Metastable Solution Thermodynamic Properties and Crystal Growth Kinetics

Soojin Kim and Allan S. Myerson*.

Department of Chemical Engineering, Polytechnic University, Six MetroTech Center, Brooklyn, New York 11201

The crystal growth rates of NH₄H₂PO₄, KH₂PO₄, (NH₄)₂SO₄, KAl(SO₄)₄·12H₂O, NaCl, and glucose and the nucleation rates of KBr, KCl, NaBr·2H₂O, (NH₄)₂Cl, and (NH₄)₂SO₄ were expressed in terms of the fundamental driving force of crystallization calculated from the activity of supersaturated solutions. The kinetic parameters were compared with those from the commonly used kinetic expression based on the concentration difference. From the viewpoint of thermodynamics, rate expressions based on the chemical potential difference provide accurate kinetic representation over a broad range of supersaturation. The rates estimated using a kinetic expression based on the concentration difference coincide with the true rates of crystallization only in the concentration range of low supersaturation and deviate from the true kinetics as the supersaturation increases.

Introduction

Crystallization is an important separation and purification process used in many areas such as the chemical, pharmaceutical, petrochemical, and electronics industries. The kinetics of crystallization is essential information required for the design of any crystallization equipment. Numerous experimental works investigating the kinetics of crystal growth and nucleation have been published in the literature. However, a standardized approach in correlating experimental results to the theoretical or semiempirical models to describe the kinetic processes has not been established. Consequently, estimating rates of crystallization from different expressions often leads to inconsistent results.

The driving force for crystallization is the degree of supersaturation which has been commonly expressed, for the sake of convenience, as the difference in concentration between the supersaturated and saturated solutions. This practice of expressing the crystallization rate as a function of the concentration difference causes confusion and inconsistency: even dimensionless supersaturations calculated from different concentration units result in different numerical values that are not proportional to one another, and thus different sets of kinetic parameters could be evaluated from a given set of experimental data.

It is well-known that the fundamental driving force of crystallization is the difference between the chemical potential of the supersaturated solution and that of the solid crystal face, which can be used independently of units (Mullin and Söhnel, 1977). Using the concentration difference in place of the fundamental driving force of crystallization is based on the assumption that the solute activity coefficient of a supersaturated solution can be closely approximated by that of the saturated solution, which may cause serious errors in evaluating the true kinetics of crystallization.

Unfortunately, the kinetic expression using the fundamental driving force seldom has been used in crystallization practices, because there had been virtually no experimental data of activity in supersaturated solutions. Recently, efforts to study thermodynamic properties of supersaturated solutions have been carried out by a number of researchers utilizing an electrodynamic microparticle levitator (Cohen et al., 1987; Na, 1992; Cohen et al., 1994, 1995). Water activities of many aqueous supersaturated solutions have been measured using a single micron-sized solution droplet that is electrically levitated and continuously weighed as the concentration is increased by a slow evaporation of water. Since the activity of the supersaturated solutions can be computed from the water activity data using the Gibbs-Duhem relation; hence, we can establish a direct relationship between the chemical potential and the concentration of a supersaturated solution.

From this relationship, many kinetic data reported in the literature can now be expressed in terms of the chemical potential difference providing kinetic expressions of more exact and thermodynamically accurate form. The purpose of this paper is to investigate the effects of using the fundamental driving force in the expression of crystallization kinetics and to quantify the associated errors associated with the conventional use of concentration-based driving force on the actual rate of crystallization.

