However, urotropine crystals from aqueous solution form typical regular rhombododecahedra and usually capture inclusions of solution. This is characteristic of growth under conditions of "diffusional depletion" (but not of normal growth). Eqn. (1) is not used much anymore. However, the correlation between the growth rate and heat of crystallisation cannot be invalidated (see Table 2), although there may be extenuating circumstances.

Eqn. (2) has previously been applied.[21,27,32,33] Calculations for urotropine using Eqn. (2) and surface tension values of the surface γ_s obtained from the kinetic data for crystal nucleation with subsequent conversion to γ_{1a} gives $\alpha = 0.1$.[27]

Thus, urotropine crystals from aqueous solution should be poorly facetted and rounded according to these calculations. This contrasts with their actual shape. The quantity γ_{1a} for Rochelle salt ($\alpha = 5.2$, well facetted crystal) was calculated[32] on the basis of the empirical correlation between γ_s and ΔH_{cy} known from the literature. The quantity γ_{1a} was analogously determined for urea crystals.[21] The α values (see Table 2) agree with the regular shape of these crystals. This correlation is not accurate enough to calculate α. It loses meaning for solutions with $\Delta H_{cy} < 0$ and for athermal solutions. The quantity γ_{1a} for octogen crystals was calculated[33] on the basis of experimental stability data for supersaturated solutions. Such determinations give γ_s close to the true values. However, these are evidently not accurate enough to calculate γ_{1a}. Furthermore, if the crystal has complicated facetting and this method is used, averaged γ_s are obtained for the crystal as a whole and not for an actual face. For octogen crystals formed from dimethylsulphoxide solution, $\alpha = 0.26$. For such an α value, the crystals of this compound should grow by the normal mechanism, be poorly facetted, and have a linear dependence of rate on supersaturation. However, they were regularly shaped and the dependence of growth rate on supersaturation was distinctly nonlinear.[33]

For octogen in cyclohexane, the agreement of theory and experiment was satisfactory. Thus, $\alpha = 0.6$, the crystals are poorly facetted, and the growth rate depends linearly on supersaturation. According to the literature,[33] the process is diffusion limited, evidently, owing to the fast growth rates. The diffusion limit should be the reason for this linear dependence. However, the fact that the growth rates are fast should argue in favour of a normal mechanism.

The quantity γ_s was converted to γ_{1a} by assuming that the surface tensions of a face and an end of an atomic layer are identical.[27,33,1] This can be disputed by considering the differences in the number of dangling chemical bonds for the species located on the smooth face and on the end of an atomic layer. Furthermore, the symbol of a step end may not coincide with that of the given face if the crystal has complicated facetting. Even for the instance where the crystal has simple facetting, the symbol of the layer end may not correspond to the symbol of this shape (for example, the crystal is cubic and the layer is oriented along [110]). However, it is well known that the surface tension of a layer end depends on its orientation.

Eqn. (3) is used most. This apparently is due to the fact that calculations using it are the easiest. The calculations are contradictory. Obviously, this equation gives small α values for a given substance the greater its solubility. Since the solubility and growth rate are correlated, a systematic inverse correlation between α calculated using Eqn. (3) and the crystal growth rate is observed (an example can be found in Table 2). The two following examples concerning the relationship between α and the crystal shape are interesting.

The entropy factor for biphenyl crystals growing from CH_3OH and toluene solution were calculated using Eqn. (3) (Table 4). The α_{cr} values for different faces were also determined. As it turned out, the faces (001) and (110), for which $\alpha > \alpha_{cr}$, are planar. The face $(20\bar{1})$, for which $\alpha \lesssim \alpha_{cr}$, is rounded. The other two faces, which have comparatively high α_{cr}, are practically unobserved in the facetting. This is quite natural in view of their fast growth rates characteristic of a normal mechanism.

The second example involves crystallisation of naphthalene[34] from solutions in biphenyl and phenanthrene at the eutectic temperatures. It can be seen from Table 5 that the face (001) has the highest σ values. Thus, this face is planar and dominates in crystals at all studied supersaturations. The crystal is platelike along this face.

The smallest α are seen on (20$\bar{1}$). This face has the fastest growth rates and becomes rounded at $\Delta T > \Delta T_{cy}$. The face (110) has an intermediate α value. In biphenyl solution, the eutectic temperature of which is comparatively far from the m.p. of naphthalene, ΔT_{cy} for (110) is much greater than for (20$\bar{1}$). For crystallisation from the eutectic with phenanthrene, the temperature of which is close to the m.p. of naphthalene, ΔT_{cy} for both faces are similar (the approach of the crystallisation temperature to the m.p. neutralises the individual features of the different faces).

