

HEAT AND MASS TRANSFER OPERATIONS - CRYSTALLIZATION

J. Ulrich and **M.J. Jones**

TVT, Martin-Luther-Univ. Halle-Wittenberg, Germany

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Summary

This chapter presents an overview of industrial crystallization both from a fundamental, scientific perspective and with an eye on the application of crystallization as a separation process in industrial processes. Crystallization as a separation process yields a solid product from a solution or a melt. The process itself, the product characteristics and the temporal behavior are determined by thermodynamics, i.e. solubility of the materials, and crystallization kinetics, respectively. The thermodynamics of solutions and melts are dependent on a range of physical parameters as discussed within. Crystallization kinetics can be divided into two separate processes, nucleation and crystal growth. Both play a significant role in the design of equipment for a given process and are treated in detail below.

Additional factors such as the effect of crystallization on product properties as well as the effect of solid-state properties on the crystallization process are discussed in section 4.

Section 5 provides details on commonly used crystallizer designs and highlights the distinction between solution and melt crystallization.

1. Introduction

Crystallization is a thermal separation, and therefore a purification process that yields a solid product from a melt, from a solution or from a vapour. As for all thermal separations, non-equilibrium conditions are required as a driving force for the process. Here, evaporation of solvent or temperature reduction (cooling) are the most frequent means employed to establish the required non-equilibrium conditions. Pressure can, in principle, also be used to enforce the non-equilibrium state necessary for a phase change. However, in industrial applications this parameter is most frequently kept constant. As a consequence, processes involving pressure change will not be discussed here.

Other technical routes to leading to crystalline products may involve chemical reactions (reactive crystallization), change of dielectric constant/ionic strength of a solution (salting-out) or crystallization induced by a change in solvent composition (drowning-out).

Those type of crystallization processes often referred to as precipitation processes will not be covered here [Söhnel/Garside].

The main feature distinguishing crystallization from other thermal separation processes is the fact that it leads to a solid product. This is one of the key reasons why it lags behind separation techniques involving liquid-liquid or liquid-gaseous phase change processes in terms of research effort expended and knowledge available. In the past chemical engineering has tended to avoid the solid state as far as possible due to the problems inherent in solids handling. Encrustation and the concomitant heat transfer problems, seizing of moving parts, generation of hazardous dust and the general difficulty inherent in solid-liquid separation are just some of the issues involved. However, the attitude towards crystallization is changing and the positive aspects of the techniques, low energy consumption and the potential for high-purity products, are more widely appreciated. [Mullin], [Myerson], [Mersmann], [Tavare], [Jones], [Nyvlt/Ulrich], [Hartl], [Jancic/Grootscholten], [Ulrich 2002 (in Kirk-Othmer)]

Crystallization is a highly selective process and operates at lower temperatures when compared to a separation by distillation for the same material. Melt crystallization has the additional advantage of not requiring a solvent, although it is not a method suitable for all materials. Manifold reasons exist for the growing importance of crystallization as an industrial separation process. On the one hand, many products are solids under ambient conditions, in particular in the specialty chemicals sector, in the pharmaceutical industry and in the manufacture of foods. On the other hand, the ability to manipulate, at a minimum, the macroscopic properties of crystals such as shape and size by judicious choice of crystallization conditions makes the technique a very attractive option in those industry sectors already mentioned, where reproducible product quality with well defined properties (flow properties, color, dissolution characteristics, polymorphic form *etc.*) are of utmost importance. [Ulrich/Glade], [Ulrich (in Hofmann 2004)],

[Arkenbout], [Jansens/van Rosmalen (in Hurle)], [Matsuoka (in Garside)], [Sloan/McGhie], [Toyokura/Hirasawa (in Mersmann)], [Ulrich 2002 (in Myerson)]