Theoretical Section

Driving Force for Crystallization. The fundamental driving force for crystallization can be expressed in dimensionless form:

\[ \frac{\mu - \mu^*}{RT} = \ln(a/a^*) \]

For electrolyte solutions, the driving force is expressed in terms of the mean ionic activity of the solute, \( \bar{a} \):

\[ \frac{\mu - \mu^*}{RT} = \zeta \ln \frac{a^+}{a^-} = \zeta \ln \left( \frac{y^+}{y^-} \frac{c}{c^*} \right) \]

where \( c \) is the concentration and \( y^+ \) is the corresponding mean ionic activity coefficient. The fundamental dimensionless driving force for an electrolyte solution is demonstrated to be the same whether the salt dissolves partially or totally in solution (Söhnel and Mullin, 1978). For solutions of hydrate salts, the term \( \mu - \mu^* \) refers to the chemical potential difference between a hydrate in supersaturated and saturated solution, respectively, even though the existence of a hydrate solution may be only hypothetical (Söhnel and Mullin, 1978).
The use of the dimensionless concentration difference
\[ \sigma = (c - c^*)/c^* \]  
(3)
as the driving force in place of \( \Delta \mu/RT \) is justified only in the case that meets the following conditions: (i) \( \gamma_x \approx \gamma_x^* \), thus \( \ln(a_x/a_x^*) \approx \ln(c/c^*) \); (ii) \( \sigma < 1 \), thus \( \ln(\sigma + 1) \approx \sigma \), and (iii) \( \nu = 1 \).

Condition i will be satisfied only for an ideal solution or for a solution whose supersaturation is small enough so that its concentration is almost the same as that of the saturated solution. There are many circumstances in crystallization practices in which a high supersaturation level (\( \sigma > 0.1 \), for example) is encountered and thus condition ii is violated. Examples are primary nucleation and precipitation processes where relatively insoluble materials are produced as a result of reaction. Condition iii will be met for only nondissociating salts and hence is inapplicable for electrolytes. Therefore, using \( \sigma \) in place of \( \Delta \mu/RT \) is an approximation that is inadequate in a number of practical situations.

**Solute Activity.** Solute activity is computed from experimental water activity data as a function of concentration. Through the Gibbs–Duhem equation relating the chemical potentials of solvent and solute at constant temperature and pressure, the water activity can be expressed in terms of solute concentration, \( m \) in molality, for example (Robinson and Stokes, 1959):
\[ -(1000/MW_w) \frac{d(\ln a_w)}{\nu} = v_m \frac{d(\ln (\gamma_1 m))}{\nu} \]
(4)
upon integration of which we get the relation:
\[ \ln(\gamma_1/y_1^*) = \phi - \phi^* + \int_{m^*}^{m} \frac{\phi - 1}{m} dm \]
(5)
where \( \phi \), the osmotic coefficient, is defined as
\[ \phi = -\frac{1000 \ln a_w}{MW_w v_m} \]

Therefore,
\[ \ln(a_x/a_x^*) = \ln(m/m^*) + \phi - \phi^* + \int_{m^*}^{m} \frac{\phi - 1}{m} dm \]
(6)

**Crystallization Kinetics. a. Power Law Expression.** For correlation purposes, a simple semiempirical power law equation of the form
\[ G = k\sigma^n \]
(7)
has been used frequently for the expression of surface integration rate of crystal growth and nucleation rate. The kinetic expression in terms of the fundamental dimensionless driving force, as shown in eq 2, is:
\[ G = k' \left( \frac{\Delta \mu}{RT} \right)^n = k' (\nu \ln(a_x/a_x^*)^n) = k' (\nu \ln(\gamma_x/y_x^* m^*)^n) \]
(8)

The kinetic orders \( n \) and \( n' \) would be the same only in the concentration range of very low supersaturations, where \( \gamma_x/y_x^* \approx 1 \) and \( \ln(\sigma + 1) \) can be approximated as \( \sigma \). The difference between experimentally obtained \( n \) and \( n' \) will be greater for the data of a kinetic experiment conducted at a higher supersaturation range. Thermodynamically, the surface integration rate of crystal growth is determined by the constant power of the fundamental driving force; therefore, true kinetics of crystallization can be described by eq 8 only. The kinetic expression (eq 7) based on constant parameters, \( k \) and \( n \), is applicable only in the restricted range of \( \sigma \) in which the experimental data were obtained to determine the parameters and cannot be used for the prediction of crystallization rates over a broader range of concentration.