Table 4. The α-factor for biphenyl crystals at 30 °C.[15]

Face	CH_3OH	Toluene	α_{kp}
(001)	7.8	6.4	2.6
(110)	4.3	3.5	2.8
(20$\bar{1}$)	3.1	2.5	2.7
(11$\bar{1}$)	3.5	2.9	3.4
(110)	2.7	2.2	3.0

Table 5. Parameters for growth of naphthalene crystals from biphenyl (x = 0.44, 39.4 °C) and phenanthrene solutions (x= 0.98, 78.9 °C).[34]

Face	ζ	Biphenyl		Phenanthrene	
		α	ΔT_{cy}	α	ΔT_{cy}
(001)	0.820	5.78	–	5.13	–
(110)	0.409	2.94	1.1	2.62	0.3
(20$\bar{1}$)	0.380	2.74	0.3	2.43	0.2

The growth of naphthalene crystals has been studied in detail.[35] It was found that rounded surfaces growing by a normal mechanism are formed in solutions of those solvents that have benzene or similar rings in their structure (benzene, toluene, pyridine, etc.). Fully facetted crystals are formed in solutions of solvents that do not have aromatic rings or are elongated or spherical (hexane, CH_3OH, $CHCl_3$, etc.). Elwenspoek et al.[35] suggest that the solvent in the first instance forms an oriented ordered adsorption layer on the naphthalene crystal surface and that the surface tension of the crystals in these solvents is relatively low. In the second instance, there is no such ordered layer and the surface tension is relatively high.

Let us illustrate examples where the observations and calculations using Eqn. (3) do not agree. The dependence of growth rate on supersaturation for the triglycerides mentioned above that is found for CCl_4 solution is much more nonlinear than for glyceryltrioleate solution although α = 2.8 in CCl_4 and α = 4.5 in trioleate.[13] For succinic acid in water and in isopropanol (Table 6), $\alpha_{(010)} > \alpha_{(001)}$; however, $V_{(010)} > V_{(001)}$. The habit changes from platelike along (001) in water to prismatic along [100] in isopropanol. This is in no way predicted on the basis of the α values. These discrepancies between theory and experiment were explained for succinic acid[17,28] as the result of solvation by isopropanol of the ends of atomic steps on the crystal faces. However, this only means that Eqn. (3) is unsatisfactory for calculating α. All varieties of interactions of the compound with the solvent are taken into consideration in Eqn. (3) only through the solubility. The individual features of the solvation of the different faces are ignored. The correction coefficient in Eqn. (3) that reflects the individual interaction of actual solution species and has previously been given[36] is difficult to calculate in practice.

Table 6. Parameters of succinic acid crystallisation.[17]

Face	ζ	Water		Isopropanol	
		α	10^6V	α	10^6V
(010)	0.67	7.8	15	8.0	1.0
(001)	0.5	5.8	4.0	6.0	0.1

Note. The growth rate is in cm sec^{-1} at σ = 0.015.

The data described suggest that in general application of α to solutions is problematical. Eqn. (3) is interesting for calculating an approximate α. Eqn. (2) is most general although it is difficult to use in practice owing to the complexity of determining the surface tension of the end of an atomic layer. The conversion to a rough surface at certain small but finite γ_{st} has been confirmed.[36,37] This contradicts the common viewpoint[31] according to which a condition for the conversion to a rough surface is the reversion of γ_{st} to zero. Regardless of the end construction (degree of roughness), the atomic step is an interface. Therefore, γ_{st} cannot revert to zero.

The method for analysing crystallisation from solutions that depends on use of α is counterposed to the method[28] based on direct analysis of solvation of a face and that[9] based on an analysis of solvation and its relation to the activational barriers. Such contrast is unfounded in view of the auxiliary nature of α. Its significance is to indicate the features of a phase transition on a crystal surface. If both methods contradict each other, α is calculated using an inaccurate formula.

Direct determinations of the activation energy during crystallisation from various media are rare. It has been established that the increase of solubility and growth rate of hexatriacontane in the series decane–heptane–pentane is accompanied by a decrease of activation energy, which equals to 205, 146 and 121 kJ mol^{-1}, respectively.[28] The increased solubility of stearic acid crystals (see Table 3) is also accompanied by a decrease of activation energy and heat of crystallisation.