In recent years a number of new monographs on industrial crystallization have appeared and these provide a good representation of the state of the art. A good overview of the developments in the field over the past 30 years can be gleaned from the proceedings of the International Symposia on Industrial Crystallization which take place at triennial intervals and are organised by the European Federation of Chemical Engineering (EFCE). [Mullin], [de Jong/Jancic], [Jancic/de Jong 1982], [Jancic/de Jong 1984], [Nývlt/Zacek], [Mersmann], [Rojkowski], [Biscans/Gabas], [Garside 1999], [Chianese], [Ulrich 2005]

The key factors in the design of any thermal separation process are the thermodynamics of the system under consideration as well as its kinetics. The thermodynamics defines the limits of what can be achieved, the kinetics define the time-scale and therefore the size of the equipment required. This general statement also holds for crystallization. As a consequence, fundamental knowledge of phase diagrams and solubilities of the materials to be separated is required prior to the design of any industrial process. In many instances the literature only provides phase diagrams for pure materials. With increasing number of components phase diagrams become progressively more complex. Realistic systems generally contain many components and determining phase behavior under operating conditions is one of the greatest challenges in crystallization.

Knowing the theoretical limits of a crystallization process as defined by the thermodynamics is only part of the picture, the other part is knowing what can be achieved in a finite and reasonable time scale and the information on this aspect of crystallization is contained in the process kinetics.

Two processes are important in crystallization, both with their own characteristic kinetics. One of these processes is nucleation [Kashehiev], the other is crystal growth. Both of these phenomena are dependent on a large number of variables that in some cases may be ill defined.

In addition, further factors that influence the number and nature of particles obtained have to be considered in the design of mass crystallization processes. Whenever suspensions of crystals in solution are involved, attrition and agglomeration have to be taken into account. In this chapter only the “real” kinetic parameters, nucleation and crystal growth, will be discussed.

Finally crystals possess an internal structure, an external shape and consequently a finite size (or size distribution in the case of a quantity of crystals). These parameters determine many bulk properties of a given crystalline material, such as dissolution rate, bio-availability, color, flow properties *etc.* A general overview of these properties will also be provided.

2. Solid-Liquid-Equilibria

This section provides an overview of solid-liquid equilibria and the type of information useful to crystallization that can be gleaned from their representation in the form of phase diagrams. Different types of – idealized – phase and solubility diagrams shall be discussed together with associated phenomena.

2.1. Solubilities and Phase Diagrams

A solution is a homogeneous mixture of two or more chemical species. For a liquid solution saturation is reached when the liquid phase, in contact with the solid phase, no longer changes its composition. A saturated solution therefore has a constant composition that is not changed by the addition of further amount of the dissolved material. For a two component system, the solubility of one component in the other is dependent on temperature and pressure. For three and more component systems the solubility of one component also depends on the relative amounts of the other components present. For liquid solutions the pressure dependence is negligible if the pressure difference is small (which is the case in most applications) and will not be considered here. However, the temperature dependence (and also the pressure dependence providing the difference is sufficiently large, see [Moritoki]) of the solubility can be considerable and it is therefore important to state the temperature for which the solubility is reported even under ‘normal’ conditions. In the following the discussion will focus on two component systems only.

It is common terminology for solutions of solids in liquids to denote the liquid component as the solvent and the solid component as the solute, even if the amount of solute in the solution exceeds the amount of solvent. Various measures of composition are in use to report solubilities and the use of a particular set of units should be carefully selected to suit the purpose the data are required for. The most common measures are

- Mass of solute per unit mass of solvent (kg/kg)
- Mass of solute per unit mass of solution (kg/kg)
- Mass of solute per unit volume of solvent (kg/m^3 or g/L)
- Molar amount of solute per unit volume of solvent (kmol/m^3 or mol/L)
- Mole fractions (dimensionless number)

From the above list it is clear that, for the first two cases, it has to be stated explicitly whether composition reported refers to the solvent or the solute in order to avoid confusion. Moreover, it is often necessary to mention the initial state of the solute, as many substances can exist as solvated or unsolvated solids (*vide infra*). For example, two solutions of sodium carbonate in water will have different compositions if in one case the decahydrate is used as starting material and in the other the same mass of monohydrate is employed. Ambiguity arises if this is not accounted for.

