Chapter 14

Crystallization

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INTRODUCTION

Throughout the history of the chemical industry, crystals have been produced via crystallization methods that range between something as simple as allowing vats of hot concentrated solution to cool to those as complex as continuous, carefully controlled, multi-step processes which yield a crystal product of a particular size or size distribution, shape, moisture content, and purity. Today, consumer demands require crystal products meet rigid specifications that can also include color, odor, particle size distribution, and caking characteristics.

Crystallization is an important mass transfer operation that is often employed in the preparation of a pure product. In the process, a crystal usually separates out as a substance of definite composition from a solution of varying composition. Any impurities in the liquid (often referred to as the *mother liquor*) are carried in the crystalline product only to the extent that they adhere to the surface or are *occluded* (retained) within the crystals that may have grown together during or after the crystallization operation.

The separation of a solid from a solution onto a crystal occurs only if there is a state of imbalance involving a mass driving force; namely, a decrease in chemical potential (or concentration) between the bulk of the liquid solution and the crystal interface exists. This effectively means that the solution must be supersaturated.

Although crystallization is ordinarily thought of as the deposition of a solid crystalline phase from a liquid phase by cooling, evaporation, or both, the same principles apply to crystal formation by precipitation caused by the addition of a third substance. This other component may either react to form a precipitate or simply decrease the solubility of the precipitated material.

One may also view crystallization as a phase equilibrium application. These solid crystals are usually formed from a homogenous liquid phase. If one starts with an unsaturated solution formed by dissolving some solid in liquid, more solid can be dissolved until the solution becomes *saturated*. More solid can still be dissolved in the solution causing it to become *supersaturated*. At this point, solids begin to deposit out of solution in a process often referred to as *nucleation*. Crystal growth continues until the solution reaches the previously attained saturation (equilibrium) point.

There are several different ways that crystallization can occur. The four most often encountered in practice are:

1 cooling,

2 evaporation,

3 cooling and evaporation (also denoted adiabatic evaporation), and

4 a salting out process.

Process (1) is most commonly employed, provided the solubility of the component being crystallized decreases with decreasing temperature.

The problems concerning crystallization, which are most frequently encountered by the practicing engineer, are:

1 yield of a given product,

2 purity of the product,

3 energy requirements for cooling, evaporation, etc.,

4 shape of the individual crystals,

5 size of the crystals,

6 uniformity or size distribution of the crystals,

7 rate of production of the desired crystals, and

8 caking.

It should also be noted that when crystallization begins, heat is evolved (liberated). The amount of heat evolved is defined as the heat (or enthalpy) of crystallization.

The following topics receive treatment in this chapter:

1 Phase diagrams.

2 The crystallization process.

3 Crystal characteristics.

4 Equipment.

5 Describing equations.

6 Design considerations.

The last two sections are highlighted with several illustrative examples.

PHASE DIAGRAMS

All two-component solid–liquid equilibrium systems may be classified according to the miscibility of the liquid phases and the nature of the solid phases which crystallize from the solution. As one might suppose, there are various types of these systems. Of these classifications, only the completely miscible liquid systems from which pure components crystallize from the solution will be examined.

Two-component systems belonging to the above class have a diagram of the general form shown in Figure 14.1. They are characterized by the fact that components (1) and (2) are completely miscible in the liquid state, and yield only pure (1) or pure (2) as solid phases. In this figure, points E and D are the melting points of pure (1) and pure (2), respectively. Line EG gives the concentrations of the solutions saturated with (1) at temperatures between E and F, or the freezing points of the solutions that yield (1) as a solid phase. Similarly, line DG gives the concentrations of solutions saturated with solid (2) at temperatures between D and F. At G, the solution is saturated with both components (1) and (2), i.e., at G, three phases are in equilibrium. It follows, therefore, that the lines DG and EG represent monovariant two-phase equilibria, while G is an *invariant point*. At this point, the temperature F of the solution must remain constant as long as three phases coexist. The temperature can be lowered below F only when one of the phases has disappeared and, on cooling, this must be the saturated solid solution. In effect, at F, solution G can completely solidify. Temperature F must consequently be the lowest temperature at which a liquid phase may exist in the system for components (1) and (2); below this temperature the system is completely solid. Temperature F is called the *eutectic temperature*, composition G the *eutectic composition*, and point G the *eutectic point* of the system.
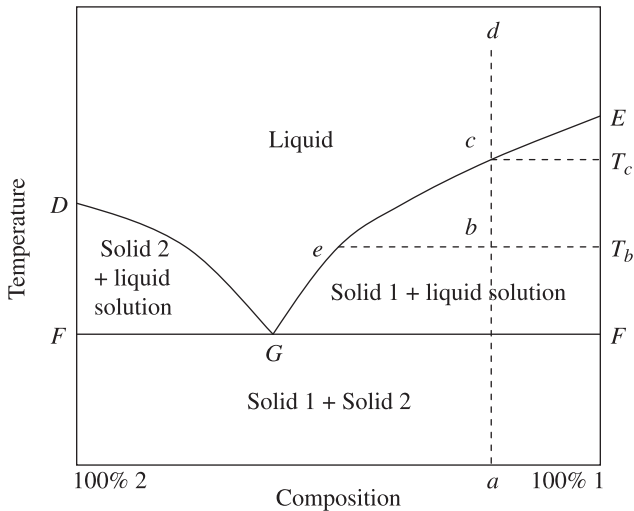

Figure 14.1   Two component solid–liquid system.

Above the lines *DG* and *EG* is the area in which the unsaturated solution exists. One phase is present in this area only. In order to define any point in this area, both the temperature and composition must be specified. The significance of the remaining portions of the diagram can be made clear by observing the behavior on the cooling of several different mixtures of components (1) and (2).

Consider a mixture of overall composition *a*. If such a mixture is heated to point *d*, an unsaturated solution is obtained. On cooling this solution, only a decrease in temperature of the liquid phase occurs until point *c*, corresponding to temperature T_c. At point *c*, the solution becomes saturated with component (1); *c* is the freezing point of the solution at temperature T_c. As cooling continues, component (1) continues to separate out, and the composition of the saturated solution changes along the line *cG*. Thus, at a temperature such as T_b, solid (1) is in equilibrium with a saturated solution of composition *e*. It is seen, therefore, that for any overall composition falling in the area *EFG*, solid (1) is in equilibrium with various compositions of solution given by the curve *EG* at each temperature. However, at temperature *F*, another solid phase of component (2) appears, and the system becomes invariant. On further extraction of heat from this system, both components (1) and (2) will completely crystallize. Once this process is over, a mixture of solid (1) and solid (2) remains and the system becomes monovariant. When cooling is continued below temperature *F* into the area *12FGF*, there is coexistence of the two solids, (1) and (2).

Consider now a three-component (ternary) system. (See also Chapter 12—Equilibrium section, Fig. 12.4) In order to better understand the equilibria associated with a three component system, it is first necessary to become acquainted with the standard method of representing such systems. Two-dimensional equilibrium diagrams for ternary systems can best be plotted on an equilateral triangle, each of whose apexes represents 100% of a particular component [see Fig. 14.2(a)–(d)]. A series of grid lines representing fractional concentrations of a particular component is drawn parallel to the base opposite the apex that represents the component. Thus, every point on the diagram corresponds to a certain percentage composition of each of the three components. It is important to note than an apex signifies a single component; a point on one of the sides describes a binary system.

There are various types of classifications of three-component systems. Only one which exhibits a simple liquid phase with crystallization of pure components will be considered in the presentation to follow. The isothermal phase diagram for a three-component system such as water (H_2O), sodium nitrate ($NaNO_3$), and sodium chloride ($NaCl$)—where only pure components crystallize from solution—takes the form shown in Figure 14.3. Details on the four phases noted in the figure are given in Table 14.1. (See also Chapter 12 for additional details).
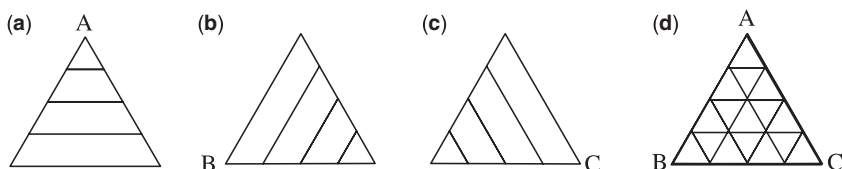

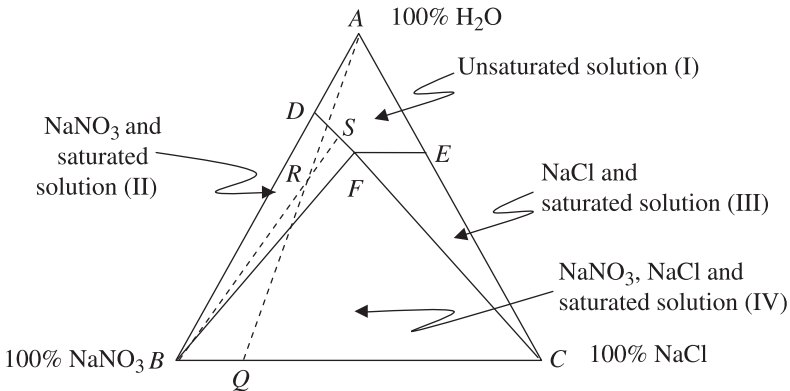**Figure 14.2** (a–d) Equilateral triangle; ternary systems.