In general, the examples of normal growth of crystals from solutions are selective and include organic compounds at formation temperatures that differ little from the m.p. Facetted growth is characteristic for crystals in solution. Faces develop owing to expansion of layers on them. Therefore, features of crystallisation from solutions should be theoretically explained by first examining layered facetted growth.

III. Experimental data analysed within the framework of the layered growth mechanism

1. Kinetic equation for the phase transition of an individual atomic species.

The known equation from the activated-complex theory[25,26,38] is usually used to describe the elementary step of crystallisation:

$$V = 0.5\nu\kappa \exp\left(-\Delta G^{\neq}/RT\right)\Pi\alpha_i^{\nu_i}. \quad (4)$$

Here ν is a frequency factor, κ is a transition coefficient, $\Pi a_i^{\nu_i}$ is the product of the activities of the starting reagents taken to powers equal to the stoichiometry coefficients ν_i of the reactants, and $\Delta G^{\neq}$ is the free energy of activation. The factor 0.5 reflects the possibility that the activated complex can decompose in the forward and reverse directions. The quantity $\Delta G^{\neq}$ consists of two terms:

$$\Delta G^{\neq} = \Delta G_{st}^{\neq} + \Delta G_{solv.}^{\neq}. \quad (5)$$

Here $\Delta G_{st}^{\neq}$ is the standard free energy of activation, $\Delta G_{solv}^{\neq}$ is the solvation energy of the activated complex determined from the expression $\Delta G_{solv}^{\neq} = RT\ln\gamma^{\neq}$, and $\gamma^{\neq}$ is the activity coefficient of the activated complex.

The coefficient κ is invariably omitted in studies on crystal growth as is the factor 0.5. Concentrations are used instead of activities. The quantity $\gamma_{st}^{\neq}$ is also ignored. Thus, $\Delta G_{st}^{\neq}$ are used although this is not always noted. In other words, an ideal systems are examined. Such simplifications are inadmissable in analysing crystallisation from solutions. Evidently, $\Delta G_{st}^{\neq}$ at these temperatures and pressures is independent of solvent, supersaturation, and the presence of impurities. Therefore, there is no basis with such an approach to make any assumptions about a change of activation barrier under the influence of these factors.

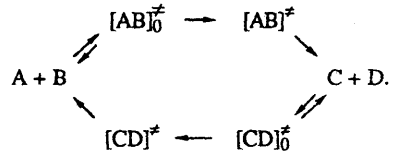
Activated-complex theory has often been criticised[39–43] (see also references in Ref. 26) mainly because the complex is postulated to be in thermodynamic equilibrium with the starting species. However, provisions are made for the further development even in the basic theory. It was noted that κ can substantially differ from unity for reactions in both gases (Ref. 25, p. 280) and in solutions (Ref. 25, p. 415). The necessity to differentiate the activated complex itself and the transition state has been pointed out (Ref. 25, pp 274–278). According to Glasstone et al.,[25] this is the reason that the transmission coefficient characterising the probability of a transfer through the activation barrier differs from unity. This idea was then further developed. According to Shakhparonov,[38] the formation of an activated complex does not imply its immediate decomposition. After it forms, there follows a fluctuating energy redistribution within it and formation of the transition state itself that ensures decomposition in the forward direction.

A detailed kinetic theory of chemical reactions in solutions that supplements the classical approach by taking into account the theory of fluctuations has been published.[38,44] The first question that arises is that of the correctness of using the Boltzmann equation, which is known to be valid only for systems with a rather large number of particles. The following considerations are relevant to this.

The activated complex during crystallisation from solutions includes the solvation sphere since the elementary step in solutions involves desolvation. The theory of fluctuations "often leads to good quantitative agreement with experiment" up to sizes of 10 nm. For smaller dimensions, it agrees qualitatively with experiment (Ref. 45, p. 129). The size of the activated complex including the solvation sphere apparently is of this order. Methods for estimating the sizes of such regions have been discussed.[40]

The refined kinetic equation for a phase transition of a separate atomic species during crystallisation from solutions is similar to that given before[38,44] for homogeneous chemical reactions in liquids. It is obtained as follows.

