11.1 INTRODUCTORY COMMENTS

Crystallization is employed heavily as a separation process in the inorganic chemical industry, particularly where salts are recovered from aqueous media. In production of organic chemicals, crystallization is also used to recover product, to refine intermediate chemicals and to remove undesired salts. The feed to a crystallization system consists of a solution from which solute is crystallized (or precipitated) via one or more of a variety of processes. The solids are normally separated from the crystallizer liquid, washed, and discharged to downstream equipment for additional treatment. High recovery of refined solute is generally the desired design objective, although sometimes the crystalline product is a residue.

The process of forming a solid phase from solution is termed **crystallization**, and the operation occurs in a vessel called a **crystallizer**. A crystallizer provides residence time for the process streams to approach equilibrium, possibly a capability of selectively removing fines or coarse product, a mixing or contacting regime to give uniform crystal growth, and may include provision for addition or removal of heat.

Crystallization is distinguished from other unit operations in that a solid phase is generated. The solid phase is characterized in part by its inherent shape (habit) and size distribution. The natural habit of the solid phase is important since it influences product purity, yield, and capacity of the crystallizer system.

11.1-1 Advantages and Disadvantages

Crystallization offers the following advantages:

1. Pure product (solute) can be recovered in one separation stage. With care in design, product purity greater than 99.0% can be attained in a single stage of crystallization, separation, and washing.

2. A solid phase is formed that is subdivided into discrete particles. Generally, conditions are controlled so that the crystals have the desired physical form for direct packaging and sale.

The major disadvantages of crystallization are:

1. Purification of more than one component is not normally attainable in one stage.
2. The phase behavior of crystallizing systems prohibits full solute recovery in one stage; thus, the use of additional equipment to remove solute completely from the remaining crystallizer solution is necessary.

Since crystallization involves processing and handling of a solid phase, the operation is normally applied when no alternative separation technique is discernible. The choice of crystallization over, say, distillation as the preferred separation technique may hinge on one or more of the following considerations:

1. Solute is heat sensitive and/or a high boiler and decomposes at temperatures required to conduct distillation.
2. Low or nil relative volatility exists between solute and contaminants and/or azeotropes formed between solute and contaminants.
3. Solute (product) is desired in particulate form. For example, if solute can be purified via distillation then it must be solidified subsequently by flaking or prilling and crystallization may be a more convenient scheme to employ in such cases.
4. Comparative economics favor crystallization. If distillation requires high temperatures and energy usage, crystallization may offer economic incentives.

Crystallization is frequently the initial step in a solids processing sequence, similar to that shown in Fig. 11.1-1, that subsequently includes solid-liquid separation and drying equipment. Since product size

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**FIGURE 11.1-1** Solids processing sequence.
and suspended solids concentration are controlled, to a large extent, in the crystallizer, predictable and reliable crystallizer performance is essential for smooth operation of the downstream system.

### 11.1-2 Crystallization Terminology

**Binary eutectic.** The location on the phase diagram at which simultaneous crystallization of solvent and solute occurs.

**Brodie purifier.** A specific type of continuous melt crystallizer.

**Crystal habit.** The external crystal shape that results from different rates of growth of the various crystal faces.

**Crystallization kinetics.** Expressions that describe crystal growth and nucleation rates from solution.

**CSD.** Crystal size distribution.

**Desupersaturation time.** The average time that solution in a crystallizer vessel has to deposit solute before entering the zone where supersaturation is created.

**Draft tube.** A device inserted in a crystallizer to induce a uniform axial flow pattern inside a crystallizer.

**Drawdown time.** The time to empty the contents of a crystallizer if the feed is stopped and product is removed at the normal rate.

**DTB.** Draft tube baffle—a crystallizer that contains a draft tube and an internal baffle to provide a crystal settling zone.

**Elutriation leg.** A settling leg in a crystallizer that classifies and washes the crystals leaving the vessel by addition of upflow liquid (usually the feed).

**Fines removal system.** System designed to increase particle size by preferential removal and subsequent destruction of smaller-size crystals.

**Forced circulation crystallization.** Continuous crystallizer in which agitation inside the vessel is created by external circulation of large quantities of liquid through a heater or cooler.

**Heterogeneous nucleation.** Nucleation induced by foreign matter in a supersaturated liquid.

**Homogeneous nucleation.** Spontaneous nucleation caused by supersaturation only.

**ICT.** Initial crystallization temperature.

**Labile zone.** Zone on concentration–temperature diagram in which spontaneous homogeneous or heterogeneous nucleation of the solid phase will occur.

**Metastable zone.** Zone on concentration–temperature diagram in which homogeneous or heterogeneous nucleation will not immediately occur but in which crystal growth will occur.

**MSMPR.** Mixed-suspension mixed-product removal crystallizer.

**Population density.** A number density function frequently described as number of crystals per unit volume of clear liquor (or slurry) per size increment (number/cm$^3$-μm).

**Product classification.** Classification device that removes large product crystals and returns smaller crystals to the crystallizer.

**Secondary nucleation.** Nucleation of a supersaturated liquid caused directly or indirectly by the presence of crystals of the same species as the solute.

**Solid solution.** Mixed crystals formed when isomorphous substances crystallize together out of a solution.

**Supersaturation.** The departure from solution saturation usually caused by cooling of the mixture and/ or by evaporating solvent.

Understanding the concept of supersaturation is necessary when discussing crystallization rate processes. Most liquids sustain a certain level of subcooling depending on the rate of cooling, temperature, and degree of agitation. Often a clear solution can be slowly subcooled several degrees below its equilibrium temperature before a profusion of nuclei appear. A diagram describing this phenomena is shown in Fig. 11.1-2. Feed $A$ is cooled to temperature $T_D$. Thus, feed is subcooled by ($T_B - T_D$) degrees or has ($T_B - T_D$) degrees of supersaturation. The temperature where nuclei first appear ($T_C$), defines the metastable limit. Inside the temperature range from $T_C$ to $T_S$ crystals grow, but spontaneous nucleation will not occur immediately. In the labile zone (temperatures less than $T_C$) crystal growth and secondary nuclei formation occur simultaneously, and both rate processes are competing for available solute. Crystallizers are designed most commonly to control supersaturation at low levels to minimize nucleation, especially by homogeneous or heterogeneous mechanisms.

### 11.2 FUNDAMENTALS

Final design of a crystallizer is the culmination of the design strategy depicted in Fig. 11.2-1. In the conceptual design stage, equilibrium data and operating mode (the method by which supersaturation is
Supersaturated region
(Metastable zone)

Supersaturated region
(Labile zone)

Unsaturated zone

Temperature $T_D$, $T_C$, $T_B$, $T_A$

Concentration

Feed

FIGURE 11.1-2 Depiction of supersaturation. The metastable limit is a function of the rate of cooling, temperature, impurities, degree of agitation, and presence of seeds.

PHASE EQUILIBRIUM

{Solvent selection:
Physical and thermal properties}

OPERATIONAL MODE

{Pressure, temperature, composition}

STYLE OF CRYSTALLIZER

{Vapor rate, operating pressure,
slurry treatment, product size}

FUNCTIONAL DESIGN

{Diameter, holding time, materials,
auxiliary equipment, circulation rate}

FIGURE 11.2-1 Process design strategy.
generated) are surveyed. Solvent choice and processing conditions are determined in this step. The type of crystallizer and finally the crystallizer functional design, that is, external and internal construction details, are then established. The discussion in this section is concerned primarily with generation, interpretation, and use of solid–liquid equilibrium data and the selection of operating mode.

11.2-1 Equilibria

Accurate solid–liquid equilibrium data must be obtained to evaluate the process design options for crystallization processes. These data are required in the earliest stages of the conceptual design phase and are necessary for the following reasons:

1. Screening the feasibility of the potential process; that is, determining if pure solute can in fact be crystallized from the feed solution.
2. Determining the best solvent to use in the process if solution crystallization is employed.
3. Establishing the temperature and/or pressure ranges of the crystallizer operation and the composition of the residue liquor exiting the crystallizer.
4. Determining the maximum recovery of solute possible. The feed composition and position of the eutectic fix the maximum attainable solute recovery. Practical limitations such as temperature of cooling medium, slurry concentration that can be pumped, or impurity level that can be tolerated may restrict solute recovery.

Phase diagrams occur in many forms. A common type of diagram is the binary eutectic in which a pure solid component is formed by cooling an unsaturated solution until solids appear. Continued cooling will increase the yield of pure component. At the eutectic temperature both components solidify and additional purification is not normally possible. A typical eutectic-forming system (naphthalene–benzene) is shown in Fig. 11.2-2:

If mixture X is cooled, crystals of benzene will form.
If mixture Y is cooled, naphthalene crystals will result.
Point Z indicates the position of the binary eutectic. Solid mixtures are formed at temperatures below this point.

A few binary systems when cooled do not deposit one of the components in a totally pure state. Instead, behavior resembles that of many vapor–liquid systems and the solid is a true solution. Figure 11.2-3 depicts

![FIGURE 11.2-2 Phase diagram for naphthalene–benzene.](image)
a phase diagram of naphthalene and 2-naphthol, which exhibit solid solution behavior. If the liquid mixture of naphthalene and 2-naphthol of composition X is cooled, a mixed crystal of composition Y is formed rather than a solid containing pure 2-naphthol. This type of behavior is found in only a small fraction of crystallizing systems.

Figure 11.2-4 shows typical solubility diagrams for solutions of various salts in water. The curve for salt (NaCl) is nearly vertical, which indicates little effect of temperature on solubility. The sodium sulfate curve shows reverse solubility as temperature increases; thus, sodium sulfate has a tendency to coat heat-exchanger surfaces where heat is added to saturated solutions of this system.

Often solid–liquid equilibrium data are not available for the system of interest, and experimental determination of the solidus–liquidus curves is required. If the system of interest is simple (i.e., two to three components) and well behaved (ideal), then reliable predictive methods are available. Techniques for predicting nonideal solid–liquid phase behavior and multicomponent equilibria are emerging.

**Predicting Solid–Liquid Equilibria**

The extent to which solids can dissolve in liquids varies enormously; in some cases a solid solute may form a highly concentrated solution and in others the solubility is barely detectable. Some of the principles...
that govern equilibrium between a solid phase and a liquid phase are discussed in this section. In many situations reliable predictive techniques are available to estimate binary and multicomponent solubility behavior, and several of these approaches also are discussed.