Figure 14.3 $H_2O–NaNO_3–NaCl$ phase diagram.

As noted in earlier chapters, Gibb's phase rule states that the number of variables that must be specified to define a system (or degrees of freedom) is determined by both the number of components and the number of phases present. This was represented mathematically by the equation:

$$F = C - P + 2 \tag{14.1}$$

where F = degrees of freedom

C = number of components present

P = number of phases present

This may be applied to the above three-component system. Since there are three components, the number of degrees of freedom is:

$$F = 5 - P \tag{14.2}$$

In order to simplify matters, two variables (temperature and pressure) are generally specified. Thus, the degrees of freedom are reduced to:

$$F = 3 - P \tag{14.3}$$

Table 14.1   Phase Diagram Details

Region	# of phases	Type of phase
I	1	Unsaturated solution
II	2	Saturated solution + Pure $NaNO_3$
III	2	Saturated solution + Pure NaCl
IV	3	Saturated solution + Pure $NaNO_3$ + Pure NaCl

This indicates that when one phase is present, two variables must be specified in order to completely define the system. If two salt phases and one liquid phase are present, the degree of freedom of the saturated solution of $NaNO_3$ and $NaCl$ is zero; this means that the composition of this point is a constant and is known as the *isothermal invariant point*.

ILLUSTRATIVE EXAMPLE 14.1

Two components are completely miscible in the liquid state and the solid phases consist of pure components. Calculate and discuss the degrees of freedom at the freezing point.

SOLUTION: At this temperature, there are two phases, liquid and solid, with the vapor being ignored. Since there are two components, the system has two degrees of freedom according to the phase rule:

$$F = C - P + 2 = 2 - 2 + 2 = 2$$

The pressure is normally fixed so that the system is univariant; hence, either the temperature or the composition of the liquid phase alone is sufficient to completely define the system.   ∎

With reference to Figure 14.3, point D represents the maximum solubility of $NaNO_3$ in H_2O, point E the maximum solubility of $NaCl$ in H_2O, and point F a saturated solution of both $NaNO_3$ and $NaCl$. This last point is not called a *eutectic point* since it does not represent a temperature but instead is defined as the aforementioned *isothermal invariant point*.

If a dry mixture of $NaNO_3$ and $NaCl$ of composition Q can, by the addition of water, be brought into the region DBF in Figure 14.3, the solid $NaNO_3$ can be separated from the solution above it containing $NaCl$ and $NaNO_3$. This can easily be accomplished by moving along the line QA until point R is reached. To calculate the amount of water to be added, the *lever rule* may be employed:

$$\frac{\text{Mass of salt mixture } Q}{\text{Mass of water to be added}} = \frac{\overline{RA}}{\overline{RQ}} \qquad (14.4)$$

In a similar manner, the mass of $NaNO_3$ that can be recovered may be determined by the following relationship:

$$\frac{\text{Mass of } NaNO_3 \text{ captured}}{\text{Mass of liquid phase above } NaNO_3} = \frac{\overline{RS}}{\overline{BR}} \qquad (14.5)$$

Obtaining *equilibrium* information for this system is demonstrated with the aid of Figure 14.4. Mixtures of various portions of the two solid components in water can be prepared and agitated until equilibrium is established. If the liquid phase is separated from the solid crystals, both can be weighted and analyzed. The composition thus
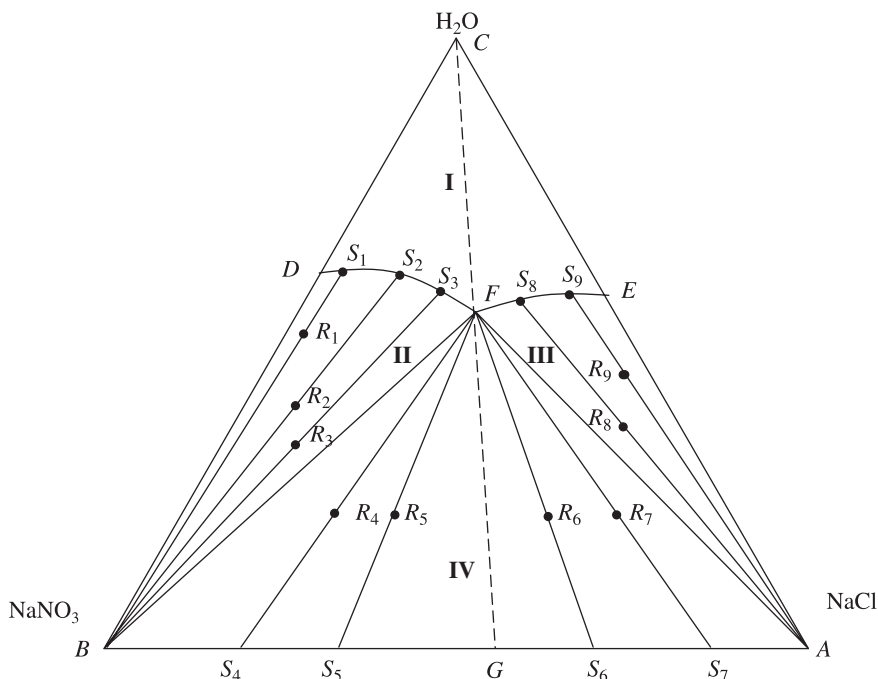
Figure 14.4 $H_2O-NaNO_3-NaCl$ phase equilibrium diagram.

obtained for the saturated solution(s) and *residue(s)* may be plotted on a triangular coordinate diagram as shown in Figure 14.4. It also shows a series of other points arrived at in this manner. If a mixture of composition R_1, R_2, R_3, ... are prepared, S_1, S_2, S_3, ..., are respectively, the composition of the saturated solutions that will result in equilibrium with $NaNO_3$.

To ascertain the nature of the solid phases in equilibrium with the various solutions, one notes that any mixture concentration point must lie on a straight line joining the composition of the solid phases and that of the saturated solution. Consequently, an *equilibrium tie-line* drawn between any corresponding pair of R and S points in region II must pass B on extension. Moreover, as several solutions may have the same solid phase, all the tie-lines for such solutions must intersect at a common point, which is the composition of the common solid phase. Therefore, it may be deduced that the solid phase for all solutions between D and F is $NaNO_3$, for those between F and E is NaCl, while area IV is composed of a saturated solution of composition F and saturated with various portions of the solid phases of both $NaNO_3$ and NaCl.

The whole diagram may be drawn once various points and tie-lines have been determined in Figure 14.4. An entire separation process can then be devised for a mixture of components $NaNO_3$ and NaCl by using the appropriate amount of water to obtain the maximum yield of each component.

> ### ILLUSTRATIVE EXAMPLE 14.2

The following laboratory data was obtained in an attempt to determine the solubility of NaCl in H_2O at 22°C:

> Weight of evaporating dish and saturated solution = 46.73 g
> Weight of evaporating dish = 34.80 g
> Weight of evaporating dish and dry salt (NaCl) = 37.90 g

SOLUTION: The mass of saturated solution is:

$$\text{Saturated solution} = 46.73 \text{ g} - 34.80 \text{ g}$$
$$= 11.93 \text{ g}$$

The mass of dry salt (NaCl) in the saturated solution is:

$$\text{NaCl} = 37.90 \text{ g} - 34.80 \text{ g}$$
$$= 3.10 \text{ g}$$

The mass percent NaCl in the saturated solution is therefore

$$\%\text{NaCl} = \left(\frac{3.10}{11.93}\right)100$$
$$= 26.0\%$$

This compares favorably with the literature value of 26.5% NaCl, 73.5% H_2O at 25°C.   ■

> ### ILLUSTRATIVE EXAMPLE 14.3

Refer to the previous example. Calculate the percent error between the calculated and literature values.