The power law correlation, eq 8, is used here to represent the process occurring at the crystal surface only. Therefore, the validity of the equation is limited by the assumption that the solute concentration at the crystal surface is equal to the bulk concentration especially at high supersaturation where the effect of the mass transfer diffusion resistance is relatively large.

**b. Boundary Layer Diffusion Model.** The overall rate of crystal growth determined both by the mass-transfer rate of solute diffusion and by surface integration to the crystal lattice has been described in terms of the concentration-based driving forces:
\[ R_g = k_d (c/c^*)^{n} \]
(9)
where \( c_i \) is the interface concentration and can be eliminated to give
\[ R_g = k_i (c/c^*)^{n} \]
(10)
which is often numerically evaluated. Equations 9 and 10 are valid only in a narrow range of concentration. Thermodynamically exact overall growth rate can be written as:
\[ R_g = k_d (\mu - \mu_i) = k_i (\mu - \mu_i) \]
(11)
or
\[ R_g = k_d (c/c^*)^{n} \]
(12)
where \( \mu_i \) is the chemical potential at the interface. Anosovically to eq 10, the overall growth rate, \( R_g \), can be evaluated numerically by eliminating the interface solute activity, \( a_i \). This overall growth rate, \( R_g \), expressed as a function of the chemical potential difference, presents the true kinetics of growth over a wide range of concentration.

**Results and Discussion**

**Kinetics of Crystal Growth. a. Surface Integration Kinetics.** Experimental data of the crystal growth rates of \( \text{NH}_4\text{H}_2\text{PO}_4 \), \( \text{KH}_2\text{PO}_4 \), \( \text{NH}_4\text{SO}_4 \), \( \text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O} \), and \( \text{NaCl} \) at 25 °C and of glycine at 20 °C are reported in the literature (Mullin and Amatavivadhana, 1967a,b; Mullin et al., 1970; Mullin and Garside, 1967; Rumford and Bain, 1960; Li and Rodriguez-Hornedo, 1992). These authors had conducted the kinetic experiments using fairly high solution velocity in order to eliminate diffusional mass-transfer resistance and thus to measure the surface integration rates. First, the supersaturation data expressed in various units in different papers were converted to be in a consistent unit of molality (mol of solute/kg of water or mol of hydrate/kg of "free" water). The data of growth rates were converted to contain the unit of kg of crystal/m² of surface area/s.

The water activity data of \( \text{NaCl} \), \( \text{NH}_4\text{SO}_4 \), and glycine solutions reported by Cohen et al. (1987) and
Table 1. Coefficients of $a_n(m)$ from the Polynomial $a_n = a_0 + a_1m + a_2m^2 + \ldots + a_n(m)$ at 20–25 °C