The chemical reaction is written in the form



Here $[AB]_0^{\neq}$ are the activated complexes in equilibrium with the starting compounds A and B, $[CD]_0^{\neq}$ are activated complexes in equilibrium with the reaction products C and D, and $[AB]^{\neq}$ and $[CD]^{\neq}$ are their respective transition states. The activated complexes in the transition state are not in thermodynamic equilibrium with other species. However, the transition states $[AB]^{\neq}$ and $[CD]^{\neq}$ are indistinguishable whereas $[AB]_0^{\neq}$ and $[CD]_0^{\neq}$ are distinguishable since they are not in thermodynamic equilibrium with each other.

The activated complex in the transition state, which includes the solvation sphere, is considered as a subsystem and the solution surrounding it, the system. According to the Boltzmann equation, the concentration of these subsystems is

$$m^{\neq} = m_0^{\neq}\exp\left(-\frac{\Delta G_{fl}^{\neq}}{RT}\right), \quad (6)$$

where $\Delta G_{fl}^{\neq}$ is the difference between the free energy of the system containing one mole of activated complexes in the transition state and its free energy in the absence of these complexes. Let us recall that this equation also forms the basis for the more expanded kinetic theory of nucleation.

The pre-exponential factor $m_0^{\neq}$ is equal to the concentration of the subsystems consisting of activated complexes for which $\Delta G_{fl}^{\neq} = 0$, i.e., in thermodynamic equilibrium with the starting compounds. The chemical potential of such complexes is

$$\mu^{\neq} = \mu_{st}^{\neq} + RT\ln\left(\gamma^{\neq}m^{\neq}\right), \quad (7)$$

where $\mu_{st}^{\neq}$ is the standard potential of the activated complexes.

Using Eqn. (7), $m_0^{\neq}$ can be expressed in terms of the activity of the starting components

$$m_0^{\neq} = K^{\neq}\frac{\Pi a_i^{\nu_i}}{\gamma^{\neq}};\ K^{\neq} = \exp\left(-\frac{\Delta G_{st}^{\neq}}{RT}\right), \quad (8)$$

where $K^{\neq}$ is the equilibrium constant of the activated complexes.

The rate of the elementary step of the reaction is determined by $V = 0.5\nu m^{\neq}$.

Substituting Eqn. (6) and taking into account Eqn. (8) we obtain

$$V = 0.5\nu\exp\left(-\frac{\Delta G_{fl}^{\neq}}{RT}\right)\exp\left(-\frac{\Delta G_{st}^{\neq}}{RT}\right)\frac{\Pi a_i^{\nu_i}}{\gamma_0^{\neq}}. \quad (9)$$

The quantity $0.5\exp(-\Delta G_{fl}^{\neq}/RT)$ can be treated as the coefficient κ. Methods for estimating it have been examined.[38] Possible methods for estimating $\gamma_0^{\neq}$, i.e. $\Delta G_{solv}^{\neq}$, have also been discussed.[46]

For this approach, the free energy of activation is

$$\Delta G^{\neq} = \Delta G_{st}^{\neq} + \Delta G_{solv}^{\neq} + \Delta G_{fl}^{\neq}. \quad (10)$$

Taking into account Eqn. (10), Eqn. (9) acquires the form

$$V = 0.5\nu\exp\left(-\frac{\Delta G^{*}}{RT}\right)\Pi a_i^{\nu_i}. \qquad (11)$$

This expression is of interest to us. It provides broad possibilities for analysing the effect on the rate of the solution composition (solution concentration, supersaturation, solvent). In a non-equilibrium process, the free energies of activation of the forward and reverse reactions are not equal: $\overrightarrow{\Delta G^{\neq}} \neq \overleftarrow{\Delta G^{\neq}}$. At equilibrium, $\overrightarrow{\Delta G_0^{\neq}} = \overleftarrow{\Delta G_0^{\neq}}$.