SOLUTION: Base the error on the *literature* value:

$$\%\text{error} = \left(\frac{26.5 - 26.0}{26.5}\right)100$$
$$= 1.89\%$$

As noted, there is excellent agreement.   ■

> ### ILLUSTRATIVE EXAMPLE 14.4

The weight of $NaNO_3$, NaCl, and H_2O in a saturated solution at 22°C is provided below:

> $NaNO_3 = 3.94$ g

NaCl = 1.92 g

Saturated solution = 13.50 g

Is the saturated solution at the invariant point? The literature value for the invariant point at 22°C is:

32% NaNO$_3$

13% NaCl

55% H$_2$O

SOLUTION: Determine the mass percent composition of the saturated solution:

$$\%NaNO_3 = \frac{3.94}{13.50}100$$

$$= 29.2\%$$

$$\%NaCl = \frac{1.92}{13.50}100$$

$$= 14.2\%$$

$$\%H_2O = 100 - (14.2 + 29.2)$$

$$= 56.6\%$$

The sample results compare favorably with the literature value for the invariant point.   ■

The reader should note that the phase diagrams presented above apply for isothermal conditions, i.e., they represent constant temperature data. A change in temperature will alter these isothermal curves. An increase in solubility generally occurs with rising temperature, i.e., as the temperature increases, the mutual solubilities of the components increase and the curves enclose smaller two-phase and three-phases areas.

THE CRYSTALLIZATION PROCESS

The crystallization process essentially involves three steps:

1 Formation of crystals.

2 Crystal growth.

3 Separation of the crystals from residual liquid.

A simple schematic of this overall process is provided in Figure 14.5.

There are various processes that can accomplish the above while meeting the desired design requirements associated with a crystallization operation and/or the rate of crystallization. As with many mass transfer (as well as heat transfer) calculations, the rate is expressed in terms of an overall coefficient which takes into account all individual resistances. This coefficient is almost always determined from experimental data and/or experience. Details on product yield, product purity, crystal
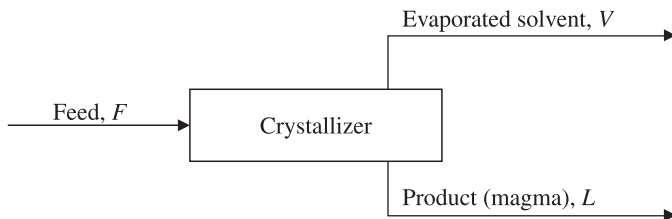
Figure 14.5   Schematic diagram of generalized crystallization process.

size and/or size distribution must also be specified. Each of these topics is discussed below with the latter topic receiving additional treatment in the next section.

The rate of crystallization involves two distinct steps:

1 The rate of formation of new crystals, or *nucleation*.

2 The rate of precipitation on crystals already present, usually referred to as *crystal growth.*

The mechanism of nucleation is essentially unknown. However, the process of crystal growth has been studied extensively, with some researchers suggesting that crystal growth occurs at erratic rates and that the solution concentration at the crystal surface is not uniform.

It is common knowledge that the solubility of small crystals is greater than that of larger crystals. Therefore, material may be *simultaneously* depositing on larger crystals while smaller crystals are dissolving when both are exposed to the same solution. As a result, it is difficult in practice to maintain uniform conditions while growing crystals. Thus, it is usually impossible to avoid locally varying conditions in the solution.

Prior to crystallization, it is common practice to inject small crystals, known as *seeds*, into the solution so that solids will be deposited more easily. Since the solubility of crystals of this size is less than that of submicroscopic crystals, the crystallization unit may be operated in such a manner as to retain the supersaturated solution with respect to the seeds, but not supersaturated with respect to crystals of the size of the aggregations that will inevitably form under the operating conditions. It should be noted that seeding is rarely used in continuous processes; it is instead used often in batch processes.

Predetermination of the yield from a crystallizer may be obtained from a material balance. The yield can usually be predicted from the solubility (see Phase Diagrams section of this chapter) of the solid phase being precipitated. It is general practice to assume equilibrium or a saturated condition. In some applications, crystallization occurs slowly and equilibrium is not attained in a short time period. In many cases, controlled precipitation does not occur unless the aforementioned seed crystals are present. If solubilities are obtained from the equilibrium diagrams discussed earlier, the prediction of the equilibrium yield can be made by applying the usual *lever arm ratio* principle between the phases which are known to be present at the specified operation temperature.

The solubilities usually reported in the literature are expressed in terms of mass of "salt" per 100 units of mass of pure solvent. The prediction of a yield of a nonhydrated

salt from a solution is simple since the amount of solvent present during crystallization is generally constant and the quantity remaining at the operating temperature is known.[1]

Impurities in crystallization operations are introduced primarily from the mother liquor that is not completely removed from the solid product. The extent of occlusion and the completeness of washing are important factors in the determination of the purity of a crystalline product. The agglomeration of crystals into larger crystals, which can occur during the growth of the crystals, makes washing more difficult and accordingly results in a lower purity of product. However, agitation decreases the tendency of the crystals to agglomerate.

Purification techniques have become increasingly important in recent years. Mechanisms by which the impurities discussed above can be incorporated into crystalline products include adsorption of impurities on crystal surfaces, solvent entrapment in cracks, crevices and agglomerates, and inclusion of pockets of liquid. The suggested recommendation for producing high purity crystals is to maintain supersaturation at a low level so that large crystals are formed. The characteristics of an impurity can also determine whether it is positioned on the surface or in the interior of the host crystal.

Although crystallization is often thought of as solely a separation operation, it is the filtration step at the end of the process that accomplishes the actual crystal separation. The residual liquid (*mixed magma underflow*) from a crystallizer typically contains approximately 30% mass solids and can be thickened further before filtration by being passed through a gravity settler. Such pre-thickening allows dewatering of the *mother liquor*, which allows either more time for the final wash step or a shorter filter cycle.

The filter cycle almost always includes a washing step at the end of the full cycle. This permits a thorough drain before the crystals are discharged. It should also be noted that the system's throughput and performance is often limited by the solids–liquid separation step; in effect, this then becomes the critical step in the overall operation.[2]

Perhaps the most troubling problem is associated with the final product. Crystalline materials have a tendency to bind together or cake on storage. Most crystalline products are required in a free-flowing form, as with sugar and table salt, or to be capable of being distributed uniformly over surfaces (e.g., fertilizers). It is also important for the crystalline product to remain in a particulate state. Caking may also require a crushing operation before the crystals can be used.

Numerous problems can arise during the operation, design, and analysis of a crystallizer. Ten of the most important problems are listed below:

1 Crystal-size distribution (CSD).
2 Purity.
3 Fouling.
4 Vapor release and location.
5 Scale-up.
6 Stability of operation.
7 Liquor–solids separation.

8 Space requirements.

9 Capital costs.

10 Operating and maintenance costs.

The proper location of the crystallization process is as important to its success as the selection of the equipment to be employed. Careful consideration must be given to the many tangible factors such as labor supply and raw material sources along with a number of intangible factors, which may be more difficult to evaluate. The selection of the site is sometimes based on a detailed study in which all factors are weighed as carefully as possible. For many processes, one or more predominant factors effectively minimize the number of possibilities for site location. Raw material and transportation costs may be such that the process must be located near a source. Thus, only the sites near sources of raw material need to be studied and these may be few in number. These and other factors serve as effective screening agents that can save both time and money.

ILLUSTRATIVE EXAMPLE 14.5

Discuss the crystallization separation process relative to the presence (or absence) of a eutectic.

SOLUTION: In cases where a complete solid solution occurs with no eutectic, it is possible to separate a binary mixture into its components. However, such systems are the rare exception; eutectic formation is the general rule. In most cases, the degree of separation attainable is therefore limited by the eutectic composition. To accomplish a complete separation, an additional step is required. ∎

CRYSTAL PHYSICAL CHARACTERISTICS

The three principle physical characteristics of crystals are size, shape, and density. Only by knowing these three properties is it possible to determine not only how they will behave in a crystallization process but also information in their later use. Although density is often not treated as an important factor, consider, for example, a ping-pong ball and a golf ball. Under a microscope, they will appear almost equal in size; however, if both were tossed into a moving fluid stream they would behave quite differently. Even though the size and shape are similar, the density is quite different and the behavior of the two objects is far from being similar. This is one of the reasons that many object to physical sizing.

A common method of specifying large crystal sizes is to designate the screen mesh that has an aperture corresponding to the crystal diameter. Since various screen scales are in use, confusion may result unless the screen scale involved is specified. The *screen mesh* generally refers to the number of screen openings per unit length or area. The aperture for a given mesh will depend on the wire size employed. The clear space between the individual wires of the screen is termed the *screen aperture*. As indicated above, the term *mesh* is applied to the number of apertures per linear inch (e.g., a 10-inch mesh screen will have 10 openings per inch and the aperture will be 0.1 inch minus the diameter of the wire).

Table 14.2   Tyler and U.S. Standard Screen Scales

Tyler mesh	Aperture microns	U.S. mesh	Aperture microns
400	37	400	37
325	43	325	44
270	53	270	53
250	61	230	62
200	74	200	74
170	88	170	88
150	104	140	105
100	147	100	149
65	208	70	210
48	295	50	297
35	417	40	420
28	589	30	590
20	833	20	840
14	1168	16	1190
10	1651	12	1680
8	2362		
6	3327		
4	4699		
3	6680		

The Tyler and the U.S. Standard Screen Scales (Table 14.2) are the most widely used in the United States. The screens are generally constructed of wire mesh cloth, with the diameters of the wire and the spacing of the wires being specified. These screens form the bottoms of metal pans about 8 inches in diameter and 2 inches high, the sides of which are fashioned so that the bottom of one sieve nests snugly on top of the next.[3,4]

ILLUSTRATIVE EXAMPLE 14.6

The size of a crystal is specified as Tyler 8-14 screen mesh. Determine its size.