**FRAMEWORK**

The fundamental relationship for equilibrium to exist between two phases (where the solute is designated by subscript 2) is

\[ f_2(\text{pure solid}) = f_2(\text{solute in solution}) \]  

or

\[ f_2(\text{pure solid}) = \gamma_2 x_2 f_2^* \]  

where \( f_2 \) is the fugacity, \( x_2 \) is the solubility (mole fraction) of the solute in the solvent, \( \gamma_2 \) is the liquid phase activity coefficient, and \( f_2^* \) is the reference-state fugacity to which \( \gamma_2 \) refers. The solubility can then be defined as

\[ x_2 = \frac{f_2}{\gamma_2 f_2^*} \]  

Thus, the solubility depends on the activity coefficient and the ratio of two fugacities. It is convenient to define the reference-state fugacity (of solute) as the fugacity of pure, subcooled liquid at the temperature of the solution. As derived elsewhere \(^1\) the pure fugacity ratio can be calculated from

\[ \ln \left( \frac{f_2(\text{pure solid})}{f_2^*(\text{pure subcooled liquid})} \right) = \frac{\Delta h_f}{RT} \left( \frac{T}{T_M} - 1 \right) \]  

where \( \Delta h_f \) is the enthalpy of fusion, \( T_M \) is the melting temperature of pure substance 2, and \( T \) is the system temperature. Correction terms associated with differences between the heat capacities of the liquid and solid are neglected.

If Eq. (11.2-4) is substituted into (11.2-3) the solubility relationship becomes

\[ \ln (\gamma_2 x_2) = \frac{\Delta h_f}{RT} \left( \frac{T}{T_M} - 1 \right) \]  

If the solution is assumed to be ideal, then \( \gamma_2 = 1.0 \) and Eq. (11.2-5) becomes

\[ \ln x_2 = \frac{\Delta h_f}{RT} \left( \frac{T}{T_M} - 1 \right) \]  

Equation (11.2-6) is often referred to as the van’t Hoff relationship. To use this equation to compute solute solubility for an ideal solution only the heat of fusion \( \Delta h_f \), and the pure-component melting temperature \( T_M \) are required. The interesting feature of this equation is that the solubility depends only on the properties of the solute and is independent of the nature of the solvent.

Another equation that is employed frequently for ideal systems uses cryoscopic constants that have been obtained empirically for a wide variety of materials in the American Petroleum Institute Research Project No. 44: \(^2\)

\[ \ln \frac{1}{x_2} = A(T_m - T)[1 + B(T_m - T) \cdots] \]  

where the cryoscopic constants \( A \) and \( B \) are defined by

\[ A = \frac{\Delta h_f}{RT_m^2} \quad \text{and} \quad B = \frac{1}{T_m} - \frac{\Delta C_p}{2 \Delta h_f} \]  

Freezing point curves were computed for para- and ortho-xylene using Eq. (11.2-6) (the van’t Hoff equation) and Eq. (11.2-7) which used cryoscopic constants. Data from Table 11.2-1 were used in the equations and calculated equilibrium compositions are shown as a function of temperature in Table 11.2-2. The computed liquid compositions are nearly identical in the high concentration range and diverge...
TABLE 11.2-1 Data Used for Freezing-Point Curve Calculations

<table>
<thead>
<tr>
<th>Data</th>
<th>p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{m}$</td>
<td>286.41 K</td>
<td>247.97 K</td>
</tr>
<tr>
<td>$\Delta h_f$</td>
<td>4090 cal/mol</td>
<td>3250 cal/mol</td>
</tr>
<tr>
<td>$A$</td>
<td>0.02599 mol frac/K</td>
<td>0.02659 mol frac/K</td>
</tr>
<tr>
<td>$B$</td>
<td>0.0028 mol frac/K</td>
<td>0.0030 mol frac/K</td>
</tr>
</tbody>
</table>

TABLE 11.2-2 Computed Freezing-Point Curves for o- and p-Xylene

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Mole Fraction in Solution</th>
<th></th>
<th>Temperature (K)</th>
<th>Mole Fraction in Solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eq. (11.2-8)</td>
<td>Eq. (11.2-9)</td>
<td></td>
<td>Eq. (11.2-8)</td>
<td>Eq. (11.2-9)</td>
</tr>
<tr>
<td>286.41</td>
<td>1.00</td>
<td>1.00</td>
<td>249.97</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>285.0</td>
<td>0.965</td>
<td>0.964</td>
<td>245.0</td>
<td>0.923</td>
<td>0.923</td>
</tr>
<tr>
<td>280.0</td>
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<td>0.844</td>
<td>240.0</td>
<td>0.803</td>
<td>0.805</td>
</tr>
<tr>
<td>270.0</td>
<td>0.646</td>
<td>0.640</td>
<td>235.0</td>
<td>0.695</td>
<td>0.699</td>
</tr>
<tr>
<td>260.0</td>
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</tr>
<tr>
<td>250.0</td>
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<td>0.172</td>
<td>0.183</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

slightly in the dilute regime. Figure 11.2-5 is a plot of freezing-point depression curves for mixtures of xylene isomers. The binary eutectic temperature for para and ortho isomers is about 236.3K. This is the temperature at which both components solidify together. Thus, the mole fraction of ortho-xylene in solution plus the mole fraction of para-xylene must equal 1 at the eutectic ($x_o + x_p = 1.0$). This condition also fixes the eutectic temperature for multicomponent systems. The ternary eutectic temperature for a mixture of xylene isomers is determined by finding the common freezing point at which the sum of the mole fractions of mixed isomers in solution equals 1 ($x_o + x_p + x_m = 1.0$). The eutectic conditions for the three xylene isomer binaries are indicated in Fig. 11.2-5. The ternary eutectic is also indicated.

FIGURE 11.2-5 Freezing-point depression curves for xylenes.
Determination of eutectic points is important since yield of a desired component is limited by the position of the eutectic. The above procedures give accurate predictions of eutectic points in ideal binary and multicomponent systems and are frequently sufficient for preliminary evaluation of a crystallization system. For the final design of a commercial system, experimental verification of the eutectic is advisable.

For nonideal systems a number of approaches are available. The method to use in a specific case may depend on the availability of thermodynamic parameters necessary to perform the specific calculation. Some of the methods are direct and others require iterative techniques best relegated to computers. Activity coefficients for solid-solubility calculations can often be estimated directly from vapor-liquid equilibrium data obtained at higher temperatures. Experimental vapor-liquid equilibrium data frequently are easier to find than solid-liquid equilibrium data; thus, this approach provides a convenient technique for conducting preliminary design calculations to determine the feasibility of a given process. Data are correlated using a semiempirical equation, such as the Wilson equation, whose characteristic binary parameters are extrapolated with respect to temperature. Muir and Howat\textsuperscript{3} have reported the results of using this technique for several ideal and nonideal systems and found good agreement with experimental data. Figures 11.2-6 and 11.2-7 compare predicted and experimental equilibrium data for acetic acid-water and caprolactam-water binaries. Agreement between predicted and experimental freezing points is good.

For nonpolar systems the activity coefficient can be estimated using the Hildebrand-Scatchard\textsuperscript{4} theory of regular solutions. To calculate the activity coefficient of a dissolved solute using regular solution theory, solubility parameters must be available for the components. For many materials these parameters can be calculated and/or are available in standard engineering references.
A group-contribution method, called UNIFAC, has been developed for estimating activity coefficients in nonelectrolyte solutions. By using this approach solubilities for several solutes in a variety of solvents may be calculated. In many cases good agreement is obtained. The activity coefficient consists of two parts, the combinatorial contribution, arising from differences in molecular size and shape, and the residual contribution, arising from differences in intermolecular forces of attraction. Group interaction parameters must be available to use this approach. Parameters are listed by Fredenslund et al. for many systems of interest.

Other approaches to the computation of solid–liquid equilibria are shown in Table 11.2-3. The Soave-Redlich-Kwong equation of state evaluates fugacities to calculate solid–liquid equilibria, while Wenzel and Schmidt developed a modified van der Waals equation of state for the representation of phase equilibria. The Wenzel-Schmidt approach generates fugacities, from which the authors developed a trial-and-error approach to compute solid–liquid equilibrium. Unno et al. recently presented a simplification of the solution of groups model (ASOG) that allows prediction of solution equilibrium from limited vapor–liquid equilibrium data.

Often complex liquid–solid equilibria cannot be predicted reliably, nor are data available in the literature. In this case, experimental determination of equilibrium behavior becomes necessary. Experimental data should be obtained at conditions that allow fitting by a model so that interpolation and extrapolation are possible.

The ASTM apparatus for determining freezing point is shown in Fig. 11.2-8. Freezing point is obtained from freezing or melting temperature versus time curves. Figure 11.2-9 shows a typical temperature-time trace from an ASTM apparatus. The freezing point can be determined from the peak of the temperature rise during slow cooldown or from the break in the temperature–time curve during heating. A DSC (differential scanning calorimeter) can be used for freezing-point determination (as well as heat of fusion) if subcooling is low. Inorganic systems usually are handled well in a DSC apparatus. If many components are present, an experimental freezing-point curve can be determined by fixing the temperature of a well-mixed slurry containing an excess of solids, allowing the system to equilibrate, and analyzing the composition of the liquid phase. By repeating this process at successively lower temperatures a freezing-point curve can be developed.

### 11.2-2 Choice of Operational Mode

The technique employed to generate supersaturation in a solution is referred to as the mode of operation. The mode chosen by the designer is strongly influenced by the phase-equilibrium characteristics of the system, and it dictates the material and energy balance requirements of the system. The common techniques for producing solids (or generating supersaturation) from a solution include:

1. Lowering the temperature of the feed solution by direct or indirect cooling. If solute solubility is strongly temperature dependent, this is the preferred approach.
2. Adding heat to the system to remove solvent and thus "salt out" the solute. This technique is effective if solubility is insensitive to temperature.
3. Vacuum cooling the feed solution without external heating. If solubility is strongly dependent on temperature, this method is attractive.
4. Combining techniques. Especially common is vacuum cooling supplemented by external heating for systems whose solubility has an intermediate dependence on temperature.
5. Adding nonsolvent. This is a common technique for precipitating solute from solution and is useful as both a laboratory technique and as an industrial process for product recovery.

The methods described above can be employed in single- or multistage crystallization or in batch operations. Multistage operations are employed where evaporative requirements exceed the capabilities of a single vessel and/or energy costs dictate staging of the operation. Sometimes, staging is useful to produce uniform and/or larger crystals. Operation of crystallizers in series generates crystal size distributions having a narrower size spread than the same volume of crystallizers in parallel. Crystal growth kinetics usually are favored at higher temperatures, so if the first stage of a two-stage crystallization system is operated at a higher temperature, the overall CSD is enhanced. Batch crystallizers produce a narrower CSD than continuous well-mixed units. For capacity requirements less than 500 kg/h, batch crystallization is often more economical. If highly uniform crystals are required, which is the case for sugar, then batch operation offers advantages. Table 11.2-4 compares the operational characteristics of several common modes of crystallization. Both advantages and disadvantages are indicated.

