Transport Processes and Unit Operations

$L_N V_{N+1}$ in Fig. 12.10-3. Its coordinates can also be calculated from Eqs. (12.10-11) and (12.10-12). The stages are stepped off as shown. The fourth stage for L_4 is slightly past the desired L_N. Hence, about 3.9 stages are required.

12.10C Constant Underflow in Countercurrent Multistage Leaching

In this case the liquid L_n retained in the underflow solids is constant from stage to stage. This means that a plot of N versus y_A is a horizontal straight line and N is constant. Then the operating-line equation (12.10-3) is a straight line when plotted as y_A versus x_A. The equilibrium line can also be plotted on the same diagram. In many cases the equilibrium line may also be straight with $y_A = x_A$. Special treatment must be given the first stage, however, since L_0 is generally not equal to L_n, since it contains little or no solvent. A separate material and equilibrium balance is made on stage 1 to obtain L_1 and V_2 (see Fig. 12.10-1). Then the straight operating line can be used and the McCabe–Thiele method used to step off the number of stages.

Since this procedure for constant underflow requires almost as many calculations as the general case for variable underflow, the general procedure can be used for constant underflow by simply using a horizontal line of N versus y_A in Fig. 12.10-2 and stepping off the stages with the Δ point.

12.11 INTRODUCTION AND EQUIPMENT FOR CRYSTALLIZATION

12.11A Crystallization and Types of Crystals

1. Introduction. Separation processes for gas–liquid and liquid–liquid systems have been treated in this and previous chapters. Also, the separation process of leaching was discussed for a solid–liquid system. Crystallization is also a solid–liquid separation process in which mass transfer occurs of a solute from the liquid solution to a pure solid crystalline phase. An important example is in the production of sucrose from sugar beet, where the sucrose is crystallized out from an aqueous solution.

Crystallization is a process where solid particles are formed from a homogeneous phase. This process can occur in the freezing of water to form ice, in the formation of snow particles from a vapor, in the formation of solid particles from a liquid melt, or in the formation of solid crystals from a liquid solution. The last process mentioned, crystallization from a solution, is the most important one commercially and will be treated in the present discussion. In crystallization the solution is concentrated and usually cooled until the solute concentration becomes greater than its solubility at that temperature. Then the solute comes out of the solution forming crystals of approximately pure solute.

In commercial crystallization the yield and purity of crystals are not only important but also the sizes and shapes of the crystals. It is often desirable that crystals be uniform in size. Size uniformity is desirable to minimize caking in the package, for ease of pouring, for ease in washing and filtering, and for uniform behavior when used. Sometimes large crystals are requested by the purchaser, even though smaller crystals are just as useful. Also, crystals of a certain shape are sometimes required, such as needles rather than cubes.

2. *Types of crystal geometry.* A crystal can be defined as a solid composed of atoms, ions, or molecules, which are arranged in an orderly and repetitive manner. It is a highly organized type of matter. The atoms, ions, or molecules are located in three-dimensional arrays or space lattices. The interatomic distances in a crystal between these imaginary planes or space lattices are measured by x-ray diffraction as are the angles between these planes. The pattern or arrangement of these space lattices is repeated in all directions.

Crystals appear as polyhedrons having flat faces and sharp corners. The relative sizes of the faces and edges of different crystals of the same material may differ greatly. However, the angles between the corresponding faces of all crystals of the same material are equal and are characteristic of that particular material. Crystals are thus classified on the basis of these interfacial angles.

There are seven classes of crystals, depending upon the arrangement of the axes to which the angles are referred:

1. Cubic system. Three equal axes at right angles to each other.
2. Tetragonal system. Three axes at right angles to each other, one axis longer than the other two.
3. Orthorhombic system. Three axes at right angles to each other, all of different lengths.
4. Hexagonal system. Three equal axes in one plane at 60° to each other, and a fourth axis at right angles to this plane and not necessarily the same length.
5. Monoclinic system. Three unequal axes, two at right angles in a plane and a third at some angle to this plane.
6. Triclinic system. Three unequal axes at unequal angles to each other and not 30, 60, or 90°.
7. Trigonal system. Three equal and equally inclined axes.

The relative development of different types of faces of a crystal may differ for a given solute crystallizing. Sodium chloride crystallizes from aqueous solutions with cubic faces only. In another case, if sodium chloride crystallizes from an aqueous solution with a given slight impurity present, the crystals will have octahedral faces. Both types of crystals are in the cubic system but differ in crystal habit. The crystallization in overall shapes of plates or needles has no relation to crystal habit or crystal system and usually depends upon the process conditions under which the crystals are grown.

12.11B Equilibrium Solubility in Crystallization

In crystallization equilibrium is attained when the solution or mother liquor is saturated. This is represented by a *solubility curve.* Solubility is dependent mainly upon temperature. Pressure has a negligible effect on solubility. Solubility data are given in the form of curves where solubilities in some convenient units are plotted versus temperature. Tables of solubilities are given in many chemical handbooks (P1). Solubility curves for some typical salts in water were given in Fig. 8.1-1. In general, the solubilities of most salts increase slightly or markedly with increasing temperature.

A very common type of curve is shown in Fig. 8.1-1 for KNO_3, where the solubility increases markedly with temperature and there are no hydrates. Over the whole range of temperatures, the solid phase is KNO_3. The solubility of NaCl is marked by its small change with temperature. In solubility plots the solubility data are ordinarily given as parts by weight of anhydrous material per 100 parts by weight of total solvent (i.e., water in many cases).

In Fig. 12.11-1 the solubility curve is shown for sodium thiosulfate, $Na_2S_2O_3$. The solubility increases rapidly with temperature, but there are definite breaks in the curve which indicate different hydrates. The stable phase up to 48.2°C is the pentahydrate $Na_2S_2O_3 \cdot 5H_2O$. This means that at concentrations above the solubility line (up to 48.2°C), the solid crystals formed are $Na_2S_2O_3 \cdot 5H_2O$. At concentrations below the solubility line, only a solution exists. From 48.2 to about 65°C, the stable phase is $Na_2S_2O_3 \cdot 2H_2O$. A half-hydrate is present between 65 to 70°C, and the anhydrous salt is the stable phase above 70°C.

