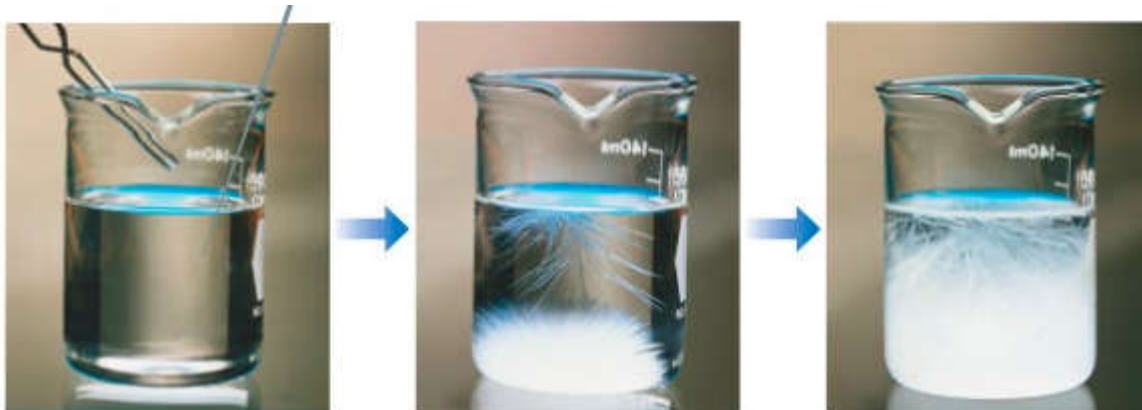


## Crystallization and Types of Crystals

*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.



### 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  $\text{KNO}_3$ , where the solubility increases markedly with temperature and there are no hydrates. Over the whole range of temperatures, the solid phase is  $\text{KNO}_3$ . The solubility of  $\text{NaCl}$  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,  $\text{Na}_2\text{S}_2\text{O}_3$ . The solubility increases rapidly with temperature, but there are definite breaks in the curve which indicate different hydrates. The stable phase up to  $48.2^\circ\text{C}$  is the pentahydrate  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . This means that at concentrations above the solubility line (up to  $48.2^\circ\text{C}$ ), the solid crystals formed are  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . At concentrations below the solubility line, only a solution exists. From  $48.2$  to about  $65^\circ\text{C}$ ; the stable phase is  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . A half-hydrate is present between  $65$  to  $70^\circ\text{C}$ , and the anhydrous salt is the stable phase above  $70^\circ\text{C}$ .

