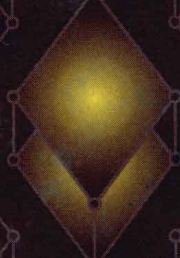# CRYSTALLIZATION

Second Edition

TECHNOLOGY

Revised and Expanded

HANDBOOK

edited by

A. Mersmann

CRYSTALLIZATION TECHNOLOGY HANDBOOK

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Preface

The aim of this book is to provide reliable information not only on the science of crystallization from solution and from melt but also on the basic design methods for laboratory and especially industrial crystallizers. Up to now the niche between scientific results and practical design and operation of large-scale crystallizers has scarcely been filled. A work devoted to this objective has to take into account relevant crystallization phenomena as well as chemical engineering processes such as fluid dynamics, multiphase flow, and heat and mass transfer. In the design of crystallizers, experiments are initially performed on laboratory crystallizers to obtain kinetic data. In this book, information is given on reliable scale-up of such crystallizers. The selection, design, and operation of large-scale industrial crystallizers based on fundamentals is the most significant objective of this work. To this end, an appendix listing important physical properties of a large number of crystallization systems is included. A selection of design data valid for industrial crystallizers with volumes up to several hundred cubic meters demonstrates the applicability of the design and scale-up rules.

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Physical and Chemical Properties of Crystalline Systems

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Unlike crystallization from melting and freezing, heat transfer is not the decisive process in cystallization from solution because the properties of the crystalline product depend primarily on supersaturation generated by cooling, evaporation, drowning out, or a reaction. The quality components of the product (i.e., its crystal size distribution, its median crystal size, its purity, and its crystal shape) are strongly influenced by (a) the geometry and type of the crystallizer, (b) the operating conditions, and (c) the properties of the liquid and solid phases.

The requirements of the product rather than the method of creating supersaturation are decisive when selecting a crystallizer. In an industrial crystallizer, there is such a variety of complex processes that it is difficult for the chemical engineer to decide on a suitable procedure for the design of a full-scale apparatus. Therefore, let us consider some general guidelines.

If the aim is to obtain a certain product having a specific crystal size distribution, grain size, and purity instead of a random product, it is necessary to control the local and mean supersaturation as well as the residence time of the solid in the supersaturated solution. Supersaturation

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is a prerequisite for nucleation and growth, which are decisive not only for the formation of a solid phase but also for its occurrence (i.e., size distribution of crystals and their shape). The degree of supersaturation is determined by the flows of materials and energies, on the one hand, and by crystallization kinetics, such as nucleation and growth, on the other hand. In addition to the conservation laws of materials and energy, the population balance is very important because in most cases, a crystalline product with a certain size distribution is required. With respect to this fact, it is necessary to take into account processes that influence the population balance (i.e., mainly agglomeration for very small crystals and attrition for large crystals).

As a rule, crystals have a higher density than that of the surrounding liquid, which results in settling. Therefore, a certain upflow current is needed in all crystallizers to compensate settling. As a result, crystallizers are equipped with rotors, such as stirrers or pump impellers, which can cause attrition of large crystals. In addition, the quality of a crystalline product may depend on the fluid dynamics of the slurry in the crystallizer. As a rule, the distribution of supersaturation and solid material in a crystallizer depends on the process of macromixing. This may be important for coarse crystalline products. With drowning-out and reaction crystallization, the local supersaturation is influenced by the process of micromixing (i.e., mixing on a molecular scale). Finally, the production rate of an industrial crystallizer may be high or low. As a rule, continuous crystallizers are used in the case of high production rates because this operation is more economical with respect to investment, energy, and labor costs. If several products are to be crystallized in the same crystallizer, a batch crystallier is chosen. Sometimes, crystallizers with circulating slurry or with fluidized beds are used instead of stirred vessels. As will be shown later, the fluid dynamics and, consequently, phenomena such as mixing and attrition differ substantially in such apparatus. Therefore, it is necesary to provide detailed information on the various crystallizers and their flow behavior. As stated earlier, the most important process parameter is supersaturation, or the difference between the actual concentration and the equilibrium concentration of the liquid.

1. MEASURES OF SOLUBILITY AND SUPERSATURATION

First, information on the phase equilibrium of solid–liquid systems and solubility and melt diagrams will be presented. Crystallization from the melt is described in detail in Chapters 13 and 14. However, because there is no distinct boundary between crystallization from solution and crystal-

lization from the melt, it is reasonable to regard phase equilibria diagrams in a general way. It will also be shown how crystallization processes can best be represented in enthalpy–concentration diagrams. Important basic principles of thermodynamics are followed by an explanation of the essential processes: the rate of nucleation and crystal growth. It is precisely these kinetic parameters that determine the crystal size distribution of a product having a large number of crystals. First, however, let us take a look at concentration and supersaturation measures.

The number of collisions of elementary units (atoms, ions, molecules) with those in the fluid phase or at the phase interface of the crystalline phase depends on the number of units per unit volume of the fluid phase:

$$\frac{\text{Number of units}}{\text{Volume of fluid phase}} = \frac{nN_A}{V} = CN_A \tag{1.1}$$

where C (mol/L or kmol/m^3) is the molar concentration and N_A is Avogadro's number. For reasons of practicality, mass concentration c is often used:

$$c = C\tilde{M} \left[\frac{\text{kmol}}{m^3} \cdot \frac{\text{kg}}{\text{kmol}} \right] \text{ or } \left[\frac{\text{kg}}{m^3} = \frac{\text{g}}{\text{dm}^3} = \frac{g}{l} \right] \tag{1.2}$$

In addition to these volumetric concentrations, it is convenient to use mole or mass fraction y or w as well as mole or mass ratios Y or W (generally, Y and Y should be used in the fluid phase and X or x in the solid phase). A scale is often used to determine the mass that can be converted to the amount of substance if the molar mass is known. Table 1.1 provides information on definition and conversions.