### 11.2-3 Crystallization Kinetics

The kinetic phenomena that influence crystal size distributions are nucleation and growth. The driving force for both these phenomena is supersaturation, and at some levels of supersaturation, both nucleation and growth occur and compete for available solute. The purpose of the present discussion is to summarize key
<table>
<thead>
<tr>
<th>System</th>
<th>Approach</th>
<th>Parameters Required</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ideal</td>
<td>van't Hoff equation</td>
<td>$\Delta h_f, T_M$</td>
<td>Prausnitz$^1$</td>
</tr>
<tr>
<td>2. Ideal</td>
<td>Cryoscopic constants</td>
<td>$A, B, T_M$</td>
<td>API Project No. 44$^2$</td>
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<tr>
<td>3. Nonideal</td>
<td>Compute $\gamma$-Wilson equation</td>
<td>Vapor-liquid equilibrium data</td>
<td>Muir and Howat$^3$</td>
</tr>
<tr>
<td>4. Nonideal</td>
<td>Compute $\gamma$-regular solution theory</td>
<td>Solubility parameters</td>
<td>Hildebrand and Scott$^4$</td>
</tr>
<tr>
<td>5. Nonideal</td>
<td>Compute $\gamma$-UNIFAC</td>
<td>Group interaction parameters</td>
<td>Gmehling et al.$^5$</td>
</tr>
<tr>
<td>6. Nonideal</td>
<td>Compute $\gamma$-groups model</td>
<td>Vapor-liquid equilibrium data</td>
<td>Unno et al.$^9$</td>
</tr>
<tr>
<td>7. Nonideal</td>
<td>Compute fugacity: modified van der Waals equation of state</td>
<td>Equation of state parameters</td>
<td>Wenzel and Schmidt$^8$</td>
</tr>
<tr>
<td>8. Nonideal</td>
<td>Compute fugacity: Soave-Redlich-Kwong equation of state</td>
<td>Vapor pressure, critical constants, acentric factors</td>
<td>Soave$^7$</td>
</tr>
</tbody>
</table>
aspects regarding the kinetics of crystal nucleation and growth and to indicate the process variables that are likely to affect each.

It is obvious that supersaturation is a key variable in setting nucleation and growth rates and, as will be shown in the following discussion, the dependence of these rates on supersaturation is affected by the mechanism through which the process is occurring. This is made plain in Fig. 11.2-10, which shows the influence of supersaturation on nucleation and growth. The key aspects in this figure are the qualitative relationships of the two forms of nucleation to growth and to each other: growth rate and secondary nucleation kinetics are low-order (shown as linear) functions of supersaturation, while primary nucleation

![Figure 11.2-9](image-url)  
**FIGURE 11.2-9** Typical temperature–time trace from freezing-point apparatus.

![Figure 11.2-8](image-url)  
**FIGURE 11.2-8** Apparatus for freezing-point determination.
Operational Characteristics: Feed enters at higher saturation temperature than is maintained in the crystallizer and is cooled in shell-and-tube or scraped-surface exchangers to remove sensible heat and heat of crystallization. Solids encrustation problems are generally confined to the cooling surfaces.

Advantages: Operation and control is simple. No vacuum equipment is necessary. Slurry density and product recovery are fixed by the feed composition and by the temperature maintained in the crystallizer body.

Disadvantages: Care must be taken to prevent fouling of the cooling surfaces by maintaining low process-to-coolant temperature differences across cooling surfaces. If severe fouling is anticipated, scraped-surface heat exchangers may be necessary to assure reliable operation.

Operational Characteristics: Feed enters at higher saturation temperature than is maintained in the crystallizer body. Crystallizer temperature, product recovery, and slurry density are regulated by vacuum control. Heat of crystallization and the sensible heat of the feed are removed by evaporation and condensation of solvent. The condensate may either be removed or a portion or all returned.

Advantages: No heater is required in this mode of operation, and condensate can be returned to wash down walls to control the formation of encrustations.
Disadvantages: Slurry concentration and product yield are fixed by material and energy balance constraints.

Mode 3. Cooling and Salting Out Crystallization

Operational Characteristics: The feed stream saturation temperature is higher than that maintained in the crystallizer body; thus, adiabatic cooling occurs. Also, external heat is added to evaporate solvent and precipitate additional solute.

Advantages: Slurry density and yield can be controlled to some degree by adjustment of external heat input.

Disadvantages: An external (or internal) heat exchanger and a vacuum system are required. Fouling at vapor release surfaces is common.

Mode 4. Salting Out Crystallization (Addition of Nonsolvent)

Operational Characteristics: Crystallizer temperature is controlled by vacuum level and ratio of nonsolvent to feed. A reflux condenser normally is used to remove heat by condensing the solvent.

Advantages: System is reliable to operate. Encrustations are minimized since heating and cooling surfaces are eliminated and vaporization is minimal.

Disadvantages: An additional component (nonsolvent) must be separated from all liquid streams and recycled. The technique is somewhat limited since the nonsolvent must be miscible in solvent.
Supersaturation

FIGURE 11.2-10 Influence of supersaturation on growth and nucleation rates.

is shown to follow a high-order dependence on supersaturation. Design of a crystallizer to produce a desired crystal size distribution requires kinetic data that quantify the relationships of nucleation and growth to externally controlled variables and to supersaturation. The following discussion necessarily is brief and simply outlines some of the major factors that influence nucleation and growth kinetics. More complete discussions of each phenomenon can be found in the references cited.

As with all kinetic phenomena, the first concept to understand is the driving force for the rate processes. While supersaturation was represented above as the driving force for nucleation and growth, no clear definition of this quantity was given. In fact, there are various ways in which the driving force or supersaturation can be defined:

1. The difference between the solute concentration and the concentration at equilibrium, $C - C^*$. 
2. The difference between the system temperature and the temperature at equilibrium, $T - T^*$. 
3. The ratio of the solute concentration and the equilibrium concentration, $C/C^*$. 
4. The ratio of the difference between the solute concentration and the equilibrium concentration to the equilibrium concentration, $s = (C - C^*)/C^*$. 

Garside\[11\] cites the analyses and restrictions which have led to the conclusion that the most appropriate driving force for crystal growth is that given by the fourth of the possibilities listed above, $s = (C - C^*)/C^*$. This definition of supersaturation will be used throughout the ensuing discussion. Garside also notes that when dealing with hydrated salts, concentration should not be based on the anhydrous solute.

NUCLEATION

In crystallization, nucleation is the formation of a solid phase from a liquid phase. The process differs from growth in that a new crystal results from the transfer of solute from the liquid to the solid; in growth, solid is deposited on an existing crystal. Because it is the phenomenon of crystal formation, nucleation sets the character of the crystallization process, and it is therefore the most critical component in relating crystallizer design and operation to crystal size distributions.

Mechanisms. Classical nucleation theory is based on homogeneous and heterogeneous mechanisms, both of which call for the formation of crystals through a process of sequentially combining the constituent units that form a crystal. These mechanisms are referred to as primary nucleation because existing crystals play no role in the nucleation. Both homogeneous and heterogeneous mechanisms require relatively high
supersaturations in order for them to occur and they exhibit a high-order dependence on supersaturation. These factors often lead to production of excessive fines in systems where primary nucleation mechanisms are important.

Mullin\textsuperscript{12} outlines the classical theoretical treatment of primary nucleation, which results in the expression

\[ B^* = A \exp \left( -\frac{16\pi \sigma v^2}{3kT^3 \ln (s + 1)^2} \right) \] (11.2-9)

where \( k \) is the Boltzmann constant, \( \sigma \) is surface energy per unit area, \( v \) is molar volume, and \( A \) is a constant. Note that this equation can be simplified by recognizing that \( s \) is often much less than 1, so that \( \ln (s + 1) \) approaches \( s \):

\[ B^* = A \exp \left( -\frac{16\pi \sigma v^2}{3kT^3 s^2} \right) \] (11.2-9a)

The most important variables affecting primary nucleation rates are shown by Eq. (11.2-9) to be interfacial energy \( \sigma \), temperature \( T \), and supersaturation \( s \). The high-order dependence of nucleation rate on supersaturation is especially important as a small variation in supersaturation may produce an enormous change in nucleation rate. This gives rise to the often observed phenomenon of having a clear liquor transformed into a slurry of very fine crystals with only a slight increase in supersaturation, for example, by decreasing the solution temperature. The catalytic effect of solid particles (as in heterogeneous nucleation) is to reduce the energy barrier to formation of a new phase. This, in effect, can reduce the interfacial energy \( \sigma \) by orders of magnitude.

An empirical approach to modeling primary nucleation requires a knowledge of the metastable limit that a given solution can withstand before spontaneous nucleation occurs. This limit, which was first observed in experiments by Miers and Issac,\textsuperscript{13} must be determined through experimentation, and nucleation rate is then correlated with the equation

\[ C^* = k(C - C_m)^\gamma \quad C^* < C_m \] (11.2-10)

where \( C \) is solute concentration, \( C_m \) is the solute concentration at which spontaneous nucleation occurs, and \( C^* \) is the solute concentration at saturation. Randolph and Larson\textsuperscript{14} indicate that \( C_m \) is very close to \( C^* \) for many inorganic systems, and they report satisfactory correlations with \( C^* \) substituted for \( C_m \) in Eq. (11.2-10).

Secondary nucleation is the formation of new crystals as a result of the presence of solute crystals, in other words, crystals of the solute must be present for secondary nucleation to occur. Garside and Davey\textsuperscript{15} and Larson\textsuperscript{16} give excellent reviews of the subject, so only a brief synopsis is provided here.

Several features of secondary nucleation make it more important than primary nucleation in industrial crystallizers. First, continuous crystallizers and seeded batch crystallizers have crystals in the magma that can participate in secondary nucleation mechanisms. Second, the requirements for the mechanisms of secondary nucleation to be operative are fulfilled easily in most industrial crystallizers. Finally, most crystallizers are operated in a low supersaturation regime so that crystal growth is regular and the resulting product is pure and of good habit; low supersaturation can support secondary nucleation but not primary nucleation.

Secondary nucleation can occur as the result of several mechanisms which have been identified and observed in selected systems. These include initial breeding, contact nucleation (also known as collision breeding), and shear breeding. Initial breeding results from immersion of seed crystals in a supersaturated solution, and it is thought to be caused by dislodging extremely small crystals that were formed on the surface of the crystals during drying. Although this mechanism is unimportant in continuous and unseeded batch crystallization, it can have a significant impact on the operation of seeded batch crystallizers. Girolami and Rousseau\textsuperscript{17} demonstrate the effects of several process variables on nucleation rates caused by initial breeding. Contact nucleation results from collisions of crystals with one another, crystallizer internals, or with an impeller of an agitator or circulation pump. It should be recognized that the collision energy for contact nucleation is small and does not necessarily result in the macroscopic degradation of the contacted crystal. Because of the importance of this mechanism it will be discussed in more detail below. Shear breeding results when supersaturated solution flows by a crystal surface and carries with it crystal precursors believed formed in the region of the growing crystal surface. Sung et al.\textsuperscript{18} observed nucleation of \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \) by this mechanism and found that very high levels of supersaturation were required for it to produce significant numbers of nuclei.