12.11C Yields and Heat and Material Balances in Crystallization

1. Yields and material balances in crystallization. In most of the industrial crystallization processes, the solution (mother liquor) and the solid crystals are in contact for a long enough time to reach equilibrium. Hence, the mother liquor is saturated at the final temperature of the process, and the final concentration of the solute in the solution can be obtained from the solubility curve. The yield of crystals from a crystallization process can then be calculated knowing the initial concentration of solute, the final temperature, and the solubility at this temperature.

In some instances in commercial crystallization, the rate of crystal growth may be quite slow, due to a very viscous solution or a small surface of crystals exposed to the solution. Hence, some supersaturation may still exist, giving a lower yield of crystals than predicted.

In making the material balances, the calculations are straightforward when the solute crystals are anhydrous. Simple water and solute material balances are made. When the crystals are hydrated, some of the water in the solution is removed with the crystals as a hydrate.

EXAMPLE 12.11-1. Yield of a Crystallization Process

A salt solution weighing 10 000 kg with 30 wt % Na_2CO_3 is cooled to 293 K (20°C). The salt crystallizes as the decahydrate. What will be the yield of $Na_2CO_3 \cdot 10H_2O$ crystals if the solubility is 21.5 kg anhydrous Na_2CO_3/100 kg of total water? Do this for the following cases.

(a) Assume that no water is evaporated.

(b) Assume that 3% of the total weight of the solution is lost by evaporation of water in cooling.

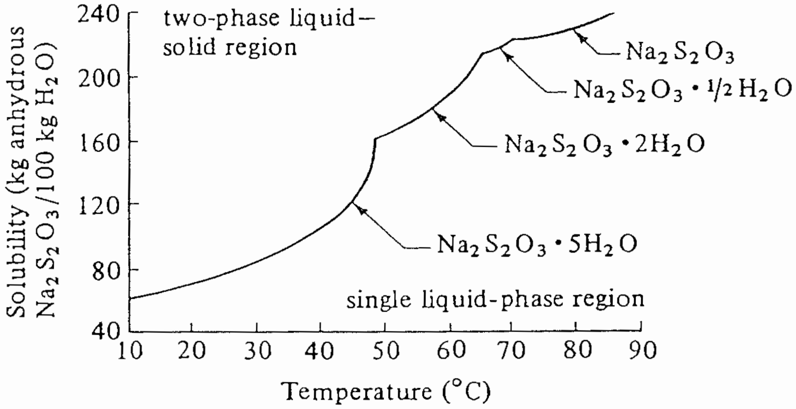


FIGURE 12.11-1. *Solubility of sodium thiosulfate, $Na_2S_2O_3$, in water.*

Solution: The molecular weights are 106.0 for Na_2CO_3, 180.2 for $10H_2O$, and 286.2 for $Na_2CO_3 \cdot 10H_2O$. The process flow diagram is shown in Fig. 12.11-2, with W being kg H_2O evaporated, S kg solution (mother liquor), and C kg crystals of $Na_2CO_3 \cdot 10H_2O$. Making a material balance around the dashed-line box for water for part (a), where $W = 0$,

$$0.70(10\,000) = \frac{100}{100 + 21.5}(S) + \frac{180.2}{286.2}(C) + 0 \qquad \textbf{(12.11-1)}$$

where (180.2)/(286.2) is wt fraction of water in the crystals. Making a balance for Na_2CO_3,

$$0.30(10\,000) = \frac{21.5}{100 + 21.5}(S) + \frac{106.0}{286.2}(C) + 0 \qquad \textbf{(12.11-2)}$$

Solving the two equations simultaneously, $C = 6370$ kg of $Na_2CO_3 \cdot 10H_2O$ crystals and $S = 3630$ kg solution.

For part (b), $W = 0.03(10\,000) = 300$ kg H_2O. Equation (12.11-1) becomes

$$0.70(10\,000) = \frac{100}{100 + 21.5}(S) + \frac{180.2}{286.2}(C) + 300 \qquad \textbf{(12.11-3)}$$

Equation (12.11-2) does not change, since no salt is in the W stream. Solving Eqs. (12.11-2) and (12.11-3) simultaneously, $C = 6630$ kg of $Na_2CO_3 \cdot 10H_2O$ crystals and $S = 3070$ kg solution.

2. *Heat effects and heat balances in crystallization.* When a compound whose solubility increases as temperature increases dissolves, there is an absorption of heat, called the *heat of solution.* An evolution of heat occurs when a compound dissolves whose solubility decreases as temperature increases. For compounds dissolving whose solubility does not change with temperature, there is no heat evolution on dissolution. Most data on heats of solution are given as the change in enthalpy in kJ/kg mol (kcal/g mol) of solute occurring with the dissolution of 1 kg mol of the solid in a large amount of solvent at essentially infinite dilution.

In crystallization the opposite of dissolution occurs. At equilibrium the heat of crystallization is equal to the negative of the heat of solution at the same concentration in solution. If the heat of dilution from saturation in the solution to infinite dilution is small, this can be neglected, and the negative of the heat of solution at infinite dilution can be used for the heat of crystallization. With many materials this heat of dilution is small

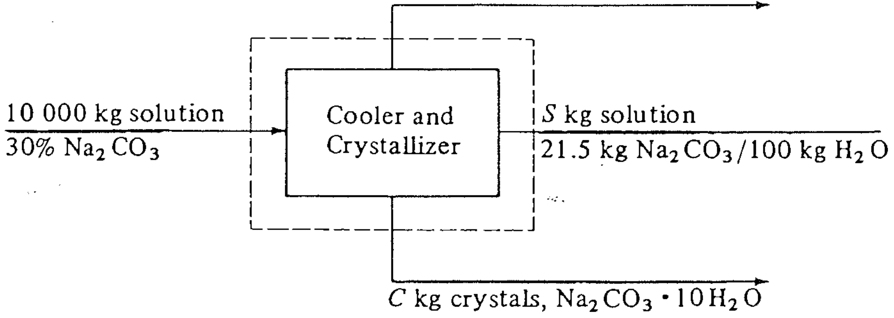


FIGURE 12.11-2. *Process flow for crystallization in Example 12.11-1.*

compared with the heat of solution, and this approximation is reasonably accurate. Heat of solution data are available in several references (P1, N1).