A saturated fluid phase having concentration C^* or c^* is in thermodynamic equilibrium with the solid phase at the relevant temperature. If the solution is liquid, the saturation concentration often depends strongly on temperature but only slightly on pressure. If a fluid phase has more units than C^*N_A, it is said to be *supersaturated*. Crystallization processes can take place only in supersaturated phases, and the rate of crystallization is often determined by the degree of supersaturation. Supersaturation is expressed either as a difference in concentration

$$\Delta C = C - C^* \quad \text{or} \quad \Delta c = c - c^* \tag{1.3}$$

or as relative supersaturation

$$S = \frac{C}{C^*} = \frac{c}{c^*} \quad \text{or} \quad \sigma = S - 1 \tag{1.4}$$

Generally, differences or ratios of molar and mass fractions can also be used; however, precise and detailed information is always required when

Table 1.1.   Definitions and Conversion of Concentration Units

	Referred to mass [kg] $M_i = c_i V$		Referred to amount of substance [kmol] $n_i = M_i/\tilde{M}_i$	
	Two components	k components	Two components	k components
Total mass	$M = M_a + M_b$	$M = \sum_{j=a}^{k} M_j$	$n = n_a + n_b$	$n = \sum_{j=a}^{k} n_j$
Mass fraction	$w_a = \dfrac{M_a}{M}$	$w_i = \dfrac{M_i}{M}$	Mole fraction $x = \dfrac{n_a}{n}$	$x_i = \dfrac{n_i}{n}$
Mass ratio	$W_a = \dfrac{M_a}{M_b}$	$W_i = \dfrac{M_i}{M_{\text{carrier}}}$	Mole ratio $X_a = \dfrac{n_a}{n_b}$	$X_i = \dfrac{n_i}{n_{\text{carrier}}}$
Conversion	Mass fraction w_i $\longrightarrow$		Mole fraction x_i $\longrightarrow$	
Mass fraction from mole fraction	$w_a = \left(1 + \dfrac{\tilde{M}_b}{\tilde{M}_a}\dfrac{1 - x_a}{x_a}\right)^{-1}$	$w_i = \dfrac{x_i \tilde{M}_i}{\sum_{j=a}^{k}(x_j \tilde{M}_j)}$	Mole fraction from mass fraction $x_a = \left(1 + \dfrac{\tilde{M}_b}{\tilde{M}_a}\dfrac{1 - w_a}{w_a}\right)^{-1}$	$x_i = \dfrac{w_i/\tilde{M}_i}{\sum_{j=a}^{k}(w_j/\tilde{M}_j)}$
Conversion	Mass ratio $\longrightarrow$		Mole ratio $\longrightarrow$	Mole fraction
	$W = \dfrac{w}{1 - w}$	$w = \dfrac{W}{1 + W}$	$X = \dfrac{x}{1 - x}$	$x = \dfrac{X}{1 + X}$

Mean molar mass: $\tilde{M}_m = \dfrac{M}{m} = \left(\dfrac{w_a}{\tilde{M}_a} + \dfrac{1 - w_a}{\tilde{M}_b}\right)^{-1}$; general: $\tilde{M}_m = \left[\sum_{j=a}^{k}\left(\dfrac{w_j}{\tilde{M}_j}\right)\right]^{-1}$

Mean density: $\rho_m = \left[\sum_{j=a}^{k}\left(\dfrac{w_j}{\rho_j}\right)\right]^{-1}$

the crystalline phase integrates (e.g., solvents, as is the case with all hydrates). The ratios kg anhydrate/kg solvent and kg hydrate/kg solvent are always different and, therefore, so are the supersaturation values. The dimensionless supersaturations S and σ also often vary considerably depending on whether, for example, values of $\sigma_1 = \Delta C/C^*$, $\sigma_2 = \Delta y/y^*$, $\sigma_3 = \Delta Y/Y^*$, $\sigma_4 = \Delta w/w^*$, or $\sigma_5 = \Delta W/W^*$ are involved. These statements also show that the expression of supersaturation as a percentage is entirely insufficient.

If the phase involved is a vapor or gaseous supersaturated phase, it is often useful to use partial pressures instead of concentrations. If the ideal law of gases applies, the following is valid:

$$C^* = \frac{p^\circ}{RT} \quad \text{or} \quad C^* = \frac{p^\circ \tilde{M}}{\Re T} \tag{1.5}$$

or

$$C = \frac{p}{RT} \quad \text{or} \quad C = \frac{p \tilde{M}}{\Re T} \tag{1.6}$$

This gives the following relative supersaturation for isothermal systems:

$$S = \frac{C}{C^*} = \frac{p}{p^\circ} \tag{1.7}$$

and

$$\sigma = \frac{p - p^\circ}{p^\circ} \tag{1.8}$$

Generally, it can be said that the difference in chemical potential $\Delta \mu = \mu_F - \mu_C$ between the fluid (index F) and the cryal (index C) phases is the kinetic driving force, which can be described via the relationship among the chemical potential μ, standard potential μ_0, the activity a, and the heat of crystallization ΔH_{CL}:

$$\mu = \mu_0 + \Re T \ln a \tag{1.9}$$

or

$$\Delta \mu^* \equiv \frac{\Delta \mu}{\Re T} = v \ln \left(\frac{a}{a^*} \right) = v \ln S_a \quad \text{(solution)} \tag{1.10a}$$

$$\Delta \mu^* \equiv \frac{\Delta \mu}{\Delta H_{CL}^*} = \frac{\Delta T}{T} \quad \text{(melt)} \tag{1.10b}$$

with the undercooling ΔT.