SOLUTION: To calculate the size of the crystal in the problem statement, refer to the Tyler screen information in Table 14.2.

$$8\text{-mesh opening} = 2362 \ \mu m$$
$$14\text{-mesh opening} = 1168 \ \mu m$$

Since an 8 by 14 mesh size indicates that an object will pass through the 8-mesh screen but not pass (be captured) through the 14-mesh screen, one size *cannot* be specified for the crystal in question. The crystal is in the size range 1168–2362 μm and the average or "mean" arithmetic size is 1765 μm.   ■

Size distributions are often characterized by a *mean* diameter. Although numerous "means" have been defined in the literature, the most common are the arithmetic mean and the geometric mean. The *arithmetic mean* diameter of a number of crystals is simply the sum of each of the diameters divided by the number of diameters measured. The *geometric mean* diameter is the nth root of the product of the n number of diameters in the sample. In addition to the arithmetic and geometric means, a size distribution may also be characterized by the *median* diameter. The median diameter is that diameter for which 50% of the crystals are larger in size and 50% are smaller in size. Another important characteristic is the measure of central tendency. It is sometimes referred to as the *dispersion* or *variability*. The most common term employed is the *standard deviation*. These terms are discussed below.

One basic way of summarizing data is by the computation of a central value. The most commonly used central value statistic is the aforementioned arithmetic average, or the "mean". This statistic is particularly useful when applied to a set of crystal size data having a fairly symmetrical distribution. The mean is an important statistic in that it summarizes all the data in the set and because each crystal is taken into account in its computation. The formula for computing the mean is

$$\overline{X} = \frac{X_1 + X_2 + X_3 + \cdots + X_n}{n} = \frac{\sum_{i=1}^{n} X_i}{n} \tag{14.6}$$

where $\overline{X} =$ arithmetic mean

$X_i =$ any individual measurement

$n =$ total number of observations

$X_1, X_2, X_3, \ldots =$ measurements 1, 2, and 3, respectively.

The most commonly used measure of dispersion, or variability, of sets of data is the *standard deviation*, s. Its defining formula is given by the expression

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}} \tag{14.7}$$

where $s =$ standard deviation (always positive)

$X_i =$ value of the ith data point

$\overline{X} =$ mean of the data sample

$n =$ number of observations

(*Note*: The above term s represents the *sample* standard deviation. In statistical circles, the symbol σ represents another, but nearly similar, standard deviation. Unfortunately, σ has often been employed to represent the *sample* standard deviation.[5])

A typical size analysis method of representation employed in the past is provided in Table 14.3. These numbers mean that 40% of the crystals by mass are greater than 5 mm in size, 27% are less than 5 mm but greater than 2.5 mm, 20% are less

Table 14.3   Early Crystal Size Distribution (CSD) Representation

—	>5.0	mm	40%
<5.0	>2.5	mm	27%
<2.5	>1.5	mm	20%
<1.5	—	mm	13%
—	—	—	100%

than 2.5 mm but greater than 1.5 mm, and the remainder (13%) is less than 1.5 mm. Another form of representing data is provided in Table 14.4.

Frequency distribution curves are usually plotted on regular coordinate (linear) paper. The curve describes the amount of material (crystals) contained within each size range. A plot of percent mass versus crystal size (d) on a linear scale gives a curve with a peak at the preferential size. Such a curve is shown in Figure 14.6. This figure shows a *normal* probability distribution that is symmetric about the preferential size. This curve is only occasionally encountered for crystal size distribution; however, this curve may occasionally be approached in some applications. Size data can also be plotted as a cumulative plot. The size for each size range is plotted on the ordinate. The cumulative percent by weight (frequency) is plotted on the abscissa. The cumulative percent by weight can be given as a cumulative percent less than stated size (%LTSS) or cumulative percent greater than stated size (%GTSS). The cumulative percent by weight can be plotted on either a linear percentage or a probability percentage scale. The size range (ordinate) is usually a logarithmic scale.

Frequently, the cumulative distribution is plotted on special coordinate paper called *log-probability* paper. The size of each size range is plotted on a logarithmic ordinate. The percent by weight larger than crystal size d is plotted on the probability scale as the abscissa. If the distribution is *lognormal*, the distribution curve plots out as a straight line. It should be noted that one can just as easily plot percent mass less than size d (%LTSS) on the abscissa. The geometric mean value of a lognormal distribution can be read directly from a plot similar to that represented in Figure 14.7. The geometric mean size is the 50% size on the plot.

As discussed previously, the *geometric standard deviation* is a measure of the dispersion or spread of a distribution. The geometric standard deviation is the root mean square deviation about the mean value and can be read directly from a plot

Table 14.4   Size Ranges in Arithmetic Increments

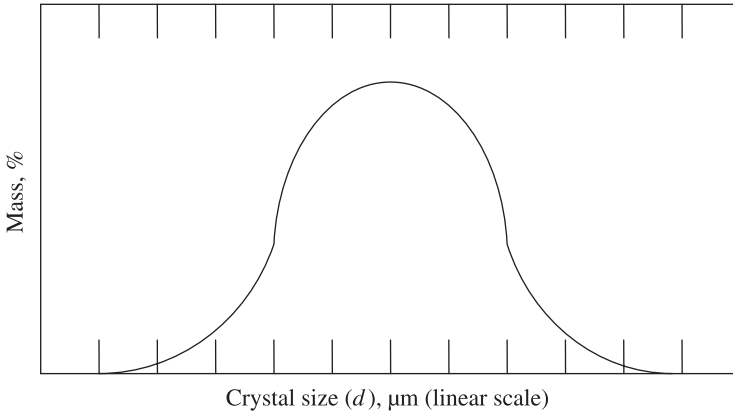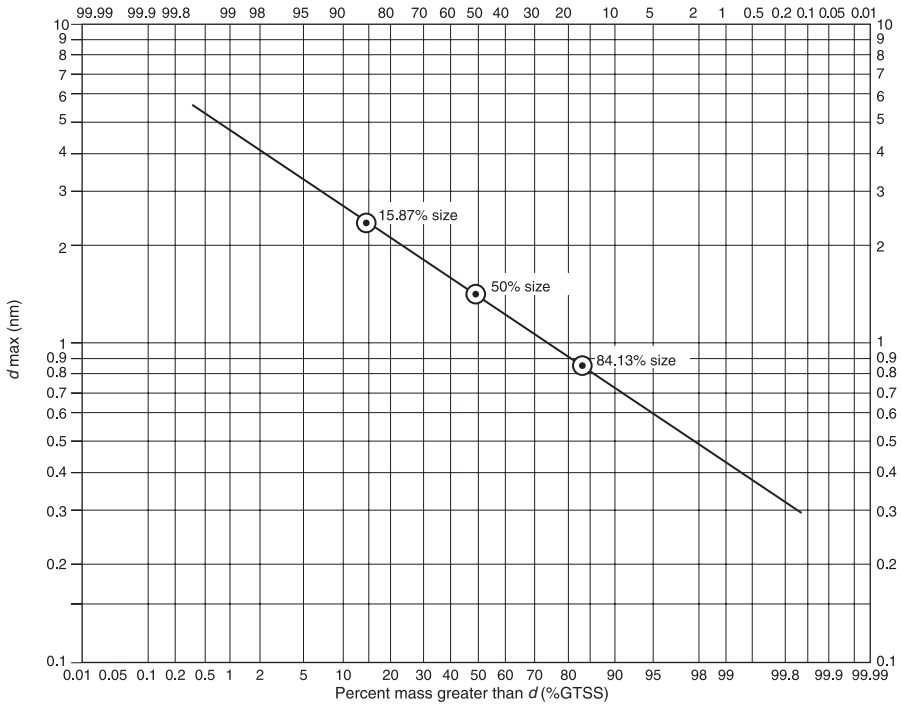| Size range, mm	Percent in size range, %
0–2	10
2–4	15
4–6	30
6–8	30
8–10	10
>10	5

Figure 14.6 Size distribution.

Figure 14.7 Lognormal distribution plot.

such as shown in Figure 14.6. For a lognormal distribution (which plots d maximum versus percent mass larger than d), the geometric standard deviation is given by

$$\sigma = \sigma_{gm} = \frac{50\% \text{ size}}{84.13\% \text{ size}} \tag{14.8}$$

or

$$\sigma = \sigma_{gm} = \frac{15.87\% \text{ size}}{50\% \text{ size}} \tag{14.9}$$

Thus, all one must do is determine the 50% size and the 84.13% size from the plot and divide to determine the geometric standard deviation.