<table>
<thead>
<tr>
<th>Salt</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$a_6$</th>
<th>$m$ range of validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$H$_2$PO$_4$</td>
<td>1.0726 (10$^{-2}$)</td>
<td>3.061 (10$^{-2}$)</td>
<td>4.0 (10$^{-2}$)</td>
<td>1.629 (10$^{-2}$)</td>
<td>2.627 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>3.4–60</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>0.9777 (10$^{-2}$)</td>
<td>1.762 (10$^{-2}$)</td>
<td>-2 (10$^{-2}$)</td>
<td>-2.128 (10$^{-2}$)</td>
<td>1.669 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>1.6–20</td>
</tr>
<tr>
<td>KAl(SO$_4$)$_2$-12H$_2$O</td>
<td>0.900 (10$^{-2}$)</td>
<td>2.076 (10$^{-2}$)</td>
<td>-2.786 (10$^{-2}$)</td>
<td>1.757 (10$^{-2}$)</td>
<td>0.97 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.2–20</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>0.9988 (10$^{-2}$)</td>
<td>2.969 (10$^{-2}$)</td>
<td>-2.244 (10$^{-2}$)</td>
<td>3.571 (10$^{-2}$)</td>
<td>5.871 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.1–18</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.998 (4.933 (10$^{-2}$)</td>
<td>8.876 (10$^{-2}$)</td>
<td>-2.157 (10$^{-2}$)</td>
<td>1.617 (10$^{-2}$)</td>
<td>1.49 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.5–14</td>
</tr>
<tr>
<td>glycine</td>
<td>0.9898 (3.081 (10$^{-2}$)</td>
<td>4.823 (10$^{-2}$)</td>
<td>-4.006 (10$^{-2}$)</td>
<td>1.629 (10$^{-2}$)</td>
<td>2.527 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.5–15</td>
</tr>
<tr>
<td>KBr</td>
<td>1.0008 (3.531 (10$^{-2}$)</td>
<td>4.890 (10$^{-2}$)</td>
<td>-6.729 (10$^{-2}$)</td>
<td>5.318 (10$^{-2}$)</td>
<td>9.040 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.1–15</td>
</tr>
<tr>
<td>KCl</td>
<td>0.9975 (2.173 (10$^{-2}$)</td>
<td>4.153 (10$^{-2}$)</td>
<td>-2.153 (10$^{-2}$)</td>
<td>4.253 (10$^{-2}$)</td>
<td>-7.780 (10$^{-2}$)</td>
<td>6.203 (10$^{-2}$)</td>
<td>-1.764 (10$^{-2}$)</td>
<td>0.1–13</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.9968 (2.511 (10$^{-2}$)</td>
<td>-1.599 (10$^{-2}$)</td>
<td>1.365 (10$^{-2}$)</td>
<td>-2.317 (10$^{-2}$)</td>
<td>-1.13 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.1–22</td>
</tr>
<tr>
<td>NaBr(2)H$_2$O</td>
<td>0.9996 (3.116 (10$^{-2}$)</td>
<td>-2.112 (10$^{-2}$)</td>
<td>9.347 (10$^{-2}$)</td>
<td>2.000 (10$^{-2}$)</td>
<td>-5.47 (10$^{-2}$)</td>
<td></td>
<td></td>
<td>0.1–24</td>
</tr>
</tbody>
</table>

* Selected data from Cohen et al., 1987; Na, 1994; and Chiou, 1994. b The molality $m$ is based on the hydrate mol/kg of free water.

The molality $m$ is based on the anhydrous mol/kg of total water.

Figure 1. Mean ionic solute activity coefficient ratio versus dimensionless supersaturation (molality-based).

Na (1993) were used to calculate the solute activity as a function of concentration. Additional measurements of the water activity for supersaturated NH$_4$H$_2$PO$_4$, KH$_2$PO$_4$, and KAl(SO$_4$)$_2$-12H$_2$O solutions were carried out in our laboratory using the spherical void electrodynamic levitator trap. Details of the experiments can be found elsewhere (Na, 1993). The water activity expressed as a polynomial function of molality (listed in Table 1) was used in the numerical calculation of eq 5 to acquire the activity coefficient ratio as a function of concentration.

The calculated ratio, $\gamma_x/\gamma^*$, is plotted as a function of dimensionless supersaturation, $\sigma$ (molality-based), in Figure 1. The ratio remains very close to unity up to the supersaturation degree of $\sigma = 0.01$, as $\sigma$ increases, the activity coefficient deviates either positively (for NaCl, KAl(SO$_4$)$_2$-12H$_2$O, glycine) or negatively (for NH$_4$H$_2$PO$_4$, KBr, KCl, glycine) from that of the saturated solution. The biggest deviation of the activity coefficient is found for solutions of NaCl and KAl(SO$_4$)$_2$-12H$_2$O and the least deviation for (NH$_4$)$_2$SO$_4$.