2. Rate equation for advance of an individual atomic step.

The rate of addition of atomic species to a step of monatomic height [mol (unit length)$^{-1}$ sec^{-1}] is defined on the basis of Eqn. (11) by

$$\vec{V}_{st} = 0.5\nu \sum_{i=1}^{3} \exp\left(-\frac{\overrightarrow{\Delta G_i^{\neq}}}{RT}\right) a_i a[M], \qquad (12)$$

where $\Delta G_i^{\neq}$ is the free energy of activation of the forward reaction for an atomic growth site i on the step and a_i is the activity of the corresponding site (mole fractions per unit length). The index of a site is 1,2,3 (isolated atom at the end of a step, an atom in a kink and at a smooth site). The index is simultaneously equal to the number of chemical bonds to nearest neighbours in the plane of the (100) face for a Kossel crystal. The variable a is the activity of the crystallising substance in solution (for simplicity, the formation of an unhydrated crystal in the absence of a chemical reaction was used). The quantity [M] is a coefficient introduced so that the dimensions of both parts of the equation are equal (omitted from here on).

It is assumed that the heights of the activation barriers $\overrightarrow{\Delta G_i^{\neq}}$ and the concentrations of different types of sites, i.e., a_i, do not change with a departure from equilibrium. Generally speaking, this is incorrect. However, this is not significant for finding the principal relations between the rate of advance of a step and the most important macroscopic parameters characterising it. Combining all quantities in Eqn. (12) except for a into a single rate coefficient for the forward reaction $\vec{k}_{st}$, we obtain

$$\vec{V}_{st} = \vec{k}_{st} a. \qquad (13)$$

It is also assumed that the removal rate of atoms from a step $\overleftarrow{V}_{st}$ is constant and equal at all supersaturations to the rate of the forward reaction at equilibrium:

$$\overleftarrow{V}_{st} = \vec{V}_{st} = \vec{k}_{st} a_0, \qquad (14)$$

where a_0 is the activity of a compound in the saturated solution.

For the step propagation rate V_{st} taking into account that $a/a_0 = \exp(\Delta\mu/RT)$, where $\Delta\mu$ is the difference of chemical potentials of the crystallising substance in the supersaturated and saturated solutions, we obtain

$$V_{st} = \vec{V}_{st} - \overleftarrow{V}_{st} = \overleftarrow{V}_{st}\left(\exp\frac{\Delta\mu}{RT} - 1\right). \qquad (15)$$

The rate of the reverse reaction $\overleftarrow{V}_{st}$ on the basis of Eqn. (11) is written

$$\overleftarrow{V}_{st} = 0.5\nu \sum_{i=1}^{3} \exp\left(-\frac{\overleftarrow{G_i^{\neq}}}{RT}\right) a_i, \qquad (16)$$

where $\overleftarrow{\Delta G_i^{\neq}}$ is the free energy of activation for removal of particles from i sites at equilibrium.

It follows from Eqn. (16) that the rate of the reverse reaction is determined by $\overleftarrow{\Delta G_i^{\neq}}$ and a_i. It is noteworthy that we are interested in crystal growth in a narrow range of supersaturation near equilibrium that corresponds to supersaturations greater than the saturation temperature by 1–3 °C. Such supersaturations are typical of bulk crystallisation and single-crystal growth. The change of thermodynamic driving force in this range of supersaturations does not exceed fractions of a kilojoule. Therefore, it is assumed to be insignificant compared with the expected activation barriers. The change of position of the upper point of the barriers should be close to that for the change of driving force. Thus, the activation barriers in the range of supersaturations usually used should be practically constant. The concentrations of various types of sites on a step and, consequently, a_i, change at the same supersaturations within narrow limits.[48] The assumption made above that the rate of the reverse reaction is constant are based on these considerations.

Let us express a_i and $\overleftarrow{\Delta G_i^{\neq}}$ for atoms at different positions on the step in terms of the corresponding value for atoms in a kink according to the scheme in Fig. 2.