**Process Variables Affecting Contact Nucleation.** As stated above, contact nucleation results from a collision of a crystal with an object, such as an impeller or other crystallizer internals, in a supersaturated medium. The pioneering studies that elucidated many factors affecting this nucleation mechanism were
carried out by Strickland-Constable and coworkers\textsuperscript{19,20} and Clontz and McCabe.\textsuperscript{21} These and subsequent works demonstrate that the number of crystals produced by a controlled impact of an object with a seed crystal depends on the energy of impact, supersaturation at impact, supersaturation at which crystals mature, material of the impacting object, area of impact, angle of impact, and system temperature. Although it is impossible to account quantitatively for each of these variables, certain generalizations can be drawn from the research on this nucleation mechanism.

Tait et al.\textsuperscript{22} demonstrate that the number of crystals produced under controlled conditions is an exponential function of impact energy \( E \). Furthermore, a threshold or minimum collision energy \( E_\text{t} \) is required for some crystalline systems. Also, Shah et al.\textsuperscript{24} and Evans et al.\textsuperscript{25} found that the material of construction of the impacting object greatly affects the number of crystals resulting from the collision. In particular, coating the crystallizer internals or manufacturing them from soft materials reduces contact nucleation rates. This is attributed to a reduction in the energy transmitted from the coated object to the impacted crystal. Based on these two experimental observations, the following expression was proposed for systems at constant supersaturation:\textsuperscript{25}

\[
B^a = k_n \exp (E - E_\text{t}) \quad E > E_\text{t}
\] (11.2-11)

In a crystallizer with a circulation pump or agitator, it has been shown that collisions between such a device and crystals in the circulating magma dominate nucleation resulting from other collisions.\textsuperscript{26} Consequently, it might be expected that a relationship of impact energy \( E \) to crystallizer variables must include the mass of the impact crystal \( M_i \), and the rotational velocity of the impeller \( \omega \). Moreover, the fraction of the available energy actually transmitted to the crystal, \( \epsilon \), should also be included in the model:

\[
E = f(\epsilon, \omega, M_i)
\] (11.2-12)

The variables shown in Eq. (11.2-12) can be manipulated to some extent, thereby modifying nucleation rates and the concomitant crystal size distribution. For example, internal classification can be used to keep larger crystals away from energetic collisions with an impeller, but doing so may create other problems with stability of the crystal size distribution. The rotational velocity of an impeller can be changed if there are appropriate controls on the pump or agitator. Caution must be exercised, however, for a reduction in circulation velocity can reduce heat transfer coefficients and increase fouling or encrustation on heat transfer surfaces. Moreover, the crystals in the magma must be kept suspended or else crystal habit and growth rates could be affected adversely. It is suspected that impact energy may have a high-order dependence on rotational velocity, and if that is the case, modest changes in this quantity could alter nucleation rates substantially. As already indicated, the fraction of the impact energy transmitted from an impeller to the crystal can be manipulated by changing the material of construction of the impeller. Tai\textsuperscript{27} also showed the hardness of the crystal surface to be important in comparing nucleation characteristics of different crystalline materials. Therefore, the importance of \( \epsilon \) may vary from one crystalline system to another: those systems in which the crystal face is soft may be more susceptible to nucleation rate changes due to the variables in Eq. (11.2-12) than those crystalline systems where the face is hard.

Correlations of nucleation rate with crystallizer variables have been developed for several systems. For example, Bennett et al.\textsuperscript{28} examined the effect of slurry circulation rate on nucleation and developed a correlation based on the tip speed of the impeller. Grootscholten et al.\textsuperscript{29} considered the scale-up of nucleation kinetics for sodium chloride crystallization, and they provide an analysis of the role of mixing and mixer characteristics in contact nucleation. Garside and Shah\textsuperscript{30} reviewed published kinetic correlations though about 1979.

Supersaturation has been observed to affect contact nucleation, but the mechanism by which this occurs is not clear. There are data\textsuperscript{22} that infer a direct relationship between contact nucleation and crystal growth. These data show that the number of nuclei produced by an impact is proportional to the linear growth rate of the impacted face. This is true even for citric acid which exhibits an unusual relationship between growth rate and supersaturation. It has been proposed that the known effect of growth rates, which are determined by mass transfer rates and supersaturation at the surface of the growing crystal, is the link between crystal growth and contact nucleation.

A second perspective is that supersaturation influences the fraction of entities formed by a collision that survive to form large crystals. This concept largely has been rejected based on the observation that such entities are much larger than the size of a critical nucleus. Recent research\textsuperscript{11,32} used photographic and electronic zone-sensing techniques to examine the size distributions of particles formed by impacts with seed crystals in a supersaturated solution. These experiments on potassium alum show that the particles produced cover a size range from 50 \( \mu m \) down to the smallest size capable of being observed by the instrument. Furthermore, the influence of supersaturation on the number of particles produced in the 20-50 \( \mu m \) range was much greater than it was on the number produced in the smaller size range. Data that will be discussed in the section on crystal growth have shown that dissolution of crystals formed by contact nucleation does not occur, but that a fraction of the crystals grow very slowly and some may not grow at all.

Still another possible role of supersaturation is that it affects the solution structure and perhaps causes
the formation of clusters of solute molecules. These clusters may participate in nucleation, although the mechanism by which this would occur is not clear. Mullin and Lecl34 present evidence for the formation of citric acid clusters in aqueous supersaturated solutions, and McMahon et al.35 have examined cluster formation in solutions of KNO₃ using Raman spectroscopy.

The ease with which nuclei can be produced by contact nucleation is a clear indication that this mechanism is dominant in many industrial crystallization operations. Research on this nucleation mechanism is continuing with the objective of building an understanding of the phenomenon that will allow its successful inclusion in models describing commercial systems.

CRYSTAL GROWTH

Crystal growth rates may be expressed in a variety of ways: as the linear advance rate of an individual crystal face, as the change in a characteristic dimension of a crystal, or as the rate of change in mass of a crystal. These different expressions can be related through an understanding of crystal geometry. However, it is often convenient to use the method of measurement as the basis of the growth rate expression. In certain instances an analysis of the crystallization process will require growth rate to be defined in a specific way; for example, the use of a population balance to describe crystal size distribution requires that growth rate be defined as the rate of change of a characteristic dimension.

Single-crystal studies of growth kinetics often involve the rate of advance of an individual crystal face or the rate of change in crystal size associated with exposure to a supersaturated solution. The latter type of study will be dealt with in discussions of multicrystal magmas. The rate of advance of a single crystal face can be quantified by observation of the face through a calibrated eyepiece of an optical microscope. Using this procedure, it is possible to examine the structure of the advancing crystal face and perhaps to isolate surface reaction kinetics from mass transfer kinetics. These phenomena will be discussed later. An additional advantage of this system is that it is possible to examine crystal growth kinetics without interference from competing processes such as nucleation.

Multicrystal magma studies usually involve examination of the rate of change of a characteristic crystal dimension or the rate of increase in the mass of crystals in a magma. The characteristic dimension in such analyses depends on the method used in the determination of crystal size; for example, the second largest dimension is measured by sieve analyses, while an equivalent spherical diameter is determined by both electronic zone-sensing and laser light-scattering instruments. A relationship between these two measured dimensions and between the measured quantity and the actual crystal dimensions can be derived from appropriate shape factors. Recall that volume and area shape factors are defined by the equations

\[ V_c = k_v L^3 \]  \hspace{1cm} (11.2-13)

and

\[ A_c = k_a L^2 \]  \hspace{1cm} (11.2-14)

where \( V_c \) and \( A_c \) are volume and area of a crystal, \( k_v \) and \( k_a \) are volume and area shape factors, and \( L \) is the characteristic dimension of the crystal. Suppose an equivalent spherical diameter \( L_s \) is obtained from an electronic zone-sensing instrument and the actual dimensions of the crystal, which is known to have a cubic habit, are to be calculated. Let \( L_e \) be the edge length of the crystal, and \( k_{vs} \) and \( k_{vc} \) be the volume shape factors for a sphere and a cube, respectively. Since the volume of the crystal is the same, regardless of the characteristic dimension,

\[ V_c = k_{vs} L_s^3 = k_{vc} L_e^3 \]  \hspace{1cm} (11.2-15)

which means that

\[ L_e = \left( \frac{k_{vc}}{k_{vs}} \right)^{1/3} L_s \]  \hspace{1cm} (11.2-16)

Since \( k_{vs} = \pi/6 \) and \( k_{vc} = 1.0 \), the numerical relationship between these two dimensions can be determined from Eq. (11.2-16).

If the rate of change of a crystal mass, \( dM_c/dt \), is measured, the quantity can be related to the rate of change in the crystal characteristic dimension by the equation

\[ \frac{dM_c}{dt} = \frac{d}{dt} \left( \frac{\rho_c k_v L^3}{A^2} \right) = 3 \rho_c k_v L^2 \frac{dL}{dt} \]  \hspace{1cm} (11.2-17)

where \( \rho_c \) is crystal density. Since \( k_a = A_c / L^2 \) and \( G \) is defined as \( dL/dt \)

\[ \frac{dM_c}{dt} = 3 \rho_c \left( \frac{k_v}{k_a} \right) A_c G \]  \hspace{1cm} (11.2-18)

\[ \frac{dM_c}{dt} = \frac{d}{dt} \left( \frac{\rho_c k_v L^3}{A^2} \right) = 3 \rho_c k_v L^2 \frac{dL}{dt} \]  \hspace{1cm} (11.2-17)
In multicrystal magma systems, growth kinetics become difficult to isolate from other phenomena, although a combined analysis, such as that described in Section 11.2-4 for the perfectly mixed crystallizer, gives a realistic view of the actual process that occurs in a crystallizer; that is, nucleation and growth kinetics are measured simultaneously and therefore at the same process conditions.

**Growth Models.** At least two resistances contribute to a determination of growth kinetics. The rate processes to which these resistances apply are (1) integration or incorporation of the crystalline unit (e.g., solute molecules) into the crystal surface (lattice) and (2) molecular or bulk transport of the unit from the surrounding solution to the crystal face. Since bulk transport is addressed elsewhere (see Chapter 2), this discussion will focus only on surface incorporation. Detailed reviews of this topic can be found elsewhere so this discussion will be brief.

Numerous models have been proposed to describe surface reaction kinetics. Among these are models that assume crystals grow by layers and other models that consider growth to occur by the movement of a continuous step. Each model results in a specific relationship between growth rate and supersaturation, but none can be used for a priori predictions of growth kinetics. Such models do provide insights as to the effects of certain process variables on growth and, with additional research, may lead to predictive capabilities. For these reasons and because of the extensive literature on the subject, all that will be pointed out here are the key aspects of the physical models and the resulting relationship between growth and supersaturation predicted by each theory.

