Crystallisation, one of the oldest of unit operations, is used to produce vast quantities of materials, including sodium chloride, sodium and aluminium sulphates and sucrose which all have production rates in excess of $10^8$ tonne/year on a world basis. Many organic liquids are purified by crystallisation rather than by distillation since, as shown by Mullin\(^1\) in Table 15.1, enthalpies of crystallisation are generally much lower than enthalpies of vaporisation and crystallisation may be carried out closer to ambient temperature thereby reducing energy requirements. Against this, crystallisation is rarely the last stage in a process and solvent separation, washing and drying stages are usually required. Crystallisation is also a key operation in the freeze-concentration of fruit juices, the desalination of sea water, the recovery of valuable materials such as metal salts from electroplating processes, the production of materials for the electronic industries and in biotechnological operations such as the processing of proteins.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point (K)</th>
<th>Enthalpy of crystallisation (kJ/kg)</th>
<th>Boiling point (K)</th>
<th>Enthalpy of vaporisation (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-cresol</td>
<td>304</td>
<td>115</td>
<td>464</td>
<td>410</td>
</tr>
<tr>
<td>m-cresol</td>
<td>285</td>
<td>117</td>
<td>476</td>
<td>423</td>
</tr>
<tr>
<td>p-cresol</td>
<td>306</td>
<td>110</td>
<td>475</td>
<td>435</td>
</tr>
<tr>
<td>o-xylene</td>
<td>246</td>
<td>128</td>
<td>414</td>
<td>347</td>
</tr>
<tr>
<td>m-xylene</td>
<td>225</td>
<td>109</td>
<td>412</td>
<td>343</td>
</tr>
<tr>
<td>p-xylene</td>
<td>286</td>
<td>161</td>
<td>411</td>
<td>340</td>
</tr>
<tr>
<td>o-nitrotoluene</td>
<td>268.9</td>
<td>120</td>
<td>495</td>
<td>344</td>
</tr>
<tr>
<td>m-nitrotoluene</td>
<td>288.6</td>
<td>109</td>
<td>506</td>
<td>364</td>
</tr>
<tr>
<td>p-nitrotoluene</td>
<td>325</td>
<td>113</td>
<td>511</td>
<td>366</td>
</tr>
<tr>
<td>water</td>
<td>273</td>
<td>334</td>
<td>373</td>
<td>2260</td>
</tr>
</tbody>
</table>

Although crystals can be grown from the liquid phase—either a solution or a melt—and also from the vapour phase, a degree of supersaturation, which depends on the characteristics of the system, is essential in all cases for crystal formation or growth to take place. Some solutes are readily deposited from a cooled solution whereas others crystallise only after removal of solvent. The addition of a substance to a system in order to alter equilibrium conditions is often used in precipitation processes where supersaturation is sometimes achieved by chemical reaction between two or more substances and one of the reaction products is precipitated.
In evaluating a crystallisation operation, data on phase equilibria are important as this indicates the composition of product which might be anticipated and the degree of supersaturation gives some idea of the driving force available. The rates of nuclei formation and crystal growth are equally important as these determine the residence time in, and the capacity of a crystalliser. These parameters also enable estimates to be made of crystal sizes, essential for the specification of liquor flows through beds of crystals and also the mode and degree of agitation required. It is these considerations that form the major part of this Section.

15.2. PHASE EQUILIBRIA

One-component systems

Temperature and pressure are the two variables that affect phase equilibria in a one-component system. The phase diagram in Figure 15.1 shows the equilibria between the solid, liquid, and vapour states of water where all three phases are in equilibrium at the triple point, 0.06 N/m² and 273.3 K. The sublimation curve indicates the vapour pressure of ice, the vaporisation curve the vapour pressure of liquid water, and the fusion curve the effect of pressure on the melting point of ice. The fusion curve for ice is unusual in that, in most one component systems, increased pressure increases the melting point, whilst the opposite occurs here.

![Phase diagram for water](image)

A single substance may crystallise in more than one of seven crystal systems, all of which differ in their lattice arrangement, and exhibit not only different basic shapes but also different physical properties. A substance capable of forming more than one different crystal is said to exhibit polymorphism, and the different forms are called polymorphs. Calcium carbonate, for example, has three polymorphs — calcite (hexagonal),
aragonite (tetragonal), and vaterite (trigonal). Although each polymorph is composed of the same single substance, it constitutes a separate phase. Since only one polymorph is thermodynamically stable at a specified temperature and pressure, all the other polymorphs are potentially capable of being transformed into the stable polymorph. Some polymorphic transformations are rapid and reversible and polymorphs may be enantiotropic (interconvertible) or monotropic (incapable of transformation). Graphite and carbon, for example, are monotropic at ambient temperature and pressure, whereas ammonium nitrate has five enantiotropic polymorphs over the temperature range 255–398 K. Figure 15.2a, taken from Mullin (2), shows the phase reactions exhibited by two enantiotropic forms, α and β, of the same substance. The point of intersection of the two vapour pressure curves is the transition point at which the two forms can co-exist in equilibrium at the specified temperature and pressure. The triple point at which vapour, liquid and β solid can co-exist may be considered as the melting point of the β form. On slow heating, solid α changes into solid β and finally melts with the reverse process taking place on slow cooling. Rapid heating or cooling can, however, result in

![Figure 15.2a](image1.png)

![Figure 15.2b](image2.png)

Figure 15.2. Phase diagram for polymorphic substances (2)
different behaviour where the vapour pressure of the $\alpha$ form follows a continuation of the vaporisation curve, and changes in the liquid are represented by the liquid vaporisation curve. The two curves intersect at a metastable triple point where the liquid, vapour, and a solid can coexist in metastable equilibrium. Figure 15.2b shows the pressure–temperature curves for a monotropic substance for which the vapour pressure curves of the $\alpha$ and $\beta$ forms do not intersect, and hence there is no transition point. In this case, solid $\beta$ is the metastable form, and the metastable triple point is as shown.

Two-component systems

Temperature, pressure, and concentration can affect phase equilibria in a two-component or binary system, although the effect of pressure is usually negligible and data can be shown on a two-dimensional temperature–concentration plot. Three basic types of binary system — eutectics, solid solutions, and systems with compound formation — are considered and, although the terminology used is specific to melt systems, the types of behaviour described may also be exhibited by aqueous solutions of salts, since, as Mullin(3) points out, there is no fundamental difference in behaviour between a melt and a solution.

An example of a binary eutectic system $\text{AB}$ is shown in Figure 15.3a where the eutectic is the mixture of components that has the lowest crystallisation temperature in the system. When a melt at X is cooled along XZ, crystals, theoretically of pure $B$, will start to be deposited at point Y. On further cooling, more crystals of pure component $B$ will be deposited until, at the eutectic point E, the system solidifies completely. At Z, the crystals C are of pure $B$ and the liquid L is a mixture of $A$ and $B$ where the mass proportion of solid phase (crystal) to liquid phase (residual melt) is given by ratio of the lengths LZ to CZ; a relationship known as the lever arm rule. Mixtures represented by points above $AE$ perform in a similar way, although here the crystals are of pure $A$. A liquid of the eutectic composition, cooled to the eutectic temperature, crystallises with unchanged composition and continues to deposit crystals until the whole system solidifies. Whilst a eutectic has a fixed composition, it is not a chemical compound, but is simply a physical mixture of the individual components, as may often be visible under a low-power microscope.

The second common type of binary system is one composed of a continuous series of solid solutions, where the term solid solution or mixed crystal refers to an intimate mixture on the molecular scale of two or more components. The components of a solid-solution system cannot be separated as easily as those of a eutectic system. This is shown in Figure 15.3b, where the liquidus represents the temperature at which mixtures of $A$ and $B$ begin to crystallise on cooling and the solidus represents temperatures at which mixtures begin to melt on heating. A melt at X begins to crystallise at Y and then at Z, the system consists of a mixture of crystals of a composition represented by C and a liquid of a composition represented by L, where the ratio of crystals to liquid is again given by the lever arm rule. The crystals do not, however, consist of a single pure component as in a simple eutectic system but are an intimate mixture of components $A$ and $B$ which must be heated and re-crystallised, perhaps many times, in order to achieve further purification. In this way, a simple eutectic system may be purified in a single-stage crystallisation operation, whereas a solid-solution system always needs multistage operation.

The solute and solvent of a binary system can combine to form one or more different compounds such as, for example, hydrates in aqueous solutions. If the compound can
co-exist in stable equilibrium with a liquid phase of the same composition, then it has a *congruent* melting point, that is where melting occurs without change in composition. If this is not the case, then the melting point is *incongruent*. In Figure 15.4a, the heating–cooling cycle follows the vertical line through point D since melting and crystallisation occur without any change of composition. In Figure 15.4b, however, compound D decomposes at a temperature $T_1$ which is below its theoretical melting point $T_2$. Thus, if
**Figure 15.4. Phase diagrams for binary systems (E - eutectic, L - liquid)**

D is heated, melting begins at $T_1$, though is not complete. At $T_1$, a system of composition D contains crystals of pure B in a melt of composition C. If this mixture is cooled, then a solid mixture of B and that represented by point C is obtained and subsequent heating and cooling cycles result in further decomposition of the compound represented by D.

There is current interest in the use of inorganic-salt hydrates as heat-storage materials, particularly for storage of solar heat in domestic and industrial space heating, where, ideally, the hydrate should have a congruent melting point so that sequences of crystallisation–melting–crystallisation can be repeated indefinitely. Incongruently melting hydrate systems tend to stratify on repeated temperature cycling with a consequent loss of efficiency as melting gives a liquid phase that contains crystals of a lower hydrate or of the anhydrous salt, which settle to the bottom of the container and fail to re-dissolve on subsequent heating. Calcium chloride hexahydrate, whilst not a true congruently melting
hydrate, appears to be one of the most promising materials\textsuperscript{(4,5)} as are sodium sulphate deca-hydrate, sodium acetate tri-hydrate, and sodium thiosulphate penta-hydrate which all do have incongruent melting points\textsuperscript{(6,7)}.

**Three-component systems**

Phase equilibria in three-component systems are affected by temperature, pressure, and the concentrations of any two of the three components. Since the effect of pressure is usually negligible, phase equilibria may be plotted on an isothermal triangular diagram and, as an example, the temperature–concentration space model for $o$-, $m$-, and $p$-nitrophenol is shown in Figure 15.5a\textsuperscript{(3)}. The three components are $O$, $M$, and $P$, respectively and points $O'$, $M'$, and $P'$ represent the melting points of the pure components $o$- (318 K), $m$- (370 K) and $p$-nitrophenol (387 K). The vertical faces of the prism represent temperature–concentration diagrams for the three binary eutectic systems $O-M$, $O-P$, and $M-P$, which are all similar to that shown in Figure 15.4. The binary eutectics are represented by points A (304.7 K, 72.5 per cent O, 27.5 per cent M), B (306.7 K, 75.5 per cent O, 24.5 per cent P), and C (334.7 K, 54.8 per cent M, 45.2 per cent P) and $AD$ within the prism represents the effect of adding $P$ to the $O-M$ binary eutectic at $A$. Similarly, curves $BD$ and $CD$ denote the lowering of freezing points of the binary eutectics represented by points $B$ and $C$, respectively, upon adding the third component. Point $D$ is a ternary eutectic point (294.7 K; 57.7 per cent $O$, 23.2 per cent $M$, 19.1 per cent $P$) at which the liquid freezes to form a solid mixture of the three components. The section above the freezing point surfaces formed by the liquidus curves represents the homogeneous liquid phase, the section below these surfaces down to a temperature, $D$ denotes solid and liquid phases in equilibrium and the section below this temperature represents a completely solidified system.

Figure 15.5b is the projection of $AD$, $BD$, and $CD$ in Figure 15.5a on to the triangular base of the prism. Again $O$, $M$ and $P$ are the pure components, points A, B, and C represent the three binary eutectic points and $D$ is the ternary eutectic point. The diagram is divided by $AD$, $BD$, and $CD$ into three regions which denote the three liquidus surfaces in the space model and the temperature falls from the apexes and sides of the triangle toward the eutectic point $D$. Several isotherms showing points on the liquidus surfaces are shown. When, for example, a molten mixture with a composition $X$ is cooled, solidification starts when the temperature is reduced to 353 K and since $X$ lies in the region $ADCM$, pure $m$-nitrophenol is deposited. The composition of the remaining melt changes along line $MX'$ and at $X'$, equivalent to 323 K, $p$-nitrophenol also starts to crystallise. On further cooling, both $m$ and $p$-nitrophenol are deposited and the composition of the liquid phase changes in the direction $X'D$. When the melt composition and temperature reach point $D$, $o$-nitrophenol also crystallises out and the system solidifies without further change in composition.

Many different types of phase behaviour are encountered in ternary systems that consist of water and two solid solutes. For example, the system $\text{KNO}_3-\text{NaNO}_3-\text{H}_2\text{O}$ which does not form hydrates or combine chemically at 323 K is shown in Figure 15.6, which is taken from Mullin\textsuperscript{(3)}. Point A represents the solubility of $\text{KNO}_3$ in water at 323 K (46.2 kg/100 kg solution), C the solubility of $\text{NaNO}_3$ (53.2 kg/100 kg solution), AB is the composition of saturated ternary solutions in equilibrium with solid $\text{KNO}_3$ and BC
Figure 15.5: Eutectic formation in the ternary system o-, m- and p-nitrophenol. (a) Temperature-concentration space model; (b) Projection on a triangular diagram. (Numerical values represent temperatures in K)

Figure 15.6: Phase diagram for the ternary system KNO$_3$-NaNO$_3$-$\text{H}_2\text{O}$ at 323 K.

Those in equilibrium with solid NaNO$_3$. The area above the line ABC is the region of unsaturated homogeneous solutions. At point B, the solution is saturated with both KNO$_3$ and NaNO$_3$. If, for example, water is evaporated isothermally from an unsaturated solution at $X_1$, the solution concentration increases along $X_1X_2$ and pure KNO$_3$ is deposited when the concentration reaches $X_2$. If more water is evaporated to give a system of composition $X_3$, the solution composition is represented by $X'_3$ on the saturation curve AB, and by point B when composition $X_4$ is reached. Further removal of water causes deposition...
of NaNO₃. After this, all solutions in contact with solid have a constant composition B, which is referred to as the *eutonic point* or *drying-up point* of the system. After complete evaporation of water, the composition of the solid residue is indicated by X₅. Similarly, if an unsaturated solution, represented by a point to the right of B is evaporated isothermally, only NaNO₃ is deposited until the solution composition reaches B. KNO₃ is then also deposited and the solution composition remains constant until evaporation is complete. If water is removed isothermally from a solution of composition B, the composition of deposited solid is given by X₆ and it remains unchanged throughout the evaporation process.

**Multi-component systems**

The more components in a system, the more complex are the phase equilibria and it is more difficult to represent phases graphically. Descriptions of multi-component solid–liquid diagrams and their uses have been given by Mullin, Findlay and Campbell, Ricci, Null and Nyvlt and techniques for predicting multi-component solid–liquid phase equilibria have been presented by Hormeyer et al., Kusik et al., and Sander et al.

**Phase transformations**

Metastable crystalline phases frequently crystallise to a more stable phase in accordance with Ostwald’s rule of stages, and the more common types of phase transformation that occur in crystallising and precipitating systems include those between polymorphs and solvates. Transformations can occur in the solid state, particularly at temperatures near the melting point of the crystalline solid, and because of the intervention of a solvent. A stable phase has a lower solubility than a metastable phase, as indicated by the solubility curves in Figures 15.7a and 15.7b for enantiotropic and monotropic systems respectively and:

![Solubility curves](image)
whilst transformation cannot occur between the metastable (I) and stable (II) phases in
the monotropic system in the temperature range shown, it is possible above the transition
temperature in an enantiotropic system. Polymorphic transformation adds complexity to a
phase diagram, as illustrated by Nancollas et al., Nancollas and Reddy who have studied dissolution–recrystallisation transformations in hydrate systems, and Cardew and Davey who have presented theoretical analyses of both solid
state and solvent-mediated transformations in an attempt to predict their kinetics.

15.2.2. Solubility and saturation

Supersaturation

A solution that is in thermodynamic equilibrium with the solid phase of its solute at a
given temperature is a saturated solution, and a solution containing more dissolved solute
than that given by the equilibrium saturation value is said to be supersaturated. The degree
of supersaturation may be expressed by:

\[ \Delta c = c - c^* \]  

(15.1)

where \( c \) and \( c^* \) are the solution concentration and the equilibrium saturation value re-
spectively. The supersaturation ratio, \( S \), and the relative supersaturation, \( \varphi \) are then:

\[ S = \frac{c}{c^*} \]  

(15.2)

and:

\[ \varphi = \frac{\Delta c}{c^*} = S - 1 \]  

(15.3)

Solution concentrations may be expressed as mass of anhydride/mass of solvent or as
mass of hydrate/mass of free solvent, and the choice affects the values of \( S \) and \( \varphi \) as
shown in the following example which is based on the data of Mullin.