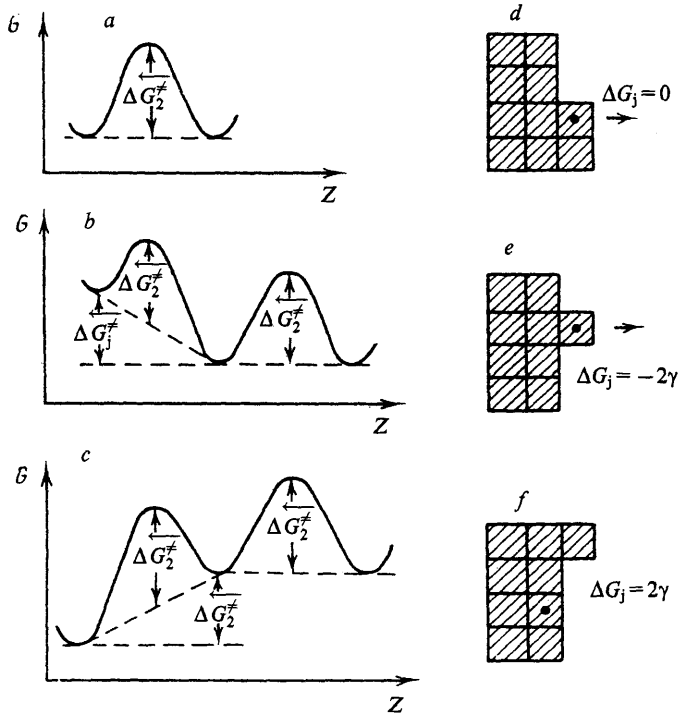


Figure 2. Free-energy activation barrier G (a–c) for transfer of atomic particles at different positions (d–f) from sites on a step into solution (from left to right).[47] The particles being removed are shown by dots.

The chemical potential of particles in solution at equilibrium μ_0 is equal to the chemical potential of particles located in a kink at the end of the step.[31] The chemical potential of an isolated particle on a step is 2γ greater than that of a particle in a kink (see Fig. 2) (γ is the specific free surface energy calculated per area of one atom at the end of a step). On the other hand, the chemical potential of a

particle at a smooth site is 2γ less than that of a particle in a kink since its removal will increase the surface energy of the step (i.e., the whole system) by 2γ. Thus,

$$\mu_{ki}(\mu_2)=\mu_0;\ \ \mu_1=\mu_{ki}+2\gamma;\ \ \mu_3=\mu_{ki}-2\gamma. \tag{17}$$

Setting the standard chemical potential of particles at all points of the step equal to the standard chemical potential of the compound in solution, we obtain from Eqn. (17)

$$a_2(a_{ki})=a_0;\ \ a_1=e^{2\gamma}a_2=e^{2\gamma}a_0;\ \ a_3=e^{-2\gamma}a_2=e^{-2\gamma}a_0. \tag{18}$$

It is noteworthy that a_i are related by the Gibbs–Duhem equation:

$$\sum_{i=1}^{3} x_i d\ln a_i = 0.$$

Here x_i are the concentrations of particles at different positions on the end of a step in fractions of the total number of sites:

$$\sum_{i=1}^{3} x_i = 1.$$

The quantities $\overleftarrow{\Delta G_i^{\neq}}$ are related as follows (see Fig. 2):

$$\overleftarrow{\Delta G_1^{\neq}}=\overleftarrow{\Delta G_2^{\neq}}-\gamma;\ \ \overleftarrow{\Delta G_3^{\neq}}=\overleftarrow{\Delta G_2^{\neq}}+\gamma. \tag{19}$$

Substituting Eqn. (16) into Eqn. (15), we obtain taking into account Eqns.(18) and (19):

$$V_{st}=0.5\exp\left(-\frac{\overleftarrow{\Delta G_2^{\neq}}}{RT}\right)a_0\left(2\cosh\frac{3\gamma_{st}}{RT}-1\right)\left(\exp\frac{\Delta\mu}{RT}-1\right). \tag{20}$$

The following points are noteworthy. According to Eqn. (20), the growth rate of a step should increase with increasing surface energy. At first glance, this seems paradoxical. However, it is just as paradoxical that the rate of advance of a step is greater the greater the rate of removal of particles from it according to Eqn. (15).

On going to nonequilibrium and increasing the supersaturation, the number of kinks and single atoms on the step increase.[48] Thus, the number of atomic particles belonging to the smooth parts of the step decreases. This means that the activities of the kinks a_2 and single particles a_1 increase whereas the activity of atomic particles at the smooth sites a_3 decreases. Thus, besides increasing the position of the free-energy minimum for particles in solution, the position of the minimum for various types of particles on the step increases or decreases (see Fig. 2). It can be assumed that the position of the minima for the latter changes to a lower value than for particles in solution. The position of the free-energy maxima (tops of the activation barriers) also changes with a change of supersaturation. However, it is not clear to what value it changes. There is no basis to think that they decrease by $\Delta\mu/2$ for the forward and increase by $\Delta\mu/2$ for the reverse reaction, as previously assumed.[47,49] These effects, as already noted above, are ignored here.

