is the fraction of liquid removed at each decantation, then a mass balance gives:

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

or:

\[ \ln(c_{in}/c_{io}) = n \ln(1 - F) \]  \hspace{1cm} (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For continuous operation, where fresh wash-liquid enters the vessel continuously and liquor is withdrawn through a filter screen, then a mass balance gives:

\[ V_L \, dc = -c_i \, dV_W \]  \hspace{1cm} (15.26)

or:

\[ \ln(c_{in}/c_{io}) = -V_W/V_L \]  \hspace{1cm} (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:

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

or:

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

As Mullin\textsuperscript{(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 salt-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.

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 Na\(_3\)PO\(_4\).12H\(_2\)O. The solubility of Na\(_3\)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:
\[
y = 2.32 \times 0.77(0.30 - 0.155(1 - 0))/(1 - 0.155(2.32 - 1)) = 0.33 \text{ kg}
\]
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 \(= (0.063 \times 146.5) = 9.2 \text{ kW}\); a total of \((9.3 + 9.2) = 18.5 \text{ kW}\)

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, \(A' = Q/U \Delta T_m = 18.5/(0.14 \times 14.4) = 9.2 \text{ m}^2\)

Assuming that the area available is, typically, 1 m²/m length, the length of exchanger required = 9.2 m. In practice 3 lengths, each of 3 m 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.

![Forced-circulation Swenson crystalliser](image)

*Figure 15.15. Forced-circulation Swenson crystalliser*
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 feedstock, enters at the base of the draught tube, and the steady movement of magma and feedstock 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.

![Diagram of Escher-Wyss Tsukishima double-propeller (DP) crystalliser](image)

**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 15.20. 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)

**Figure 15.20.** Effect of seeding on cooling crystallisation

If crystallisation occurs only on the added seeds, the mass $m_s$ 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:

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

(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:

\[
T_t = T_0 - (T_0 - T_f)(t/t_b)^3
\]

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 Abegg 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 m\(^3\)/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(72) 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(37) 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 (37) is:

\[
n' = n^o \exp(-d/GdT) \tag{15.32}
\]

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:

\[
B = k_1 \Delta c^b \tag{15.33}
\]

and:

\[
G_d = k_2 \Delta c^s \tag{15.34}
\]
These empirical expressions may be combined to give:

\[
B = k_3 G^i
\]  
(15.35)

where:

\[
i = b/s \quad \text{and} \quad k_3 = k_1 / k_2^i
\]  
(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_url)

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:

$$\rho_m = 6\alpha \rho n^o (G_{dT})^4$$

(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:

$$d_D = 3 G_{dT}$$

(15.40)

and this can be related to the crystallisation kinetics by:

$$d_D \propto t^{(i-1)/(i+3)}$$

(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 $n^o = 10^{11}/\text{m}^4$, 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 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 $\mu$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 $\mu$m

**Solution**

Draw-down time $= (4/0.00017) = 23530$ s

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

$$c_s = 6\alpha \rho n^o (G_{dT})^4$$

(equation 15.39)

$$= (6 \times 0.6 \times 2660 \times 10^{11})(10^{-8} \times 23530)^4$$

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

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

\[
\frac{n}{n_0} = \exp(-L/G_d t_r) \tag{equation 15.32}
\]

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

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

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

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

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

and:

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

Thus:

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

and:

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

**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 GRIFFITHS\(^{(74)}\) 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:

\[S.I. = d_p P'/V \tag{15.42}\]

where \(d_p\) is the product crystal size, \(P'/\text{kg/s}\) is the crystal production rate and \(V\) (m\(^3\)) is the suspension volume.
Mullin 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 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

<table>
<thead>
<tr>
<th>Basic Data:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance: potassium sulphate at 293 K</td>
<td></td>
</tr>
<tr>
<td>Product: 0.278 kg/s of 1 mm crystals</td>
<td></td>
</tr>
<tr>
<td>Growth constant: ( k_d = 0.75 \Delta c^{-2} ) kg/m²s</td>
<td></td>
</tr>
<tr>
<td>Nucleation constant: ( k_n = 2 \times 10^6 \Delta c^{-7.3} ) kg/s</td>
<td></td>
</tr>
<tr>
<td>Crystal size: Smallest in fluidised bed = 0.3 mm, (free settling velocity = 40 mm/s)</td>
<td></td>
</tr>
<tr>
<td>Smallest in system = 0.1 mm</td>
<td></td>
</tr>
<tr>
<td>Crystal density = 2660 kg/m³, Solution density = 1082 kg/m³</td>
<td></td>
</tr>
<tr>
<td>Solution viscosity = 0.0012 Ns/m², Solubility, ( c^* = 0.1117 ) kg/kg water</td>
<td></td>
</tr>
</tbody>
</table>

| Desupersaturation | 1.0 | 0.9 | 0.5 | 0.1 |
| Maximum growth rate (\( \mu \)m/s) | 5.6 | 5.6 | 5.6 | 5.6 |
| Up-flow velocity (m/s) | 0.04 | 0.04 | 0.04 | 0.04 |
| Circulation rate (m³/s) | 0.029 | 0.032 | 0.058 | 0.286 |
| Crystal residence time (ks) | 1469 | 907 | 51.8 | 12.6 |
| Mass of crystals (Mg) | 145 | 90 | 5.1 | 1.25 |
| Volume of crystal suspension (m³) | 364 | 225 | 12.8 | 3.15 |
| Cross-sectional area of crystalliser (m²) | 0.72 | 0.80 | 1.45 | 7.2 |
| Crystalliser diameter (m) | 0.96 | 1.01 | 1.36 | 3.02 |
| Crystalliser height (m) | 505 | 281 | 8.8 | 0.44 |
| Height/diameter | 525 | 280 | 6.5 | 0.15 |
| Separation intensity | 3.0 | 4.5 | 78 | 320 |
| Economically possible | no | no | yes | no |