Example 15.1

At 293 K, a supersaturated solution of sucrose contains 2.45 kg sucrose/kg water. If the equilibrium
saturation value is 2.04 kg/kg water, what is the supersaturation ratio in terms of kg/kg water and
kg/kg solution?

Solution

For concentrations in kg sucrose/kg water:

\[ c = 2.45 \text{ kg/kg, } c^* = 2.04 \text{ kg/kg} \]

and:

\[ S = \frac{c}{c^*} = \frac{2.45}{2.04} = 1.20 \]

For concentrations in kg sucrose/kg solution:

\[ c = \frac{2.45}{(2.45 + 1.0)} = 0.710 \text{ kg/kg solution,} \]

\[ c^* = \frac{2.04}{(2.04 + 1.0)} = 0.671 \text{ kg/kg solution} \]

and:

\[ S = \frac{0.710}{0.671} = 1.06 \]
Whilst the fundamental driving force for crystallisation, the true thermodynamic supersaturation, is the difference in chemical potential, in practice supersaturation is generally expressed in terms of solution concentrations as given in equations 15.1–15.3. Mullin and Söhnle\(^\text{[19]}\) has presented a method of determining the relationship between concentration-based and activity-based supersaturation by using concentration-dependent activity-coefficients.

In considering the state of supersaturation, Ostwald\(^{[20]}\) introduced the terms labile and metastable supersaturation to describe conditions under which spontaneous (primary) nucleation would or would not occur, and Miers and Isaac\(^{[21]}\) have represented the metastable zone by means of a solubility–supersolubility diagram, as shown in Figure 15.8.

![Solubility supersolubility diagram](image)

Figure 15.8. Solubility supersolubility diagram

Whilst the (continuous) solubility curve can be determined accurately, the position of the (broken) supersolubility curve is less certain as it is influenced by factors such as the rate at which the supersaturation is generated, the degree of agitation and the presence of crystals or impurities. In the stable unsaturated zone, crystallisation is impossible. In the metastable supersaturated zone, spontaneous nucleation is improbable although a crystal would grow, and in the unstable or labile saturated zone, spontaneous nucleation is probable but not inevitable. If a solution at A is cooled without loss of solvent along ABC, spontaneous nucleation cannot occur until C is reached. Although the tendency to nucleate increases once the labile zone is reached, some solutions become too viscous to permit nucleation and set to a glass. Supersaturation can also be achieved by removing solvent and ADE represents such an operation carried out at constant temperature. Because the solution near the evaporating surface is more highly supersaturated than the bulk solution, penetration into the labile zone rarely occurs and crystals at the surface fall into the solution and induce nucleation, often before bulk conditions at E have been reached. Industrial crystallisers often combine cooling and evaporation. The width of the metastable zone is often expressed as a temperature difference, \(\Delta T\) which is related to the corresponding concentration difference, \(\Delta c\) by the point slope of the solubility curve, \(dc^*/dT\) or:

\[
\Delta c \approx \frac{dc^*}{dT} \Delta T
\]  \hspace{1cm} (15.4)
Table 15.2. Maximum allowable supercooling $\Delta T_{\text{max}}$ for aqueous salt solutions at 298 K$^{(3)}$

<table>
<thead>
<tr>
<th>Substance</th>
<th>deg K</th>
<th>Substance</th>
<th>deg K</th>
<th>Substance</th>
<th>deg K</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$Cl</td>
<td>0.7</td>
<td>Na$_2$CO$_3$·10H$_2$O</td>
<td>0.6</td>
<td>Na$_2$S$_2$O$_5$·5H$_2$O</td>
<td>1.0</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>0.6</td>
<td>Na$_2$CrO$_4$·10H$_2$O</td>
<td>1.6</td>
<td>K alum</td>
<td>4.0</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>1.8</td>
<td>NaCl</td>
<td>4.0</td>
<td>KBr</td>
<td>1.1</td>
</tr>
<tr>
<td>NH$_4$H$_2$PO$_4$</td>
<td>2.5</td>
<td>Na$_2$B$_4$O$_7$·10H$_2$O</td>
<td>4.0</td>
<td>KCl</td>
<td>1.1</td>
</tr>
<tr>
<td>CuSO$_4$·5H$_2$O</td>
<td>1.4</td>
<td>NaI</td>
<td>1.0</td>
<td>KI</td>
<td>0.6</td>
</tr>
<tr>
<td>FeSO$_4$·7H$_2$O</td>
<td>0.5</td>
<td>NaHPO$_4$·12H$_2$O</td>
<td>0.4</td>
<td>KH$_2$PO$_4$</td>
<td>9.0</td>
</tr>
<tr>
<td>MgSO$_4$·7H$_2$O</td>
<td>1.0</td>
<td>NaNO$_3$</td>
<td>0.9</td>
<td>KNO$_3$</td>
<td>0.4</td>
</tr>
<tr>
<td>NiSO$_4$·6H$_2$O</td>
<td>4.0</td>
<td>NaNO$_2$</td>
<td>0.9</td>
<td>KNO$_2$</td>
<td>0.8</td>
</tr>
<tr>
<td>NaBr·2H$_2$O</td>
<td>0.9</td>
<td>Na$_2$SO$_4$·10H$_2$O</td>
<td>0.3</td>
<td>K$_2$SO$_4$</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Data measured in the presence of crystals with slow cooling and moderate agitation. The working value for a normal crystalliser may be 50 per cent of these values or less.

The measurement of the width of the metastable zone is discussed in Section 15.2.4, and typical data are shown in Table 15.2. Provided the actual solution concentration and the corresponding equilibrium saturation concentration at a given temperature are known, the supersaturation may be calculated from equations 15.1–15.3. Data on the solubility for two- and three-component systems have been presented by SEIDELL and LINKE$^{(22)}$, STEPHEN et al.$^{(23)}$ and BROUL et al.$^{(24)}$. Supersaturation concentrations may be determined by measuring a concentration-dependent property of the system such as density or refractive index, preferably in situ on the plant. On industrial plant, both temperature and feedstock concentration can fluctuate, making the assessment of supersaturation difficult. Under these conditions, the use of a mass balance based on feedstock and exit-liquor concentrations and crystal production rates, averaged over a period of time, is usually an adequate approach.

### Prediction of solubilities

Techniques are available for estimating binary and multi-component solubility behaviour. One example is the van’t Hoff relationship which, as stated by MOYERS and ROUSSEAU$^{(25)}$, takes the following form for an ideal solution:

$$\ln x = \frac{H_f}{RT} \left( \frac{T}{T_M} - 1 \right)$$  \hfill (15.5)

where $x$ is the mole fraction of solute in solution, $H_f$ is the heat of fusion and $T_M$ is the melting point of the pure component. One interesting consequence of this equation is that solubility depends only on the properties of the solute occurring in the equation. Another equation frequently used for ideal systems incorporates cryoscopic constants, values of which have been obtained empirically for a wide variety of materials in the course of the American Petroleum Research Project 44$^{(26)}$. This takes the form:

$$\ln(1/x) \equiv z_1(T_M - T)[1 + z_2(T_M - T)] \ldots$$  \hfill (15.6)

where:

$$z_1 = \frac{H_f}{RT_M^2} \quad \text{and} \quad z_2 = \frac{1}{T_M} = \frac{C_p}{2H_f^2}$$

MOYERS and ROUSSEAU$^{(25)}$ have used equations 15.5 and 15.6, to calculate the freezing point data for $o$- and $p$-xylene shown in Table 15.3.
Table 15.3: Calculated freezing point curves for \( o- \) and \( p- \) xylene\(^{(22)} \)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Mole fraction in solution</th>
<th>( p- ) xylene</th>
<th>( o- ) xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Eqn. 15.5} )</td>
<td>( \text{Eqn. 15.6} )</td>
<td>( \text{Eqn. 15.5} )</td>
</tr>
<tr>
<td>286.41</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>0.848</td>
<td>0.844</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td>0.646</td>
<td>0.640</td>
<td></td>
</tr>
<tr>
<td>260</td>
<td>0.482</td>
<td>0.478</td>
<td></td>
</tr>
<tr>
<td>249.97</td>
<td>0.249</td>
<td>0.256</td>
<td>1.00</td>
</tr>
<tr>
<td>240</td>
<td>0.172</td>
<td>0.183</td>
<td>0.803</td>
</tr>
<tr>
<td>235</td>
<td></td>
<td></td>
<td>0.695</td>
</tr>
<tr>
<td>230</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crystal size and solubility

If very small solute particles are dispersed in a solution, the solute concentration may exceed the normal equilibrium saturation value. The relationship between particle size and solubility first applied to solid–liquid systems by Ostwald\(^{(20)} \) may be expressed as:

\[
\ln \frac{c_r}{c^*} = \frac{2M_\sigma}{n_iRT\rho_s} \rho_r \quad (15.7)
\]

where \( c_r \) is the solubility of particles of radius \( r \), \( \rho_s \) the density of the solid, \( M \) the relative molecular mass of the solute in solution, \( \rho_r \) the interfacial tension of the crystallisation surface in contact with its solution and \( n_i \) the moles of ions formed from one mole of electrolyte. For a non-electrolyte, \( n_i = 1 \) and for most inorganic salts in water, the solubility increase is really only significant for particles of less than 1 \( \mu \)m. The use of this equation is illustrated in the following example which is again based on data from Mullin\(^{(3)} \).

Example 15.2

Compare the increase in solubility above the normal equilibrium values of 1, 0.1 and 0.01 \( \mu \)m particles of barium sulphate and sucrose at 298 K. The relevant properties of these materials are:

<table>
<thead>
<tr>
<th></th>
<th>barium sulphate</th>
<th>sucrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative molecular mass (kg/kmol)</td>
<td>233</td>
<td>342</td>
</tr>
<tr>
<td>number of ions (( - ))</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>solid density (kg/m(^3))</td>
<td>4500</td>
<td>1590</td>
</tr>
<tr>
<td>interfacial tension (J/m(^2))</td>
<td>0.13</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Solution

Taking the gas constant, \( R \) as 8314 J/kmol K, then in equation 15.7:
For barium sulphate:
\[
\ln\left(\frac{c_r}{c^*}\right) = \frac{(2 \times 233 \times 0.13)}{(2 \times 8314 \times 298 \times 4500r)} = 2.72 \times 10^{-9}/r
\]

For sucrose:
\[
\ln\left(\frac{c_r}{c^*}\right) = \frac{(2 \times 342 \times 0.01)}{(1 \times 8314 \times 298 \times 1590r)} = 1.736 \times 10^{-9}/r
\]

Substituting 0.5 \times 10^{-7}, 0.5 \times 10^{-8} and 0.5 \times 10^{-9} m for \( r \) gives the following data:

<table>
<thead>
<tr>
<th>particle size</th>
<th>( d (\mu\text{m}) )</th>
<th>( r (\mu\text{m}) )</th>
<th>( c_r/c^* )</th>
<th>increase (per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>barium sulphate</td>
<td>1</td>
<td>0.5</td>
<td>1.005</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.05</td>
<td>1.06</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.005</td>
<td>1.72</td>
<td>72</td>
</tr>
<tr>
<td>sucrose</td>
<td>1</td>
<td>0.5</td>
<td>1.004</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.05</td>
<td>1.035</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.005</td>
<td>1.415</td>
<td>41.5</td>
</tr>
</tbody>
</table>

**Effect of impurities**

Industrial solutions invariably contain dissolved impurities that can increase or decrease the solubility of the prime solute considerably, and it is important that the solubility data used to design crystallisation processes relate to the actual system used. Impurities can also have profound effects on other characteristics, such as nucleation and growth.

**15.2.3. Crystal nucleation**

Nucleation, the creation of crystalline bodies within a supersaturated fluid, is a complex event, since nuclei may be generated by many different mechanisms. Most nucleation classification schemes distinguish between *primary nucleation* - in the absence of crystals and *secondary nucleation* - in the presence of crystals. STRICKLAND-CONSTABLE\(^{27}\) and KASHCHEV\(^{28}\) have reviewed nucleation, and GARSIDE and DAVEY\(^{29}\) have considered secondary nucleation in particular.

**Primary nucleation**

Classical theories of primary nucleation are based on sequences of bimolecular collisions and interactions in a supersaturated fluid that result in the build-up of lattice-structured bodies which may or may not achieve thermodynamic stability. Such primary nucleation is known as *homogeneous*, although the terms *spontaneous* and *classical* have also been used. As discussed by UBELHÖDE\(^{30}\) and GARTEN and HEAD\(^{31}\), ordered solute-clustering can occur in supersaturated solutions prior to the onset of homogeneous nucleation, and BERGLUND et al.\(^{32}\) has detected the presence of quasi-solid-phase species even in unsaturated solutions. MULLIN and LECI\(^{33}\) discussed the development of concentration gradients in supersaturated solutions of citric acid under the influence of gravity, and LARSON and GARSIDE\(^{34}\) estimated the size of the clusters at 4–10 nm. Primary nucleation may also be initiated by suspended particles of foreign substances, and this mechanism is generally
referred to as heterogeneous nucleation. In industrial crystallisation, most primary nucleation is almost certainly heterogeneous, rather than homogeneous, in that it is induced by foreign solid particles invariably present in working solutions. Although the mechanism of heterogeneous nucleation is not fully understood, it probably begins with adsorption of the crystallising species on the surface of solid particles, thus creating apparently crystalline bodies, larger than the critical nucleus size, which then grow into macro-crystals.

Homogeneous nucleation. A consideration of the energy involved in solid-phase formation and in creation of the surface of an arbitrary spherical crystal of radius \( r \) in a supersaturated fluid gives:

\[
\Delta G = 4\pi r^2 \sigma + (4\pi/3)r^3 \Delta G_v
\]

where \( \Delta G \) is the overall excess free energy associated with the formation of the crystalline body, \( \sigma \) is the interfacial tension between the crystal and its surrounding supersaturated fluid, and \( \Delta G_v \) is the free energy change per unit volume associated with the phase change. The term \( 4\pi r^2 \sigma \), which represents the surface contribution, is positive and is proportional to \( r^2 \) and the term \( (4\pi/3)r^3 \Delta G_v \) which represents the volume contribution, is negative and is proportional to \( r^3 \). Any crystal smaller than the critical nucleus size \( r_c \) is unstable and tends to dissolve whilst any crystal larger than \( r_c \) is stable and tends to grow. Combining equations 15.7 and 15.8, and expressing the rate of nucleation \( J \) in the form of an Arrhenius reaction rate equation, gives the nucleation rate as:

\[
J = F \exp\left[-\frac{16\pi^3 v^2}{3 k^3 T^3 (\ln S)^2}\right]
\]

where \( F \) is a pre-exponential factor, \( v \) is molar volume, \( k \) is the Boltzmann constant and \( S \) is the supersaturation ratio. Since equation 15.9 predicts an explosive increase in the nucleation rate beyond some so-called critical value of \( S \), it not only demonstrates the powerful effect of supersaturation on homogeneous nucleation, but also indicates the possibility of nucleation at any level of supersaturation.

Heterogeneous nucleation. The presence of foreign particles or heteronuclei enhances the nucleation rate of a given solution, and equations similar to those for homogeneous nucleation have been proposed to express this enhancement. The result is simply a displacement of the nucleation rate against supersaturation curve, as shown in Figure 15.9, indicating that nucleation occurs more readily at a lower degree of supersaturation. For primary nucleation in industrial crystallisation, classical relationships similar to those based on equation 15.9 have little use, and all that can be justified is a simple empirical relationship such as:

\[
J = K_N(\Delta c)^n
\]

which relates the primary nucleation rate \( J \) to the supersaturation \( \Delta c \) from equation 15.1. The primary nucleation rate constant \( K_N \), and the order of the nucleation process \( n \), which is usually greater than 2, depend on the physical properties and hydrodynamics of the system.

Secondary nucleation

Secondary nucleation can, by definition, take place only if crystals of the species under consideration are already present. Since this is usually the case in industrial crystallisers, secondary nucleation has a profound influence on virtually all industrial crystallisation processes.
Apart from deliberate or accidental introduction of tiny seed crystals to the system, and productive interactions between existing crystals and quasi-crystalline embryos or clusters in solution, the most influential mode of new crystal generation in an industrial crystalliser is contact secondary nucleation between the existing crystals themselves, between crystals and the walls or other internal parts of the crystalliser, or between crystals and the mechanical agitator. Secondary nucleation rates (in m$^{-3}$s$^{-1}$) are most commonly correlated by empirical relationships such as:

$$B = K_b \rho_m^i N^l \Delta c^b$$

(15.11)

where $B$ is the rate of secondary nucleation or birthrate, $K_b$ is the birthrate constant, $\rho_m$ is the slurry concentration or magma density and $N$ is a term that gives some measure of the intensity of agitation in the system such as the rotational speed of an impeller. The exponents $j$, $l$, and $b$ vary according to the operating conditions.