3. Rate equation for growth of a crystal face.

Dislocations, as a rule, are the source of growth layers on faces during formation of crystals from solutions. A two-dimensional nucleus can predominate only during growth of perfect crystals from carefully purified solutions. During crystallisation under ordinary conditions, it begins to contribute to growth of faces only at rather large supersaturations. The presence of dislocations ensures that steps are always present on a face, even where the crystal is in equilibrium with the medium. Therefore, the face growth rate is

$$V=V_{st}B, \tag{21}$$

where B is the total length of dislocation steps of atomic height per unit area of face at a given supersaturation.† Let us substitute Eqn. (20) into Eqn. (21) and find a linear approximation to Eqn. (21) near equilibrium (i.e. the first term in the expansion of the latter equation in a Maclaurin series):

$$V=0.5v\exp\left(-\frac{\overleftarrow{\Delta G_{ki}^{\neq}}}{RT}\right)B_0\left(2\cosh\frac{3\gamma_{st}}{RT}-1\right)a_0\sigma. \tag{22}$$

Here B_0 is the density of dislocation steps at equilibrium. The supersaturation is $\sigma\approx\Delta\mu/RT$. Introducing for simplification the parameter B_0, we obtain, according to Eqn. (22), an expression for the kinetic coefficient β, which determines the slope of the curve for the growth rate at zero coordinates:

$$\beta=\beta_0B_0\exp\left(-\frac{\overleftarrow{\Delta G_{ki}^{\neq}}}{RT}\right)\left(2\cosh\frac{3\gamma_{st}}{RT}+1\right). \tag{23}$$

The parameter β is calculated in practice (see Section II). According to the resulting equation, the solution composition affects the growth rate through B_0, the free energy of activation $\overleftarrow{\Delta G_{ki}^{\neq}}$ and the specific free surface energy of a step γ_{st}. The density of steps depends on the crystal imperfection, which in turn is determined by the impurities in solution. Two other quantities reflect the degree of solvation of crystallising particles and the solvation of the actual crystal face.

Thus, at large departures from equilibrium we have:

$$V=\beta\frac{\Delta\mu}{RT}\equiv\beta\frac{\Delta a}{a}\equiv\beta\sigma. \tag{24}$$

This means that if the driving force is represented as $\Delta\mu/RT$ (i.e., $\Delta a_0/a_0$ or σ), then the kinetic coefficient is equal to the rate of reverse reaction $\overleftarrow{V}$ at equilibrium [mol (unit area)$^{-1}$)]. If the driving force is represented as the difference of the activities, then

$$V=\overleftarrow{k}_0\Delta a, \tag{25}$$

where $\overleftarrow{k}_0$ is the rate constant of the forward reaction at equilibrium. Thus, $\beta=\overleftarrow{k}_0a_0$. Since a_0 = const regardless of the solvent, then β and $\overrightarrow{k}_0$ in all solutions for a single substance at a given temperature differ only by a constant factor.

The apparent Arrhenius activation energy of the reverse reaction is found as usual from the temperature dependence of β

$$\partial\ln\beta/\partial(1/T)=-\overleftarrow{E}^{*}/R. \tag{26}$$

The Arrhenius activation energy of the forward reaction is found from the temperature dependence of $\overrightarrow{k}_0$:

$$\partial\ln\overrightarrow{k}_0/\partial\ (1/T)=-\overrightarrow{E}^{*}/R. \tag{27}$$

The free energy of activation in Eqn. (23) is determined using the known equations

$$\overleftarrow{\Delta G_{ki}^{\neq}}=\Delta\overrightarrow{G}_{ki}^{\neq}=\overleftarrow{\Delta H_0^{\neq}}-T\Delta\overleftarrow{S}_0^{\neq}=\Delta\overrightarrow{H}_0^{\neq}-T\Delta\overrightarrow{S}_0^{\neq}, \tag{28}$$

where $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the enthalpy and entropy of activation for the forward and reverse reactions. The subscript

† The possibility that atomic and larger steps may be present on the crystal faces is ignored. They form through consolidation of atomic steps, like other cooperative effects arising between steps, owing to impurities and solvent diffusion. These factors are peripheral to our examination. Furthermore, these factors at small supersaturations have a comparatively weak effect on the growth of steps.

zero indicates that these quantities refer to equilibrium conditions. The activation energy $\vec{E}^{\neq}$ is evidently related to $\Delta H^{\neq}$; $\overleftarrow{E}^{\neq}$, to $\Delta H^{\neq}$.