Probably the most satisfactory method of calculating heat effects during a crystallization process is to use the enthalpy–concentration chart for the solution and the various solid phases which are present for the system. However, only a few such charts are available, including the following systems: calcium chloride–water (H1), magnesium sulfate–water (P2), and ferrous sulfate–water (K2). When such a chart is available, the following procedure is used. The enthalpy H_1 of the entering solution at the initial temperature is read off the chart, where H_1 is kJ (btu) for the total feed. The enthalpy H_2 of the final mixture of crystals and mother liquor at the final temperature is also read off the chart. If some evaporation occurs, the enthalpy H_V of the water vapor is obtained from the steam tables. Then the total heat absorbed q in kJ is

$$q = (H_2 + H_V) - H_1 \qquad \textbf{(12.11-4)}$$

If q is positive, heat must be added to the system. If it is negative, heat is evolved or given off.

EXAMPLE 12.11-2. Heat Balance in Crystallization
A feed solution of 2268 kg at 327.6 K (54.4°C) containing 48.2 kg $MgSO_4$/100 kg total water is cooled to 293.2 K (20°C), where $MgSO_4 \cdot 7H_2O$ crystals are removed. The solubility of the salt is 35.5 kg $MgSO_4$/100 kg total water (P1). The average heat capacity of the feed solution can be assumed as 2.93 kJ/kg · K (H1). The heat of solution at 291.2 K (18°C) is -13.31×10^3 kJ/kg mol $MgSO_4 \cdot 7H_2O$ (P1). Calculate the yield of crystals and make a heat balance to determine the total heat absorbed, q, assuming that no water is vaporized.

Solution: Making a water balance and a balance for $MgSO_4$ using equations similar to (12.11-1) and (12.11-2) in Example 12.11-1, $C = 616.9$ kg $MgSO_4 \cdot 7H_2O$ crystals and $S = 1651.1$ kg solution.

To make a heat balance, a datum of 293.2 K (20°C) will be used. The molecular weight of $MgSO_4 \cdot 7H_2O$ is 246.49. The enthalpy of the feed is H_1.

$$H_1 = 2268(327.6 - 293.2)(2.93) = 228\,600 \text{ kJ}$$

The heat of solution is $-(13.31 \times 10^3)/246.49 = -54.0$ kJ/kg crystals. Then the heat of crystallization is $-(-54.0) = +54.0$ kJ/kg crystals, or $54.0(616.9) = 33\,312$ kJ. This assumes that the value at 291.2 K is the same as at 293.2 K. The total heat absorbed, q, is

$$q = -228\,600 - 33\,312 = -261\,912 \text{ kJ } (-248\,240 \text{ btu})$$

Since q is negative, heat is given off and must be removed.

12.11D Equipment for Crystallization

1. Introduction and classification of crystallizers. Crystallizers may be classified according to whether they are batch or continuous in operation. Batch operation is done for certain special applications. Continuous operation of crystallizers is generally preferred.

Crystallization cannot occur without *supersaturation.* A main function of any crystallizer is to cause a supersaturated solution to form. A classification of crystallizing equipment can be made based on the methods used to bring about supersaturation as follows: (1) supersaturation produced by cooling the solution with negligible evaporation—tank and batch-type crystallizers; (2) supersaturation produced by evaporation of the solvent with little or no cooling—evaporator–crystallizers and crystallizing evaporators; (3) supersaturation by combined cooling and evaporation in adiabatic evaporator—vacuum crystallizers.

In crystallizers producing supersaturation by cooling the substances must have a solubility curve that decreases markedly with temperature. This occurs for many substances, and this method is commonly used. When the solubility curve changes little with temperature, such as for common salt, evaporation of the solvent to produce supersaturation is often used. Sometimes evaporation with some cooling will also be used. In the method of cooling adiabatically in a vacuum, a hot solution is introduced into a vacuum, where the solvent flashes or evaporates and the solution is cooled adiabatically. This method to produce supersaturation is the most important one for large-scale production.

In another method of classification of crystallizers, the equipment is classified according to the method of suspending the growing product crystals. Examples are crystallizers where the suspension is agitated in a tank, is circulated by a heat exchanger, or is circulated in a scraped surface exchanger.

An important difference in many commercial crystallizers is the manner in which the supersaturated liquid contacts the growing crystals. In one method, called the *circulating magma method*, the entire magma of crystals and supersaturated liquid is circulated through both the supersaturation and crystallization steps without separating the solid from the liquid into two streams. Crystallization and supersaturation are occurring together in the presence of the crystals. In the second method, called the *circulating liquid method*, a separate stream of supersaturated liquid is passed through a fluidized bed of crystals, where the crystals grow and new ones form by nucleation. Then the saturated liquid is passed through an evaporating or cooling region to produce supersaturation again for recycling.

2. Tank crystallizers. In tank crystallization, which is an old method still used in some specialized cases, hot saturated solutions are allowed to cool in open tanks. After a period of time the mother liquor is drained and the crystals removed. Nucleation and the size of crystals are difficult to control. Crystals contain considerable amounts of occluded mother liquor. Labor costs are very high. In some cases the tank is cooled by coils or a jacket and an agitator used to improve the heat-transfer rate. However, crystals often build up on these surfaces. This type has limited application and sometimes is used to produce some fine chemicals and pharmaceutical products.

3. Scraped surface crystallizers. One type of scraped surface crystallizer is the Swenson–Walker crystallizer, which consists of an open trough 0.6 m wide with a semicircular bottom having a cooling jacket outside. A slow-speed spiral agitator rotates and suspends the growing crystals on turning. The blades pass close to the wall and break off any deposits of crystals on the cooled wall. The product generally has a somewhat wide crystal-size distribution.

In the double-pipe scraped surface crystallizer, cooling water passes in the annular space. An internal agitator is fitted with spring-loaded scrapers that wipe the wall and provide good heat-transfer coefficients. This type is called a *votator* and is used in crystallizing ice cream and plasticizing margarine. A sketch is shown in Fig. 4.13-2.

4. Circulating-liquid evaporator–crystallizer. In a combination evaporator–crystallizer shown in Fig. 12.11-3a, supersaturation is generated by evaporation. The circulating liquid is drawn by the screw pump down inside the tube side of the condensing steam heater. The heated liquid then flows into the vapor space, where flash evaporation occurs giving some supersaturation. The vapor leaving is condensed. The supersaturated liquid flows down the downflow tube and then up through the bed of fluidized and agitated crystals, which are growing in size. The leaving saturated liquid then goes back as a recycle stream to the heater, where it is joined by the entering feed. The larger crystals settle out and a slurry of crystals and mother liquor is withdrawn as product. This type is also called the *Oslo crystallizer*.