**Nucleation measurements**

One of the earliest attempts to derive nucleation kinetics for solution crystallisation was proposed by Nyvlt$^{(35)}$ and Nyvlt et al.$^{(36)}$ whose method is based on the measurement of metastable zone widths shown in Figure 15.8, using a simple apparatus, shown in Figure 15.10, consisting of a 50 ml flask fitted with a thermometer and a magnetic stirrer, located in an external cooling bath. Nucleation is detected visually and both primary and secondary nucleation can be studied in this way. Typical results$^{(35)}$ shown in Figure 15.11 demonstrate that seeding has a considerable influence on the nucleation process, and the difference between the slopes of the two lines indicates that primary and secondary nucleation occur by different mechanisms. Solution turbulence also affects nucleation and, in general, agitation reduces the metastable zone width. For example, the metastable zone width for gently agitated potassium sulphate solutions is about 12 deg K whilst vigorous agitation reduces this to around 8 deg K. The presence of crystals also induces secondary
nucleation at a supercooling of around 4 deg K. The relation between supercooling $\Delta T$ and supersaturation $\Delta c$ is given by equation 15.4. Useful information on secondary nucleation kinetics for crystalliser operation and design can be determined only from model experiments that employ techniques such as those developed for MSMPR (mixed-suspension mixed-product removal) crystallisers. As discussed by, Nyvlt et al\(^{30}\) and Randolph and Larson\(^{37}\), in a real crystalliser, both nucleation and growth proceed together and interact with other system parameters in a complex manner.
**Induction periods**

A delay occurs between attainment of supersaturation and detection of the first newly created crystals in a solution, and this so-called *induction period*, $t_i$, is a complex quantity that involves both nucleation and growth components. If it is assumed that $t_i$ is essentially concerned with nucleation, that is $t_i \propto 1/J$, then MULLIN\(^3\) has shown, from equation 15.9, that:

$$\frac{1}{t_i} \propto \exp \left( \frac{\sigma^3}{T^3(\log S)^2} \right)$$

(15.12)

Thus, for a given temperature, a logarithmic plot of $t_i$ against $(\log S)^{-\frac{1}{2}}$ should yield a straight line which, if the data truly represent homogeneous nucleation, will allow the calculation of the interfacial tension $\sigma$ and the evaluation of the effect of temperature on $\sigma$. NIELSEN and SÖHNEL\(^38\) has attempted to derive a general correlation between interfacial tension and the solubility of inorganic salts as shown in Figure 15.12a, although the success of this method depends on precise measurement of the induction period $t_i$, which presents problems if $t_i$ is less than a few seconds.

SÖHNEL and MULLIN\(^39\) have shown that short induction periods can be determined by a technique that detects rapid changes in the conductivity of a supersaturated solution. Typical results for CaCO$_3$, SrCO$_3$, and BaCO$_3$, produced by mixing an aqueous solution of Na$_2$CO$_3$ with a solution of the appropriate chloride, are shown in Figure 15.12b. The slopes of the linear, high-supersaturation regions are used to calculate the interfacial tensions (0.08 – 0.12 J/m$^2$), which compare reasonably well with the values predicted from the interfacial tension–solubility relationship in Figure 15.12a. Although interfacial tensions evaluated from experimentally measured induction periods are somewhat unreliable, measurements of the induction period can provide useful information on other crystallisation phenomena, particularly the effect of impurities.

### 15.2.4. Crystal growth

#### Fundamentals

As with nucleation, classical theories of crystal growth\(^3,20,21,35,40–42\) have not led to working relationships, and rates of crystallisation are usually expressed in terms of the supersaturation by empirical relationships. In essence, overall mass deposition rates, which can be measured in laboratory fluidised beds or agitated vessels, are needed for crystalliser design, and growth rates of individual crystal faces under different conditions are required for the specification of operating conditions.

In simple terms, the crystallisation process may be considered to take place in two stages — a diffusional step in which solute is transported from the bulk fluid through the solution boundary layer adjacent to the crystal surface, and a deposition step in which adsorbed solute ions or molecules at the crystal surface are deposited and integrated into the crystal lattice. These two stages which are shown in Figure 15.13, may be described by:

$$\frac{dm}{dt} = k_d A(c - c_i) = k_r A(c_i - c^*)$$

(15.13)

where $m$ is the mass deposited in time $t$, $A$ is the crystal surface area, $c$, $c_i$ and $c^*$ are the solute concentrations in the bulk solution, at the interface and at equilibrium saturation and $k_d$ and $k_r$ are the diffusion and deposition or reaction mass transfer coefficients.
Figure 15.12: (a) Interfacial tension as a function of solubility (k)^{390} (b) Induction period as a function of initial supersaturation (k)^{391}
Because it is not possible to determine the interfacial concentration, this is eliminated by using the overall concentration driving force $\Delta c = (c - c^*)$, where:

$$(c - c^*) = \left( \frac{1}{k_d} \right) \frac{dm}{dt} + \left( \frac{1}{k_r} \right) \left( \frac{dm}{dt} \right)^{1/2}$$

Eliminating $c$ and introducing an overall crystal growth coefficient, $K_G$ gives the approximate relation:

$$\frac{dm}{dt} = K_G (\Delta c)^s$$

(15.14)

The exponents $i$ and $s$ in equations 15.13 and 15.14, referred to as the order of integration and overall crystal growth process, should not be confused with their more conventional use in chemical kinetics where they always refer to the power to which a concentration should be raised to give a factor proportional to the rate of an elementary reaction. As Mullin\textsuperscript{(3)} points out, in crystallisation work, the exponent has no fundamental significance and cannot give any indication of the elemental species involved in the growth process. If $i = 1$ and $s = 1$, $c_i$ may be eliminated from equation 15.13 to give:

$$\frac{1}{K_G} = \frac{1}{k_d} + \frac{1}{k_r}$$

(15.15)

Where the rate of integration is very high, $K_G$ is approximately equal to $k_d$ and the crystallisation is diffusion controlled. When the diffusional resistance is low, $K_G$ is approximately equal to $k_r$ and the process is controlled by the deposition step. Whilst the diffusional step is generally proportional to the concentration driving force, the integration process is rarely first-order and for many inorganic salts crystallising from aqueous solution, $s$ lies in the range 1 – 2.

Comprehensive reviews of theories of crystal growth have been presented by Garside\textsuperscript{(43)}, Nielsen\textsuperscript{(44)}, Pampin\textsuperscript{(45)} and Kaldis and Scheel\textsuperscript{(46)}.
**Measurement of growth rate**

Methods used for the measurement of crystal growth rates are either a) direct measurement of the linear growth rate of a chosen crystal face or b) indirect estimation of an overall linear growth rate from mass deposition rates measured on individual crystals or on groups of freely suspended crystals\(^3,\,35,\,41,\,47,\,48\).

**Face growth rates.** Different crystal faces grow at different rates and faces with a high value of \(s\) grow faster than faces with low values. Changes in growth environment such as temperature, supersaturation pH, and impurities can have a profound effect on growth, and differences in individual face growth rates give rise to habit changes in crystals. For the measurement of individual crystal-face growth-rates, a fixed crystal in a glass cell is observed with a travelling microscope under precisely controlled conditions of solution temperature, supersaturation and liquid velocity\(^3\). The solution velocity past the fixed crystal is often an important growth-determining parameter, sometimes responsible for the so-called size-dependent growth effect often observed in agitated and fluidised-bed crystallisers. Large crystals have higher settling velocities than small crystals and, if their growth is diffusion-controlled, they tend to grow faster. Salts that exhibit solution velocity dependent growth rates include the alums, nickel ammonium sulphate, and potassium sulphate, although salts such as ammonium sulphate and ammonium or potassium dihydrogen phosphate are not affected by solution velocity.

**Overall growth rates.** In the laboratory, growth rate data for crystalliser design can be measured in fluidised beds or in agitated vessels, and crystal growth rates measured by growing large numbers of carefully sized seeds in fluidised suspension under strictly controlled conditions. A warm undersaturated solution of known concentration is circulated in the crystalliser and then supersaturated by cooling to the working temperature. About 5 g of closely sized seed crystals with a narrow size distribution and a mean size of around 500 \(\mu m\) is introduced into the crystalliser, and the upward solution velocity is adjusted so that the crystals are maintained in a reasonably uniform fluidised state in the growth zone. The crystals are allowed to grow at a constant temperature until their total mass is some 10 g, when they are removed, washed, dried, and weighed. The final solution concentration is measured, and the mean of the initial and final supersaturations is taken as the average for the run, an assumption which does not involve any significant error because the solution concentration is usually not allowed to change by more than about 1 per cent during a run. The overall crystal growth rate is then calculated in terms of mass deposited per unit area per unit time at a specified supersaturation.

**Expression of growth rate**

Because the rate of growth depends, in a complex way, on temperature, supersaturation, size, habit, system turbulence and so on, there is no simple way of expressing the rate of crystal growth, although, under carefully defined conditions, growth may be expressed as an overall mass deposition rate, \(R_G\) (kg/m\(^2\) s), an overall linear growth rate, \(G_d(=\ t\ /\ dt)\) (m/s) or as a mean linear velocity, \(u'(=\ t\ /\ dt)\) (m/s). Here \(d\) is some characteristic size of the crystal such as the equivalent aperture size, and \(r\) is the radius corresponding to the
equivalent sphere where \( r = 0.5d \). The relationships between these quantities are:

\[
R_G = K_G \Delta c^s = \left( \frac{1}{A} \right) \frac{3 \alpha \rho \frac{d\rho}{dt}}{\beta} = \left( \frac{6 \alpha \rho}{\beta} \right) \frac{dr}{dt} = \frac{6 \alpha \rho u'}{\beta}
\]

(15.16)

where \( \rho \) is the density of the crystal and the volume and surface shape factors, \( \alpha \) and \( \beta \), are related to particle mass \( m \) and surface area \( A \), respectively, by:

\[
m = \alpha \rho d^3
\]

(15.17)

and:

\[
A = \beta d^2
\]

(15.18)

Values of \( 6\alpha/\beta \) are 1 for spheres and cubes and 0.816 for octahedra and typical values of the mean linear growth velocity, \( u' = 0.5 \ G_d \) for crystals 0.5 – 1 mm growing in the presence of other crystals are given in Table 15.4 which is taken from Mullin(3).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Supersaturation ratio</th>
<th>( S )</th>
<th>( u' ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>313</td>
<td>1.05</td>
<td>8.5 × 10⁻⁷</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>303</td>
<td>1.05</td>
<td>2.5 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>1.05</td>
<td>4.0 × 10⁻⁷</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>293</td>
<td>1.02</td>
<td>4.5 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.01</td>
<td>8.0 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.02</td>
<td>1.5 × 10⁻⁷</td>
</tr>
<tr>
<td>KCl</td>
<td>313</td>
<td>1.01</td>
<td>6.0 × 10⁻⁷</td>
</tr>
<tr>
<td>KNO₃</td>
<td>293</td>
<td>1.05</td>
<td>4.5 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>1.05</td>
<td>1.5 × 10⁻⁷</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>293</td>
<td>1.09</td>
<td>2.8 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>1.18</td>
<td>1.7 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.07</td>
<td>4.2 × 10⁻⁸</td>
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<td></td>
<td>323</td>
<td>1.06</td>
<td>7.0 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.12</td>
<td>3.2 × 10⁻⁷</td>
</tr>
<tr>
<td>NaCl</td>
<td>323</td>
<td>1.002</td>
<td>2.5 × 10⁻⁸</td>
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<tr>
<td></td>
<td>323</td>
<td>1.003</td>
<td>6.5 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>1.002</td>
<td>9.0 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>1.003</td>
<td>1.5 × 10⁻⁷</td>
</tr>
</tbody>
</table>

**Dependence of growth rate on crystal size**

Experimental evidence indicates that crystal growth kinetics often depend on crystal size, possibly because the size depends on the surface deposition kinetics and different crystals of the same size can also have different growth rates because of differences in surface structure or perfection. In addition, as discussed by White et al.(49), Jones and Mullin(50), Janse and de Jong(51) and Garside and Jančič(52), small crystals of many substances grow much more slowly than larger crystals, and some do not grow at all. The behaviour of very small crystals has considerable influence on the performance of continuously operated crystallisers because new crystals with a size of 1 – 10 µm are constantly generated by secondary nucleation and these then grow to populate the full crystal size distribution.
Growth - nucleation interactions

Crystal nucleation and growth in a crystalliser cannot be considered in isolation because they interact with one another and with other system parameters in a complex manner. For a complete description of the crystal size distribution of the product in a continuously operated crystalliser, both the nucleation and the growth processes must be quantified, and the laws of conservation of mass, energy, and crystal population must be applied. The importance of population balance, in which all particles are accounted for, was first stressed in the pioneering work of Randolph and Larson.\(^{37}\)

Crystal habit modification

Differences in the face growth-rates of crystals give rise to changes in their habit or shape. Although the growth kinetics of individual crystal faces usually depend to various extents on supersaturation so that crystal habit can sometimes be controlled by adjusting operating conditions, the most common cause of habit modification is the presence of impurities. Although a soluble impurity will often remain in the liquid phase so that pure crystals are formed, in many cases, both the rate of nucleation and the crystal growth rate are affected. More usually, the effect is one of retardation, thought to be due to the adsorption of the impurity on the surface of the nucleus or crystal. Materials with large molecules such as tannin, dextrin or sodium hexametaphosphate, added in small quantities to boiler feed water, prevent the nucleation and growth of calcium carbonate crystals and hence reduce scaling. In a similar way, the addition of 0.1 per cent of HCl and 0.1 per cent PbCl\(_2\) prevent the growth of sodium chloride crystals. In some cases the adsorption occurs preferentially on one particular face of the crystal, thus modifying the crystal shape. One example is that sodium chloride crystallised from solutions containing traces of urea forms octahedral instead of the usual cubic crystals. In a similar way, dyes are preferentially adsorbed on inorganic crystals,\(^{53}\) although the effect is not always predictable. Garrett\(^{54}\) has described a number of uses of additives as habit modifiers, and industrial applications of habit modification are reported in several reviews\(^{3,55,56}\) in which the factors that must be considered in selecting a suitable habit modifier are discussed. In the main, solid impurities act as condensation nuclei and cause dislocations in the crystal structure.

Inclusions in crystals

Inclusions are small pockets of solid, liquid, or gaseous impurities trapped in crystals that usually occur randomly although a regular pattern may be sometimes observed. As described by Mullin\(^{53}\), a simple technique for observing inclusions is to immerse the crystal in an inert liquid of similar refractive index or, alternatively, in its own saturated solution when, if the inclusion is a liquid, concentration streamlines will be seen as the two fluids meet and, if it is a vapour, a bubble will be released. Industrial crystals may contain significant amounts of included mother liquor that can significantly affect product purity and stored crystals may cake because of liquid seepage from inclusions in broken crystals. In order to minimise inclusions, the crystallising system should be free of dirt and other solid debris, vigorous agitation or boiling should be avoided, and ultrasonic irradiation may be used to suppress adherence of bubbles to a growing crystal face. As fast crystal growth is probably the
most common cause of inclusion formation, high supersaturation levels should be avoided. 

D. Eiacha, Powers, Wilcox and Kuo and Saska and Myerson have published detailed accounts of crystal inclusion.

15.2.5. Crystal yield

The yield of crystals produced by a given degree of cooling may be estimated from the concentration of the initial solution and the solubility at the final temperature, allowing for any evaporation, by making solvent and solute balances. For the solvent, usually water, the initial solvent present is equal to the sum of the final solvent in the mother liquor, the water of crystallisation within the crystals and any water evaporated, or:

\[ w_1 = w_2 + y \left( \frac{R - 1}{R} \right) + w_1 E \]  \hspace{1cm} (15.19)

where \( w_1 \) and \( w_2 \) are the initial and final masses of solvent in the liquor, \( y \) is the yield of crystals, \( R \) is the ratio (molecular mass of hydrate/molecular mass of anhydrous salt) and \( E \) is the ratio (mass of solvent evaporated/mass of solvent in the initial solution). For the solute:

\[ w_1 c_1 = w_2 c_2 + \frac{y}{R} \]  \hspace{1cm} (15.20)

where \( c_1 \) and \( c_2 \) are the initial and final concentrations of the solution expressed as (mass of anhydrous salt/mass of solvent). Substituting for \( w_2 \) from equation 15.19:

\[ w_1 c_1 = c_2 \left[ w_1 (1 - E) - y \left( \frac{R - 1}{R} \right) \right] + \frac{y}{R} \]  \hspace{1cm} (15.21)

from which the yield for aqueous solutions is given by:

\[ y = \frac{R w_1 (c_1 - c_2 (1 - E))}{1 - c_2 (R - 1)} \]  \hspace{1cm} (15.22)

The actual yield may differ slightly from that given by this equation since, for example, when crystals are washed with fresh solvent on the filter, losses may occur through dissolution. On the other hand, if mother liquor is retained by the crystals, an extra quantity of crystalline material will be deposited on drying. Since published solubility data usually refer to pure solvents and solutes that are rarely encountered industrially, solubilities should always be checked against the actual working liquors.