The model used to describe the growth of crystals by layers calls for a two-step process: (1) formation of a two-dimensional nucleus on the surface and (2) spreading of the solute from the two-dimensional nucleus across the surface. The relative rates at which these two steps occur give rise to the mononuclear two-dimensional nucleation theory and the polynuclear two-dimensional nucleation theory. In the mononuclear two-dimensional nucleation theory, the surface nucleation step occurs at a finite rate while the spreading across the surface occurs at an infinite rate. The reverse is true for the polynuclear two-dimensional nucleation theory. From the mononuclear two-dimensional nucleation theory, growth is related to supersaturation by the equation

$$G = C_1hA[\ln(1 + s)]^{1/2} \exp \left( -\frac{C_2}{T^2 \ln(1 + s)} \right)$$

(11.2-19)

where \(C_1\) and \(C_2\) are system-dependent constants, \(h\) is the height of the nucleus, \(A\) is surface area, and \(s\) and \(T\) are as defined earlier. The polynuclear two-dimensional theory produces the equation

$$G = \left( \frac{C_3}{T^2[\ln(1 + s)]^{5/2}} \right) \exp \left( -\frac{C_2}{T^2 \ln(1 + s)} \right)$$

(11.2-20)

where \(C_3\) is a system-dependent constant. Finally, if both formation of the two-dimensional nucleus and spreading of the surface layer are important in determining growth rate, the following equation can be derived:

$$G = C_4s^{2/3}[\ln(1 + s)]^{1/6} \exp \left( -\frac{C_2}{3T^2 \ln(1 + s)} \right)$$

(11.2-21)

where \(C_4\) is a system-dependent constant.

Equations (11.2-19), (11.2-20), and (11.2-21) can be simplified considerably by recognizing that in many systems the quantity \(s\) is much less than 1. In that case, \(\ln(1 + s)\) is approximately \(s\). Making this substitution, the growth rate from the mononuclear two-dimensional theory becomes

$$G = C_1hA^{1/2} \exp \left( -\frac{C_2}{Ts} \right)$$

(11.2-22)

For the polynuclear two-dimensional nucleation theory

$$G = \left( \frac{C_3}{T^{5/2}s^{5/2}} \right) \exp \left( -\frac{C_2}{Ts} \right)$$

(11.2-23)

For both steps occurring at similar rates

$$G = C_4s^{5/6} \exp \left( -\frac{C_2}{T^{5/2}s} \right)$$

(11.2-24)

The screw dislocation theory, which was formulated by Burton, Cabrera, and Frank and is often referred to as the BCF theory, shows that the dependence of growth rate on supersaturation can vary from a parabolic relationship at low supersaturations to a linear relationship at high supersaturations. In the BCF
theory, growth rate is given by

\[ G = C \left( \frac{es}{a_1} \right) \tanh \left( \frac{a_1}{es} \right) \]  

(11.2-25)

where \( e \) is screw dislocation activity and \( a_1 \) is a system-dependent quantity that is inversely proportional to temperature. The dependence of growth rate on supersaturation is linear if the ratio \( a_1/es \) is small, but this dependence becomes parabolic as the ratio becomes large. This is because \( \tanh x \) approaches \( x \) as \( x \) becomes small (supersaturation becomes large), and \( \tanh x \) approaches 1.0 as \( x \) becomes large (supersaturation becomes small). It is possible then to observe variations in the dependence of growth rate on supersaturation for a given crystal-solvent system.

An empirical approach can also be used to relate growth kinetics to supersaturation. This approach simply fits the data with a power-law function of the form

\[ G = k_G s^g \]  

(11.2-26)

where \( k_G \) and \( g \) are constants determined by fitting the equation to growth rate data. Such an approach should be valid over small ranges of supersaturation. In fact, careful analysis of the theories discussed above will show that the more fundamental equations can be fit by Eq. (11.2-26) over limited ranges of supersaturation.

**Effects of Impurities and Solvent.** The presence of impurities can alter substantially the growth rates of crystalline materials. The alteration that is most common is for the growth rates to be decreased. It is often thought that impurities must be molecularly similar to the solute to have an impact on crystal growth. However, impurities with few similarities to the crystallizing species have been observed to reduce growth rates. This may be because structurally similar complexes have been formed between the impurity and solvent or another species in the solution, but such events are difficult to identify. Because additions of impurities to a crystallizing system most often result in a reduced crystal growth rate, it is critical that feed solutions be as free from contamination as possible. This is one way in which the operation of process units upstream of a crystallizer can affect crystal size distribution. Therefore, it is suggested that a strict protocol be followed in operating units such as reactors or other separation equipment upstream of the crystallizer. Equally important is monitoring the composition of recycle streams so as to detect the accumulation of impurities. Moreover, crystallization kinetics obtained on small-scale equipment for use in design or analysis should be obtained using solutions as similar as possible to that expected in the full-scale process.

Another important effect associated with the presence of impurities is that they may change the crystal habit. Habit alteration is considered to result from unequal changes in the growth rates of different crystal faces. Davey\textsuperscript{41} reviews the role of impurities in the general context of habit modification. Surfactants, especially, have been observed to modify growth rates of individual faces and thereby change the habit of a crystal.\textsuperscript{42}

The mechanism by which an impurity affects crystal growth rate is considered to involve adsorption of the impurity onto the crystal surface. Once located on the surface, the impurity forms a barrier to solute transfer from the solution to the crystal. This model has been used to relate the growth rate of a crystal to the concentration of impurity in solution through an adsorption isotherm.\textsuperscript{43,44} An alternative theory calls for the adsorbed impurity to occupy active growth sites, thereby preventing attachment of solute to the surface. Still another concept of the impact of impurities on growth rate calls for integration of the impurity into the crystal structure, which leads to two deleterious effects: reduction of growth rate and production of impure product. Few generalities exist in describing the role of impurities in crystallization phenomena, and it is usual to rely on experimental data that are often correlated empirically. Mullin\textsuperscript{12} lists several systems in which habit modifiers have been used effectively. An interesting prospect raised by the work of McMahon et al.\textsuperscript{35} is that impurities may have a strong effect on the formation of solute clusters and ultimately crystal growth.

The solvent from which a material is crystallized can influence the crystal habit and growth rate. Bourne\textsuperscript{45} ascribes the effects of a solvent to two sets of factors: one has to do with the effects of solvent on mass transfer of the solute through adjustments in viscosity, density, and diffusivity; the second is concerned with the structure of the interface between the crystal and solvent. The analysis provided by Bourne concludes that a solute-solvent system having a high solubility is likely to produce a rough interface and concomitantly large crystal growth rates.

**Crystal Growth in Mixed Crystallizers.** As described earlier, crystal growth rates in mult-crystal magmas are defined in terms of the rate of change of a characteristic dimension

\[ G = \frac{dL}{dt} \]  

(11.2-27)
It will be shown in a later section that the solution of a differential population balance requires a knowledge of the relationship between growth rate and size of the growing crystals. Moreover, this relationship can often be deduced from the form of population density data. A special condition, which simplifies such balances, results when all crystals in the magma grow at the same constant rate. Crystal-solvent systems that show this behavior are said to follow the $\Delta L$ Law proposed by McCabe,\textsuperscript{46} while systems that do not are said to exhibit anomalous growth.

Anomalous growth is a term used here to indicate that growth rates of crystals in a magma are not identical or that the growth rate of an individual crystal or mass of crystals is not constant. Two theories have been used to explain growth rate anomalies: size-dependent growth and growth rate dispersion. As with systems that follow the $\Delta L$ Law, anomalous growth results in characteristic forms of population density data. Unfortunately, such data cannot be used to distinguish between size-dependent growth and growth rate dispersion, because both have the same qualitative effects on population density.

**Size-Dependent Crystal Growth.** A number of empirical expressions that correlate the apparent effect of crystal size on growth rate are summarized by White et al.\textsuperscript{47} However, only a few of these meet the following requirements for use in population balances: (1) the expression must be continuous over the entire size range including $L = 0$; (2) the growth rate of zero-size crystals must not be zero; (3) the growth rate expression must allow convergence of moments of the crystal size distribution. The most often used correlation of size-dependent growth kinetic data is the Abegg–Stevens–Larson (ASL) growth rate expression.\textsuperscript{48} This equation uses three empirical parameters to correlate growth rate with crystal size:

$$G = G^0 (1 + \gamma L)^b \quad b < 1$$

(11.2-28)

where $G^0$, $\gamma$, and $b$ are determined from experimental data.

There have been attempts to relate the kinetic parameter $b$ to crystallizer variables; Garside and Jancic\textsuperscript{49} showed a qualitative dependence on crystallizer volume, and Rousseau and Parks correlated $b$ with $G^0$ and $r$. Several theories have been proposed to explain size-dependent growth kinetics, but none has been substantiated by direct observation or used to predict the onset of such behavior. One explanation seems particularly appealing: larger crystals impact impellers and other crystallizer internals with higher frequency and energy than smaller crystals; the larger crystals are therefore recipients of more surface breaks and irregularities that lead to higher growth rates.

At the small end of the size range, crystals in mixed magmas have been observed\textsuperscript{50,51,52} to give the appearance of growing at much reduced rates. Theories proposed to explain these observations are as follows: (1) it is assumed that smaller crystals have fewer surface defects to enhance crystal growth; (2) smaller crystals are assumed to have an increased solubility; (3) when small crystals are formed they are more spherical than more-developed crystals and a high surface energy is involved when the crystal shape goes from spherical to that characteristic of the crystal.

**Growth Rate Dispersion.** The phenomenon of growth rate dispersion is the exhibition of different growth rates by crystals in a magma, even though they have the same size and are exposed to identical conditions. Both zero growth and abrupt changes in growth rates of individual crystals can be exhibited. This dispersion in growth rates can have significant effects on crystal population, leading in general to a broadening of the size distribution. As was discussed under size-dependent growth, growth rate dispersion may lead to population densities with characteristics that are different from those following the $\Delta L$ Law. These characteristics will become more apparent in Section 11.2-4. The phenomenological aspects of growth rate dispersion are discussed in the following paragraphs.

White and Wright\textsuperscript{53} first characterized the effects of growth rate dispersion on a population of sucrose crystals by correlating the variance of the population about a mean size $\bar{L}$. They correlated the variance with the extent of growth of the crystals in a seeded batch crystallizer. The original crystals were of uniform size and the mean of the crystal size distribution was used as a measure of the extent of growth. The relationship between the variance and extent of growth was linear and had slope $p$, which was proportional to the rate of spreading of the distribution. Growth rate dispersion for sucrose was found to be significant ($p = 67 \mu m$), but negligible dispersion ($p = 1 \mu m$) was observed for aluminum trihydroxide. The slope $p$ did not depend on the initial seed size (10–500 $\mu m$) or the stirring rate in the crystallizer; it decreased when growth rate or impurity concentration increased, or when brief intervals of dissolution occurred. Janse and de Jong\textsuperscript{54,55} found growth rate dispersion important in the growth of large potassium dichromate and potassium alum crystals and demonstrated that this phenomenon could account for anomalous characteristics in the population density of crystals obtained from continuous, steady-state crystallizers. They concluded that growth rate dispersion could provide an explanation of what had been considered to be size-dependent growth, but they also indicated that both phenomena could occur simultaneously and cause the aforementioned anomalous behavior; in other words, the occurrence of growth rate dispersion does not rule out the possibility that single-crystal growth may be size dependent.