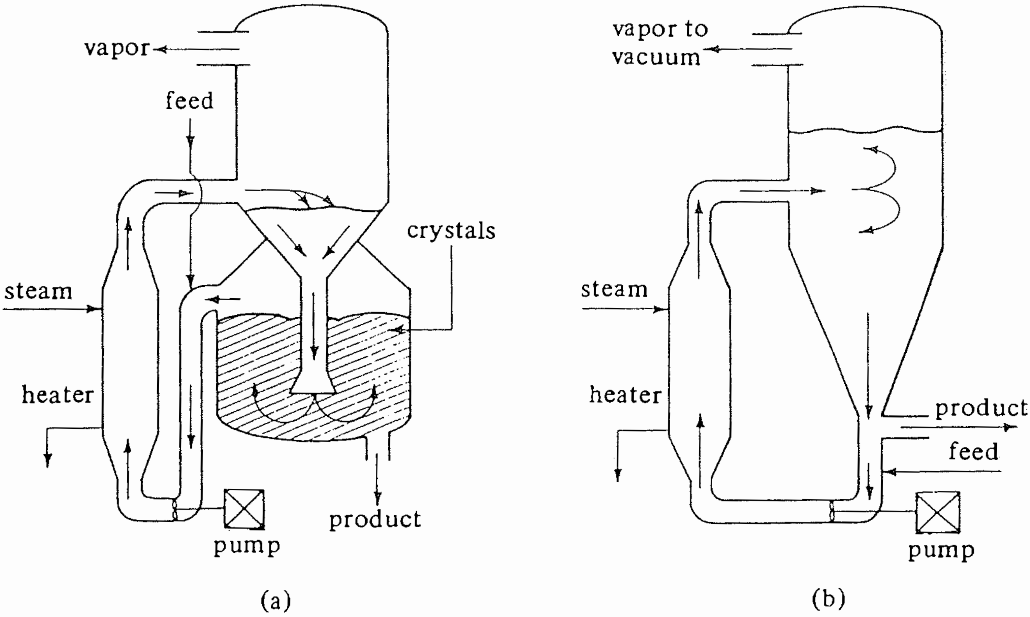
5. Circulating-magma vacuum crystallizer. In this circulating-magma vacuum-type crystallizer in Fig. 12.11-3b, the magma or suspension of crystals is circulated out of the main body through a circulating pipe by a screw pump. The magma flows through a heater, where its temperature is raised 2 to 6 K. The heated liquor then mixes with body slurry and boiling occurs at the liquid surface. This causes supersaturation in the swirling liquid near the surface, which causes deposits on the swirling suspended crystals until they leave again via the circulating pipe. The vapors leave through the top. A steam-jet ejector provides the vacuum.

12.12 CRYSTALLIZATION THEORY

12.12A Introduction and Nucleation Theories

1. Introduction. When crystallization occurs in a homogeneous mixture, a new solid phase is created. An understanding of the mechanisms by which crystals form and then grow is helpful in designing and operating crystallizers. Much experimental and theoretical work has been done to help understand crystallization. However, the differences between predicted and actual performance in commercial crystallizers are still often quite large.

The overall process of crystallization from a supersaturated solution is considered to consist of the basic steps of nucleus formation or nucleation and of crystal growth. If the solution is free of all solid particles, foreign or of the crystallizing substance, then nucleus formation must first occur before crystal growth starts. New nuclei may continue to form



(a) (b)

FIGURE 12.11-3. *Types of crystallizers: (a) circulating-liquid evaporator–crystallizer, (b) circulating-magma vacuum crystallizer.*

while the nuclei present are growing. The driving force for the nucleation step and the growth step is supersaturation. These two steps do not occur in a saturated or undersaturated solution.

2. Nucleation theories. *Primary nucleation* is a result of rapid local fluctuations on a molecular scale in a homogeneous phase. Particles or molecules of solute happen to come together and form clusters. More solute molecules may be added to one or more clusters so they grow, whereas others may break up and revert to individual molecules. The growing clusters become crystals and continue to absorb solute molecules from the solution.

This type of nucleation is called *homogeneous* or *primary nucleation.* The larger the crystal, the smaller its solubility. The solubility of small crystals in the micrometer size range is greater than that of a large crystal. The ordinary solubility data apply to large crystals. Hence, in a supersaturated solution a small crystal can be in equilibrium. If a large crystal is also present, the larger crystal will grow and the smaller one will dissolve. This effect of particle size is an important factor in nucleation. In magma crystallization, primary nucleation happens to a small degree.

An early qualitative explanation of crystallization by Miers attempts to explain formation of nuclei and crystals in an unseeded solution. This theory is shown in Fig. 12.12-1, where line AB is the normal solubility curve. If a sample of solution at point a is cooled, it first crosses the solubility curve. The sample will not crystallize until it has supercooled to some point b where crystallization begins, and the concentration drops to point c if no further cooling is done. The curve CD, called the *supersolubility curve*, represents the limit at which nucleus formation starts spontaneously and hence where crystallizaton can start. Any crystal in the metastable region will grow. The present tendency is to regard the supersolubility curve as a zone where the nucleation rate increases sharply. However, the value of Miers' explanation is that it points out that the greater the degree of supersaturation, the greater the chance of more nuclei forming.

Secondary or *contact nucleation*, which is the most effective method of nucleation, occurs when crystals collide with each other, with the impellors in mixing, or with the walls of the pipe or container. This type of nucleation is, of course, affected by the intensity of agitation. It occurs at low supersaturation, where the crystal growth rate is at the optimum for good crystals. This type of contact nucleation has been isolated and demonstrated experimentally. It is the most effective and common method of nucleation in magma crystallization. The precise mechanisms of contact nucleation are not known, nor is a complete theory available to predict these rates.