It is safe to say that crystals produced via the crystallization process have a distribution of sizes that can vary over large ranges, and the crystal size distribution (CSD) is expressed as a number or mass distribution in terms of the size. Other crystal factors include appearance, purity, the solid–liquid separation process, and other properties involving shape and surface area.

ILLUSTRATIVE EXAMPLE 14.7

The following crystal sizes (in mm) in a sample were recorded from a crystallizer:

$$22, \ 10, \ 8, \ 15, \ 13, \ 18$$

Find the median, the arithmetic mean, and the geometric mean of these crystal sizes.

SOLUTION: The *median* is simply the middle value of a distribution, or the quantity above which half the data lie and below which the other half lie. If n data points are listed in their order of magnitude, the median is the $[(n + 1)/2]$th value. If the number of data is even, then the numerical value of the median is the value midway between the two data nearest the middle. The median, being a positional value, is less influenced by extreme values in a distribution than the mean. However, the median for these data is 14 mm and 15 mm since this data set has an even number of measurements. Another measure of central tendency used in specialized applications is the aforementioned *geometric mean* X_G. The geometric mean can be calculated using the following equation

$$\overline{d}_G = \sqrt[n]{(d_1)(d_2) \cdots (d_n)} \tag{14.10}$$

For the particle sizes given above, one obtains

$$\overline{d}_G = [(8)(10)(13)(15)(18)(22)]^{1/6} = 13.54 \, \text{mm}$$

while the arithmetic mean $\overline{d}$ is

$$\overline{d} = (8 + 10 + 13 + 15 + 18 + 22)/6$$
$$= 14.33 \, \text{mm} \qquad \blacksquare$$

ILLUSTRATIVE EXAMPLE 14.8

Refer to the previous example. Calculate the standard deviation of the six crystal sizes.

SOLUTION: The following algebraically equivalent formula makes computation much easier (now applied to the crystal diameter d):

$$s = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}} = \sqrt{\frac{n \sum d_i^2 - \left(\sum d_i\right)^2}{n(n - 1)}} \tag{14.11}$$

The standard deviation may be calculated for the data at hand:

$$\sum d_i^2 = (8)^2 + (10)^2 + (13)^2 + (15)^2 + (18)^2 + (22)^2 = 1366$$

$$\left(\sum d_i\right)^2 = (8 + 10 + 13 + 15 + 18 + 22)^2 = 7396$$

Thus,

$$s = \sqrt{\frac{6(1366) - 7396}{(6)(5)}} = 5.16 \, \text{mm} \qquad \blacksquare$$

ILLUSTRATIVE EXAMPLE 14.9

A tiny spherical crystal has a diameter of 100 nanometers (nm). Calculate the volume (cm^3) and surface area (cm^2) of the crystal.

SOLUTION: The volume (V) of the crystal is

$$V = \pi D^3 / 6$$

$$= 0.524(100)^3$$

$$= 0.524 \times 10^6 \, \text{nm}^3$$

Since there are $10^7 \, \text{nm/cm}$,

$$V = 0.524(10^6)(10^{-7})^3 = 0.524 \times 10^{-15} \, \text{cm}^3$$

The surface area (A) is given by

$$A = \pi D^2$$

$$= 3.14 \times (100)^2$$

$$= 3.14 \times 10^4 \, \text{nm}^2$$

Converting leads to

$$A = 3.14(10^4)(10^{-7})^2$$

$$= 3.14 \times 10^{-10} \, \text{cm}^2 \qquad \blacksquare$$

ILLUSTRATIVE EXAMPLE 14.10

Compare a 10 μm spherical crystal to one with a diameter of 100 mm. Include the ratio of volumes and surface area in the calculation.

SOLUTION: The ratio of diameters (RD) is

$$RD = \frac{100\,\text{mm}}{10\,\mu\text{m}} = \frac{(100)(1000)}{10}$$
$$= 10^4$$

Since the volume and surface area are a function of the (diameter)^3 and (diameter)^2, respectively, the volume ratio (VR) and surface area ratio (SAR) are

$$VR = (10^4)^3 = 10^{12}$$
$$SAR = (10^4)^2 = 10^8 \qquad\blacksquare$$

With reference to the crystallization process, the average size to which crystals are grown is usually dictated by the manner in which they are to be used. As noted earlier, fine crystals have less opportunity for agglomeration and accordingly occlude less mother liquor; however, fine crystals have a greater surface and offer greater difficulty of complete removal of mother liquor entrained on the crystals. In addition, producing crystalline material of a given size range (a specific upper and lower limit) is difficult to accomplish.

It should be noted that the removal rate of crystals of a given size can greatly alter a crystallizer's ability to continue the production of crystals having that same size and/or size distribution. This effect is particularly pronounced in a separation unit where the crystals of a desired size–distribution range are preferentially removed and the under-sized particles recycled to the crystallizer. This can shift the distribution to a smaller and narrower size range.

ILLUSTRATIVE EXAMPLE 14.11

The crystal size separation efficiency information for a filtration unit is provided in Table 14.5. Calculate the overall separation efficiency for the filter on a

  1 number basis
  2 mass basis
  3 volume basis

Table 14.5   Crystal Size–Separation Efficiency Data

d, mm	Efficiency, %	Number of crystals
1.0	0	10,000
100	100	1

SOLUTION:

1 On a number basis

$$E_N = \frac{(10{,}000)(0) + (1)(1.0)}{10{,}000 + 1}$$

$$= \frac{1}{10{,}000 + 1} = \frac{1}{10{,}001}$$

$$= 0.0001 = 0.01\%$$

2 On a mass basis

$$E = \frac{(1)(100)^3(1.0) + (10{,}000)(1.0)^3(0)}{(1)(100)^3 + (10{,}000)(1.0)^3}$$

$$= \frac{10^6 + 0}{10^6 + 10^4}$$

$$= 0.99 = 99\%$$

3 On a volume basis

$$E_V = 0.99 = 99\%$$

since volume is proportional to mass.   ■

ILLUSTRATIVE EXAMPLE 14.12

Calculate the overall efficiency of the crystallization separation unit using the data provided in Table 14.6.

Table 14.6   Crystal Size Distribution and Separation Information

CSR, mm	% in PSR	%LTSS	%GTSS	$\bar{d}$, mm	E_i, %
0–5	2	2	98	2.5	0.6
5–10	2	4	96	7.5	7.7
10–15	1	5	95	12.5	19.2
15–20	4	9	91	17.5	38.3
20–30	6	15	85	25.0	56.2
30–50	11	26	74	40.0	79.1
50–100	13	39	61	75.0	98.9
100+	61	–	–	100.0+	100

SOLUTION: Refer to Table 14.6. The overall efficiency is obtained from the cross-product of columns 2 and 6 for each CSR and summing the results:

$$E = \sum_{i=1}^{n} [(2) \times (6)]/100; \text{ percent basis}$$

The calculated results are provided in Table 14.7.

Table 14.7   Calculation of Overall Efficiency

CSR, mm	2×6
0–5	1.2
5–10	15.4
10–15	19.2
15–20	153.2
20–30	337.2
30–50	870.1
50–100	1285.7
100+	6100.0
	8782.0

From Table 14.7, one obtains

$$E = \frac{8782.0}{100} = 87.82\%$$ ∎

Finally, two of the goals of the design and practicing engineers who work on the CSD problem are to be able to:

1 understand CSD so as to analyze and modify what a particular operating crystallizer can and cannot do in the way of producing acceptable crystal size and crystal size ranges, and

2 include the effects of CSD on the design of new units, i.e., to design an original process that is not yet operating.[2]

EQUIPMENT

Equipment and equipment selection procedures are usually based on maximum throughput capacities for a new crystallization process. The reason for this is to enable the equipment to perform satisfactorily under the most extreme operating conditions. Material and energy balances based on these conditions are also required before the individual equipment is selected. Most importantly, this procedure is also influenced by the manner in which crystallization occurs. As noted in the Introduction, the methods to accomplish this are crystallization via cooling, via

evaporation, cooling and evaporation (adiabatic evaporation), and a salting out process. Details on the equipment that can accomplish these tasks are provided below.

Perhaps the simplest type of equipment for crystallization is a tank in which natural cooling is allowed to lower the temperature of a solution. A hot concentrated solution with the solute is simply poured into the tank where it cools by natural convection. However, there are several drawbacks when employing this practice. This type of crystallizer is inefficient relative to the quantity produced per unit space or per unit of time because of the slow cooling rate. It offers no control of size or size distribution of crystals and it also favors the formation of large crystals that are subject to occlusion of the mother liquor since the crystals tend to grow together. This agglomeration phenomena can be reduced with agitation. This class of equipment is employed when precipitating small quantities of a material and where the size range of the product is not critical.