Before equation 15.22 can be applied to vacuum or adiabatic cooling crystallisation, the quantity \( E \) must be estimated, where, from a heat balance:

\[ E = \frac{q R (c_1 - c_2) + C_p (T_1 - T_2) (1 + c_1) [1 - c_2 (R - 1)]}{\lambda [1 - c_2 (R - 1)] - q R c_2} \]  \hspace{1cm} (15.23)

In this equation, \( \lambda \) is the latent heat of evaporation of the solvent (J/kg), \( q \) is the heat of crystallisation of the product (J/kg), \( T_1 \) is the initial temperature of the solution (K), \( T_2 \) is the final temperature of the solution (K) and \( C_p \) is the specific heat capacity of the solution (J/kg K).
Example 15.3

What is the theoretical yield of crystals which may be obtained by cooling a solution containing 1000 kg of sodium sulphate (molecular mass = 142 kg/kmol) in 5000 kg water to 283 K? The solubility of sodium sulphate at 283 K is 9 kg anhydrous salt/100 kg water and the deposited crystals will consist of the deca-hydrate (molecular mass = 322 kg/kmol). It may be assumed that 2 per cent of the water will be lost by evaporation during cooling.

Solution

The ratio, \( R = \frac{322}{142} = 2.27 \)

The initial concentration, \( c_1 = \frac{1000}{5000} = 0.2 \text{ kg Na}_2\text{SO}_4/\text{kg water} \)

The solubility, \( c_2 = \frac{9}{100} = 0.09 \text{ kg Na}_2\text{SO}_4/\text{kg water} \)

The initial mass of water, \( w_1 = 5000 \text{ kg} \) and the water lost by evaporation, \( E = \frac{2}{100} = 0.02 \text{ kg/kg} \)

Thus, in equation 15.22:

\[
y = \frac{(5000 \times 2.27)[0.2 - 0.09(1 - 0.02)]/[1 - 0.09(2.27 - 1)]}{1432 \text{ kg Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}}
\]

Example 15.4

What is the yield of sodium acetate crystals (\( \text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O} \)) obtainable from a vacuum crystalliser operating at 1.33 kN/m\(^2\) when it is supplied with 0.56 kg/s of a 40 per cent aqueous solution of the salt at 353 K? The boiling point elevation of the solution is 11.5 deg K.

Data:

- Heat of crystallisation, \( q = 144 \text{ kJ/kg trihydrate} \)
- Heat capacity of the solution, \( C_p = 3.5 \text{ kJ/kg deg K} \)
- Latent heat of water at 1.33 kN/m\(^2\), \( \lambda = 2.46 \text{ MJ/kg} \)
- Boiling point of water at 1.33 kN/m\(^2\) = 290.7 K
- Solubility of sodium acetate at 290.7 K, \( c_2 = 0.539 \text{ kg/kg water} \)

Solution

Equilibrium liquor temperature = \( (290.7 + 11.5) = 302.2 \text{ K} \).

Initial concentration, \( c_1 = 40/(100 - 40) = 0.667 \text{ kg/kg water} \)

Final concentration, \( c_2 = 0.539 \text{ kg/kg water} \)

Ratio of molecular masses, \( R = (136/82) = 1.66 \)

Thus, in equation 15.23:

\[
E = \frac{144 \times 1.66(0.667 - 0.539) + 3.5(353 - 302.2)(1 + 0.667)[1 - 0.539(1.66 - 1)]}{2460[1 - 0.539(1.66 - 1)] - (144 \times 1.66 \times 0.539)}
\]

\[
e = 0.153 \text{ kg/kg water originally present.}
\]
The yield is then given by equation 15.22 as:

\[ y = (0.56(100 - 40)/100)1.66[0.667 - 0.539(1 - 0.153)]/[1 - 0.539(1.66 - 1)] \]

\[ = 0.183 \text{ kg/s} \]

### 15.2.6. Caking of crystals

Crystalline materials frequently cake or cement together on storage and crystal size, shape, moisture content, and storage conditions can all contribute to the caking tendency. In general, caking is caused by a dampening of the crystal surfaces in storage because of inefficient drying or an increase in atmospheric humidity above some critical value that depends on both substance and temperature. The presence of a hygroscopic trace impurity in the crystals, can also greatly influence their tendency to absorb atmospheric moisture. Moisture may also be released from inclusions if crystals fracture under storage conditions and, if crystal surface moisture later evaporates, adjacent crystals become firmly joined together with a cement of re-crystallised solute. Caking may be minimised by efficient drying, packaging in airtight containers, and avoiding compaction on storage. In addition, crystals may be coated with an inert dust that acts as a moisture barrier. Small crystals are more prone to cake than large crystals because of the greater number of contact points per unit mass, although actual size is less important than size distribution and shape and the narrower the size distribution and the more granular the shape, the lower is the tendency of crystals to cake. Crystal size distribution can be controlled by adjusting operating conditions in a crystalliser and crystal shape may be influenced by the use of habit modifiers. A comprehensive account of the inhibition of caking by trace additives has been given by Phoenix(61).

### 15.2.7. Washing of crystals

The product from a crystalliser must be subjected to efficient solid–liquid separation in order to remove mother liquor and, whilst centrifugal filtration can reduce the liquor content of granular crystals to 5–10 per cent, small irregular crystals may retain more than 50 per cent. After filtration, the product is usually washed to reduce the amount of liquor retained still further and, where the crystals are very soluble in the liquor, another liquid in which the substance is relatively insoluble is used for the washing, although this two-solvent method means that a solvent recovery unit is required. When simple washing is inadequate, two stages may be required for the removal of mother liquor with the crystals removed from the filter, re-dispersed in wash liquor and filtered again. This may cause a loss of yield although this is much less than the loss after a complete re-crystallisation.

If, for simplicity, it is assumed that the soluble impurity is in solution and that solution concentrations are constant throughout the dispersion vessel, then wash liquor requirements for decantation washing may be estimated as follows:

If, in batch operation, \( c_{i0} \) and \( c_{iN} \) denote the impurity concentrations in the crystalline material (kg impurity/kg product) initially and after washing stage \( n \) respectively, and \( F \)
is the fraction of liquid removed at each decantation, then a mass balance gives:

\[ c_{in} = c_{io}(1 - F)^n \]  
(15.24)

or:

\[ \ln\left(\frac{c_{in}}{c_{io}}\right) = n \ln(1 - F) \]  
(15.25)

For continuous operation, where fresh wash-liquid enters the vessel continuously and liquor is withdrawn through a filter screen, then a mass balance gives:

\[ V_L \, dc = -c_i \, dV_W \]  
(15.26)

or:

\[ \ln\left(\frac{c_{in}}{c_{io}}\right) = -\frac{V_W}{V_L} \]  
(15.27)

where \( c_{io} \) and \( c_{in} \) are the initial and final concentrations and \( V_L \) and \( V_W \) are the volumes of liquor in the vessel and of the wash-water respectively. Combining equations 15.25 and 15.27:

\[ n \ln(1 - F) = -\frac{V_W}{V_L} \]  
(15.28)

or:

\[ \frac{1}{nFV_L} = \ln \frac{1 - F}{F} \]  
(15.29)

As Mullin\(^{(3)}\) points out, this equation can be used for comparing batch and continuous processing since \( V_W \) and \( nFV_L \) represent the wash liquor requirements for both cases.

### 15.3. CRystallisation FROM SOLUTIONs

Solution crystallisers are usually classified according to the method by which supersaturation is achieved, that is by cooling, evaporation, vacuum, reaction and salting out. The term controlled denotes supersaturation control whilst classifying refers to classification of product size.

#### 15.3.1. Cooling crystallisers

**Non-agitated vessels**

The simplest type of cooling crystalliser is an unstirred tank in which a hot feedstock solution is charged to an open vessel and allowed to cool, often for several days, by natural convection. Metallic rods may be suspended in the solution so that large crystals can grow on them thereby reducing the amount of product that sinks to the bottom of the unit. The product is usually removed manually. Because cooling is slow, large interlocked crystals are usually produced. These retain mother liquor and thus the dried crystals are generally impure. Because of the uncontrolled nature of the process, product crystals range from a fine dust to large agglomerates. Labour costs are high, but the method is economical for small batches since capital, operating, and maintenance costs are low, although productivity is low and space requirements are high.

**Agitated vessels**

Installation of an agitator in an open-tank crystalliser gives smaller and more uniform crystals and reduces batch times. Because less liquor is retained by the crystals after filtration
and more efficient washing is possible, the final product has a higher purity. Water jackets are usually preferred to coils for cooling because the latter often become encrusted with crystals and the inner surfaces of the crystalliser should be smooth and flat to minimise encrustation. Operating costs of agitated coolers are higher than for simple tanks and, although the productivity is higher, product handling costs are still high. Tank crystallisers vary from shallow pans to large cylindrical tanks.

The typical agitated cooling crystalliser, shown in Figure 15.14a, has an upper conical section which reduces the upward velocity of liquor and prevents the crystalline product from being swept out with the spent liquor. An agitator, located in the lower region of a draught tube circulates the crystal slurry through the growth zone of the crystalliser; cooling surfaces may be provided if required. External circulation, as shown in Figure 15.14b, allows good mixing inside the unit and promotes high rates of heat transfer between liquor and coolant, and an internal agitator may be installed in the crystallisation tank if required. Because the liquor velocity in the tubes is high, low temperature differences are usually adequate, and encrustation on heat transfer surfaces is reduced considerably. Batch or continuous operation may be employed.

![Diagram of cooling crystalliser](image)

**Figure 15.14. Cooling crystallisers**
Scraped-surface crystallisers

The Swenson-Walker scraped-surface unit, which is used for processing inorganic salts that have a high temperature solubility coefficient with water, is a shallow semi-cylindrical trough, about 600 mm wide and 3–12 m long, fitted with a water-cooled jacket. A helical scraper rotating at 0.8–1.6 Hz, keeps the cooling surfaces clean and enhances growth of crystals by moving them through the solution which flows down the sloping trough. Several units may be connected in series and the capacity is determined by the heat transfer rate which should exceed 60 kW\(^{(1)}\) for economic operation, with heat transfer coefficients in the range 50–150 W/m\(^2\) deg K. High coefficients and hence high production rates are obtained with double-pipe, scraped-surface units such as Votator and Armstrong crystallisers in which spring-loaded internal agitators scrape the heat transfer surfaces. With turbulent flow in the tube, coefficients of 50–700 W/m\(^2\) deg K are achieved. Such units range from 75 to 600 mm in diameter and 0.3 to 3 m long. They are used mainly for processing fats, waxes and other organic melts, as outlined in Section 15.4, although the processing of inorganic solutions such as sodium sulphate from viscose spin-bath liquors, has been reported by Armstrong\(^{(62)}\).

Example 15.5

A solution containing 23 per cent by mass of sodium phosphate is cooled from 313 to 298 K in a Swenson-Walker crystalliser to form crystals of \(\text{Na}_3\text{PO}_4\cdot12\text{H}_2\text{O}\). The solubility of \(\text{Na}_3\text{PO}_4\) at 298 K is 15.5 kg/100 kg water, and the required product rate of crystals is 0.063 kg/s. The mean heat capacity of the solution is 3.2 kJ/kg deg K and the heat of crystallisation is 146.5 kJ/kg. If cooling water enters and leaves at 288 and 293 K, respectively, and the overall coefficient of heat transfer is 140 W/m\(^2\) deg K, what length of crystalliser is required?

Solution

The molecular mass of hydrate/molecular mass of anhydrate, \(R = (380/164) = 2.32\)

It will be assumed that the evaporation is negligible and that \(E = 0\).

The initial concentration, \(c_1 = 0.23\) kg/kg solution or 0.23/(1 – 0.23) = 0.30 kg/kg water

The final concentration, \(c_2 = 15.5\) kg/kg water or 0.155 kg/kg water

In 1 kg of the initial feed solution, there is 0.23 kg salt and 0.77 kg water and hence \(w_1 = 0.77\) kg

The yield is given by equation 15.22:

\[
y = 2.32 \times 0.77[0.30 - 0.155(1 - 0)]/[1 - 0.155(2.32 - 1)]
\]

= 0.33 kg

In order to produce 0.063 kg/s of crystals, the required feed is:

\[
= (1 \times 0.063/0.33) = 0.193 \text{ kg/s}
\]

The heat required to cool the solution = 0.193 \times 3.2(313 - 298) = 9.3 kW
Heat of crystallisation = (0.063 \times 146.5) = 9.2 \, kW; a total of (9.3 + 9.2) = 18.5 \, kW

Assuming countercurrent flow, \( \Delta T_1 = (313 - 293) = 20 \, \text{deg K} \)
\( \Delta T_2 = (298 - 288) = 10 \, \text{deg K} \)

and the logarithmic mean, \( \Delta T_m = (20/10) / \ln(20/10) = 14.4 \, \text{deg K} \)

The heat transfer area required, \( A' = \frac{Q}{U \Delta T_m} = \frac{18.5}{(0.14 \times 14.4)} = 9.2 \, \text{m}^2 \)

Assuming that the area available is, typically, 1 \, \text{m}^2/\text{m} \, \text{length}, the length of exchanger required = 9.2 \, \text{m}. In practice 3 lengths, each of 3 \, \text{m} \, \text{length} would be specified.

**Direct-contact cooling**

The occurrence of crystal encrustation in conventional heat exchangers can be avoided by using direct-contact cooling (DCC) in which supersaturation is achieved by allowing the process liquor to come into contact with a cold heat-transfer medium. Other potential advantages of DCC include better heat transfer and lower cooling loads, although disadvantages include product contamination from the coolant and the cost of extra processing required to recover the coolant for further use. Since a solid, liquid, or gaseous coolant can be used with transfer of sensible or latent heat, the coolant may or may not boil during the operation, and it can be either miscible or immiscible with the process liquor, several types of DCC crystallisation are possible:

(a) immiscible, boiling, solid or liquid coolant where heat is removed mainly by transfer of latent heat of sublimation or vaporisation;
(b) immiscible, non-boiling, solid, liquid, or gaseous coolant with mainly sensible heat transfer;
(c) miscible, boiling, liquid coolant with mainly latent heat transfer; and
(d) miscible, non-boiling, liquid coolant with mainly sensible heat transfer.

Crystallisation processes employing DCC have been used successfully in the de-waxing of lubricating oils\(^{63}\), the desalination of water\(^{64}\), and the production of inorganic salts from aqueous solution\(^{65}\).

**15.3.2. Evaporating crystallisers**

If the solubility of a solute in a solvent is not appreciably decreased by lowering the temperature, the appropriate degree of solution supersaturation can be achieved by evaporating some of the solvent and the oldest and simplest technique, the use of solar energy, is still employed commercially throughout the world\(^{66}\). Common salt is produced widely from brine in steam-heated evaporators, multiple-effect evaporator-crystallisers are used in sugar refining and many types of forced-circulation evaporating crystallisers are in large-scale use\(^{3,40,67}\). Evaporating crystallisers are usually operated under reduced pressure to aid solvent removal, minimise heat consumption, or decrease the operating temperature of the solution, and these are described as reduced-pressure evaporating crystallisers.
15.3.3. Vacuum (adiabatic cooling) crystallisers

A vacuum crystalliser operates on a slightly different principle from the reduced-pressure unit since supersaturation is achieved by simultaneous evaporation and adiabatic cooling of the feedstock. A hot, saturated solution is fed into an insulated vessel maintained under reduced pressure. If the feed liquor temperature is higher than the boiling point of the solution under the low pressure existing in the vessel, the liquor cools adiabatically to this temperature and the sensible heat and any heat of crystallisation liberated by the solution evaporate solvent and concentrate the solution.

15.3.4. Continuous crystallisers

The majority of continuously operated crystallisers are of three basic types: forced-circulation, fluidised-bed and draft-tube agitated units.

Forced-circulation crystallisers

A Swenson forced-circulation crystalliser operating at reduced pressure is shown in Figure 15.15. A high recirculation rate through the external heat exchanger is used to provide good heat transfer with minimal encrustation. The crystal magma is circulated from the lower conical section of the evaporator body, through the vertical tubular heat exchanger, and reintroduced tangentially into the evaporator below the liquor level to create a swirling action and prevent flashing. Feed-stock enters on the pump inlet side of the circulation system and product crystal magma is removed below the conical section.

![Figure 15.15. Forced-circulation Swenson crystalliser](image-url)
**Fluidised-bed crystallisers**

In an *Oslo fluidised-bed crystalliser*, a bed of crystals is suspended in the vessel by the upward flow of supersaturated liquor in the annular region surrounding a central downcomer, as shown in Figure 15.16. Although originally designed as classifying crystallisers, fluidised-bed Oslo units are frequently operated in a mixed-suspension mode to improve productivity, although this reduces product crystal size\(^{(68)}\). With the classifying mode of operation, hot, concentrated feed solution is fed into the vessel at a point directly above the inlet to the circulation pipe. Saturated solution from the upper regions of the crystalliser, together with the small amount of feedstock, is circulated through the tubes of the heat exchanger and cooled by forced circulation of water or brine. In this way, the solution becomes supersaturated although care must be taken to avoid spontaneous nucleation. Product crystal magma is removed from the lower regions of the vessel.