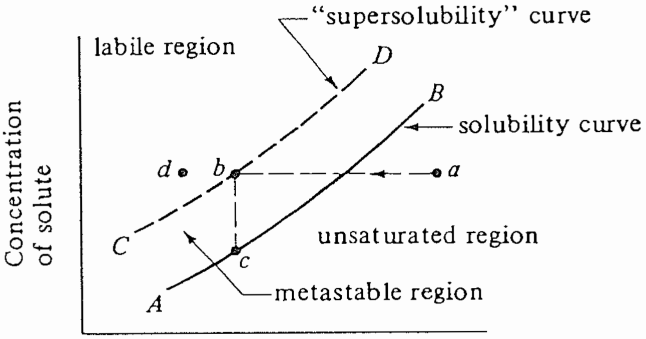


FIGURE 12.12-1. *Miers' qualitative explanation of crystallization: solubility curve (AB) and "supersolubility" curve (CD).*

12.12B Rate of Crystal Growth and ΔL Law

1. Rate of crystal growth and growth coefficients. The rate of growth of a crystal face is the distance moved per unit time in a direction that is perpendicular to the face. The crystal growth is a layer-by-layer process, and since the growth can occur only at the outer face of the crystal, the solute material must be transported to that face from the bulk of the solution. The solute molecules reach the face by diffusion through the liquid phase. The usual mass-transfer coefficient k_y applies in this case. At the surface the resistance to integration of the molecules into the space lattice at the face must be considered. This reaction at the surface occurs at a finite rate, and the overall process consists of two resistances in series. The solution must be supersaturated for the diffusion and interfacial steps to proceed.

The equation for mass transfer of solute A from the bulk solution of supersaturation concentration y_A, mole fraction of A, to the surface where the concentration is y'_A, is

$$\frac{\bar{N}_A}{A_i} = k_y(y_A - y'_A) \tag{12.12-1}$$

where k_y is the mass-transfer coefficient in kg mol/s · m^2 · mol frac, $\bar{N}_A$ is rate in kg mol A/s, and A_i is area in m^2 of surface i. Assuming that the rate of reaction at the crystal surface is also dependent on the concentration difference,

$$\frac{\bar{N}_A}{A_i} = k_s(y'_A - y_{Ae}) \tag{12.12-2}$$

where k_s is a surface reaction coefficient in kg mol/s · m^2 · mol frac and y_{Ae} is the saturation concentration. Combining Eqs. (12.12-1) and (12.12-2),

$$\frac{\bar{N}_A}{A_i} = \frac{y_A - y_{Ae}}{1/k_y + 1/k_s} = K(y_A - y_{Ae}) \tag{12.12-3}$$

where K is the overall transfer coefficient.

The mass-transfer coefficient k_y can be predicted by methods given in Section 7.4 for convective mass-transfer coefficients. The correlation for mass transfer through fixed and fluidized beds of solids can be used. The velocity obtained from the terminal settling velocity of particles can be used in the correlation or the velocity of the solution relative to the crystals in the suspension. The Schmidt number of the saturated solution is also needed for the prediction.

When the mass-transfer coefficient k_y is very large, the surface reaction is controlling and $1/k_y$ is negligible. Conversely, when the mass-transfer coefficient is very small, diffusional resistance is controlling. Surface reaction coefficients and overall transfer coefficients have been measured and reported on a number of systems (B4, H2, P3, V1). Much of the information in the literature is not directly applicable, because the conditions of measurement differ greatly from those in a commercial crystallizer. Also, the velocities and the level of supersaturation in a system are difficult to determine, and vary with position of the circulating magma in the crystallizer.

2. The ΔL law of crystal growth. McCabe (M1) has shown that all crystals that are geometrically similar and of the same material in the same solution grow at the same rate. The growth is measured as the increase in length ΔL, in mm, in linear dimension of one crystal. This increase in length is for geometrically corresponding distances on all crystals. This increase is independent of the initial size of the initial crystals, provided that all the crystals are subject to the same environmental conditions. This law follows from Eq. (12.12-3), where the overall transfer coefficient is the same for each face of all crystals.

Mathematically, this can be written

$$\frac{\Delta L}{\Delta t} = G \qquad \textbf{(12.12-4)}$$

where Δt is time in h and growth rate G is a constant in mm/h. Hence, if D_1 is the linear dimension of a given crystal at time t_1 and D_2 at time t_2,

$$\Delta L = D_2 - D_1 = G(t_2 - t_1) \qquad \textbf{(12.12-5)}$$

The total growth $(D_2 - D_1)$ or ΔL is the same for all crystals.

The ΔL law fails in cases where the crystals are given any different treatment based on size. It has been found to hold for many materials, particularly when the crystals are under 50 mesh in size (0.3 mm). Even though this law is not applicable in all cases, it is reasonably accurate in many situations.

12.12C Particle-Size Distribution of Crystals

An important factor in the design of crystallization equipment is the expected particle-size distribution of the crystals obtained. Usually, the dried crystals are screened to determine the particle sizes. The percent retained on different-sized screens is recorded. The screens or sieves used are the Tyler standard screens, whose sieve or clear openings in mm are given in Appendix A.5.

The data are plotted as particle diameter (sieve opening in screen) in mm versus the cumulative percent retained at that size on arithmetic probability paper. Data for urea particles from a typical crystallizer (B5) are shown in Fig. 12.12-2. Many types of such data will show an approximate straight line for a large portion of the plot.

A common parameter used to characterize the size distribution is the coefficient of variation, CV, as a percent.

$$\mathrm{CV} = 100\,\frac{\mathrm{PD}_{16\%} - \mathrm{PD}_{84\%}}{2\mathrm{PD}_{50\%}} \qquad \textbf{(12.12-6)}$$

where $\mathrm{PD}_{16\%}$ is the particle diameter at 16 percent retained. By giving the coefficient of variation and mean particle diameter, a description of the particle-size distribution is obtained if the line is approximately straight between 90 and 10%. For a product removed from a mixed-suspension crystallizer, the CV value is about 50% (R1). In a

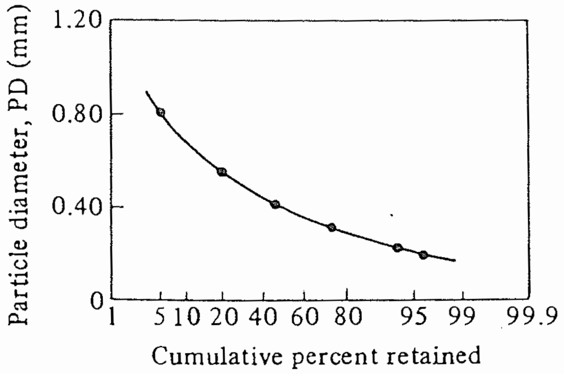


FIGURE 12.12-2. *Typical particle-size distribution from a crystallizer,* [*From R. C. Bennett and M. Van Buren, Chem. Eng. Progr. Symp., 65(95), 46 (1969).*]

mixed-suspension system, the crystallizer is at steady state and contains a well-mixed-suspension magma with no product classification and no solids entering with the feed.