Recent microscopic studies of individual secondary nuclei have observed growth rate dispersion and size-dependent growth directly.\textsuperscript{51,56} Garside et al.\textsuperscript{52} report that two types of potassium alum secondary
nuclei form after gentle contact of a seed crystal. Those less than 4 μm in size were created in larger numbers and were formed even if the solution was undersaturated. The number of such nuclei was relatively independent of supersaturation. These nuclei grew more slowly than larger ones and, in some cases, did not grow at a measurable rate. The number and size of nuclei between 4 and 50 μm in size increased as supersaturation was increased. Large crystals were not formed in saturated or undersaturated solution and in supersaturated solutions tended to grow more rapidly than small crystals.

Girolami and Rousseau analyzed batch data to show that apparent size-dependent growth of potassium alum crystals is in fact a manifestation of growth rate dispersion. Crystals of citric acid monohydrate generated by contact nucleation were found by Berglund and Larson to exhibit growth rate dispersion but not size-dependent growth. Very slow or zero growth rates for small secondary nuclei have been reported for aqueous solutions of pentaerythritol and sodium chloride. Several types of nuclei were distinguished by their size, shape, and individual growth behavior.

Two distinctly different mechanisms that lead to growth rate dispersion have experimental support. The first, which was proposed by Randolph and White, assumes that all crystals have the same time-averaged growth rate but the growth rates of individual crystals fluctuate about some mean value. Direct evidence of random fluctuations in growth rates has been reported for magnesium sulfate heptahydrate and potassium alum. The second proposed mechanism for growth rate dispersion assumes that crystals are born with a characteristic distribution of growth rates but individual crystals retain a constant growth rate throughout their residence in a crystallizer. This mechanism is supported by findings on citric acid, potassium nitrate, and ammonium dihydrogen phosphate. All these studies found nuclei to have a distribution of growth rates and individual crystals to have constant growth rates.

The surface integration step for crystal growth is thought to be the primary factor in both mechanisms of growth rate dispersion, and the BCF growth theory can be used to provide a qualitative explanation of the growth rate dispersion phenomenon. From the BCF theory, the growth rate of a crystal face is dependent on the number, sign, and location of screw dislocations on the surface of a growing crystal. Collisions of crystals with each other and crystallizer internals result in changes in the dislocation network of a crystal and lead to the random fluctuations of growth rates. Changes in the dislocation networks also occur simply due to the imperfect growth of crystal faces. A distribution of growth rates is a result of the varying dislocation networks and densities among nuclei and seed crystals.

Although evidence for both mechanisms of growth rate dispersion exists, separate mathematical models have been developed for incorporating the two mechanisms into descriptions of crystal populations. Random growth rate fluctuations were characterized by Randolph and White with a growth rate diffusivity parameter $D_G$ which is representative of the magnitude of the growth rate fluctuations. This model is similar to that used to describe molecular diffusion and axial dispersion associated with velocity fluctuations. Mathematical models of growth rate dispersion due only to the growth rate distribution mechanism have been developed using different methods by Janse and de Jong and Larson and coworkers. These models characterize the growth rate distribution mechanism of growth rate dispersion by a distribution function having a mean growth rate $\bar{G}$ and a growth rate variance $\sigma_G^2$. Zumstein and Rousseau have extended such models by showing how both mechanisms of growth rate dispersion can be included and by illustrating the relative effects of the two mechanisms on CSD from batch and continuous crystallizers.

Experimental efforts to determine the importance of the two mechanisms of growth rate dispersion have been involved mainly with the measurement of the spread in crystal size distribution during constant-supersaturation, isothermal batch crystallizations. The model for random growth rate fluctuations predicts the variance of the crystal size distribution will increase linearly with the extent of growth, while the model for a distribution of constant crystal growth rates predicts the variance to increase with the extent of growth squared. The original work by White and Wright on sucrose supports the growth rate fluctuation mechanism, while the mechanism associated with a growth rate distribution is supported by data on contact nuclei of ammonium dihydrogen phosphate and citric acid. Although there is experimental support for both mechanisms, it is still unclear how crystallizing conditions affect the relative importance of the two mechanisms.

### 11.2.4 MODEL OF A WELL-MIXED CRYSTALLIZER

In this section, the principles involved in using a population balance to describe the crystal size distribution in the product from a well-mixed continuous crystallizer are illustrated. The primary objective of this treatment is to show how nucleation and growth kinetics can be evaluated from data on the crystal size distribution produced in such crystallizers. Detailed development of the theory and extensions of these principles to crystallizers that employ selective removal of crystals from the crystallizer internals or to batch or transient continuous crystallizers is provided by Randolph and Larson.

#### APPLICATION OF A POPULATION BALANCE

The basis of a population balance is that the number of crystals in a system is a balanceable quantity. Such balances are coupled to the usual mass and energy balances describing any system, and the crystals are
assumed to be sufficiently small and numerous so that the crystal size distribution may be considered to be a continuous function of a variable with which individual crystals are to be characterized. In this discussion, the variable is the characteristic dimension (size) of the crystal.

A balance on the number of crystals in any size range—say $L_1$ to $L_2$—must account for crystals that enter and leave that size range by convective flow into and out of the control volume $V_7$ and for crystals that enter and leave the size range by growth. Crystal breakage and agglomeration are ignored in this discussion, and it is assumed that crystals are formed by nucleation at or near size zero. Now define a quantity called population density $n$ so that the number of crystals $dN(L)$ in the size range $L$ to $L + dL$ is given by

$$dN(L) = V_7 n(L) dL$$

(11.2-29)

It is important to note that either clear liquor volume or slurry volume can be taken as a basis for the definition of $n$. For example, if clear liquor volume is taken as the basis, $V_7$ becomes the volume of clear liquor in the control volume. With this definition of the population density, it can be shown that the population balance on a well-mixed continuous crystallizer is given by

$$V_7 \frac{\partial (nG)}{\partial L} + Q_o n - Q_i n_i = - \left( V_7 \frac{\partial n}{\partial t} + n \frac{\partial V_7}{\partial t} \right)$$

(11.2-30)

where $Q_i$ and $Q_o$ are volumetric flow rates of either clear liquor or slurry into and out of the crystallizer, respectively. Equation (11.2-30) can now be simplified as follows: assume that the feed liquor contains no crystals ($n_i = 0$); restrict growth to follow the $AL$ Law $[d(nG)/dL = G\partial n/dL]$; specify that the magma volume is constant ($\partial V_7/\partial t = 0$); and operate the crystallizer at steady state ($dn/dt = 0$).

If all four of these restrictions apply, and if a mean residence time $\tau$ (often called drawdown time) is defined as $V_7/Q_o$, the population balance can be written

$$G \frac{\partial n}{\partial L} + n \frac{1}{\tau} = 0$$

(11.2-31)

which may be integrated, using the boundary condition $n(0) = n^0$, to give

$$n = n^0 \exp \left(-\frac{L}{Gr}\right)$$

(11.2-32)

If the assumptions that lead to Eq. (11.2-32) are valid, and they often are, a straight line will result if $n$ is plotted versus $L$ on semilog coordinates. Furthermore, the growth rate of crystals can be determined from the slope of the plot, which is $-1/Gr$. The nucleation rate is related to the intercept of the plot, $n^0$, by the expression

$$B^0 = n^0 G$$

(11.2-33)

Equations (11.2-32) and (11.2-33) can be used to obtain nucleation and growth rates from population density measurements on a crystallizer that conforms to the assumptions stated above. This means that $n$ must be determined as a function of $L$. There are various techniques for obtaining particle size distributions, and the procedures for determining $n$ from these data varies according to the device used for the analysis. Although complete coverage of the advantages and disadvantages of available particle size analyzers is beyond the scope of this chapter, two common techniques are discussed briefly in the following paragraphs.

**Sieves.** Dry and/or wet sieve analyses provide differential or cumulative weight distributions. Obviously, crystals must be in the size range appropriate for a given set of sieves in order for this procedure to be used. The processes of sampling, sample treatment, and sieving can modify the crystal size distribution if care is not taken to prevent agglomeration, crystal abrasion, and crystal breakage. In most sieving techniques, obtaining representative material for sieving requires that crystals be filtered carefully from the mother liquor and dried, and prior to drying it may be necessary to wash the crystals with a nonsolvent to prevent agglomeration. When working the first time with a crystalline material, some experimentation may be necessary to develop a good sieving practice and to find an appropriate wash liquor.

Once satisfactory sieving has been accomplished, $n(L)$ is determined from the following relationship derived from the definition of the cumulative weight distribution data:

$$n(L) = \frac{M_{T} \Delta W(L)}{\Delta L \rho c_k L^3}$$

(11.2-34)
where \( M_T \) is magma density or mass of crystals per unit volume of clear liquor or slurry, \( \Delta W(L) \) is the fraction of the total mass of crystals retained on the sieve having an average size \( L \), \( \Delta L \) is the interval in size between the sieve and the next largest sieve in the nest, \( \rho_c \) is the density of the crystal, \( k \) is the volume shape factor, and \( L \) is the average of the size of the sieve and the next largest sieve in the nest.

**Electronic Particle Size Analyzers.** These devices typically measure changes in a property such as light diffraction, light scattering, light blockage, or electrical conductance to determine the size of a particle. Changes in these measured quantities depend on the volume of the particle being sized, and hence this is the property actually determined by the instrument. The characteristic dimension assigned to the particle is that of a sphere having a volume equivalent to the measured volume. The output from these instruments can be in two forms: a particle volume distribution or a number distribution. The volume distribution data can be converted to population densities using Eq. (11.2-34) and assigning the particles the shape factor of a sphere, \( \pi/6 \). Several devices give population density data directly, and conversions to other forms are unnecessary.

There is considerable technique required in appropriately interpreting the data from electronic particle size analyzers. Vendors can be quite helpful in the development of a measurement procedure, but some experimentation should be expected with each new system.

**KINETIC MODELS**

Once nucleation and growth kinetics have been obtained using the procedures outlined above, correlations of them as functions of process variables are required to use the population balance model for predictive purposes. As discussed in Section 11.2-3, the important variables affecting nucleation and growth kinetics include temperature, supersaturation, magma density, and external stimuli that can cause nucleation, such as agitation or circulation rate of the magma. In Section 11.2-3 some of the important mechanisms by which nucleation and growth occur were described. These mechanisms should be the basis of models of crystallization kinetics, even though the actual correlations are empirical. Power-law functions are used most frequently in correlating nucleation and growth rates, but the choice of the independent variables can be justified from a mechanistic perspective. For example, systems that are believed to follow secondary nucleation mechanisms should include a variable reflecting the character of crystals in the crystallizer, such as magma density. The most commonly used power-law functions are

\[
B^o = k_1 s^b M_T^b
\]

and

\[
G = k_2 s^c
\]

Several methods for expressing supersaturation were described in Section 11.2-3; it is often very difficult to measure this quantity, especially in systems that have high growth rates. In these systems, supersaturation is often so small that it is difficult to measure accurately, and it can be neglected in writing a solute mass balance. However, it is important in setting nucleation and growth rates. A useful technique in such instances is to substitute growth rate for supersaturation by combining Eqs. (11.2-35) and (11.2-36). This gives

\[
B^o = k_n G^i M_T^j
\]

The constant \( k_n \) depends on process variables other than supersaturation and magma density, such as temperature, rate of agitation or circulation, and presence of impurities. If sufficient data are available, these variables may be separated from the constant by adding more terms in a power-law correlation. However, \( k_n \) is essentially a constant specific to the operating equipment and not transferable from one scale of equipment to another. The solute-solvent-specific constants \( i \) and \( j \) are obtainable from experimental data and may be used in scale-up.