![Figure 15.16. Oslo cooling crystalliser](image)

**Draught-tube agitated vacuum crystallisers**

A *Swenson draught-tube-baffled (DTB) vacuum unit* is shown in Figure 15.17. A relatively slow-speed propellor agitator is located in a draught tube that extends to a small distance below the liquor level. Hot, concentrated feed-stock, enters at the base of the draught tube, and the steady movement of magma and feed-stock to the surface of the liquor produces a gentle, uniform boiling action over the whole cross-sectional area of the crystalliser. The degree of supercooling thus produced is less than 1 deg K and, in the absence of violent vapour flashing, both excessive nucleation and salt build-up on the inner walls are minimised. The internal baffle forms an annular space free of agitation and provides a settling zone for regulating the magma density and controlling the removal of excess nuclei. An integral elutriating leg may be installed below the crystallisation zone to effect some degree of product classification.

The *Standard-Messo turbulence crystalliser*, Figure 15.18, is a draught-tube vacuum unit in which two liquor flow circuits are created by concentric pipes: an outer ejector
Figure 15.17. Swenson draught-tube-baffled (DTB) crystalliser

Figure 15.18. Standard-Messo turbulence crystalliser
tube with a circumferential slot, and an inner guide tube in which circulation is effected by a variable-speed agitator. The principle of the Oslo crystalliser is utilised in the growth zone, partial classification occurs in the lower regions, and fine crystals segregate in the upper regions. The primary circuit is created by a fast upward flow of liquor in the guide tube and a downward flow in the annulus. In this way, liquor is drawn through the slot between the ejector tube and the baffle, and a secondary flow circuit is formed in the lower region of the vessel. Feedstock is introduced into the draught tube and passes into the vaporiser section where flash evaporation takes place. In this way, nucleation occurs in this region, and the nuclei are swept into the primary circuit. Mother liquor may be drawn off by way of a control valve that provides a means of controlling crystal slurry density.

The Escher-Wyss Tsukishima double-propeller (DP) crystalliser, shown in Figure 15.19, is essentially a draught-tube agitated crystalliser. The DP unit contains an annular baffled zone and a double-propellor agitator which maintains a steady upward flow inside the draught tube and a downward flow in the annular region, thus giving very stable suspension characteristics.

15.3.5. Controlled crystallisation

Carefully selected seed crystals are sometimes added to a crystalliser to control the final product crystal size. The rapid cooling of an unseeded solution is shown in Figure 15.20a in which the solution cools at constant concentration until the limit of the metastable zone is reached, where nucleation occurs. The temperature increases slightly due to the release of latent heat of crystallisation, but on cooling more nucleation occurs. The temperature and concentration subsequently fall and, in such a process, nucleation and growth cannot
be controlled. The slow cooling of a seeded solution, in which temperature and solution composition are controlled within the metastable zone throughout the cooling cycle, is shown in Figure 15.20b. Crystal growth occurs at a controlled rate depositing only on the added seeds and spontaneous nucleation is avoided because the system is never allowed to become labile. Many large-scale crystallisers are operated on this batch operating method that is known as *controlled crystallisation*.

![Cooling curve](image)

(a) Rapid cooling—unseeded

(b) Slow cooling—seeded

Figure 15.20. Effect of seeding on cooling crystallisation

If crystallisation occurs only on the added seeds, the mass $m$, of seeds of size $d_s$ that can be added to a crystalliser depends on the required crystal yield $y$ and the product crystal size $d_p$, as follows:

$$m_s = y \left( \frac{d_p^3}{d_s^3} - 1 \right)$$  \hspace{1cm} (15.30)

The product crystal size from a batch crystalliser can also be controlled by adjusting the rates of cooling or evaporation. Natural cooling, for example, produces a supersaturation
peak in the early stages of the process when rapid, uncontrolled heavy nucleation inevitably occurs, although nucleation can be controlled within acceptable limits by following a cooling path that maintains a constant low level of supersaturation. As MULLIN and NYVLT(69) has pointed out, the calculation of optimum cooling curves for different operating conditions is complex, although the following simplified relationship is usually adequate for general application:

\[ T_t = T_0 - (T_0 - T_f)(t/t_b)^3 \]  \hspace{1cm} (15.31)

where \( T_0 \), \( T_f \), and \( T_t \) are the temperatures at the beginning, end and any time \( t \) during the process, respectively, and \( t_b \) is the overall batch time.

15.3.6. Batch and continuous crystallisation

Continuous, steady-state operation is not always the ideal mode for the operation of crystallisation processes, and batch operation often offers considerable advantages such as simplicity of equipment and reduced encrustation on heat-exchanger surfaces. Whilst only a batch crystalliser can, in certain cases, produce the required crystal form, size distribution, or purity, the operating costs can be significantly higher than those of a comparable continuous unit, and problems of product variation from batch to batch may be encountered. The particular attraction of a continuous crystalliser is its built-in flexibility for control of temperature, supersaturation nucleation, crystal growth, and other parameters that influence the size distribution of the crystals. The product slurry may have to be passed to a holding tank, however, to allow equilibrium between the crystals and the mother liquor to be reached if unwanted deposition in the following pipelines and effluent tanks is to be avoided. One important advantage of batch operation, especially in the pharmaceutical industry, is that the crystalliser can be cleaned thoroughly at the end of each batch, thus preventing contamination of the next charge with any undesirable products that might have been formed as a result of transformations, rehydration, dehydration, air oxidation and so on during the batch cycle. In continuous crystallisation systems, undesired self-seeding may occur after a certain operating time, necessitating frequent shutdowns and washouts.

Semi-continuous crystallisation processes which often combine the best features of both batch and continuous operation are described by NYVLT(35), RANDOLPH(37), ROBINSON and ROBERTS(70), and ABEC and BALAKRISHNAM(71). It may be possible to use a series of tanks which can then be operated as individual units or in cascade. MULLIN(3) suggests that for production rates in excess of 0.02 kg/s (70 kg/h) or liquor feeds in excess of 0.005 m³/s, continuous operation is preferable although sugar may be produced batch-wise at around 0.25 kg/s (900 kg/h) per crystalliser.

15.3.7. Crystalliser selection

The temperature–solubility relationship for solute and solvent is of prime importance in the selection of a crystalliser and, for solutions that yield appreciable amounts of crystals on cooling, either a simple cooling or a vacuum cooling unit is appropriate. An evaporating crystalliser would be used for solutions that change little in composition on cooling and
salting-out would be used in certain cases. The shape, size and size distribution of the product is also an important factor and for large uniform crystals, a controlled suspension unit fitted with suitable traps for fines, permitting the discharge of a partially classified product, would be suitable. This simplifies washing and drying operations and screening of the final product may not be necessary. Simple cooling-crystallisers are relatively inexpensive, though the initial cost of a mechanical unit is fairly high although no costly vacuum or condensing equipment is required. Heavy crystal slurries can be handled in cooling units without liquor circulation, though cooling surfaces can become coated with crystals thus reducing the heat transfer efficiency. Vacuum crystallisers with no cooling surfaces do not have this disadvantage but they cannot be used when the liquor has a high boiling point elevation. In terms of space, both vacuum and evaporating units usually require a considerable height.

Once a particular class of unit has been decided upon, the choice of a specific unit depends on initial and operating costs, the space available, the type and size of the product, the characteristics of the feed liquor, the need for corrosion resistance and so on. Particular attention must be paid to liquor mixing zones since the circulation loop includes many regions where flow streams of different temperature and composition mix. These are all points at which temporary high supersaturations may occur causing heavy nucleation and hence encrustation, poor performance and operating instabilities. As Toussaint and Donders stresses, it is essential that the compositions and enthalpies of mixer streams are always such that, at equilibrium, only one phase exists under the local conditions of temperature and pressure.

15.3.8. Crystalliser modelling and design

Population balance

Growth and nucleation interact in a crystalliser in which both contribute to the final crystal size distribution (CSD) of the product. The importance of the population balance is widely acknowledged. This is most easily appreciated by reference to the simple, idealised case of a mixed-suspension, mixed-product removal (MSMPR) crystalliser operated continuously in the steady state, where no crystals are present in the feed stream, all crystals are of the same shape, no crystals break down by attrition, and crystal growth rate is independent of crystal size. The crystal size distribution for steady state operation in terms of crystal size $d$ and population density $n'$ (number of crystals per unit size per unit volume of the system), derived directly from the population balance over the system is:

$$n' = n^o \exp(-d/G_d)$$

where $n^o$ is the population density of nuclei and $t_r$ is the residence time. Rates of nucleation $B$ and growth $G_d(=dd/dt)$ are conventionally written in terms of supersaturation as:

$$B = k_1 \Delta c^b$$

and:

$$G_d = k_2 \Delta c^s$$
These empirical expressions may be combined to give:

\[ B = k_3 G^i \]  

(15.35)

where:

\[ i = \frac{b}{s} \quad \text{and} \quad k_3 = \frac{k_1}{k_2^i} \]  

(15.36)

where \( b \) and \( s \) are the kinetic orders of nucleation and growth, respectively, and \( i \) is the relative kinetic order. The relationship between nucleation and growth may be expressed as:

\[ B = n^o G_d \]  

(15.37)

or:

\[ n^o = k_4 G_d^{i-1} \]  

(15.38)

In this way, experimental measurement of crystal size distribution, recorded on a number basis, in a steady-state MSMPR crystalliser can be used to quantify nucleation and growth rates. A plot of \( \log n \) against \( d \) should give a straight line of slope \(- (G_d t_r)^{-1}\) with an intercept at \( d = 0 \) equal to \( n^o \) and, if the residence time \( t_r \) is known, the crystal growth rate \( G_d \) can be calculated. Similarly, a plot of \( \log n^o \) against \( \log G_d \) should give a straight line of slope \( (i - 1) \) and, if the order of the growth process \( s \) is known, the order of nucleation \( b \) may be calculated. Such plots are shown in Figure 15.21.

![Population plots for a continuous mixed-suspension mixed-product removal (MSMPR) crystalliser](image)

Figure 15.21. Population plots for a continuous mixed-suspension mixed-product removal (MSMPR) crystalliser.
The mass of crystals per unit volume of the system, the so-called magma density, $\rho_m$ is given by:

$$\rho_m = 6\alpha \rho n^\circ (G_d t_r)^4$$  \hspace{1cm} (15.39)

where $\alpha$ is the volume shape factor defined by $\alpha = \text{volume}/d^3$ and $\rho$ is the crystal density.

The peak of the mass distribution, the dominant size $d_D$ of the CSD, is given by Mullin\(^{(1)}\) as:

$$d_D = 3 G_d t_r$$  \hspace{1cm} (15.40)

and this can be related to the crystallisation kinetics by:

$$d_D \propto t_r^{i/(i+3)}$$  \hspace{1cm} (15.41)

This interesting relationship\(^{(37)}\) enables the effect of changes in residence time to be evaluated. For example, if $i = 3$, a typical value for many inorganic salt systems, a doubling of the residence time would increase the dominant product crystal size by only 26 per cent. This could be achieved either by doubling the volume of the crystalliser or by halving the volumetric feed rate, and hence the production rate. Thus, residence time adjustment is usually not a very effective means of controlling product crystal size.

CSD modelling based on population balance considerations may be applied to crystalliser configurations other than MSMPR\(^{(37)}\) and this has become a distinct, self-contained branch of reaction engineering\(^{(56,59,60,73)}\).

**Example 15.6**

An MSMPR crystalliser operates with a steady nucleation rate of $n^\circ = 10^{13} / \text{m}^4$, a growth rate, $G_d = 10^{-8} \text{ m/s}$ and a mixed-product removal rate, based on clear liquor of $0.00017 \text{ m}^3/\text{s}$. The volume of the vessel, again based on clear liquor, is $4 \text{ m}^3$, the crystal density is $2660 \text{ kg/m}^3$ and the volumetric shape factor is $0.7$. Determine:

(a) the solids content in the crystalliser
(b) the crystal production rate
(c) the percent of nuclei removed in the discharge by the time they have grown to $100 \mu\text{m}$.
(d) the liquor flowrate which passes through a trap which removes 90 per cent of the original nuclei by the time they have grown to $100 \mu\text{m}$

**Solution**

Draw-down time = $(4/0.00017) = 23530 \text{ s}$

(a) From a mass balance, the total mass of solids is:

$$c_s = 6\alpha n^\circ (G_d t_r)^4$$  \hspace{1cm} (equation 15.39)

$$= (6 \times 0.6 \times 2660 \times 10^{13}) (10^{-8} \times 23530)^4$$

$$= 343 \text{ kg/m}^3$$

(b) The production rate = $(343 \times 0.00017) = 0.058 \text{ kg/s} (200 \text{ kg/h})$
(c) The crystal population decreases exponentially with size or:

\[
n/n_0 = \exp(\frac{-L}{G_d \tau})
\]

\[
= \exp\left(\frac{(-100 \times 10^{-6})}{(10^{-8} \times 23530)}\right)
\]

\[
= 0.66 \text{ or 66 per cent}
\]

Thus: \((100 - 66) = 34\) per cent have been discharged by the time they reach 100 µm.

(d) If \((100 - 90) = 10\) per cent of the nuclei remain and grow to \(>100\) µm, then in equation 15.32:

\[
(1/0.10) = \exp\left(\frac{(-100 \times 10^{-6})}{(10^{-8} \tau)}\right)
\]

and:

\[
\tau = 4343 \text{ s}
\]

Thus:

\[
4343 = 4/(0.00017 + Q_F)
\]

and:

\[
Q_F = 0.00075 \text{ m}^3/\text{s (2.68 m}^3/\text{h)}
\]

**Design procedures**

MULLIN\(^{[3]}\) has given details of a procedure for the design of classifying crystallisers in which the calculation steps are as follows.

(a) The maximum allowable supersaturation is obtained and hence the working saturation, noting that this is usually about 30 per cent of the maximum.

(b) The solution circulation rate is obtained from a materials balance.

(c) The maximum linear growth-rate is obtained based on the supersaturation in the lowest layer which contains the product crystals and assuming that \((\beta/\alpha) = 6\).

(d) The crystal growth time is calculated from the growth rate for different relative desupersaturations (100 per cent desuperation corresponding to the reduction of the degree of supersaturation to zero).

(e) The mass of crystals in suspension and the suspension volume are calculated assuming a value for the voidage which is often about 0.85.

(f) The solution up-flow velocity is calculated for very small crystals (< 0.1 mm) using Stokes’ Law although strictly this procedure should not be used for particles other than spheres or for \(Re > 0.3\). In a real situation, laboratory measurements of the velocity are usually required.

(g) The crystalliser area and diameter are first calculated and then the height which is taken as (volume of suspension/cross-sectional area).

(h) A separation intensity (S.I.), defined by GRATTHIS\(^{[74]}\) as the mass of equivalent 1 mm crystals produced in 1 m\(^3\) of crystalliser volume in 1 s, is calculated. Typical values are 0.015 kg/m\(^3\) s at 300 K and up to 0.05 at higher temperatures and, for crystals >1 mm, the intensity is given by:

\[
\text{S.I.} = \frac{d_p P'}{V} \quad (15.42)
\]

where \(d_p\) is the product crystal size, \(P'\) (kg/s) is the crystal production rate and \(V\) (m\(^3\)) is the suspension volume.
MULLIN(3) has used this procedure for the design of a unit for the crystallisation of potassium sulphate at 293 K. The data are given in Table 15.5 from which it will be noted that the cross-sectional area depends linearly on the relative degree of de-supersaturation and the production rate depends linearly on the area but is independent of the height. If the production rate is fixed, then the crystalliser height may be adjusted by altering the sizes of the seed or product crystals. MULLIN and NYVLT(75) have proposed a similar procedure for mixed particle-size in a crystalliser fitted with a classifier at the product outlet which controls the minimum size of product crystals.