Figure 2 shows the calculated fundamental driving force, $\Delta\mu/RT (= \nu \ln(a_1/a^n))$, as a function of $\sigma$. The big differences between $\Delta\mu/RT$ and $\sigma$ for KAl(SO$_4$)$_2$-12H$_2$O and NaCl are due to relatively large deviations of $\gamma_x$ from $\gamma^*$ and the values of $\nu$ ($\nu = 4$ for KAl(SO$_4$)$_2$-12H$_2$O, $\nu = 2$ for NaCl). For (NH$_4$)$_2$SO$_4$, which had a relatively small deviation of $\gamma_x/\gamma^*$ in all ranges of $\sigma$, the difference is mainly due to the value of $\nu = 3$. Although it is not apparent from the plots, all the curves have a linear section with slope $\nu$ in the region of $\sigma$ below 0.01. The leveling down curvature at high $\sigma$ (above 0.5) is due mainly to the fact that $\ln(\sigma + 1)$ becomes relatively smaller than $\sigma$ as $\sigma$ increases.

Figure 2. Fundamental driving forces calculated as functions of dimensionless supersaturation (molality-based).

Parts a–d of Figure 3 show the experimental data points of the growth rate versus $\sigma$ and versus $\Delta\mu/RT$. The kinetic parameters for the rate expressions of the forms in eqs 7 and 8 were determined from linear regressions of the logarithmic plots. The evaluated kinetic parameters are listed in Table 2. It should be noted that the kinetic parameters $k$ and $n$ are good only for the experimental range of $\sigma$ indicated in the table, whereas $k'$ and $n'$ are valid for all ranges of supersaturation. The values of $n$ and $n'$ are close for the data measured at the range of very low $\sigma$ (less than 0.01); in which the fundamental driving force and concentration driving force remain more or less proportional to each other. For example, the values of $n$ and $n'$ are almost identical for (NH$_4$)$_2$SO$_4$ (measure at $\sigma < 0.007$) and NaCl (measured at $\sigma < 0.004$). On the other hand, KAl(SO$_4$)$_2$-12H$_2$O (measured at $0.1 < \sigma < 0.2$) shows much different $n$ and $n'$.

The solid lines (extrapolated from the growth rate data with respect to $\Delta\mu/RT$ shown in Figure 3a) represent the true kinetics of crystal growth over a wide range of the driving force. The true rates of growth determined from the fundamental driving force were plotted against $\sigma$ (broken solid lines). These are the growth rates that would be measured in kinetic experiments conducted over a wide range of $\sigma$. The plots clearly show that different values of the kinetic parameters $k$ and $n$ would be obtained from experiments conducted at different ranges of supersaturation. The dotted lines, which were extrapolated from the growth rate range of very low $\sigma$.
rate data with respect to $\sigma$, are included only to illustrate the inadequacy of the rate expression based on $\sigma$ (eq 7).

In general, the order $n$ obtained from the experimental data of low $\sigma$ ($<0.01$) can be considered a close approximation of the true kinetic order $n'$. We are interested in how $n$ (determined from experiment) deviates from $n'$ as $\sigma$ increases. The true growth rate $G$ can be expressed as:

$$ G = k'(\Delta\mu/RT)^{n'} = k(\sigma) \sigma^{n(\sigma)} $$  \hspace{1cm} (13)
changing functions of \( \sigma \). Taking the logarithm of both sides produces:

\[
\log k' + n' \log(\Delta \mu/RT) = \log k(\sigma) + n(\sigma) \log \sigma \quad (14)
\]