The solubility of most materials increases with temperature. However, a number of examples exist, where the solubility shows the reverse trend (sodium sulfate, calcium carbonate, iron sulfate dihydrate, to name but a few). The dependence of the solubility upon temperature is best represented graphically in the form of a solubility curve, which maps the composition of a solution at the solubility limit onto the temperature. A generalized solubility curve is shown in Figure 1 below. The solubility is a continuous

function of temperature for a given form of a given material. Polymorphs of the same material, solvates and hydrates (*vide infra*) generally have different solubilities. A change in solid form is normally evidenced by a discontinuity in the solubility curve, which results from different slope, that is, temperature dependence, of the solubility of the respective forms. In Figure 1 the solubility of a fictitious substance A that forms three phases, two hydrates and one anhydrous phase, is shown. Two discontinuities can be seen marking the transition points between the stable regions for the trihydrate and monohydrate (left) and the monohydrate and anhydrous phase (right). The solubilities of the respective stable phases are indicated by the solid line. In addition, the solubilities of the different metastable forms are indicated by the dotted line.

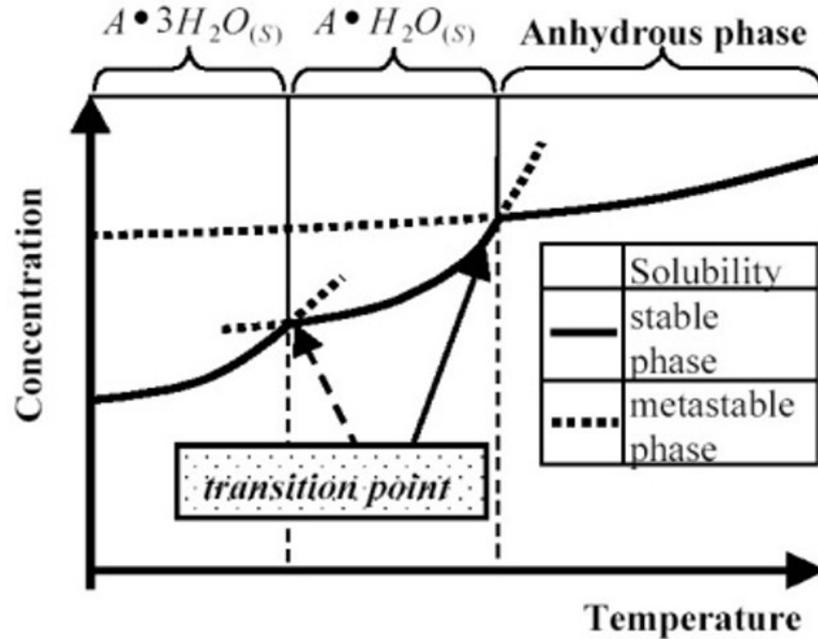


Figure 1: Typical solubility diagram showing the dependence of solution phase concentration in equilibrium versus temperature. Transition points between different phases are highlighted. (from [Nordhoff]). The full line represents the solubility of the stable phase in a given region, the dashed line represents the solubility of the respective metastable phases.

Solubilities are determined experimentally and any convenient analytical technique that provides a quantitative measure of composition can be employed. Not every technique is suitable for every situation and the decision as to which method is used has to be made on a case by case basis. In the simplest case of a two component system containing a solute that is non-volatile and stable with respect to temperature the composition can be determined by taking a given mass of the solution, evaporating to dryness and weighing the remaining solid (solubility measurements should always be based upon a mass of solution due to the higher accuracy compared to volume measurements). The more components present and the more complex the system, the more difficult it becomes to accurately determine the composition by a single analytical technique.