Table 15.5: Design of a continuous classifying crystalliser(75)

<table>
<thead>
<tr>
<th>Basic Data:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance:</td>
<td>potassium sulphate at 293 K</td>
</tr>
<tr>
<td>Product:</td>
<td>0.278 kg/s of 1 mm crystals</td>
</tr>
<tr>
<td>Growth constant:</td>
<td>$k_d = 0.75 \Delta c^{1/2}$ kg/m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Nucleation constant:</td>
<td>$k_n = 2 \times 10^{10} \Delta c^{-1/3}$ kg/s</td>
</tr>
<tr>
<td>Crystal size:</td>
<td>Smallest in fluidised bed = 0.3 mm, (free settling velocity = 40 mm/s)</td>
</tr>
<tr>
<td></td>
<td>Smallest in system = 0.1 mm</td>
</tr>
<tr>
<td>Crystal density</td>
<td>2660 kg/m$^3$</td>
</tr>
<tr>
<td>Solution density</td>
<td>1082 kg/m$^3$</td>
</tr>
<tr>
<td>Solution viscosity</td>
<td>0.0012 Ns/m$^2$</td>
</tr>
<tr>
<td>Solubility, $c^*$</td>
<td>0.1117 kg/kg water</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Desupersaturation</th>
<th>1.0</th>
<th>0.9</th>
<th>0.5</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum growth rate ($\mu$m/s)</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Up-flow velocity (m/s)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Circulation rate (m$^3$/s)</td>
<td>0.029</td>
<td>0.032</td>
<td>0.058</td>
<td>0.286</td>
</tr>
<tr>
<td>Crystal residence time (ks)</td>
<td>4.69</td>
<td>9.07</td>
<td>51.8</td>
<td>12.6</td>
</tr>
<tr>
<td>Mass of crystals (Mg)</td>
<td>145</td>
<td>90</td>
<td>5.1</td>
<td>1.25</td>
</tr>
<tr>
<td>Volume of crystal suspension (m$^3$)</td>
<td>364</td>
<td>225</td>
<td>12.8</td>
<td>3.15</td>
</tr>
<tr>
<td>Cross-sectional area of crystalliser (m$^2$)</td>
<td>0.72</td>
<td>0.80</td>
<td>1.45</td>
<td>7.2</td>
</tr>
<tr>
<td>Crystalliser diameter (m)</td>
<td>0.96</td>
<td>1.01</td>
<td>1.36</td>
<td>3.02</td>
</tr>
<tr>
<td>Crystalliser height (m)</td>
<td>505</td>
<td>281</td>
<td>8.8</td>
<td>0.44</td>
</tr>
<tr>
<td>Height/diameter</td>
<td>525</td>
<td>280</td>
<td>6.8</td>
<td>0.15</td>
</tr>
<tr>
<td>Separation intensity</td>
<td>3.0</td>
<td>4.5</td>
<td>78</td>
<td>320</td>
</tr>
<tr>
<td>Economically possible</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>

**Scale-up problems**

Crystalliser design is usually based on data measured on laboratory or pilot-scale units or, in difficult cases, both. One of the main problems in scaling up is characterisation of the particle–fluid hydrodynamics and the assessment of its effects on the kinetics of nucleation and crystal growth. In fluidised-bed crystallisers, for example, the crystal suspension velocity must be evaluated—a parameter which is related to crystal size, size distribution, and shape, as well as bed voidage and other system properties—such as density differences between particles and liquid and viscosity of the solution. Possible ways of estimating suspension velocity are discussed in the literature(3,41,43,76,77), although, as MULLIN(13) points out, determination of suspension velocities on actual crystal samples is often advisable. In agitation vessels, the "just-suspended" agitator speed $N_{JS}$, that is the minimum rotational speed necessary to keep all crystals in suspension, must be determined since, not only do all the crystals have to be kept in suspension, but the development of "dead spaces" in the vessel must also be avoided as these are unproductive zones and regions of high supersaturation in which vessel surfaces can become encrusted. Fluid and crystal
properties, together with vessel and agitator geometries, are important in establishing $N_{JS}$ values\(^{(3,43)}\). As discussed in Volume 1, Section 7.3, agitated vessel crystallisers are often scaled up successfully on the crude basis of either constant power input per unit volume or constant agitator tip speed, although Bennett et al.\(^{(75)}\) have suggested that, in draughttube agitated vessels, the quantity \((\text{tip speed})^2/(\text{vessel volume}/\text{volumetric circulation rate})\) should be kept constant.

15.4. CRYSTALLISATION FROM MELTS

15.4.1. Basic techniques

A melt is a liquid or a liquid mixture at a temperature near its freezing point and melt crystallisation is the process of separating the components of a liquid mixture by cooling until crystallised solid is deposited from the liquid phase. Where the crystallisation process is used to separate, or partially separate, the components, the composition of the crystallised solid will differ from that of the liquid mixture from which it is deposited. The ease or difficulty of separating one component from a multi-component mixture by crystallisation may be represented by a phase diagram as shown in Figures 15.4 and 15.5, both of which depict binary systems — the former depicts a eutectic, and the latter a continuous series of solid solutions. These two systems behave quite differently on freezing since a eutectic system can deposit a pure component, whereas a solid solution can only deposit a mixture of components.

Two basic techniques of melt crystallisation are:

(a) gradual deposition of a crystalline layer on a chilled surface in a static or laminar-flowing melt, and
(b) fast generation of discrete crystals in the body of an agitated vessel.

Gradual deposition (a) occurs in the Proabd refiner\(^{(79)}\) which essentially utilises a batch cooling process in which a static liquid feedstock is progressively crystallised on to extensive cooling surfaces, such as fin-tube heat-exchangers, supplied with a cold heat-transfer fluid located inside a crystallisation tank. As crystallisation proceeds, the liquid becomes increasingly impure and crystallisation may be continued until virtually the entire charge has solidified. When the crystallised mass is then slowly melted by circulating a hot fluid through the heat exchanger, the impure fraction melts first and drains out of the tank. As melting proceeds, the melt run-off becomes progressively richer in the desired component, and fractions may be taken off during the melting stage. A typical flow diagram, based on a scheme for the purification of naphthalene, is shown in Figure 15.22 where the circulating fluid is usually cold water that is heated during the melting stage by steam injection. Another example of gradual deposition occurs in the rotary drum crystalliser which consists of a horizontal cylinder, partially immersed in the melt, or otherwise supplied with feedstock. The coolant enters and leaves the inside of the hollow drum through trunnions and, as the drum rotates, a crystalline layer forms on the cold surface and is removed with a scraper knife. Two feed and discharge arrangements are shown in Figure 15.23. Rotary drum behaviour and design have been discussed by Gelperin and
Figure 15.22. Batch cooling crystallisation of melts: flow diagram for the Proabd refiner

Figure 15.23. Feed and discharge arrangements for drum crystallisers

Nosov\cite{80} and Ponomarenko et al.\cite{81}. Wintermantel\cite{82} has shown that the structure and impurity levels of growing crystal layers are determined primarily by mass-transfer effects at the layer front.

Fast-melt crystallisation (b) takes place in the scraped-surface heat exchanger, which consists of a cylindrical tube surrounded by a heat-exchange jacket. The tube is surrounded by close-clearance scraper blades and rotates at relatively low speed. Two basic types are available: the large (>200 mm in diameter, >3 m long) slow-speed (<0.15 Hz) unit, and the small (<150 mm in diameter, <1.5 m long) high-speed (>8 Hz) machine. Both types can handle viscous magmas, operating at temperatures as low as 190 K, and are widely used in the manufacture of margarine (crystallisation of triglycerides), de-waxing of lubricating oils (crystallisation of higher n-alkanes), and large-scale processing of many organic substances, such as naphthalene, p-xylene, chlorobenzenes and so on. The magma
emerging from a scraped-surface crystalliser generally contains very small crystals, often less than 10 \( \mu \text{m} \), which are difficult to separate and can subsequently cause reprocessing problems unless the crystals are first grown to a larger size in a separate holdup tank.

15.4.2. Multistage-processes

A single-stage crystallisation process may not always achieve the required product purity and further separation, melting, washing, or refining may be required. Two approaches are used:

a) a repeating sequence of crystallisation, melting, and re-crystallisation;
b) a single crystallisation step followed by countercurrent contacting of the crystals with a relatively pure liquid stream.

The first approach is preferred if the concentration of impurities in the feedstock is high, and is essential if the system forms a continuous series of solid solutions. The second approach is used where the concentration of impurities is low, although some industrial operations require a combination of both systems. Atwood\(^{(83)}\) has offered an analysis of different types of multistage crystallisation schemes.

As described by Mullin\(^{(3)}\), Bennett et al.\(^{(78)}\) and Rittner and Steiner\(^{(184)}\), many industrial melt-crystallisation processes have been developed, and further interest is being stimulated by the energy-saving potential in large scale processing, as compared with distillation. One example is the Newton-Chambers process, described by Molinari et al.\(^{(79)}\), in which benzene is produced from a coal-tar benzole fraction by contacting the impure feedstock with brine. The slurry is centrifuged, yielding benzene crystals (freezing point 278.6 K) and a mixture of brine and mother liquor which is then allowed to settle. The brine is returned for refrigeration and the mother liquor is reprocessed to yield motor fuel. The process efficiency depends to a large extent on the efficient removal of impure mother liquor that adheres to the benzene crystals, and several modes of operation are possible. In the thaw-melt method shown in Figure 15.24, benzene crystals are washed in the centrifuge with brine at a temperature above 279 K. Some of the benzene crystals partially melt, which helps to wash away the adhering mother liquor. The thawed liquor may then be recycled. Multistage operation can be employed, in which the first crop of crystals is removed as product and the second, from the liquor, is melted for recycle. The Sulzer MWB process, described by Fischer et al.\(^{(85)}\), involves crystallisation on a cold surface and, since it may be operated effectively as a multistage separation device, it can be used to purify solid solutions. In an effective multistage countercurrent scheme, only one crystalliser, a vertical multi-tube heat exchanger, is required and the crystals do not have to be transported since they remain deposited on the internal heat-exchange surfaces in the vessel until they are melted for further processing. The intermediate storage tanks and crystalliser are linked by a control system consisting of a programme timer, actuating valves, pumps, and cooling loop, as shown in Figure 15.25. This process has been used on a large scale for the purification of organics, such as chloronitrobenzenes, nitrotoluenes, cresols, and xylanols, and in the separation of fatty acids.
Figure 15.24: Newton—Chambers process for the purification of benzene

Figure 15.25: Sulzer MWB process
15.4.3. Column crystallisers

Because the components of the melt feedstock can form both eutectic and solution systems with one another, sequences of washing, partial or complete melting, and re-crystallisation are often necessary to produce one of the components in near-pure form. Because the operation of a sequence of melt crystallisation steps can be time-consuming and costly, many attempts have been made to carry out some of these operations in a single unit, such as a column crystalliser. One example is the Schildknecht column developed in the 1950’s which is shown in Figure 15.26. Liquid feedstock enters the column continuously at an intermediate point and freezing at the bottom of the column and melting at the top are achieved using, respectively, a suitable refrigerant and a hot fluid or an electrical heating element. Crystals and liquid pass through the column countercurrently, and the solid phase is transported downward by a helical conveyor fixed on a central shaft. The purification zone is usually operated at a virtually constant temperature, intermediate between the temperatures of the freezing and melting sections. Crystals are formed mainly in the freezing section, although some may also be deposited on the inner surface of the column and removed by the helical conveyor. During this operation, crystals make contact with the counter-flowing liquid melt and are thereby surface-washed. A system in which an upward flowing liquid is in contact with crystals being conveyed downward has also been used and, in this case, the locations of the freezer and melter are the reverse of those shown in Figure 15.26. Gates and Powers\(^{86}\) and Henry and Powers\(^{87}\) have discussed the modelling of column crystallisers.

![Figure 15.26: Schildknecht column](image)

Whilst the Schildknecht column is essentially a laboratory-scale unit, a melt-crystalliser of the wash-column type was developed by Phillips Petroleum Company in the 1960s for large-scale production of \(p\)-xylene. The key features of this *Phillips pulsed-column crystalliser*, as described by McKee et al.\(^{88}\), are shown in Figure 15.27. A cold slurry
feed, produced in a scraped-surface chiller, enters at the top of the column and crystals are pulsed downward in the vertical bed by a piston, whilst impure mother liquor leaves through a filter. The upward-flowing wash liquor is generated at the bottom by a heater that melts pure crystals before they are removed from the column.

Whilst the Brodie purifier\textsuperscript{89} developed in the late 1960s incorporates several features of the column crystallisers described previously, it also has the potential to deal effectively with solid-solution systems. As shown in Figure 15.28, it is essentially a centre-fed column that can convey crystals from one end to the other. As the crystals move through the unit, their temperature is gradually increased along the flow path and thus they are subjected to partial melting which encourages the release of low-melting impurities. The interconnected scraped-surface heat exchangers are of progressively smaller diameter so as to maintain reasonably constant axial flow velocities and to prevent back-mixing. The vertical purifying column acts as a countercurrent washer in which descending, nearly pure, crystals meet an upward stream of pure melt. The Brodie purifier has been used in the large-scale production of high-purity 1,4-dichlorobenzene and naphthalene.

The Tsukishima Kikai (TSK) countercurrent cooling crystallisation process described by TAKEGAMI\textsuperscript{90} is, in effect, a development of Brodie technology. A typical system, consisting of three conventional cooling crystallisers connected in series is shown in Figure 15.29. Feed enters the first-stage vessel and partially crystallises, and the slurry is then concentrated in a hydrocyclone before passing into a Brodie purifying column. After passage through a settling zone in the crystalliser, clear liquid overflows to the next stage. Slurry pumping and overflow of clear liquid in each stage result in countercurrent flow of liquid and solid. This process has been applied in the large-scale production of p-xylene.
Units have been developed by Sulzer Chemtech which consist of vertical tubes where the product flows as a film down the inside surface of the tubes, and the liquid used for cooling and heating is distributed so as to wet the external surface of the tubes. During the initial freezing stage, the heat transfer medium chills the tubes, partial melting is then induced by raising the temperature of the heat transfer medium and higher temperatures are
then applied for the final melting stage. A distribution system equalises the flow through the tubes and optimum performance is achieved by accurate control of the heating and cooling profiles. Sulzer also produce a unit for static melt crystallisation which employs cooled plates immersed in a stagnant melt. After a crystal layer has formed, sweating is induced, as with the falling-film device, and the sweated fraction is removed. The remaining crystal layer is then melted and passed to storage. A higher degree of purity may be obtained by using the intermediate product as feedstock and repeating the procedure and, in a similar way, the residue drained from the first phase of operation may be further depleted by additional melt-freezing processes to give an enhanced yield. A relatively new development is the use of a heat pump in which one crystalliser operates in the crystallisation mode as an evaporator, and a further identical unit operates in the sweating or melting mode as a condenser. In this way, energy costs are reduced due to the use of the enthalpy of condensation for crystal melting. Auxiliary exchangers are required only for the elimination of excess energy and for the start-up operation.

A further development, discussed by Moritoki(91), is high-pressure crystallisation, which is considered in Section 15.9.

15.4.4. Prilling and granulation

Prilling, a melt-spray crystallisation process in which solid spherical granules are formed, is used particularly in the manufacture of fertilisers such as ammonium nitrate and urea. Shearon and Dunwoody(92) describe the prilling of ammonium nitrate, in which a very concentrated solution containing about 5 per cent of water is sprayed at 415 K into the top of a 30 m high, 6 m diameter tower, and the droplets fall countercurrently through an upwardly flowing air stream that enters the base of the tower at 293 K. The solidified droplets, which leave the tower at 353 K and contain about 4 per cent water, must be dried to an acceptable moisture content at a temperature below 353 K in order to prevent any polymorphic transitions. Nunnally and Cartney(93) describe a melt granulation technique for urea in which molten urea is sprayed at 420 K on to cascading granules in a rotary drum. Seed granules of less than 0.5 mm diameter can be built up to the product size of 2–3 mm. Heat released by the solidifying melt is removed by the evaporation of a fine mist of water sprayed into the air as it passes through the granulation drum.

An important application of granulation is in improving the 'flowability' of very fine (submicron) particles which stick together because of the large surface forces acting in materials with very high surface/volume ratios.

15.5. CRYSTALLISATION FROM VAPOURS

15.5.1. Introduction

The term sublimation strictly refers to the phase change: solid → vapour, with no intervention of a liquid phase. In industrial applications, however, the term usually includes the reverse process of condensation or desublimation: solid → vapour → solid. In practice, it is sometimes desirable to vaporise a substance from the liquid state and hence the
complete series of phase changes is then: solid → liquid → vapour → solid, and, on the condensation side of the process, with the supersaturated vapour condensing directly to the crystalline solid state without the creation of a liquid phase.

Common organic compounds that can be purified led by sublimation include:

- 2-aminophenol, anthracene, anthranilic acid, anthraquinone, benzanthrone, benzoic acid, 1,4-benzoquinone, camphor, cyanuric chloride, iso-phthalic acid, naphthalene, 2-napththol, phthalic anhydride, phthalimide, pyrogallol, salicylic acid, terephthalic acid and thymol.

and the following elemental and inorganic substances for which the process is suitable include:

- aluminum chloride, arsenic, arsenic(III) oxide, calcium, chromium(III) chloride, hafnium tetrachloride, iodine, iron(III) chloride, magnesium, molybdenum trioxide, sulphur, titanium tetrachloride, uranium hexafluoride and zirconium tetrachloride.

In addition, the sublimation of ice in freeze-drying, discussed in Chapter 16, has become an important operation particularly in the biological and food industries. The various industrial applications of sublimation techniques are discussed by several authors, and the principles underlying vaporisation and condensation, and the techniques for growing crystals from the vapour phase are also presented in the literature.