12.12D Models for Crystallizers

In order to analyze data from a mixed-suspension crystallizer, an overall theory combining the effects of nucleation rate, growth rate, heat balance, and material balance is needed. Some progress has been made and an idealized model has been investigated by Randolph and Larson and their co-workers (R1, R2, R3, M2, S2, P1, P3, C2). Their equations are rather complicated but allow determination of some fundamental factors of growth rate and nucleation rate from experimental data.

A crystal product sample from the actual crystallizer is first obtained and a screen analysis run. The slurry density and retention time in the crystallizer are also needed. By converting the size analysis to a population density of crystals of various sizes and plotting the data, the nucleation rate and the growth rate in mm/h can be obtained for the actual conditions tested in the crystallizer. Then experiments can be conducted to determine the effects of operation effects on growth rate and nucleation rate. A sample calculation for this method is given elsewhere (P1). A contact nucleation model for the design of magma crystallizers has been developed (B6) based on single-particle-contact nucleation experiments (C4, M3). Larson (L2, P1) gives examples of design of crystallizing systems.

PROBLEMS

12.1-1. *Equilibrium Isotherm for Glucose Adsorption.* Equilibrium isotherm data for adsorption of glucose from an aqueous solution to activated alumina are as follows (H3):

c (g/cm^3)	0.0040	0.0087	0.019	0.027	0.094	0.195
q (g solute/g alumina)	0.026	0.053	0.075	0.082	0.123	0.129

Determine the isotherm that fits the data and give the constants of the equation using the given units.

Ans. Langmuir isotherm, $q = 0.145c/(0.0174 + c)$

12.2-1. *Batch Adsorption for Phenol Solution.* A wastewater solution having a volume of 2.5 m^3 contains 0.25 kg phenol/m^3 of solution. This solution is mixed thoroughly in a batch process with 3.0 kg of granular activated carbon until equilibrium is reached. Use the isotherm from Example 12.2-1 and calculate the final equilibrium values and the percent phenol extracted.

12.3-1. *Scale-Up of Laboratory Adsorption Column Data.* Using the break-point time and other results from Example 12.3-1, do as follows:

(a) The break-point time for a new column is to be 8.5 h. Calculate the new total length of the column required, column diameter, and the fraction of total capacity used up to the break point. The flow rate is to remain constant at 754 cm^3/s.

(b) Use the same conditions as part (a), but the flow rate is to be increased to 2000 cm^3/s.

Ans. (a) $H_T = 27.2$ cm, 0.849 fraction; (b) $D = 6.52$ cm

12.3-2. *Drying of Nitrogen and Scale-Up of Column.* Using molecular sieves, water vapor was removed from nitrogen gas in a packed bed (C3) at 28.3°C. The column height was 0.268 m, with the bulk density of the solid bed being equal to 712.8 kg/m^3. The initial water concentration in the solid was 0.01 kg water/kg solid and the mass velocity of the nitrogen gas was 4052 kg/m$^2\cdot$ h.

The initial water concentration in the gas was $c_o = 926 \times 10^{-6}$ kg water/kg nitrogen. The breakthrough data are as follows.

t (h)	0	9	9.2	9.6	10	10.4
c (kg H_2O/kg $N_2 \times 10^6$)	<0.6	0.6	2.6	21	91	235
t (h)	10.8	11.25	11.5	12.0	12.5	12.8
c (kg H_2O/kg $N_2 \times 10^6$)	418	630	717	855	906	926

A value of $c/c_o = 0.02$ is desired at the break point. Do as follows.

(a) Determine the break-point time, the fraction of total capacity used up to the break point, the length of the unused bed, and the saturation loading capacity of the solid.

(b) For a proposed column length $H_T = 0.40$ m, calculate the break-point time and fraction of total capacity used.

Ans. (a) $t_b = 9.58$ h, fraction used = 0.878

12.4-1. ***Scale-Up of Ion-Exchange Column.*** An ion-exchange process using a resin to remove copper ions from aqueous solution is conducted in a 1.0-in.-diameter column 1.2 ft high. The flow rate is 1.5 gph and the break point occurred at 7.0 min. Integrating the breakthrough curve gives a ratio of usable capacity to total capacity of 0.60. Design a new tower that will be 3.0 ft high and operating at 4.5 gph. Calculate the new tower size and break-point time.

Ans. $t_b = 24.5$ min, $D = 1.732$ in.

12.4-2. ***Height of Tower in Ion-Exchange.*** In a given run using a flow rate of 0.2 m^3/h in an ion-exchange tower with a column height of 0.40 m, the break point occurred at 8.0 min. The ratio of usable capacity to total equilibrium capacity is 0.65. What is the height of a similar column operating for 13.0 min to the break point at the same flow rate?

12.4-3. ***Ion Exchange of Copper in Column.*** An ion-exchange column containing 99.3 g of amberlite ion-exchange resin was used to remove Cu^{2+} from a solution where $c_o = 0.18$ M $CuSO_4$. The tower height = 30.5 cm and the diameter = 2.59 cm. The flow rate was 1.37 cm^3 solution/s to the tower. The breakthrough data are shown below.

t (s)	420	480	510	540	600	660
c (g mol Cu/L)	0	0.0033	0.0075	0.0157	0.0527	0.1063
t (s)	720	780	810	870	900	
c (g mol Cu/L)	0.1433	0.1634	0.1722	0.1763	0.180	

The concentration desired at the break point is $c/c_o = 0.010$. Determine the break-point time, fraction of total capacity used up to the break point, length of unused bed, and the saturation loading capacity of the solid.

12.5-1. ***Composition of Two Liquid Phases in Equilibrium.*** An original mixture weighing 200 kg and containing 50 kg of isopropyl ether, 20 kg of acetic acid, and 130 kg of water is equilibrated in a mixer–settler and the phases separated. Determine the amounts and compositions of the raffinate and extract layers. Use equilibrium data from Appendix A.3.

12.5-2. ***Single-Stage Extraction.*** A single-stage extraction is performed in which 400 kg of a solution containing 35 wt % acetic acid in water is contacted with 400 kg of pure isopropyl ether. Calculate the amounts and compositions of the extract and raffinate layers. Solve for the amounts both algebraically and by the lever-arm rule. What percent of the acetic acid is removed? Use equilibrium data from Appendix A.3.

Ans. $L_1 = 358$ kg, $x_{B1} = 0.715$, $x_{C1} = 0.03$, $V_1 = 442$ kg, $y_{A1} = 0.11$, $y_{C1} = 0.86$, 34.7% removed.