Crystallization can also be achieved by cooling a hot concentrated solution on a surface. The cooling, in turn, produces results in solute solubility that favor solid-phase precipitation. This type of equipment is available in several designs. The most popular of these in earlier years was the *Swenson–Walker crystallizer.* The unit contains a water-jacketed open trough with a semicylindrical bottom. Hot concentrated solution enters at one end of the trough and the crystals that accumulate on the cooling surface are lifted and pushed along by a spiral stirrer to the other end of the crystallizer. Crystals are removed at the end of the crystallizer by an inclined spiral flight conveyor that lifts them onto a draining board or a conveyor which carries the crystals to centrifuges or any other drying and/or separation operation that may be required. This, as well as other units in this category, are usually employed for systems with a *steep solubility slope* for which a relatively large yield of crystals can be achieved with a modest drop in temperature.

The *vacuum crystallizer* accomplishes cooling via a flashing process. It is a device that cools the solution by the evaporation of a portion of the solvent. The energy for vaporization is obtained from the sensible enthalpy (heat) of the feed. The unit is usually evacuated to a low pressure by steam jet ejectors. The flashing of the feed due to the lower pressure results in both the cooling and concentration of the solution. One of the problems that can arise is that the operating pressure required to attain the desired crystallization is so low that the evolved vapor cannot be condensed by any cooling water available. These units work for systems of intermediate solubility slopes (see Chapter 12 for a further explanation of solubility slopes). It also has the advantage of vaporizing some of the solvent to bring about additional yield.

In the *evaporative crystallizer*, crystallization is caused by evaporating the solvent from the feed, which can either be a weak unsaturated solution or a hot concentrated mixture. These classes of crystallizers are employed when the solute has a small, low slope temperature-solubility curve. The operation of the evaporator seldom allows much flexibility as to the size, size distribution, and shape of crystals produced. Some classifying action does occur in that fine crystals are usually carried in the circulating mother liquor until they attain a size that will result in their precipitation out of the circulating stream into the solid-removal equipment.[1] These units are normally steam-heated although the heating can also be accomplished by passing hot gases

through the solution. If a traditional evaporator is employed, the classic equation for heat transfer may be applied:[4]

$$Q = UA\Delta T \qquad (14.12)$$

where Q is the rate of heat transfer, U is the overall heat transfer coefficient (the resistance to heat transfer), A is the available area for heat exchange, and ΔT is the temperature difference driving force across the heat transfer area.

The *salting-out crystallizer* uses a third component that does not chemically react to induce supersaturation, but instead displaces the solubility of the solute in the mixture. The term salting-out is employed because sodium chloride (NaCl) is usually added as the third component although any substance that depresses the solubility of the original solute can be added (as the third component). In some applications, the process is referred to as an *antisolvent crystallization*. Examples include alcohols and ketones.

Reactor crystallizers are another category of units, but are rarely employed. In such units, a mass-transfer step (e.g., gas absorption), occurs in the mother liquor. This results in supersaturation and provides additional mass transfer from the liquid to the solid phase in the form of crystallization.[2]

Auxiliary equipment for a crystallization process can include slurry pumps, vacuum pumps, mixers, condensers, steam traps, and entrainment separators. These latter units are not different than those described earlier (and required) for other mass transfer operations.[3]

ILLUSTRATIVE EXAMPLE 14.13

Define the terms *occlusion* and *magma*.

SOLUTION: *Occulsion* is a word that describes a process that "prevents the passage of." It is employed with reference to the mother liquor retained within crystals.

The word *magma* is simply "a suspension of precipitated matter in a water substance."   ∎

DESCRIBING EQUATIONS

Overall and componential material balances have already been described in rather extensive detail in Part I. Some of these calculations in the chemical process industry include transient effects that can account for process upsets, startups, shutdowns, and so on. The describing equations for these time-varying (unsteady-state) systems are differential. The equations usually take the form of a first-order derivative with respect to time, where time is the independent variable. However, calculations for most crystallization processes assume steady-state conditions with the ultimate or final design based on the aforementioned worst-case or maximum flow conditions. This greatly simplifies the calculations since the describing equations are no longer differential, but rather algebraic.

The development of mass (and energy to follow) balances follow the same pro-
cedure(s) presented in Part I. Consider, as with other mass transfer operations, material
and energy balances and any heat transfer equations that can be written for the various
crystallization processes. The material balances can provide the process yield, i.e., the
mass of crystals formed from a given mass of solution. The effect of evaporation or of
cooling must be included if applicable.

As an example, the evaporation of solvent from a crystallizer is pictured in
Figure 14.8. A solute componential and total material balance equation (on a mole
basis) may be written:

$$F = V + L + P; \quad \text{total} \tag{14.13}$$

$$x_F F = V(0) + x_L L + x_C P; \quad \text{componential} \tag{14.14}$$

where F is the feed, V is the quantity of evaporation, L is liquid (filtrate) withdrawal,
P is the crystal production, and x represents the solute content of a stream in units con-
sistent with the flow rate. There is also an equilibrium expression relating x_L and x_C.

Once the material balance is completed, one may then proceed directly to the
energy calculations, some of which can play a significant role in crystallizer design.
As with material balance calculations, energy calculations for crystallizers almost
always are based on steady-state conditions. One of the principal jobs of a practicing
engineer involved with crystallizers is to account for the energy that flows into and out
of the unit and to determine overall energy requirements. This is accomplished by
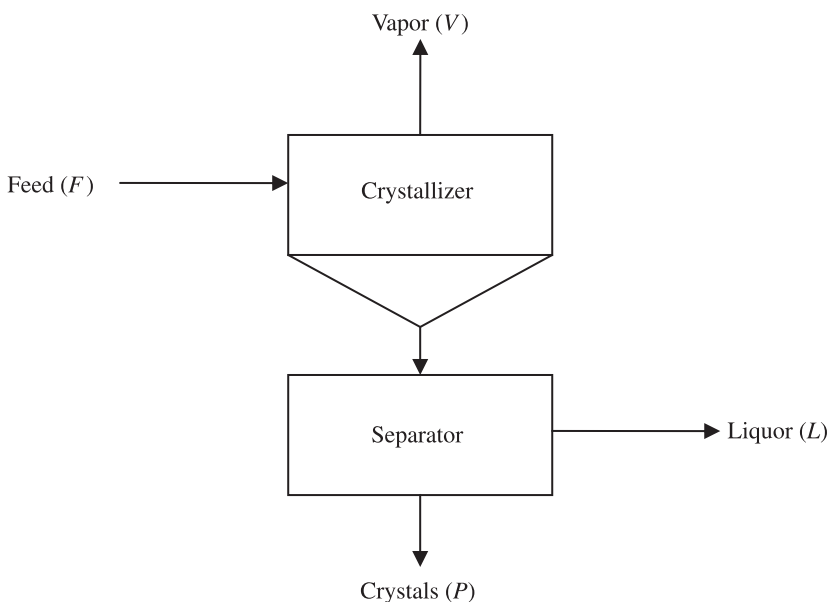performing energy balances on the unit.

Figure 14.8   Line diagram of an evaporative crystallizer.

As noted earlier, crystallization operations may be carried out either by cooling a solution or by evaporative concentration, or by both. The cooling of a solution may be accomplished by the removal (transfer) of heat to cooling water or air of both the sensible heat and the heat evolved during crystallization of the product. If the solution is crystallized by evaporation, the required heat may be supplied by the sensible heat of solution as in vacuum crystallizers, or it may be supplied from an external source. In the former case, the heat of vaporization of the solvent from the solution may safely be assumed equal to the heat of vaporization of the pure solvent. In the latter case, the heat of solution (data for which is rarely available) may be assumed equal to the heat of solution at infinite dilution.[1] Obviously, for crystallization problems requiring energy balances, e.g., where evaporation occurs or when the temperature of an adiabatic crystallizer is unknown, enthalpy data must be provided or made available.

Referring once again to Figure 14.8, one may also write an energy balance

$$F\hat{H}_F + Q = V\hat{H}_V + L\hat{H}_L + P\hat{H}_C \tag{14.15}$$

The enthalpies in this equation can be determined, provided the temperatures of the product streams are known. In addition, the operation is usually either adiabatic or may be safely assumed to be adiabatic, so that $Q = 0$.

Five illustrative examples concerned with the describing equations associated with crystallizers follow. Several excellent additional examples are available in the literature.[6]

ILLUSTRATIVE EXAMPLE 14.14

Devise a process that will produce 2000 lb/hr of $NaNO_3$ crystals from a 90% (by mass) $NaNO_3$–NaCl mixture.