15.5.2. Fundamentals

**Phase equilibria**

A sublimation process is controlled primarily by the conditions under which phase equilibria occur in a single-component system, and the phase diagram of a simple one-component system is shown in Figure 15.30 where the sublimation curve is dependent on the vapour pressure of the solid, the vaporisation curve on the vapour pressure of the liquid, and the fusion curve on the effect of pressure on the melting point. The slopes of these three curves can be expressed quantitatively by the Clapeyron equation:

\[
\frac{dP}{dT}_{\text{sub}} = \frac{\lambda_s}{T} (v_g - v_l) \quad (15.43)
\]

\[
\frac{dP}{dT}_{\text{vap}} = \frac{\lambda_v}{T} (v_g - v_l) \quad (15.44)
\]

\[
\frac{dP}{dT}_{\text{fus}} = \frac{\lambda_f}{T} (v_l - v_s) \quad (15.45)
\]

where \( P \) is the vapour pressure, and \( v_s, v_l \) and \( v_g \) are the molar volumes of the solid, liquid, and gas phases, respectively. The molar latent heats (enthalpies) of sublimation, vaporisation, and fusion \( \lambda_s, \lambda_v \) and \( \lambda_f \) respectively) are related at a given temperature by:

\[
\lambda_s = \lambda_v + \lambda_f \quad (15.46)
\]
Although there are few data available on sublimation-desublimation, a considerable amount of information can be calculated using the Clausius-Clapeyron equation provided that information on vapour pressure is available at two or more temperatures. In this way:

\[
\ln \frac{P_1}{P_2} = \frac{\lambda_v'}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

(15.47)

where \(\lambda_v'\) is latent heat of vaporisation per mole.

**Example 15.7**

The vapour pressures of naphthalene at 463 and 433 K are 0.780 and 0.220 kN/m\(^2\) respectively. If \(\lambda_v'\) does not vary greatly over the temperature range considered, what is the vapour pressure at 393 K?

**Solution**

In equation 15.47:

\[
\ln \left( \frac{780}{220} \right) = \frac{\lambda_v'(463 - 433)}{[8314 \times 463 \times 433]}
\]

and:

\(\lambda_v' = 70340 \text{ kJ/kmol}\)

Thus:

\[
\ln \left( \frac{220}{P} \right) = \frac{70340(433 - 393)}{[8.314 \times 433 \times 393]}
\]

and:

\(P = 30 \text{ kN/m}^2\)

The position of the **triple point** \(T\), which represents the temperature and pressure at which the solid, liquid, and gas phases co-exist in equilibrium, is of the utmost importance in
sublimation-desublimation processes. If it occurs at a pressure above atmospheric, the solid cannot melt under normal atmospheric conditions, and true sublimation (solid → vapour) is easily achieved. For example, since the triple point for carbon dioxide is at 216 K and 500 kN/m², liquid CO₂ is not formed when solid CO₂ is heated at atmospheric pressure and the solid simply vaporises. If the triple point occurs at a pressure less than atmospheric, certain precautions are necessary if the phase changes solid → vapour and vapour → solid are to be controlled. For example, since the triple point for water is 273.21 K and 0.6 kN/m², ice melts when it is heated above 273.2 K at atmospheric pressure. For ice to sublime, both the temperature and the pressure must be kept below the triplepoint values. If the solid → liquid stage takes place before vaporisation, the operation is often called pseudo-sublimation. Both true sublimation and pseudo-sublimation cycles are depicted in Figure 15.31. For a substance with a triple point at a pressure greater than atmospheric, true sublimation occurs. The solid at A is heated to a temperature B and the increase in vapour pressure is given by AB. The condensation is given by BCDE. Since the vapour passing to the condenser may cool slightly and be diluted with an inert gas such as air, C can be taken as the condition at the condenser inlet. After entering the condenser, the vapour is mixed with more inert gas, and the partial pressure and temperature drop to D. The vapour then cools at essentially constant pressure to E which is the condenser temperature. When the triple point of the substance occurs at a pressure lower than atmospheric; heating may result in the temperature and vapour pressure of the solid exceeding the values at the triple-point, and the solid will then melt in the vaporiser along AB. In the condensation stage, the partial pressure in the vapour stream entering the condenser must be reduced below the pressure at the triple-point to prevent initial condensation to a liquid by diluting the vapour with an inert gas, although the frictional pressure drop in the vapour line is often sufficient to effect the required drop in partial pressure. C' then represents the conditions at the entry into the condenser and the condensation path is C'DE.

Figure 15.31: Phase diagram showing true sublimation (ABCDE) and pseudosublimation (AB'C'DE) cycles.
**Fractional sublimation.** If two or more sublimable substances form true solid solutions, their separation by fractional sublimation is theoretically possible. The phase diagram for a binary solid-solution system at a pressure below the triple-point pressures of the two components is shown in Figure 15.32, where points A and B represent the equilibrium sublimation temperatures of pure components A and B, respectively, at a given pressure. The lower curve represents the sublimation temperatures of mixtures of A and B, while the upper curve represents the solid-phase condensation temperatures, generally called snow points. Figure 15.33 shows that if a solid solution at S is heated to some temperature X, the resulting vapour phase at Y and residual solid solution at Z contain different proportions of the original components, quantified by the lever arm rule. The sublimate and the residual solid may then each be subjected again to this procedure and, therefore, the possibility of fractionation exists, although the practical difficulties may be considerable. G. L. Chlort and G. Oldberger, Vitovec et al., and Eggers et al. have described experimental studies of fractional sublimation, and nucleation and growth rates, of organic condensates. Matsouka et al. has also applied the procedure to the fractionation of mixed vapours.

**Vaporisation and condensation**

(Vaporisation.) The maximum theoretical vaporisation rate \( v' \) (kg/m\(^2\) s) from the surface of a pure liquid or solid is limited by its vapour pressure and is given by the Hertz-Knudsen equation, which can be derived from the kinetic theory of gases:

\[
v' = \frac{P_s}{(M'/2\pi RT_s)^{0.5}}
\]  

(15.48)
where $P_s$ is the vapour pressure at the surface temperature $T_s$, $M'$ is the molecular weight and $R$ is the gas constant. In practice, the actual vaporisation rate may be lower than predicted by equation 15.48, and a correction factor $e$, generally referred to as an evaporation coefficient, is included to give:

$$v' = e P_s (M'/2\pi R T_s)^{0.5}$$  \hspace{1cm} (15.49)

A laboratory technique used to measure values of $e$ for sublimable solid materials is described by Plewe and Klassen\(^{105}\).

Sublimation rates of pure solids into turbulent air streams have been successfully correlated by the Gilliland–Sherwood equation\(^{102}\):

$$d'/x' = 0.023 Re^{0.38} Sc^{0.44}$$  \hspace{1cm} (15.50)

where $d'$ is a characteristic dimension of the vaporisation chamber, $x'$ is the effective film thickness for mass transfer at the vapour–solid interface, and $Re$ and $Sc$ are the dimensionless Reynolds and Schmidt numbers, respectively.

Condensation is generally a transient operation in which, as discussed by Ueda and Takashima\(^{100}\), simultaneous heat and mass transfer are further complicated by the effects of spontaneous condensation in the bulk gaseous phase. After the creation of supersaturation in the vapour phase, nucleation normally occurs which may be homogeneous in special circumstances, but more usually heterogeneous. This process is followed by both crystal growth and agglomeration which lead to the formation of the final crystal product. As a rate process, the condensation of solids from vapours is less well understood than vaporisation\(^{98}\). Strickland-Constable\(^{107}\) has described a simple laboratory technique...
for measuring kinetics in subliming systems which has been used to compare the rates of solid evaporation and crystal growth of benzophenone under comparable conditions.

The two most common ways of creating the supersaturation necessary for crystal nucleation and subsequent growth are: (a) cooling by a metal surface to give either a glassy or multi-crystalline deposit that requires mechanical removal and (b) dilution with an inert gas to produce a loose crystalline mass that is easy to handle. Blik and Krupiczka\(^{108}\) have described the measurement and correlation of heat transfer rates during condensation of phthalic anhydride in a pilot plant connected to an industrial desublimation unit, Chikowski and Wrenski\(^{109}\) have reported on the condensation of several sublimable materials in a fluidised bed, and Knuth and Weisnach\(^{110}\) have summarised an extensive study on heat- and mass-transfer processes in a fluidised-bed desublimation unit.

### 15.5.3. Sublimation processes

**Simple and vacuum sublimation**

*Simple sublimation* is a batch-wise process in which the solid material is vaporised and then diffuses towards a condenser under the action of a driving force attributable to difference in partial pressures at the vaporising and condensing surfaces. The vapour path between the vaporiser and the condenser should be as short as possible in order to reduce mass-transfer resistance. Simple sublimation has been used for centuries, often in very crude equipment, for the commercial production of ammonium chloride, iodine, and flowers of sulphur.

*Vacuum sublimation* is a development of simple sublimation, which is particularly useful if the pressure at the triple-point is lower than atmospheric, where the transfer of vapour from the vaporiser to the condenser is enhanced by the increased driving force attributable to the lower pressure in the condenser. Iodine, pyrogallol, and many metals have been purified by vacuum sublimation processes in which the exit gases from the condenser are usually passed through a cyclone or scrubber to protect the vacuum equipment and to minimise product loss.

**Entrainer sublimation**

In entainer sublimation, an entainer gas is blown into the vaporisation chamber of a sublimer in order to increase the vapour flowrate to the condensing equipment, thereby increasing the yield. Air is the most commonly used entainer, though superheated steam can be employed for substances such as anthracene that are relatively insoluble in water. If steam is used, the vapour may be cooled and condensed by direct contact with a spray of cold water. Although the recovery of the sublimate is efficient, the product is wet. The use of an entainer gas in a sublimation process also provides the heat needed for sublimation and an efficient means of temperature control. If necessary, it may also provide dilution for the fractional condensation at the desublimation stage. Entainer sublimation, whether by gas flow over a static bed of solid particles or through a fluidised bed, is ideally suited to continuous operation.

A general-purpose, continuous entainer–sublimation plant is shown in Figure 15.34. The impure feedstock is pulverised in a mill and, if necessary, a suitable entainer gas,
such as hot air, is used to blow the fine particles, which volatilise readily, into a series of separators, such as cyclones, where nonvolatile solid impurities are removed. A filter may also be located in the vapour line to remove final traces of inert, solid impurities. The vapour then passes to a series of condensers from which the sublimate is subsequently discharged. The exhaust gases may be recycled, or passed to the atmosphere through a cyclone or wet scrubber to recover any entrained product.

Although the application of fluidisation techniques to sublimation–desublimation processes was first proposed by Matz(111), the technique has not yet been widely adopted for large-scale commercial use, despite its obvious advantage of improving both heat and mass transfer rates. Cedro(112) has, however, reported on a fluidised-bed de-sublimation unit operating in the United States for the production of aluminium chloride at the rate of 3 kg/s (11 tonne/h).

The product yield from an entrainer–sublimation process may be estimated as follows. The mass flowrate $G'$ of the inert gas and the mass sublimation rate $S'$ are related by:

$$\frac{G'}{S'} = \frac{\rho_s P'_s}{\rho_g P_g}$$

where $P_g$ and $P'_s$ are the partial pressures of the inert gas and vaporised material, respectively, in the vapour stream, and $\rho_g$ and $\rho_s$ are their respective vapour densities. The total pressure $P_t$ of the system is the sum of the partial pressures of the components or:

$$P_t = P'_s + P_g$$

From equation 15.51:

$$S' = G' \left( \frac{\rho_s}{P_g} \right) \left( \frac{P'_s}{P_t} \right)$$

or, in terms of the molecular weights of the inert gas, $M_g$ and of the material being sublimed, $M_s$:

$$S' = G' \left( \frac{M_s}{M_g} \right) \left( \frac{P'_s}{P_g} \right)$$

The theoretical maximum yield from an entrainer sublimation process is the difference between the calculated sublimation rates corresponding to the conditions in the vaporisation and condensation stages.
Example 15.8

Salicylic acid ($M_s = 138 \text{ kg/kmol}$) is to be purified by entrainer sublimation with air ($M_g = 29 \text{ kg/kmol}$) at 423 K. The vapour is fed at 101.5 kN/m$^2$ to a series of condensers, the internal temperature and pressure of the last condenser being 313 K and 100 kN/m$^2$ respectively. The air flowrate is 0.56 kg/s and the pressure drop between the vaporiser and the last condenser is 1.5 kN/m$^2$.

The vapour pressures of salicylic acid at 423 and 313 K are 1.44 and 0.0023 kN/m$^2$ respectively. What are the mass sublimation rates in the vaporiser and condenser?

Solution

Under saturated conditions:

**Vaporisation stage:** $P_t = 101.5 \text{ kN/m}^2$, $P'_s = 1.44 \text{ kN/m}^2$

Thus, in equation 15.54:

$$S'_v = 0.56(138/29)(1.44/(101.5 - 1.44)) = 0.038 \text{ kg/s (38 g/s)}$$

**Condensation stage:** $P_t = 100 \text{ kN/m}^2$, $P'_s = 0.0023 \text{ kN/m}^2$

Thus, in equation 15.54:

$$S'_c = 0.56(138/29)(0.0023/(100 - 0.0023)) = 0.000061 \text{ kg/s (0.061 g/s)}$$

In this example, the loss from the condenser exit gases is only 0.061 g/s whilst the theoretical maximum yield is 38 g/s. This maximum yield is obtained, however, only if the air is saturated with salicylic acid vapour at 423 K, and saturation is approached only if the air and salicylic acid are in contact for a sufficiently long period of time at the required temperature. A fluidised-bed vaporiser may achieve these optimum conditions though, if air is simply blown over bins or trays containing the solid, saturation will not be achieved and the actual rate of sublimation will be lower than that calculated. In some cases, the degree of saturation achieved may be as low as 10 per cent of the calculated value. The actual loss of product in the exit gases from the condenser is then greater than the calculated value. There are other losses which can be minimised by using an efficient scrubber.

Comparison of entrainer-sublimation and crystallisation

An analysis by KUDELA and SAMPSON$^{(97)}$ of the processes for commercial purification of naphthalene suggests that sublimation is potentially more economical than conventional melt crystallisation. In the sublimation method, the feedstock is completely vaporised in a nitrogen stream and then partially condensed. Heat is removed by vaporising water at the top of the condenser and, in order to prevent deposition of sublimate on the vessel walls, the inner wall of the condenser is sufficiently permeable to allow it to pass some of the entrainer gas. Impurities remain in the vapour stream and are subsequently condensed in a cooler located after the compressor used to circulate the entrainer. The stream carrying impurities and wastewater from the separator is washed with benzene in an extractor. Sublimation gives a higher yield of naphthalene at a lower cost, and with a smaller space requirement, than crystallisation$^{(94)}$. Although steam and electricity consumption is higher for sublimation, this is offset by a much lower cooling-water requirement.
Fractional sublimation

As discussed in Section 15.5.2, the separation of two or more sublimable substances by fractional sublimation is theoretically possible if the substances form true solid solutions. GILLOT and GOLDBERGER\textsuperscript{100} have reported the development of a laboratory-scale process known as thin-film fractional sublimation which has been applied successfully to the separation of volatile solid mixtures such as hafnium and zirconium tetrachlorides, 1,4-dibromobenzene and 1-bromo-4-chlorobenzene, and anthracene and carbazole. A stream of inert, non-volatile solids fed to the top of a vertical fractionation column falls counter-currently to the rising supersaturated vapour which is mixed with an entrainer gas. The temperature of the incoming solids is maintained well below the snow-point temperature of the vapour, and thus the solids become coated with a thin film (10 $\mu$m) of sublimate which acts as a reflux for the enriching section of the column above the feed entry point.

15.5.4. Sublimation equipment

Very few standard forms of sublimation or de-sublimation equipment are in common use and most industrial units, particularly on the condensation side of the process, have been developed on an ad hoc basis for a specific substance and purpose. The most useful source of information on sublimation equipment is the patent literature, although as HOLDEN and BRYANT\textsuperscript{95} and KEMP et al.\textsuperscript{96} point out, it is not clear whether a process has been, or even can be, put into practice.

Vaporisers

A variety of types of vapourisation units has been used or proposed for large-scale operation\textsuperscript{95}, the design depending on the manner in which the solid feedstock is to be vapourised. These include:

- (a) a bed of dry solids without entrainer gas;
- (b) dry solids suspended in a dense non-volatile, liquid;
- (c) solids suspended in a boiling (entrainer) liquid where the entrainer vapour is formed in situ;
- (d) entrainer gas flowing through a fixed bed of solid particles;
- (e) entrainer gas bubbling through molten feedstock such that vaporisation takes place above the triple-point pressure;
- (f) entrainer gas flowing through a dense phase of solid particles in a fluidised bed;
- (g) entrainer gas flowing through a dilute phase of solid particles, such as in a transfer-line vaporiser where the solid and gas phases are in co-current flow, or in a raining solids unit where the solids and entrainer may be in countercurrent flow.