12.5-3. ***Single-Stage Extraction with Unknown Composition.*** A feed mixture weighing 200 kg of unknown composition containing water, acetic acid, and isopropyl ether is contacted in a single stage with 280 kg of a mixture containing 40 wt % acetic acid, 10 wt % water, and 50 wt % isopropyl ether. The resulting raffinate layer weighs 320 kg and contains 29.5 wt % acetic acid, 66.5 wt % water, and 4.0 wt % isopropyl ether. Determine the original composition of the feed mixture and the composition of the resulting extract layer. Use equilibrium data from Appendix A.3.

Ans. $x_{A0} = 0.030, x_{B0} = 0.955, y_{A1} = 0.15$

12.5-4. ***Extraction of Acetone in a Single Stage.*** A mixture weighing 1000 kg contains 23.5 wt % acetone and 76.5 wt % water and is to be extracted by 500 kg methyl isobutyl ketone in a single-stage extraction. Determine the amounts and compositions of the extract and raffinate phases. Use equilibrium data from Appendix A.3.

12.7-1. ***Multiple-Stage Extraction with Fresh Solvent in Each Stage.*** Pure water is to be used to extract acetic acid from 400 kg of a feed solution containing 25 wt % acetic acid in isopropyl ether. Use equilibrium data from Appendix A.3.

(a) If 400 kg of water is used, calculate the percent recovery in the water solution in a one-stage process.

(b) If a multiple four-stage system is used and 100 kg fresh water is used in each stage, calculate the overall percent recovery of the acid in the total outlet water. (*Hint*: First, calculate the outlet extract and raffinate streams for the first stage using 400 kg of feed solution and 100 kg of water. For the second stage, 100 kg of water contacts the outlet organic phase from the first stage. For the third stage, 100 kg of water contacts the outlet organic phase from the second stage, and so on.)

12.7-2. ***Overall Balance in Countercurrent Stage Extraction.*** An aqueous feed of 200 kg/h containing 25 wt % acetic acid is being extracted by pure isopropyl ether at the rate of 600 kg/h in a countercurrent multistage system. The exit acid concentration in the aqueous phase is to contain 3.0 wt % acetic acid. Calculate the compositions and amounts of the exit extract and raffinate streams. Use equilibrium data from Appendix A.3.

12.7-3. ***Minimum Solvent and Countercurrent Extraction of Acetone.*** An aqueous feed solution of 1000 kg/h containing 23.5 wt % acetone and 76.5 wt % water is being extracted in a countercurrent multistage extraction system using pure methyl isobutyl ketone solvent at 298–299 K. The outlet water raffinate will contain 2.5 wt % acetone. Use equilibrium data from Appendix A.3.

(a) Calculate the minimum solvent that can be used. [*Hint*: In this case the tie line through the feed L_0 represents the condition for minimum solvent flow rate. This gives $V_{1\,\text{min}}$. Then draw lines $L_N V_{1\,\text{min}}$ and $L_0 V_{N+1}$ to give the mixture point M_{min} and the coordinate $x_{AM\,\text{min}}$. Using Eq. (12.7-4), solve for $V_{N+1\,\text{min}}$, the minimum value of the solvent flow rate V_{N+1}.]

(b) Using a solvent flow rate of 1.5 times the minimum, calculate the number of theoretical stages.

12.7-4. ***Countercurrent Extraction of Acetic Acid and Minimum Solvent.*** An aqueous feed solution of 1000 kg/h of acetic acid–water solution contains 30.0 wt % acetic acid and is to be extracted in a countercurrent multistage process with pure isopropyl ether to reduce the acid concentration to 2.0 wt % acid in the final raffinate. Use equilibrium data in Appendix A.3.

(a) Calculate the minimum solvent flow rate that can be used. (*Hint*: See Problem 12.7-3 for the method to use.)

(b) If 2500 kg/h of ether solvent is used, determine the number of theoretical stages required. (*Note*: It may be necessary to replot on an expanded scale the concentrations at the dilute end.)

Ans. (a) Minimum solvent flow rate $V_{N+1} = 1630$ kg/h; (b) 7.5 stages

12.7-5. ***Number of Stages in Countercurrent Extraction.*** Repeat Example 12.7-2 but use an exit acid concentration in the aqueous phase of 4.0 wt %.

12.7-6. ***Extraction with Immiscible Solvents.*** A water solution of 1000 kg/h containing 1.5 wt % nicotine in water is stripped with a kerosene stream of 2000 kg/h containing 0.05 wt % nicotine in a countercurrent stage tower. The exit water is to contain only 10% of the original nicotine, i.e., 90% is removed. Use equilibrium data from Example 12.7-3. Calculate the number of theoretical stages needed.

Ans. 3.7 stages

12.7-7. ***Analytical Equation for Number of Stages.*** Example 12.7-3 gives data for extraction of nicotine from water by kerosene where the two solvents are immiscible. A total of 3.8 theoretical stages were needed. Use the analytical equations (10.3-21)–(10.3-26) to calculate the number of theoretical stages and compare with the value obtained graphically.

12.7-8. ***Minimum Solvent Rate with Immiscible Solvents.*** Determine the minimum solvent kerosene rate to perform the desired extraction in Example 12.7-3. Using 1.25 times this minimum rate, determine the number of theoretical stages needed graphically and also by using Eqs. (10.3-21)–(10.3-26).

12.7-9. ***Stripping Nicotine from Kerosene.*** A kerosene flow of 100 kg/h contains 1.4 wt % nicotine and is to be stripped with pure water in a countercurrent multistage tower. It is desired to remove 90% of the nicotine. Using a water rate of 1.50 times the minimum, determine the number of theoretical stages required. (Use the equilibrium data from Example 12.7-3.)

12.8-1. ***Effective Diffusivity in Leaching Particles.*** In Example 12.8-1 a time of leaching of the solid particle of 3.11 h is needed to remove 80% of the solute. Do the following calculations.

(a) Using the experimental data, calculate the effective diffusivity, $D_{A\,\text{eff}}$.

(b) Predict the time to leach 90% of the solute from the 2.0 mm particle.

Ans. (a) $D_{A\,\text{eff}} = 1.0 \times 10^{-5}$ mm^2/s; (b) $t = 5.00$ h

12.9-1. ***Leaching of Oil from Soybeans in a Single Stage.*** Repeat Example 12.9-1 for single-stage leaching of oil from soybeans. The 100 kg of soybeans contains 22 wt % oil and the solvent feed is 80 kg of solvent containing 3 wt % soybean oil.