Equation 14 indicates that \( d(\log(\Delta \mu/RT))/d(\log \sigma) \) is equal to the ratio of the kinetic orders, \( n(\sigma)/n' \). Therefore, in the logarithmic plots of \( \Delta \mu/RT \) versus \( \sigma \) (shown in Figure 4), slopes of the tangent lines at varying \( \sigma \) should be equal to \( n(\sigma)/n' \). It is easily seen from the figure that the plots have the tangent lines with slopes very close to unity when \( \sigma < 0.01 \), and the slopes decrease with increasing \( \sigma \). The ratio \( n(\sigma)/n' \) determined from the slopes with varying \( \sigma \) is plotted in Figure 5. In all of the crystallizing systems considered here, \( n(\sigma) \) is within 5% below \( n' \) in the range of \( \sigma \) below 0.1. As indicated in the figure, the range of \( \sigma \) at which \( n(\sigma)/n' < 0.9 \) can be considered as the concentration region where \( n(\sigma) \) significantly deviates from \( n' \).

b. Diffusion-Limited Crystallization. The overall growth rates of \( \text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O} \) measured by Mullin and Garside (1968) at 32 °C were investigated in terms of the fundamental driving force using the boundary

Figure 5. \( n(\sigma)/n' \) determined from the tangent lines of the plots in Figure 4 versus \( \sigma \).
Nomenclature

\( \sigma = \text{activity of solute} \)

\( \sigma_w = \text{activity of water in aqueous solution} \)

\( c = \text{concentration of solute in any unit} \)

\( c_i = \text{concentration of solute at the interface between the solution and the boundary layer} \)

\( G = \text{crystal growth rate (surface integration), kg/m}^2s \)

\( J = \text{crystal nucleation rate, kg/m}^3s \)

\( k = \text{crystallization rate constant, kg/m}^2s \)

\( k' = \text{crystallization rate constant with respect to } \Delta \mu/RT, \text{ kg/m}^2s \)

\( k_1 = \text{mass-transfer diffusion coefficient, kg/m}^2s \)

\( k_n = \text{nucleation rate constant, kg/m}^3s \)

\( k_n' = \text{nucleation rate constant with respect to } \Delta \mu/RT, \text{ kg/m}^3s \)

\( n = \text{order of crystal nucleation rate expression based on } \sigma \)

\( n' = \text{order of crystal growth rate expression based on } \sigma \)

\( \Delta \mu = \text{chemical potential difference between supersaturated and saturated solution, } J/\text{mol} \)

\( T = \text{temperature, K} \)

\( \phi = \text{osmotic coefficient} \)

\( \gamma = \text{mean ionic activity coefficient} \)

\( \mu = \text{chemical potential at the interface between the solution and the boundary layer, } J/\text{mol} \)

\( m = \text{molar concentration of solute, mol/kg of water} \)

\( m = \text{order of crystal nucleation rate expression based on } \Delta \mu/RT \)

\( M_W = \text{molecular weight of water, g/mol} \)

\( R = \text{gas constant, J/mol-K} \)

\( R_g = \text{overall rate of diffusion-limited crystal growth, kg/m}^2s \)

\( c_0 = \text{initial concentration of solute} \)

\( c_m = \text{mean concentration of solute} \)

\( c_{	ext{ss}} = \text{steady-state concentration of solute} \)

\( 

\text{Literature Cited} \)


Table 3. Kinetic Parameters of Nucleation of Various Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>range of ( \sigma ) measured</th>
<th>( G = k_\sigma \sigma^m ) order m</th>
<th>( G = k_n'(\Delta \mu/RT)^{n'} ) order n'</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>0.01–0.04</td>
<td>2.49</td>
<td>2.51</td>
</tr>
<tr>
<td>KCl</td>
<td>0.01–0.02</td>
<td>5.98</td>
<td>5.99</td>
</tr>
<tr>
<td>NaBr-2H2O</td>
<td>0.03–0.07</td>
<td>2.11</td>
<td>2.14</td>
</tr>
<tr>
<td>NH4Cl</td>
<td>0.01–0.02</td>
<td>4.57</td>
<td>4.61</td>
</tr>
<tr>
<td>(NH4)2SO</td>
<td>0.01–0.02</td>
<td>4.85</td>
<td>4.87</td>
</tr>
</tbody>
</table>


Received for review June 1, 1995
Revised manuscript received October 4, 1995
Accepted October 16, 1995