Condensers

Sublimate condensers are usually large, air-cooled chambers which tend to have very low heat-transfer coefficients (5–10 W/m$^2$ deg K) because sublimate deposits on the condenser walls act as an insulator, and vapour velocities in the chambers are generally very low.
Quenching the vapour with cold air in the chamber may increase the rate of heat removal although excessive nucleation is likely and the product crystals will be very small. Condenser walls may be kept free of solid by using internal scrapers, brushes, and other devices, and all vapour lines in sublimation units should be of large diameter, be adequately insulated, and if necessary, be provided with supplementary heating to minimise blockage due to the buildup of sublimate. One of the main hazards of air-entrainment sublimation is the risk of explosion since many solids that are considered safe in their normal state can form explosive mixtures with air. All electrical equipment should therefore be flame-proof, and all parts of the plant should be efficiently earthed to avoid build-up of static electricity.

The method of calculating the density of deposited layers of sublimate and of other variables and the optimisation of sublimate condenser design, has been discussed by Wintermantel et al. It is generally assumed that the growth rate of sublimate layers is governed mainly by heat and mass transfer. The model which is based on conditions in the diffusion boundary layer takes account of factors such as growth rate, mass transfer, and concentrations in the gas. The model shows a reasonably good fit to experimental data.

In a variant of the large-chamber de-sublimation condenser, the crystallisation chamber may be fitted with gas-permeable walls as described by Vitovec et al. The vapour and the entrainer gas are cooled by evaporation of water dispersed in the pores of the walls, and an inert gas passes through the porous walls into the cooling space and protects the internal walls from solid deposits. Crystallisation takes place in the bulk vapour–gas mixture as a result of direct contact with the dispersed water. This arrangement has been used, for example, for the partial separation of a mixture of phthalic anhydride and naphthalene by using nitrogen as the entrainer. Although fluidised-bed condensers have been considered for large-scale application, most of the published reports are concerned with laboratory-scale investigations.

15.6. FRACTIONAL CRYSTALLISATION

A single crystallisation operation performed on a solution or a melt may fail to produce a pure crystalline product for a variety of reasons including:

(a) the impurity may have solubility characteristics similar to those of the desired pure component, and both substances consequently co-crystallise,
(b) the impurity may be present in such large amounts that the crystals inevitably become contaminated,
(c) a pure substance cannot be produced in a single crystallisation stage if the impurity and the required substance form a solid solution.

Re-crystallisation from a solution or a melt is, therefore, widely employed to increase crystal purity.

Example 15.9

Explain how fractional crystallisation may be applied to a mixture of sodium chloride and sodium nitrate given the following data. At 293 K, the solubility of sodium chloride is 36 kg/100 kg water
and of sodium nitrate 88 kg/100 kg water. Whilst at this temperature, a saturated solution comprising both salts will contain 25 kg sodium chloride and 59 kg of sodium nitrate per 100 kg of water. At 373 K, these values, again per 100 kg of water, are 40 and 176 and 17 and 160, respectively.

Solution

The data enable a plot of kg NaCl/100 kg of water to be drawn against kg NaNO₃/100 kg of water as shown in Figure 15.35. On the diagram, points C and E represent solutions saturated with respect to both NaCl and NaNO₃ at 293 K and 373 K respectively. Fractional crystallisation may then be applied to this system as follows:

(a) A solution saturated with both NaCl and NaNO₃ is made up at 373 K. This is represented by point E, and, on the basis of 100 kg water, this contains 17 kg NaCl and 160 kg NaNO₃.
(b) The solution is separated from any residual solid and then cooled to 293 K. In so doing, the composition of the solution moves along EG.
(c) Point G lies on CB which represents solutions saturated with NaNO₃ but not with NaCl. Thus the solution still contains 17 kg NaCl and in addition is saturated with 68 kg NaNO₃. That is (168 − 68) = 92 kg of pure NaNO₃ crystals have come out of solution and this may be drained and washed.

Figure 15.35. Effect of sodium chloride on the solubility of sodium nitrate

In this way, relatively pure NaNO₃, depending on the choice of conditions and particle size, has been separated from a mixture of NaNO₃ and NaCl.

The amount of NaNO₃ recovered from the saturated solution at 373 K is:

\[
\frac{(92 \times 100)}{160} = 57.5\% 
\]

An alternative approach is to note that points C and B represent 59 and 88 kg NaNO₃/100 kg water and assuming CB to be a straight line, then by similar triangles:

\[
\text{concentration of NaNO}_3 = 59 + [(88 - 59)(25 - 17)]/24 \\
= 68.3 \text{ kg/100 kg water}
\]

and:

\[
\text{yield of NaNO}_3 = (160 - 68.3) = 91.7 \text{ kg/100 kg water}.
\]

whilst all the sodium chloride remains in solution.
If the cycle is then repeated, during the evaporation stage the sodium chloride is precipitated (and
removed!) whilst the concentration of the nitrate re-attains 160 kg/100 kg water. On cooling again,
the amount of sodium nitrate which crystallises out is 91.7 kg/100 kg water,

or: \[(91.7 \times 100)/160 = 57.3\] per cent of the nitrate in solution, as before.

The same percentage of the chloride will be precipitated on re-evaporation.

**15.6.1. Recrystallisation from solutions**

Most of the impurities from a crystalline mass can often be removed by dissolving the
crystals in a small amount of fresh hot solvent and cooling the solution to produce a
fresh crop of purer crystals. The solubility of the impurities in the solvent must, however,
be greater than that of the main product. Re-crystallisation may have to be repeated
many times before crystals of the desired purity are obtained. A simple recrystallisation
scheme is:

\[
\begin{array}{c}
S \\
\downarrow \\
AB \\
\downarrow \\
X_1 \\
\downarrow \\
X_2 \\
\downarrow \\
X_3 \\
\downarrow \\
L_1 \\
\downarrow \\
L_2 \\
\downarrow \\
L_3
\end{array}
\]

An impure crystalline mass \(AB\), where \(A\) is the less soluble, desired component, is dissolved
in the minimum amount of hot solvent \(S\) and then cooled. The first crop of crystals \(X_1\) will
contain less impurity \(B\) than the original mixture, and \(B\) is concentrated in the liquor \(L_1\).
To achieve a higher degree of crystal purity, the procedure can be repeated. In each stage
of such a sequence, losses of the desired component \(A\) can be considerable, and the final
amount of “pure” crystals may easily be a small fraction of the starting mixture \(AB\). Many
schemes have been designed to increase both the yield and the separation efficiency of
fractional re-crystallisation. The choice of solvent depends on the characteristics of the
required substance \(A\) and the impurity \(B\). Ideally, \(B\) should be very soluble in the solvent
at the lowest temperature employed and \(A\) should have a high temperature coefficient of
solubility, so that high yields of \(A\) can be obtained from operation within a small temperature
range.

**15.6.2. Recrystallisation from melts**

Schemes for recrystallisation from melts are similar to those for solutions, although a solvent
is not normally added. Usually, simple sequences of heating (melting) and cooling (partial
crystallisation) are followed by separation of the purified crystals from the residual melt.
Selected melt fractions may be mixed at intervals according to the type of scheme employed,
and fresh feed-stock may be added at different stages if necessary. As Bailey[114] reports,
several such schemes have been proposed for purification of fats and waxes.

As described in Section 15.2.1, eutectic systems can be purified in theory by single-stage
recrystallisation, whereas solid solutions always require multistage operations. Countercurrent
fractional crystallisation processes in column crystallisers are described in Section 15.4.3.
15.6.3. Recrystallisation schemes

A number of fractional crystallisation schemes have been devised by Mullin\textsuperscript{(3)} and Gordon et al.\textsuperscript{(115)}, and the use of such schemes has been discussed by Joy and Payne\textsuperscript{(116)} and Salutsky and Sites\textsuperscript{(117)}.

15.7. FREEZE CRYSTALLISATION

Crystallisation by freezing, or freeze crystallisation, is a process in which heat is removed from a solution to form crystals of the solvent rather than of the solute. This is followed by separation of crystals from the concentrated solution, washing the crystals with near-pure solvent, and finally melting the crystals to produce virtually pure solvent. The product of freeze crystallisation can be either the melted crystals, as in water desalination, or the concentrated solution, as in the concentration of fruit juice or coffee extracts. Freeze crystallisation is applicable in principle to a variety of solvents and solutions although, because it is most commonly applied to aqueous systems, the following comments refer exclusively to the freezing of water.

One of the more obvious advantages of freezing over evaporation for removal of water from solutions is the potential for saving heat energy resulting from the fact that the enthalpy of crystallisation of ice, 334 kJ/kg, is only one-seventh of the enthalpy of vaporisation of water, 2260 kJ/kg, although it has to be acknowledged that the cost of producing ‘cold’ is many times more than the cost of producing ‘heat’. Process energy consumption may be reduced below that predicted by the phase-change enthalpy, however, by utilising energy recycle methods, such as multiple-effect or vapour compression, as commonly employed in evaporation as discussed in Chapter 14. In freeze-crystallisation plants operating by direct heat exchange, vapour compression has been used to recover refrigeration energy by using the crystals to condense the refrigerant evaporated in the crystalliser. Another advantage of freeze crystallisation, important in many food applications, is that the volatile flavour components normally lost during conventional evaporation can be retained in the freeze-concentrated product. Despite earlier enthusiasm, large-scale applications in desalination, effluent treatment, dilute liquor concentration and solvent recovery and so on have not been developed as yet.

All freeze separation processes depend on the formation of pure solvent crystals from solution, as described for eutectic systems in Section 15.2.1, which allows single-stage operation. Solid-solution systems, requiring multistage-operation, are not usually economic. Several types of freeze crystallisation processes may be designated according to the kind of refrigeration system used as follows:

(a) In indirect-contact freezing, the liquid feedstock is crystallised in a scraped-surface heat exchanger as described in Section 15.4, fitted with internal rotating scraper blades and an external heat-transfer jacket through which a liquid refrigerant is passed. The resulting ice-brine slurry passes to a wash column where the ice crystals are separated and washed before melting. Van Pelt and van Nistelrooij\textsuperscript{(118)} have described one of the commercial systems which are based on this type of freezing process.
(b) Direct-contact freezing processes utilise inert, immiscible refrigerants and are suitable for desalination. A typical scheme taken from BARDUN(64) is shown in Figure 15.36: Sea-water, at a temperature close to its freezing point, is fed continuously into the crystallisation vessel where it comes in direct contact with a liquid refrigerant such as $n$-butane which vaporises and causes ice crystals to form due to the exchange of latent heat. The ice-brine slurry is fed to a wash column where it is washed countercurrently with fresh water. The emerging brine-free ice is melted by the enthalpy of the condensation of the vapour released from the compressed refrigerant. A major part of the energy input is that required for the compressors.

(c) Vacuum freezing processes do not require a conventional heat exchanger, and the problems of scale formation on heat-transfer surfaces are avoided. Cooling is effected by flash evaporating some of the solvent as the liquid feedstock enters a crystallisation vessel maintained at reduced pressure. Although vacuum freezing is potentially attractive for aqueous systems it has not, as yet, achieved widespread commercial success.

THIJSSEN and SPICER(119) has given a general review of freeze concentration as an industrial separation process and BUSHELL and EAGEN(63) have discussed the status of freeze desalination. The potential of freeze crystallisation in the recycling and re-use of wastewater has been reviewed by HEST(120), and the kinetics of ice crystallisation in aqueous sugar solutions and fruit juice are considered by OMRAH and KING(121).
15.8. HIGH PRESSURE CRYSTALLISATION

As noted previously, high pressure crystallisation in which an impure liquid feedstock is subjected to pressures of up to 300 MN/m$^2$ in a relatively small chamber, 0.001 m$^3$ in volume, under adiabatic conditions is a relatively recent development. As the pressure and temperature of the charge increase, fractional crystallisation takes place and the impurities are concentrated in the liquid phase which is then discharged from the pressure chamber. At the end of the cycle, further purification is possible since residual impurities in the compressed crystalline plug may then be 'sweated out' when the pressure is released. Moritoki$^{[91]}$ has claimed that a single-cycle operation lasting less than 300 s is capable of substantially purifying a wide range of organic binary melt systems.

The principle of operation is illustrated in Figure 15.37 which shows the pressure-volume relationship. Curve $a$ shows the phase change of a pure liquid as it is pressurised isothermally. Crystallisation begins at point $A_1$ and proceeds by compression without any pressure change until it is complete at point $A_2$. Beyond this point, the solid phase is compressed resulting in a very sharp rise in pressure. If the liquid contains impurities, these nucleate at point $B_1$. As the crystallisation of the pure substance progresses, the impurities are concentrated in the liquid phase and a higher pressure is required to continue the crystallisation process. As a result, the equilibrium pressure of the liquid–solid system rises exponentially with increase of the solid fraction, as shown by curve $b$ which finally approaches

![Figure 15.37](image_url)  
Figure 15.37: Relationship between pressure and volume for isothermal conditions
the solidus curve. A liquid–solid equilibrium line in terms of pressure and temperature is shown in Figure 15.38a. The liquid–solid equilibrium line moves from line a to line b with increase in impurities and line c represents the liquid–solid equilibrium for eutectic composition. On the industrial scale, a liquid is adiabatically compressed first from point A to point B, accompanied by heat generation and then to point C at which nucleation occurs accompanied by a temperature rise due to the release of the latent heat. Again, it is during this step that the impurities are concentrated into the mother liquor. At this stage, the liquid is separated from the solid phase and removed from the vessel at point C which is at a slightly lower pressure than the eutectic line. When the greater part of the liquid has been removed, its pressure decreases at first gradually and then rapidly to atmospheric pressure whilst the crystals are maintained at the initial separation pressure. In this way, the crystals are compacted and their surfaces are purified by slight melting, or by the so-called ‘sweating’ phenomenon. After the separation at point D, the crystals are highly purified and the line representing the equilibrium state gradually approaches line a. The basic pattern of operation as a function of time is shown in Figure 15.38b.

Pilot scale investigations by Kobe Steel have shown, for example, that the impurity level in a feed of mesitylene is reduced from 0.52 to 0.002 per cent in a single operating cycle at 15 MN/m$^2$ and a concentration of greater than 99 per cent p-xylene is obtained from a mixture of p-xylene and mesitylene containing 80 per cent p-xylene. It has also been shown that whilst crystals of cumenealdehyde are very difficult to obtain by cooling, nucleation and crystal growth occur at pressures of 50–70 MN/m$^2$ and, where the crystals obtained are then used as seed material, cumenealdehyde is then easily crystallised and purified at pressures below 20 MN/m$^2$. In this work, even though the capacity of the pilot unit was only 0.0015 m$^3$, some 360 tonne/year of raw material could be processed in 120 s cycles over a period of 8000 h.

Kobe Steel claim that, in terms of running costs, not only is the energy consumption low, being 10–50 per cent compared with conventional processes, but high pressure operation is ideally suited to the separation of isomers which are difficult to purify by other processes. These substances may have close boiling points or may be easily decomposed by temperature elevation. In this respect, recent work on supercritical fluids, as described by POLOAKOFF et al.$^{[122]}$, is of great importance.

As discussed in Chapter 14, supercritical fluids are gases that are compressed until their densities are close to those of liquids. They are extremely non-ideal gases in which interactions between molecules of a supercritical fluid and a potential solute can provide a ‘solvation energy’ for many solids to dissolve. The higher the pressure and hence the density of the supercritical fluid, the greater are the solvent–solute interactions and hence the higher the solubility of the solid. In other words the solvent power of a supercritical fluid is ‘tunable’ and this is the key factor in the use of supercritical fluids for a wide range of processes. As discussed in Chapter 14, supercritical fluids in common use include ethene, ethane and propane together with supercritical carbon dioxide and these have all been widely discussed in the literature$^{[123–127]}$. Although supercritical fluids have considerable advantages in the field of process intensification and can also replace environmentally undesirable solvents and indeed most organics, their most important property as far as crystallisation is concerned is that they can be tuned to dissolve the desired product, or indeed any impurities, which are then separated by crystallisation at high pressure. It is in this way that crystallisation is moving from the simple production of
(a) Adiabatic application of pressure

(b) Pressure and temperature variation during a cycle

Figure 15.38: High pressure crystallisation
hydrates from salt solutions towards a fully fledged separation technique which has and will have many advantages in comparison with more traditional operations in the years to come.

15.9. FURTHER READING

AIChE Symp. Ser. (a) 65 (1969) no. 95, Crystallization from solutions and melts; (b) 67 (1971) no. 110; Factors affecting size distribution; (c) 68 (1972) no. 121; Crystallization from solutions; Nucleation phenomena in growing crystal systems; (d) 72 (1976) no. 153; Analysis and design of crystallisation processes; (e) 76 (1980) no. 193, Design, control and analysis of crystallisation processes; (f) 78 (1982) no. 215, Nucleation, growth and impurity effects in crystallisation process engineering; (g) 80 (1984) no. 240, Advances in crystallisation from solutions.
15.10. REFERENCES

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15.11. NOMENCLATURE

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<tr>
<th>SYMBOL</th>
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<td>ρ</td>
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<td>L²T⁻²</td>
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<td>$\lambda$</td>
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