**PARAMETER EVALUATION**

As shown above, growth rate \( G \) can be obtained from the slope of a plot of the log of population density data against crystal size; nucleation rate \( B^o \) can be obtained from the same data by using the relationship

\[
B^o = n^o G
\]

where \( \ln n^o \) is the intercept of the plot with the axis at \( L = 0 \). Nucleation rates obtained by these procedures should be checked by comparison with values obtained from a mass balance. It can be shown that the magma density of a slurry in a perfectly mixed crystallizer is given by

\[
M_T = 6 \rho_c k_n n^o (Gr)^4
\]

Rearranging this equation and substituting \( n^o = B^o/G \), we obtain

\[
B^o = \frac{M_T}{6 \rho_c k_n G^i r^4}
\]
TABLE 11.2-5 Typical Kinetic Orders Reported

<table>
<thead>
<tr>
<th>System</th>
<th>Mode of Crystallization</th>
<th>Kinetic Order</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium sulfate-phosphoric acid</td>
<td>Precipitation</td>
<td>2.6-2.8</td>
<td>Indication that homogeneous nucleation dominates</td>
</tr>
<tr>
<td>Ammonium sulfate-water</td>
<td>Cooling</td>
<td>1.7</td>
<td>No enhancement in crystal size with increased suspension density noted</td>
</tr>
<tr>
<td>Ammonium alum-water</td>
<td>Cooling</td>
<td>2.1</td>
<td>Strong secondary nucleation effects were noted</td>
</tr>
<tr>
<td>Ammonium alum-water-ethanol</td>
<td>Salting out</td>
<td>1.0</td>
<td>Increased residence time had no effect on crystal size distribution</td>
</tr>
<tr>
<td>Ammonium sulfate-water-methanol</td>
<td>Salting out</td>
<td>4.0</td>
<td>Increased residence time had moderate effect on CSD</td>
</tr>
<tr>
<td>Sodium chloride-water-ethanol</td>
<td>Salting out</td>
<td>9.0</td>
<td>Increasing residence time strongly affected CSD</td>
</tr>
<tr>
<td>Ammonium alum-water-ethanol</td>
<td>Salting out</td>
<td>2.0</td>
<td>Used MSMPR theory to analyze data. Secondary nucleation effects not accounted for</td>
</tr>
<tr>
<td>Cyclonite-water-nitric acid</td>
<td>Precipitation</td>
<td>1.0</td>
<td>Used MSMPR theory to obtain kinetic order</td>
</tr>
</tbody>
</table>

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After nucleation and growth rates have been obtained from population density data, the exponents $i$ and $j$ in Eq. (11.2-37) can be determined using graphical techniques or multivariable linear regression. For example, $i$ can be obtained from data on several runs of varying residence times. Each run will yield values of $B^*, n^*$, and $G$. If slurry concentration (magma density) $M_T$ is the same for all runs, the slope of a logarithmic plot of $n^*$ versus $G$ will give $i$. If slurry concentration varies slightly from run to run, then a logarithmic plot of $B^*/M_T$ versus $G$ will smooth the data so that $i$ can be obtained from the slope of the plot. Confidence in the parameters $i$ and $j$ requires that sufficient data be accumulated to make such correlations statistically reliable. Typical values of kinetic orders are given in Table 11.2-5, and a more complete list is given by Garside and Shah.

**Characteristics of Crystal Size Distributions from MSMPR Crystallizers**

The preceding discussion centered on the development of expressions for the population density function in terms of nucleation and growth kinetics. It is also possible to express the properties of a crystal size distribution in terms of a mass density function $m$. The two density functions can be shown to be related by the expression

$$m = \rho_k L_D^2 n$$  \hspace{1cm} (11.2-40)

The perfectly mixed, continuous, steady-state mixed-suspension mixed-product removal (MSMPR) crystallizer is restrictive in the degree to which characteristics of a crystal size distribution can be varied. Indeed, examination of Eqs. (11.2-32) and (11.2-40) shows that once nucleation and growth kinetics are fixed in these systems the crystal size distribution is determined in its entirety. In addition, such distributions have the following characteristics:

1. The mode or maximum of the mass density function occurs at the dominant crystal size $L_D$, which is given by

$$L_D = 3Gr$$  \hspace{1cm} (11.2-41)

2. *Moments* of the population density are given by the expression

$$m_i = i! n^* (Gr)^{i-1}$$  \hspace{1cm} (11.2-42)

3. The *coefficient of variation* of the mass density function, which is a measure of the spread of the distribution about the dominant crystal size, is 50%. Such a distribution may be too broad to be acceptable for certain crystalline products, such as sugar.
4. The magma density $\rho_f$ (mass of crystals per unit volume of slurry or liquor) may be obtained from the third moment of the population density function. As shown above, this quantity is related to nucleation and growth rates by Eq. (11.2-38). Although magma density is a function of the kinetic parameters $n^o$ and $G$, it can be measured independently of crystal size distribution and, where possible, it should be used, as indicated above, as a constraint in evaluating nucleation and growth rates from measured crystal size distributions.

5. A pair of kinetic parameters, one for nucleation rate and another for growth rate, describe the crystal size distribution for a given set of crystallizer operating conditions. Furthermore, variation in one of the kinetic parameters without changing the other is not possible.

6. Properties of the distribution may be evaluated explicitly from the moment equations:

$$N = \text{total number of crystals per unit volume}$$

$$= \int_0^\infty n \, dL = m_0 = n^o G r \quad (11.2-43a)$$

$$L_T = \text{total length of crystals per unit volume}$$

$$= \int_0^\infty nL \, dL = m_1 = n^o (Gr)^2 \quad (11.2-43b)$$

$$A_T = \text{total area of crystals per unit volume}$$

$$= k_o \int_0^\infty nL^2 \, dL = k_o m_2 = 2k_o n^o (Gr)^3 \quad (11.2-43c)$$

$$V_c = \text{total volume of crystals per unit volume}$$

$$= k_v \int_0^\infty nL^3 \, dL = k_v m_3 = 6k_v n^o (Gr)^4 \quad (11.2-43d)$$

PARAMETERS FROM SYSTEMS EXHIBITING ANOMALOUS GROWTH

Two types of anomalous growth behavior were described in Section 11.2-3: growth rate dispersion and size-dependent growth. As pointed out, the effects of these mechanistically different phenomena on crystal size distributions are the same; both cause curvature in semilog plots of population density against size. Moreover, when size-dependent growth rates increase with crystal size, both cause a broadening of the distribution. In this discussion, methods will be presented that illustrate evaluation of the parameters in systems following size-dependent growth kinetics. Research is in progress on development of similar procedures for systems deemed to follow growth rate dispersion anomalies, and the current literature should be followed for such cases.

A number of empirical size-dependent growth expressions have been developed. Of these, the ASL model given in Eq. (11.2-28) is the most commonly used. Substituting this equation into the differential population balance given by Eq. (11.2-31), the steady-state population density function can be derived as

$$n = n^o (1 + \gamma L)^{-b} \exp \left( \frac{1 - (1 + \gamma L)^{1-b}}{G^o \gamma (1 - b)} \right) \quad (b < 1) \quad (11.2-44)$$

This equation is often simplified by restricting $\gamma$ to be equal to $1/G^o \sigma$, which reduces the number of model parameters by one and often results in a fit to data that is nearly as good as the three-parameter model. The reduced ASL model ($\gamma = 1/G^o \sigma$) leads to the following equation for population density:

$$n = n^o \left(1 + \frac{L}{G^o \sigma} \right)^{-b} \exp \left( \frac{1 - (1 + L/G^o \sigma)^{1-b}}{1 - b} \right) \quad (11.2-45)$$

Garside and Jancic\textsuperscript{49} noted the relationship of several magma properties to the parameter $b$ in the ASL growth model. O'Dell and Rousseau\textsuperscript{53,74} derived formulas for estimating the characteristics of crystal size distributions in terms of parameters in size-dependent growth kinetic models and for crystallizers with selective removal of fines and/or product. For systems whose growth follows the reduced ASL equation, it was shown that total length of crystals per unit volume of magma or liquor, surface area of crystals per unit volume, mass of crystals per unit volume (magma density), mass average size, coefficient of variation, and dominant size could be calculated from the equations

$$L_T = C_r n^o (G^o \sigma)^2 \quad (11.2-46)$$

$$A_T = k_o C_r n^o (G^o \sigma)^3 \quad (11.2-47)$$
TABLE 11.2-6 Constants for Evaluating Magma Properties of Systems that Follow Reduced ASL Kinetics

<table>
<thead>
<tr>
<th>b</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_L$</th>
<th>CV</th>
<th>$C_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>3.6602</td>
<td>526.71</td>
<td>5,8409 E06</td>
<td>307680.0</td>
<td>333.40</td>
<td>1681.2</td>
</tr>
<tr>
<td>0.8</td>
<td>2.5104</td>
<td>48.373</td>
<td>5205.4</td>
<td>606.09</td>
<td>154.28</td>
<td>57.003</td>
</tr>
<tr>
<td>0.7</td>
<td>2.0041</td>
<td>18.058</td>
<td>539.05</td>
<td>78.417</td>
<td>108.47</td>
<td>19.032</td>
</tr>
<tr>
<td>0.6</td>
<td>1.7038</td>
<td>9.9331</td>
<td>140.86</td>
<td>28.428</td>
<td>86.786</td>
<td>10.748</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5000</td>
<td>6.5000</td>
<td>57.750</td>
<td>15.351</td>
<td>74.203</td>
<td>7.4314</td>
</tr>
<tr>
<td>0.4</td>
<td>1.3502</td>
<td>4.6865</td>
<td>29.933</td>
<td>10.064</td>
<td>66.014</td>
<td>5.6882</td>
</tr>
<tr>
<td>0.3</td>
<td>1.2344</td>
<td>3.5929</td>
<td>17.862</td>
<td>7.3600</td>
<td>60.256</td>
<td>4.6220</td>
</tr>
<tr>
<td>0.2</td>
<td>1.1414</td>
<td>2.8732</td>
<td>11.696</td>
<td>5.7630</td>
<td>55.975</td>
<td>3.9044</td>
</tr>
<tr>
<td>0.1</td>
<td>1.0646</td>
<td>2.3964</td>
<td>8.1769</td>
<td>4.7239</td>
<td>52.656</td>
<td>3.3887</td>
</tr>
<tr>
<td>0.0</td>
<td>1.0000</td>
<td>2.0000</td>
<td>6.0000</td>
<td>4.0000</td>
<td>50.000</td>
<td>3.0000</td>
</tr>
</tbody>
</table>

The constants in Eqs. (11.2-46)-(11.2-51) are functions of $b$ only, and they are given in Table 11.2-6. The table can be used to estimate the desired property of a crystal size distribution from the model parameters and Eqs. (11.2-46)-(11.2-51), or it can be used in evaluating the model parameters from experimental data as described below.