SOLUTION: This is obviously an open-ended process design problem. One possible flow diagram is provided in Figure 14.9.   ∎
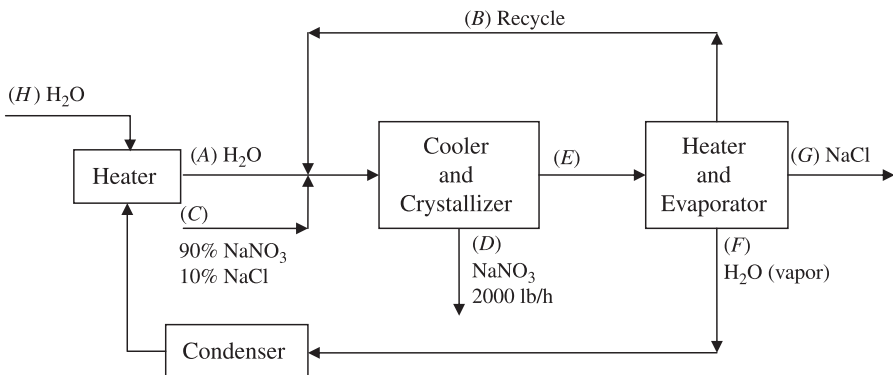

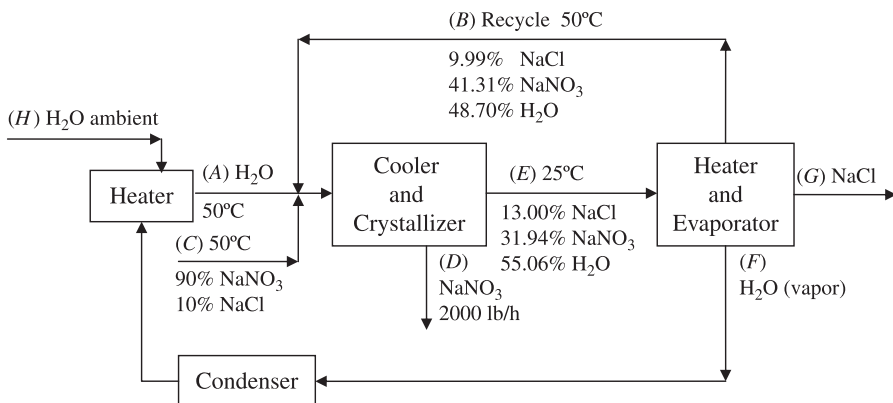**Figure 14.9**   Process flow diagram.

Figure 14.10   Process flow diagram with system data.

ILLUSTRATIVE EXAMPLE 14.15

Refer to the previous example. Write pertinent material balance equations around the cooler and crystallizer for the system provided in Figure 14.10.

SOLUTION:

Overall material balance:

$$A + B + C - E - D = 0; \quad D = 2000$$

Water balance:

$$A + 0.487(B) - 0.5506(E) = 0$$

NaCl balance:

$$0.1(C) + 0.0999(B) - 0.13(E) = 0$$

NaNO$_3$ balance:

$$0.9(C) + 0.4131(B) - 0.3194(E) - 2000 = 0$$

Since there are three components—(H$_2$O, NaNO$_3$, and NaCl)—only three independent equations may be employed.   ■

ILLUSTRATIVE EXAMPLE 14.16

Refer to the previous example. Write pertinent material balance equations around the heater and evaporator in Figure 14.10.

SOLUTION:

Overall material balance:

$$E - G - F - B = 0$$

Water balance:

$$0.5506(E) - F - 0.487(B) = 0$$

NaCl balance:

$$0.13(E) - G - 0.0999(B) = 0$$

$NaNO_3$ balance:

$$0.3194(E) - 0.4131(B) = 0$$

Once again, only three independent equations may be written.   ■

ILLUSTRATIVE EXAMPLE 14.17

Obtain the flow rates for each of the eight streams noted in Figure 14.10.

SOLUTION: First, examine the material balance equations provided in the three previous examples. Although there are eight equations, one notes that there are a total of only seven independent equations. Since there are seven unknown streams—*A*, *B*, *C*, *D*, *E*, *F*, and *G*—a unique solution is possible. That unique solution, in lb/hr can be shown to be:

$$A = 733$$
$$B = 3254$$
$$C = 2222$$
$$D = 2000$$
$$E = 4209$$
$$F = 733$$
$$G = 222$$
$$H = 0$$ ■

DESIGN CONSIDERATIONS

As with any mass transfer device, there are usually five conceptual steps to be considered with the design of equipment. These are:

1 the identification of the parameters that must be specified,

2 the application of fundamentals underlying theoretical equations or concepts,

3 the enumeration, explanation, and application of simplifying assumptions,

4 the possible use of correction factors for "nonideal" behavior, and

5 the identification of other factors that must be considered for adequate equipment specification.

Since design calculations are generally based on the maximum throughput capacity for the proposed crystallizer or process, these calculations are never completely accurate. It is usually necessary to apply reasonable safety or "fudge" factors when setting the final design for the crystallizer. Safety factors vary widely, particularly with crystallizers, and are a strong function of the accuracy of the data involved, calculational procedures, and past experience. Nonetheless, simple qualitative design procedures are provided below.

Assuming a crystallizer is the mass transfer operation of choice, the class of crystallizer is normally selected first. For high feed rate (e.g., greater that 50,000 lb/hr), a continuous—as opposed to a batch—process is normally selected. Overall process decisions are based on capital, operating and maintenance costs, space, location, production rate, crystal characteristics, size and size distribution of crystals, physical and chemical characteristics of the feed liquor and slurry, corrosion concerns, and so on.

Regarding a new design, scale-up problems can be expected when the design is based on pilot-plant or laboratory units. Even after the equipment is finally constructed, significant startup problems are the norm. Finally, it should be noted that the scaling-up of crystallization equipment is probably more difficult than that for any of the other mass transfer operations.

If the pilot or small-scale crystallizer produces a satisfactory product, then the design of the larger crystallizer must simulate a number of different conditions obtained in the smaller unit. The four most important conditions are:[7]

1 identical flow characteristics of liquids and solid particles,

2 identical degrees of supersaturation in all equivalent regions of the crystallizer,

3 identical initial seed sizes (if applicable) and magma densities, and

4 identical contact times between growing crystals and supersaturated liquor.

ILLUSTRATIVE EXAMPLE 14.18

Discuss problems associated with the design of crystallization equipment.

SOLUTION: As discussed earlier, the design of crystallization equipment can be difficult. Knowledge of the phase equilibrium and physical properties does not allow one to predict the behavior of the actual process. Bench-scale and pilot-plant experiments on the actual stream are usually recommended and some equipment vendors require a pilot-plant test before designing the equipment. Even with such testing, operating adjustments must usually be made on the actual commercial installation before the equipment will operate to yield an acceptable product.   ■

Marnell[8] has provided a step-by-step procedure for the design of a single solute forced circulation crystallization, as pictured in Figure 14.10. The nine specifications required and listed below are:

1 production rate of crystals, P,
2 feed (liquid) mass fractions,
3 desired CSD and appropriate residence time to achieve it,
4 feed temperature,
5 design temperature and corresponding mother liquor saturation mass fractions,
6 centrifuge wash water ratio,
7 crystal bulk density, ρ_B,
8 magma density, ρ_M, and
9 liquor density, ρ_L.

Specifications (5)–(9) are generally drawn from experience.

ILLUSTRATIVE EXAMPLE 14.19

Complete a material balance for the process pictured in Figure 14.11. The following information is provided:[8]

> Production rate: 3125 kg/h
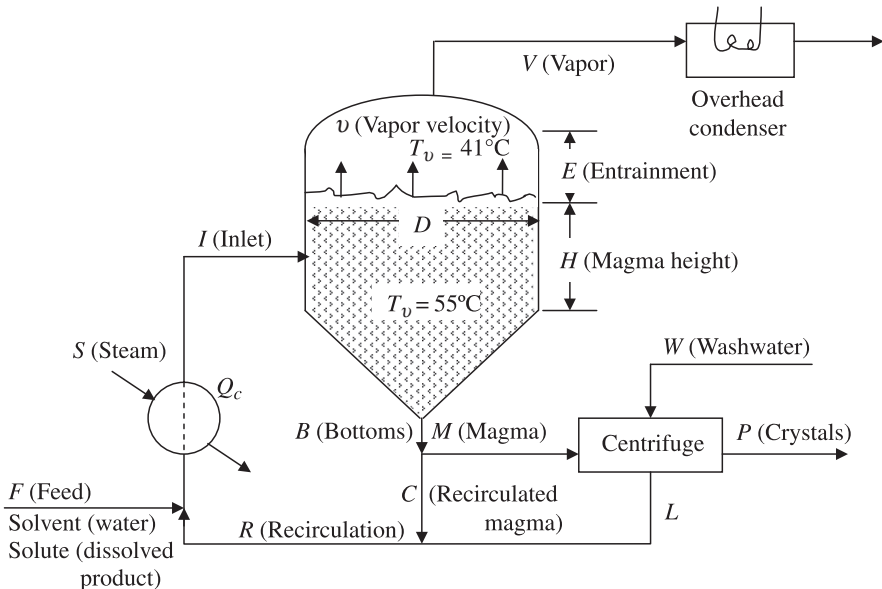> Feed composition: 75% urea, 25% water

Figure 14.11   Forced circulation crystallizer.