Ans. $L_1 = 52.0$ kg, $y_{A1} = 0.239$, $V_1 = 50.0$ kg, $x_{A1} = 0.239$, $N_1 = 1.5$

12.9-2. ***Leaching a Soybean Slurry in a Single Stage.*** A slurry of flaked soybeans weighing a total of 100 kg contains 75 kg of inert solids and 25 kg of solution with 10 wt % oil and 90 wt % solvent hexane. This slurry is contacted with 100 kg of pure hexane in a single stage so that the value of N for the outlet underflow is 1.5 kg insoluble solid/kg solution retained. Calculate the amounts and compositions of the overflow V_1 and the underflow L_1 leaving the stage.

12.10-1. ***Constant Underflow in Leaching Oil from Meal.*** Use the same conditions as given in Example 12.10-1, but assume constant underflow of $N = 1.85$ kg solid/kg solution. Calculate the exit flows and compositions and the number of stages required. Compare with Example 12.10-1.

Ans. $y_{AN} = 0.111$, $x_{A1} = 0.623$, 4.3 stages

12.10-2. ***Effect of Less Solvent Flow in Leaching Oil from Meal.*** Use the same conditions as given in Example 12.10-1, but the inlet fresh solvent mixture flow rate per hour is decreased by 10%, to 1179 kg of benzene and 18 kg of oil. Calculate the number of stages needed.

12.10-3. ***Countercurrent Multistage Washing of Ore.*** A treated ore containing inert solid gangue and copper sulfate is to be leached in a countercurrent multistage extractor using pure water to leach the $CuSO_4$. The solid charge rate per hour consists of 10 000 kg of inert gangue (B), 1200 kg of $CuSO_4$ (solute A), and 400 kg of water (C). The exit wash solution is to contain 92 wt % water and 8 wt % $CuSO_4$. A total of 95% of the $CuSO_4$ in the inlet ore is to be recovered. The underflow is constant at $N = 0.5$ kg inert gangue solid/kg aqueous solution. Calculate the number of stages required.

12.10-4. ***Countercurrent Multistage Leaching of Halibut Livers.*** Fresh halibut livers containing 25.7 wt % oil are to be extracted with pure ethyl ether to remove 95% of the oil in a countercurrent multistage leaching process. The feed rate is 1000 kg of fresh livers per hour. The final exit overflow solution is to contain 70 wt % oil. The retention of solution by the inert solids (oil-free liver) of the liver varies as follows (C1), where N is kg inert solid/kg solution retained and y_A is kg oil/kg solution.

N	y_A	N	y_A
4.88	0	1.67	0.6
3.50	0.2	1.39	0.81
2.47	0.4		

Calculate the amounts and compositions of the exit streams and the total number of theoretical stages.

12.10-5. ***Countercurrent Leaching of Flaked Soybeans.*** Soybean flakes containing 22 wt % oil are to be leached in a countercurrent multistage process to contain 0.8 kg oil/100 kg inert solid using fresh and pure hexane solvent. For every 1000 kg soybeans, 1000 kg hexane is used. Experiments (S1) give the following retention of solution with the solids in the underflow, where N is kg inert solid/kg solution retained and y_A is wt fraction of oil in solution.

N	y_A
1.73	0
1.52	0.20
1.43	0.30

Calculate the exit flows and compositions and the number of theoretical stages needed.

12.11-1. ***Crystallization of $Ba(NO_3)_2$.*** A hot solution of $Ba(NO_3)_2$ from an evaporator contains 30.6 kg $Ba(NO_3)_2$/100 kg H_2O and goes to a crystallizer where the solution is cooled and $Ba(NO_3)_2$ crystallizes. On cooling, 10% of the original water present evaporates. For a feed solution of 100 kg total, calculate the following.

(a) The yield of crystals if the solution is cooled to 290 K (17°C), where the solubility is 8.6 kg $Ba(NO_3)_2$/100 kg total water.

(b) The yield if cooled instead to 283 K, where the solubility is 7.0 kg $Ba(NO_3)_2$/100 kg total water.

Ans. (a) 17.47 kg $Ba(NO_3)_2$ crystals

12.11-2. ***Dissolving and Subsequent Crystallization.*** A batch of 1000 kg of KCl is dissolved in sufficient water to make a saturated solution at 363 K, where the solubility is 35 wt % KCl in water. The solution is cooled to 293 K, at which temperature its solubility is 25.4 wt %.

(a) What is the weight of water required for solution and the weight of crystals of KCl obtained?

(b) What is the weight of crystals obtained if 5% of the original water evaporates on cooling?

Ans. (a) 1857 kg water, 368 kg crystals; (b) 399 kg crystals

12.11-3. ***Crystallization of $MgSO_4 \cdot 7H_2O$.*** A hot solution containing 1000 kg of $MgSO_4$ and water having a concentration of 30 wt % $MgSO_4$ is cooled to 288.8 K, where crystals of $MgSO_4 \cdot 7H_2O$ are precipated. The solubility at 288.8 K is 24.5 wt % anhydrous $MgSO_4$ in the solution. Calculate the yield of crystals obtained if 5% of the original water in the system evaporates on cooling.

12.11-4. ***Heat Balance in Crystallization.*** A feed solution of 10 000 lb_m at 130°F containing 47.0 lb $FeSO_4$/100 lb total water is cooled to 80°F, where $FeSO_4 \cdot 7H_2O$ crystals are removed. The solubility of the salt is 30.5 lb $FeSO_4$/100 lb total water (P1). The average heat capacity of the feed solution is 0.70 btu/$lb_m \cdot$ °F. The heat of solution at 18°C is -4.4 kcal/g mol (-18.4 kJ/g mol) $FeSO_4 \cdot 7H_2O$ (P1). Calculate the yield of crystals and make a heat balance. Assume that no water is vaporized.

Ans. 2750 lb_m $FeSO_4 \cdot 7H_2O$ crystals, $q = -428\,300$ btu ($-451\,900$ kJ)

12.11-5. ***Effect of Temperature on Yield and Heat Balance in Crystallization.*** Use the conditions of Example 12.11-2, but the solution is cooled instead to 283.2 K, where the solubility is 30.9 kg $MgSO_4$/100 kg total water (P1). Calculate the effect on yield and the heat absorbed by using 283.2 K instead of 293.2 K for the crystallization.

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