### 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, although, as Mullin points out, determination of suspension velocities on actual crystal samples is often advisable. In agitated 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.\(^{(78)}\) have suggested that, in draught-tube 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\(^{(80)}\) and PONOMARENKO \textit{et al.}\(^{(81)}\). WINTERMANT\textit{EL}\(^{(82)}\) 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 µm, 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(84), 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 xylenols, 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 components can form both eutectic and solid-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_url)

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 McKay 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 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 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. Nunnelly 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 vapourise 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:\(^{(94)}\):

- 2-aminophenol, anthracene, anthranilic acid, anthraquinone, benzanthrone, benzoic acid, 1,4-benzoquinone, camphor, cyanuric chloride, \textit{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\(^{(3,40,95,96,97)}\), and the principles underlying vaporisation and condensation\(^{(98)}\) and the techniques for growing crystals from the vapour phase\(^{(99)}\) 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 \textit{sublimation curve} is dependent on the vapour pressure of the solid, the \textit{vaporisation curve} on the vapour pressure of the liquid, and the \textit{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:

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

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

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

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:

\[
\lambda_s = \lambda_v + \lambda_f
\]
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:

\[
\ln \frac{P_1}{P_2} = \frac{\lambda_v'}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \tag{15.47}
\]

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/m² 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: \(\ln(780/220) = [\lambda_v'(463 - 433)]/[8314 \times 463 \times 433]\)

and: \(\lambda_v' = 70340\) kJ/kmol

Thus: \(\ln(220/P) = [70340(433 - 393)]/[8.314 \times 433 \times 393]\)

and: \(P = 30\) kN/m²

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 $\rightarrow$ vapour) is easily achieved. For example, since the triple point for carbon dioxide is at 216 K and 500 kN/m$^2$, liquid CO$_2$ is not formed when solid CO$_2$ 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 $\rightarrow$ vapour and vapour $\rightarrow$ solid are to be controlled. For example, since the triple point for water is 273.21 K and 0.6 kN/m$^2$, 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 triple-point values. If the solid $\rightarrow$ 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](image_url)
**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. GILLOT and GOLDBERGER\(^{(100)}\), VITOVEC et al.\(^{(101)}\) and EGgers et al.\(^{(102)}\) have described experimental studies of fractional sublimation, and nucleation and growth rates, of organic condensates. MATSOUKA et al.\(^{(103)}\) 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\(^{(104)}\), which can be derived from the kinetic theory of gases:

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

(15.48)
Temperature

Mass fraction of component B

Figure 15.33. Fractional sublimation of two components A and B demonstrated on a solid-solution phase diagram

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:

\[
v' = e P_s \left( \frac{M'}{2 \pi R T_s} \right)^{0.5}
\] (15.49)

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

Sublimation rates of pure solids into turbulent air streams have been successfully correlated by the Gilliland–Sherwood equation\(^{(105)}\):

\[
d'/x' = 0.023 Re^{0.38} Sc^{0.44}
\] (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\(^{(106)}\), 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. BILJK and KRUPCZKA \(^{108}\) 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, CIBOROWSKI and WRENSKI \(^{109}\) have reported on the condensation of several sublimable materials in a fluidised bed, and KNUTH and WEINSPACH \(^{110}\) 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 entrainer sublimation, an entrainer 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 entrainer, 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 entrainer 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. Entrainer 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 entrainer–sublimation plant is shown in Figure 15.34. The impure feedstock is pulverised in a mill and, if necessary, a suitable entrainer 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 aluminum 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:

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

(15.51)

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:

\[
P_t = P_g + P'_s
\]

(15.52)

From equation 15.51:

\[
S' = G' \left( \frac{\rho_s}{\rho_g} \right) \left( \frac{P'_s}{P'_s - P'_g} \right)
\]

(15.53)

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

\[
S' = G' \left( \frac{M_s}{M_g} \right) \left( \frac{P'_s}{P_t - P'_g} \right)
\]

(15.54)

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 \((M_r = 138 \text{ kg/kmol})\) is to be purified by entrainer sublimation with air \((M_e = 29 \text{ kg/kmol})\) 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:** \(P_t = 101.5 \text{ kN/m}^2\), \(P'_t = 1.44 \text{ kN/m}^2\)

Thus, in equation 15.54:

\[
S'_v = 0.56 \times (138/29) \times (1.44/\left(101.5 - 1.44\right)) = 0.038 \text{ kg/s (38 g/s)}
\]

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

Thus, in equation 15.54:

\[
S' = 0.56 \times (138/29) \times (0.0023/\left(100 - 0.0023\right)) = 0.000061 \text{ kg/s (0.061 g/s)}
\]

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\(^{(100)}\) 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 µm) 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\(^{(95)}\) and KEMP et al.\(^{(96)}\) point out, it is not clear whether a process has been, or even can be, put into practice.

Vaporisers

A variety of types of vaporisation units has been used or proposed for large-scale operation\(^{(95)}\), 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.\textsuperscript{(113)}. 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.\textsuperscript{(101)}. 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\textsuperscript{(110)}.

\section*{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.

\section*{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