A number of factors have to be accounted for when determining solubilities. First and foremost, it is important to ensure that the solution is indeed in equilibrium. This is

particularly important in the case of highly concentrated, viscous solutions where dissolution rates may become vanishingly small the closer one approaches the equilibrium composition. Here it is important to provide good agitation and to allow for sufficient time before taking a measurement. One method to assess whether equilibrium has been reached is to take measurements from two solutions, one where saturation is approached from an undersaturated state, the other where saturation is approached from a supersaturated state. Both compositions should be identical within experimental error limits if equilibrium has been achieved.

At this point it is important to stress that crystallization is a non-equilibrium process. The value of knowing the equilibrium properties of solutions lies in the fact that they dictate the operating conditions for the crystallization process. The driving force required for nucleation and crystal growth is the level of supersaturation in the solution (supercooling in melts). This means, that crystallization can only occur at solution compositions where the amount of solute exceeds the solubility limit. Such solutions are called supersaturated solutions and the region of phase space where supersaturated solutions exist is known as the metastable zone. The driving force for crystallization (both nucleation and crystal growth, see section on kinetics below) increases with increasing supersaturation. Supersaturation can be achieved in a number of ways, most commonly by cooling a saturated solution (for solutes where solubility increases with temperature, solutes with reverse temperature dependence must, of course, be heated) or by evaporation of solvent. As is the case for solubility, several measures exist to express supersaturation. These are the difference between the equilibrium composition at the temperature of the supersaturated solution c^* and the actual composition in the supersaturated solution c

$$\Delta c = c - c^*, \quad (1)$$

the ratio of these two concentrations

$$S = c / c^*, \quad (2)$$

and, relating these two, the relative supersaturation

$$\sigma = \Delta c / c^* = S - 1 \quad (3)$$

For melts, the driving force is usually expressed in terms of the supercooling

$$\Delta \theta = \theta^* - \theta, \quad (4)$$

which represents the difference between the equilibrium temperature of the melt θ^* and the actual temperature θ . Occasionally supercooling also finds use in solution crystallization.

Quantifying the supersaturation is important for two reasons. As mentioned above the supersaturation is a measure of the driving force for the crystallization process. The second reason concerns the theoretical yield of the process. The theoretical yield of any crystallization is easy to calculate as it is given by the difference between the actual

composition of the feed solution at the starting point of the process and the equilibrium composition at the end-point of the process. This definition already accounts for any temperature gradients employed in the process. Of course the real yield of the process may differ from the theoretical yield. As the supersaturation decreases, crystal growth rates also decrease and the theoretical yield will only be reached in the limit of infinite time. The consequence of this is a lower yield than possible. On the other hand, yields may be higher than theoretically possible if growth is fast and if the crystals obtained contain a significant amount of liquid and/or impurity inclusions.

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Biographical Sketches

Joachim Ulrich received the Diplom-Ingenieur degree from the Technical University Clausthal-Zellerfeld in Germany, the Dr.-Ing. from the Rheinisch-Westfälische Technische Hochschule Aachen and the Habilitation from the Universität Bremen. He has held a post-doctoral position at the Waseda University, Tokio, Japan and in 1999 was appointed chair of thermal process engineering at the Martin-Luther-Universität Halle-Wittenberg in Halle (Saale). He is currently chair of the European Federation of Chemical Engineering. His interests include all aspects of industrial crystallization, especially melt crystallization and batch crystallization.

Matthew Jonathan Jones received the Diplom-Chemiker degree from the Westfälische Wilhelms-Universität Münster in Germany and the PhD from the University of London (University College), UK. After post-doctoral positions at the University of St. Andrews and Heriot-Watt University, Edinburgh and a teaching fellowship at the University of Leeds, he took up the position of senior scientist in the thermal process engineering group at the Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Germany in 2003. His research interests include the industrial crystallization of proteins and the application of molecular modeling to crystallization and materials in the solid state.