Magma density: 1170 kg/m^3

Magma crystal concentration: 450 kg crystals/m^3 magma

Liquor density: 1340 kg/m^3

Magma recirculation rate: 567,900 kg/h

Centrifuge washwater ratio: 0.12 kg H_2O/kg urea

SOLUTION: First calculate the feed ratio, F:

$$F = \frac{P}{x_{F,U}}; \quad x_{F,U} = \text{mass fraction urea}$$

$$= \frac{3125}{0.75}$$

$$= 4167 \text{ kg/h}$$

The wash rate, W, is

$$W = (0.12)P$$

$$= (0.12)(3125)$$

$$= 375 \text{ kg/h}$$

The water vaporization rate, V, is given as

$$V = (F)(x_{F,W}) + W; \quad x_{F,U} = \text{mass fraction urea}$$

$$= (4167)(0.25) + 375$$

$$= 1417 \text{ kg/h}$$

Calculate the magma flow, M,

$$M = \frac{(P)(\rho_M)}{\rho_{C,M}}; \quad \rho_M = \text{magma density, } \rho_{C,M} = \text{crystal density in magma}$$

$$= \frac{(3125)(1170)}{450}$$

$$= 8120 \text{ kg/h}$$

The liquor flow, L, is obtained by a total mass balance around the centrifuge:

$$W + M = P + L$$

$$L = W + M - P$$

$$= 375 + 8120 - 3125$$

$$= 5370 \text{ kg/h}$$

The bottoms, B, is

$$B = M + C$$

$$= 8120 + 567,900$$

$$= 576,000 \text{ kg/h}$$

The recycle, R, is

$$R = C + L$$
$$= 567{,}900 + 5370$$
$$= 573{,}300 \text{ kg/h}$$

Finally, the inlet to the crystallizer, I, is

$$I = F + R$$
$$= 4167 + 573{,}300$$
$$= 577{,}500 \text{ kg/h} \qquad \blacksquare$$

ILLUSTRATIVE EXAMPLE 14.20

Refer to Example 14.19. Size the crystallizer. Design information is provided below:

Average residence time, τ (based on M): 3.38 h
Maximum (with safety factor) vapor velocity,

$$v = C_f \left(\frac{\rho_l - \rho_v}{\rho_v} \right)^{0.5} ; \ C_f = 0.0122 \text{ m/s}$$

Crystallizer diameter, D, is based on the maximum vapor velocity, v
Crystallizer magma cylinder height, H: $H = 1.15D$
Freeboard height (for droplet disengagement): 2 m

Refer to Figure 14.11 for additional details.

SOLUTION: The crystallizer area and diameter are to be based on entrainment to ensure vapor droplet disengagement. The vapor velocity is given in:

$$v = C_f \left(\frac{\rho_l - \rho_v}{\rho_v} \right)^{0.5} ; \ C_f = 0.0122 \text{ m/s}$$

For steam at atmospheric pressure, set $\rho_v = 0.0563 \text{ kg/m}^3$. Therefore,

$$v = 0.0122 \left(\frac{1340}{0.0543} \right)^{0.5}$$

$$= 1.917 \text{ m/s}$$
$$= 6899 \text{ m/h}$$

The crystallizer area, A, and diameter, D, are therefore

$$A = \frac{V}{(\rho_v)(v)}$$

$$= \frac{1417}{(0.0543)(6899)}$$

$$= 3.78\,\text{m}^2$$

In addition,

$$D = \left(\frac{4A}{\pi}\right)^{0.5}$$

$$= \left(\frac{4(3.78)}{\pi}\right)^{0.5}$$

$$= 2.19\,\text{m}$$

The magma occupies two sections (of volume) in the crystallizer—the cylinder of height H and the cone below the cylinder. The magma volume MV is therefore

$$MV = \text{cone volume} + \text{cylinder volume}$$

The volume of the cone can be shown to be $0.2267D^3$.[9] Thus,

$$MV = 0.2267D^3 + \left(\frac{\pi}{4}\right)D^2H;\ H = 1.15D$$

$$= (0.2267 + 0.903)D^3$$

$$= (1.13)D^3$$

The volume occupied by the magma

$$MV = \frac{M}{\rho_M}\tau$$

$$= \left(\frac{8120}{1170}\right)(3.38)$$

$$= 23.5\,\text{m}^3$$

Setting the above two equations equal to each other,

$$23.5 = (1.13)D^3$$

$$D = 2.75\,\text{m}$$

In addition,

$$H = 1.15D$$

$$= (1.15)(2.75)$$

$$= 3.16\,\text{m}$$

The total crystallizer volume, *TC*, is

$$TC = 3.16 + 2.0$$
$$= 5.16\,\text{m}$$

∎

ILLUSTRATIVE EXAMPLE 14.21

Quick-size the heat exchanger in Figure 14.11. Assume $U = 200\,\text{Btu/h} \cdot \text{ft}^2 \cdot {}^\circ\text{F}$.

SOLUTION: In order to size the exchanger, first calculate the steam requirement. An energy balance around the entire process allows one to estimate the heat exchanger steam load, $\dot{Q}_s$:

$$\dot{Q}_s = V\hat{H}_V - F\hat{H}_F - W\hat{H}_W + P\hat{H}_P$$

Neglecting sensible enthalpy changes associated with *F*, *W*, and *P* reduces the above to

$$\dot{Q}_s = V\hat{H}_V = V\lambda_w;\ \ \lambda_w = \text{enthalpy of vaporization of water}$$

Thus,

$$\dot{Q}_s = (1417\,\text{kg/h})(2403\,\text{kJ/kg})$$
$$= 3{,}405{,}000\,\text{kJ/h}$$

Quick-size the magma exchanger by applying the standard heat transfer equation:

$$\dot{Q}_S = UA_S\Delta T_{LM} \tag{14.16}$$

Employing atmospheric steam at 100°C,

$$\Delta T_{LM} \approx 100 - 55 = 45{}^\circ\text{C}$$

The overall boiling and convective water coefficient (assumed) of $200\,\text{Btu/h} \cdot \text{ft}^2 \cdot {}^\circ\text{F}$ is converted to $4088\,\text{kJ/h} \cdot \text{m}^2 \cdot {}^\circ\text{C}$. Substituting,

$$A_S = \frac{\dot{Q}_S}{U\Delta T_{LM}} = \frac{3{,}405{,}000\,\text{kJ/h}}{\left(4088\,\text{kJ/h} \cdot \text{m}^2 \cdot {}^\circ\text{C}\right)(45{}^\circ\text{C})}$$
$$= 18.5\,\text{m}^2$$
$$= (18.5\,\text{m}^2)\left(\frac{1\,\text{ft}}{0.3048\,\text{m}}\right)^2$$
$$= 60.73\,\text{ft}^2$$

This is a small area. Normally, a double pipe exchanger is used if the area is below $500\,\text{ft}^2$. However, to avoid the numerous bends in such a design, a conventional shell and tube exchanger with a single tube and shell pass is recommended. ∎

Chapter 14 Crystallization

ILLUSTRATIVE EXAMPLE 14.22

Outline how to quick-size the overhead condenser. Assume $U = 300\,\text{Btu/h} \cdot \text{ft}^2 \cdot {}^\circ\text{F}$.

SOLUTION: The heat load, $\dot{Q}_C$, is given by

$$\dot{Q}_C = V\lambda_w$$

with (once again),

$$\dot{Q}_C = UA_C\Delta T_{LM}$$

Therefore,

$$A_C = \frac{\dot{Q}_C}{U\Delta T_{LM}}$$

A vacuum system is often recommended and a steam jet ejector should be adequate for this design. Note that the urea in the solution elevates the operating boiling temperature of water by $55 - 41 = 14^\circ\text{C}$ (per Fig. 14.11) . Assume cooling water is available at 30°C and employ an approach temperature of 3°C. Thus,

$$\Delta T_{LM} = \frac{(41 - 30) - (41 - 38)}{\ln\left(\dfrac{41 - 30}{41 - 38}\right)} = 6.16^\circ\text{C}$$

Set $U = 300\,\text{Btu/h} \cdot \text{ft}^2 \cdot {}^\circ\text{F} = 6132\,\text{kJ/h} \cdot \text{m}^2 \cdot {}^\circ\text{C}$ for a water–water condenser. Using the duty found in Illustrative Example 14.21,

$$\dot{Q}_C = 3{,}405{,}000\,\text{kJ/h}$$

one may now solve for A_C:

$$A_C = \frac{3{,}405{,}000}{(6132)(6.16^\circ\text{C})}$$

$$= 90.14\,\text{m}^2$$

$$= 970\,\text{ft}^2 \qquad\blacksquare$$

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