It should be clear that the form of the population density function given by Eq. (11.2-32) (systems that follow the $\Delta L$ Law) is much simpler than those of Eqs. (11.2-44) and (11.2-45). This increase in complexity for systems that exhibit anomalous growth makes extraction of model parameters more difficult. Not only do anomalous growth models have more parameters, but the curvature in plots of the log of the population density against size means that parameters must be determined by using nonlinear least-squares regressions. For example, fitting the reduced form of the ASL equation requires evaluation of the parameters $n^o$, $G^o$, and $b$ in Eq. (11.2-45), and the estimate of $n^o$ is extremely sensitive to the few data points frequently obtained at very small sizes. Moreover, nonlinearities in the semilogarithmic relationship between population density and size frequently are most severe at small sizes. Consequently, it is very difficult to determine $n^o$ with any real accuracy.

Rousseau and Parks simplified this problem by substituting Eq. (11.2-48) into Eq. (11.2-45) to eliminate $n^o$

$$M_T = k_c n^o (G^o \tau)^4$$ (11.2-48)

$$\bar{L} = \left( \frac{C_3}{C_1} \right) G^o \tau = C_L G^o \tau$$ (11.2-49)

$$CV = \left( \frac{C_3 C_5}{C_4^2} - 1 \right)^{1/2} \times 100\%$$ (11.2-50)

$$L_D = C_D G^o \tau$$ (11.2-51)

Experimentally determined population density, measured $M_T$, and the values of $C_3$ in Table 11.2-6 can then be used to evaluate the two remaining adjustable parameters $b$ and $G^o$. Interpolation of $C_3$ is assisted by a polynomial fit to $b$

$$\ln C_3(b) = 1.8881 + 1.5829b + 5.5316b^2 + 7.618b^3 - 32.36b^4 + 34.22b^5$$ (11.2-52)

The effects of the two growth rate dispersion mechanisms on the CSD in a mixed-suspension, mixed-product removal (MSMPR) continuous crystallizer are different. Random growth rate fluctuations do not affect the spread of the CSD from an MSMPR crystallizer and the resulting population density function is indistinguishable from that obtained assuming applicability of the $\Delta L$ Law. However, growth rate fluctuations do increase the mean crystal size from that which is expected from the $\Delta L$ Law. On the other hand, CSD from a continuous crystallizer is affected noticeably by assigning a distribution of constant crystal growth rates to the nuclei. This mechanism causes the type of curvature in population density plots that typically has been ascribed to size-dependent growth.
A model that combines growth rate dispersion mechanisms has been derived by Zumstein and Rousseau. The expression for population density derived from their model is

\[
n(L) = \frac{B^g}{\int_0^{\infty} [Gf^g(G)/S] dG} \int_0^{\infty} f^g(G) \exp \left( -\frac{SL}{G^r} \right) dG
\]

(11.2-54)

where \( f^g(G) \) is the distribution of nuclei growth rates and \( S \), which is between 0 and 1, is given by

\[
S = \left( \frac{rG^2}{2D_G} \right) \left[ \left( 1 + \frac{4D_G}{rG^2} \right)^{1/2} - 1 \right]
\]

(11.2-55)

The other terms are as defined earlier. This equation was used to demonstrate that random growth rate fluctuations may damp out the effect of the growth rate distribution function, thereby causing the effects of growth rate dispersion to be unobservable in a continuous crystallizer. Moreover, it is shown that an understanding of growth rate dispersion may be a key factor in obtaining realistic models for scale-up.

**PREFERENTIAL REMOVAL OF CRYSTALS**

Crystal size distributions produced in a perfectly mixed crystallizer are highly constrained, and nucleation and growth kinetics are determined exclusively by the crystalline system and the variables that define the state of the crystallizer. Accordingly, specification of the feed variables (flow rate, temperature, pressure, and solute concentration), the crystallizer variables (temperature, pressure in an adiabatic cooling process, agitation or magma circulation rate, and solids fraction in an evaporative crystallizer), and crystallizer geometry determines magma density and other characteristics of the crystal size distribution.

Crystallizers are made more flexible by the introduction of selective removal devices that alter the residence time distribution of materials flowing from the crystallizer. The functions of classified removal are best described in terms of idealized models of clear-liquor advance, classified-fines removal, and classified-product removal. Clear-liquor advance is the removal of mother liquor from the crystallizer without simultaneous removal of crystals. The effects of implementing this removal function are described in Section 11.5-2. The primary objective of fines removal is preferential withdrawal from the crystallizer of crystals whose size is below some specified value; with the withdrawal, dissolution, and return of the solution to the crystallizer, the growth of larger crystals is enhanced. Classified-product removal is carried out to remove preferentially those crystals whose size is larger than some specified value.

The effects of each of the selective removal functions on crystal size distributions can be described in terms of the population density function \( n \). If it is assumed that perfect classification of fines and product crystals is implemented, then the following expression for population density results:

**For \( L \leq L_f \)**

\[
n = n^o \exp \left( -\frac{RL}{G^r} \right)
\]

(11.2-56)

**For \( L_f < L < L_c \)**

\[
n = n^o \exp \left( -\frac{(R-1)L_f}{G^r} \right) \exp \left( -\frac{L}{G^r} \right)
\]

(11.2-57)

**For \( L \geq L_c \)**

\[
n = n^o \exp \left( -\frac{(R-1)L_f}{G^r} \right) \exp \left( \frac{(Z-1)L_c}{G^r} \right) \exp \left( -\frac{ZL}{G^r} \right)
\]

(11.2-58)

where the fines are below size \( L_f \) and have a removal rate \( R \) times what would exist for perfect mixing, the coarse product is greater than size \( L_c \) and has a removal rate \( Z \) times that of the perfectly mixed crystallizer. If fines removal is implemented alone, \( Z = 1 \), and if classified product removal is implemented without fines removal, \( R = 1 \). Selection of a crystallizer that has both classified-fines and classified-product removal functions usually is done so as to combine the best features of each: increased dominant size and
narrower distribution. The model of the crystallizer and selective removal devices that led to Eqs. (11.2-56)-(11.2-58) is referred to as the R-Z crystallizer. It is an obvious idealization of actual crystallizers because of the perfect cuts assumed at \( L_F \) and \( L_C \). However, it is a useful approximation to many systems and it allows qualitative analyses of complex operations.

Although many commercial crystallizers operate with some form of selective crystal removal, devices that implement these functions add to the complexity of the operation. In addition, Randolph et al.\(^{76} \) have established that classified-product removal can lead to cycling of the crystal size distribution. A review of the simulation and control of crystal size distributions has been provided by Randolph.\(^ {77} \) Properties of the crystal size distribution have been given in terms of \( R \) and \( Z \) and the moments of the crystal size distribution.\(^ {74} \)

**Batch Crystallization**

As with continuous crystallizers, the mode by which supersaturation is generated affects the yield and crystal size distribution, but batch crystallizers are strongly influenced by the rate at which supersaturation is generated. For example, in a cooling mode there are several avenues that can be followed in reducing the temperature of the batch system: natural cooling in which a batch is simply allowed to release heat to a constant-temperature heat sink, cooling in which the rate of heat transfer is constant, cooling in which the supersaturation is maintained constant, and size-optimal cooling whose objective is to vary the cooling rate so that the supersaturation in the crystallizer is adjusted to produce an optimal crystal size distribution. The effects of these and other modes of operation on crystal size distribution are discussed by Tavare et al.\(^ {74} \) Other important features of batch crystallizers are reviewed by Wey\(^ {79} \) and Randolph and Larson.\(^ {14} \)

Perhaps the most troublesome aspect of batch crystallizers is the difficulty associated with reproducing crystal size distributions in going from one batch to the next. This may be overcome through seeding\(^ {49} \) and control of mixing conditions. In general, however, the development of methods for design and analysis of batch crystallizers lags those for continuous systems.

### 11.3 Solution Crystallization

Crystallization is a commonly used industrial separation and purification technique. If the desired product is an evaporate (or filtrate) rather than a crystalline phase, then the process emphasis is primarily that of separation rather than purification. In either case there is a strong interaction and dependence between both degree of separation and purification and the particulate nature of the solid phase produced. Fundamental research on crystallization has focused mainly on understanding the variables that influence the structure and size of the crystalline phase, recognizing that better knowledge and control of this aspect would permit improvement of the unit operation of crystallization, both as a separation and purification technique.

#### 11.3-1 State-of-the-Art

Use of mathematical models for designing industrial crystallizers has lagged other chemical processing operations because of the complexities of rationally describing and interrelating growth and nucleation kinetics with the process configuration and mechanical features of the crystallizer. Crystallizers have traditionally been designed by scale-up of pilot- or bench-scale data, taking care to control supersaturation levels and to maintain similar crystal residence time, vessel configuration, and hydraulic regimes. System kinetics, even though controlling the ultimate crystal size distribution, were thought to be subjects better relegated to the laboratory and were rarely used for crystallizer design.

The design and analysis of crystallization processes of the continuous well-mixed suspension type have developed into formal design algorithms which can now be applied in situations of industrial importance. Specific process configurations that can be modeled rigorously include fines destruction, clear-liquor advance, classified-product removal, vessel staging, and seeding. Such process configurations can be modeled rigorously with a population balance CSD algorithm or, in many cases, with an alternative mass-based formulation. Crystal size distribution transients and stability can also be evaluated as well as the effects of size-dependent growth rate and suspension concentration-dependent secondary nucleation. Simulation capabilities have in fact outstripped the ability to monitor appropriate control variables and to manipulate and control liquid and solids residence-time distributions in a crystallizing environment.

A considerable amount of skepticism naturally is expressed by crystallization practitioners concerning the unbridled use of parameters generated in well-controlled small-scale equipment to predict performance of industrial-scale crystallizers. Many factors contribute to the nonideal behavior of industrial crystallizers, and not all can be easily explained.

The ability to predict crystal behavior in complex systems is ahead of our ability to manipulate crystal and liquid residence times. Generalizations of the MSMPR equations have been made to predict CSD with arbitrary process configurations and kinetics; however, there is no guarantee that an assumed process residence-time distribution can be physically implemented to produce a customized product CSD. Size distributions in cascaded crystallizers, for example, multiple-effect evaporators, can be computed if kinetic