The quantity B_0 should be practically constant if crystals of a given compound obtained under identical conditions are used as seeds to grow crystals from various solvents. This occurs because the dislocation density in them in all instances will be about the same. It is even better if the same crystals are used as seeds in the experiments, as was previously done.[21] Thus, the solvent effect can change only the parameters of $\Delta G^{\neq}$ and γ_{st}. These quantities are related to the enthalpy of crystallisation. Let us examine first the relation of $\Delta H^{\neq}$ to ΔH_{cy}.

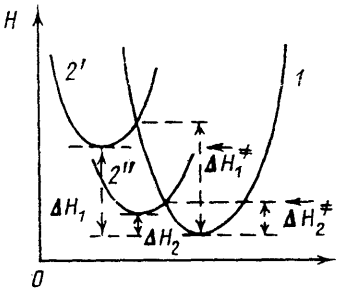


Figure 3. Enthalpy of a crystal–solution system as a function of coordinates of crystallising particles.

Suppose, in analogy with the previous potential curves,[46] that line *1* in Fig. 3 is the curve for the enthalpy change of the system after a position change of an atomic particle belonging to the crystal along the reaction coordinate z (calculated per mole of substance). Obviously, the minimum on this curve does not depend on solvent. Intermediate steps (position of the particle on a step on the face, adsorbed on the surface) are not considered. The line *2'* is the curve for the enthalpy change of the system after a position change of a dissolved particle in solvent 1; line *2''*, the same after a position change of a particle in solvent 2. The quantities ΔH_1 and ΔH_2 are the enthalpies of the phase transition in the first and second instances. The quantity $\Delta H_1 > \Delta H_2$. Therefore, the activation enthalpy of the reverse reaction is greater in the first instance than in the second. Thus, the heat of crystallisation and the enthalpy of activation of the forward reaction are directly correlated. In exactly the same way, the heat of the process and the enthalpy of activation of the forward reaction should be directly correlated since β and $\vec{k}_0$ are related by a constant factor. This means that the minimum on curve *2* in Fig. 3 must shift along the z axis on going from one solvent to another (the reaction radius changes). If the curve does not shift, then the activation energy of the forward and reverse reactions should change in opposite directions on going from one medium to another, which is impossible.

This theory was previously used[21] to explain the features described in Section II.

It is well known that an increase of the free energy of activation owing to an increase of the enthalpy of activation is usually accompanied by a decrease due to an increase of the entropy of activation (the so-called "compensation effect") since the change of the enthalpy and entropy of activation, as a rule, have the same sign. This was also confirmed for crystallisation.[50] However, the enthalpy of activation still plays the dominant role. Thus, there should be an inverse correlation between the heat of crystallisation and the growth rate. This is observed for urea (see Table 2). Furthermore, it is also possible that the entropy of activation (more accurately, the term $T\Delta S^{\neq}$) in Eqn. (28) changes more than the enthalpy of activation $\Delta H^{\neq}$. As a result, despite the decrease of activation energy, the crystal growth rate will decrease. It has been pointed out[26] that situations are also possible where the enthalpy and entropy of activation change differently.

The heat of crystallisation in solutions is determined using the known equation,[51] according to which, to a first approximation, $\Delta H_{cy} \sim m_0^{-1}$. This explains the direct correlation between the growth rate and the solubility of a given substance in the series of solvents described in Section II.

The specific surface free energy of crystals and their solubility are inversely correlated.[52] Thus, if the role of surface energy were to dominate over the effect of growth, then the increase of solubility would lead, in agreement with Eqn. (22), to a reduction of growth rate. However, as a rule, the opposite is experimentally observed. This means that the role of surface energy in the solvent effect on facetted growth of crystals is second-order compared with the role of activation barriers. Special instances ($\Delta H_{cy} < 0$) and isolated examples of a rate reduction with an increase of solubility require special investigations.

We emphasise that the described examination of the crystallisation is limited to layered dislocation growth. Its signature is the formation of well formed crystals with stable growth layers centered on the faces. The skeletal nature of the growth faces is not consistent with the normal mechanism and is only an indication of unequal diffusion of a substance to the faces (diffusional depletion due to a rate that is too fast). Rounding of the faces (antiskeletal growth) is not an unambiguous indication of the normal growth mechanism since it can be the result, like in the known example of KH_2PO_4 crystallisation, of layered growth that is hindered by trace impurities adsorbed on the faces.

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