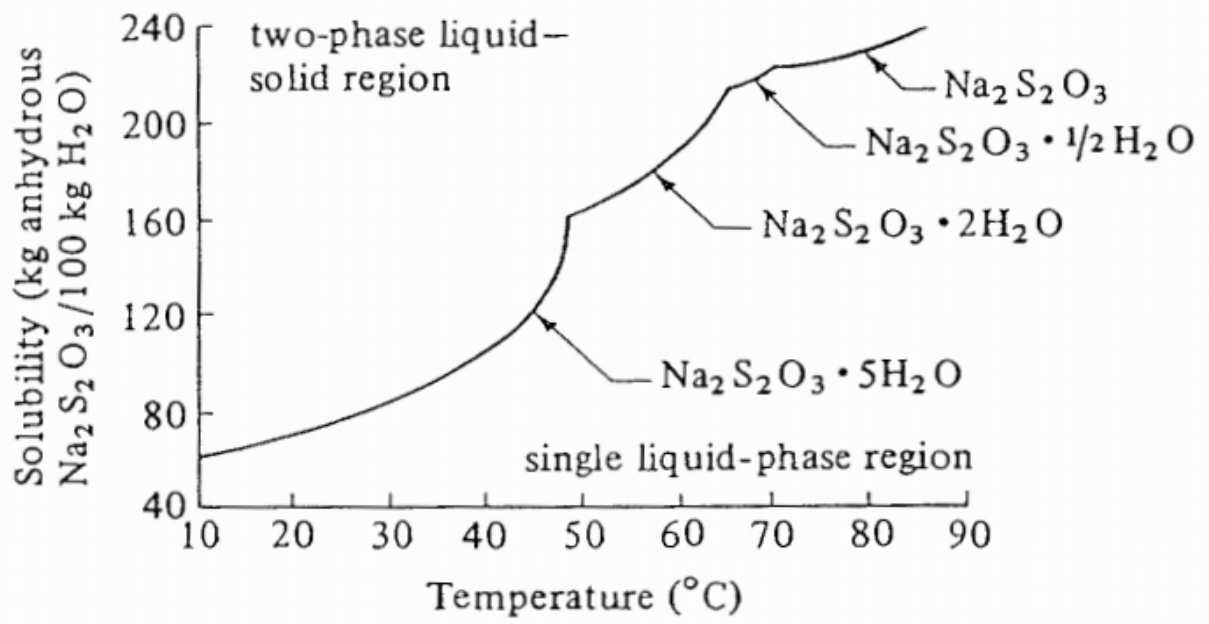


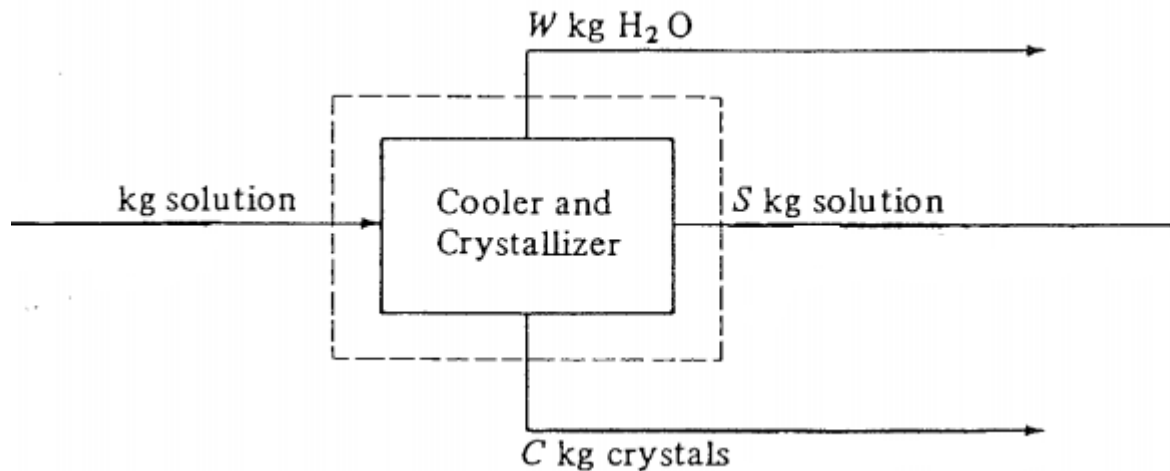
FIGURE 12.11-1. Solubility of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , in water.

### 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.

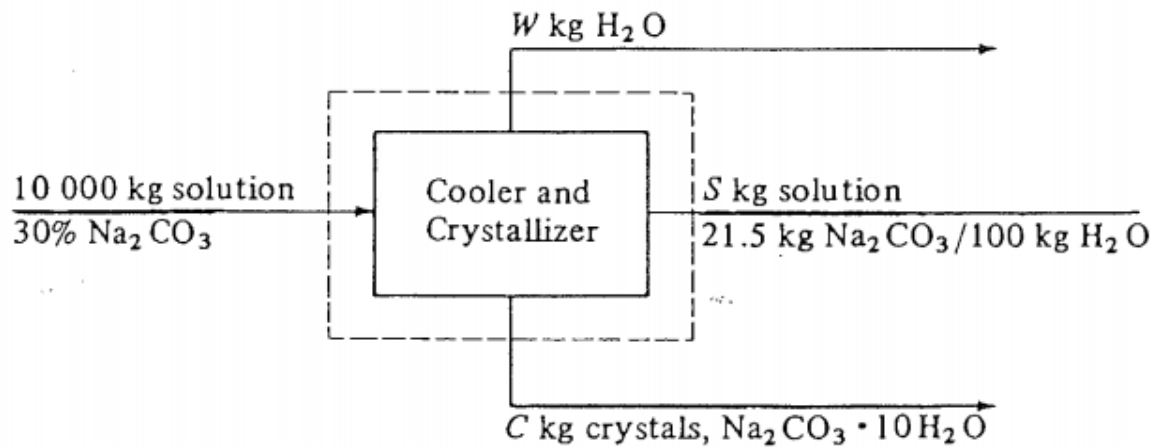
In making the material balances, the calculations are straightforward when the solute crystals are anhydrous. Simple water and solute material balances are made. When the crystals are hydrated, some of the water in the solution is removed with the crystals as a hydrate.



**EXAMPLE 12.11-1. Yield of a Crystallization Process**

A salt solution weighing 10 000 kg with 30 wt %  $\text{Na}_2\text{CO}_3$  is cooled to 293 K (20°C). The salt crystallizes as the decahydrate. What will be the yield of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  crystals if the solubility is 21.5 kg anhydrous  $\text{Na}_2\text{CO}_3/100$  kg of total water? Do this for the following cases.

- Assume that no water is evaporated.
- Assume that 3% of the total weight of the solution is lost by evaporation of water in cooling.



**Solution:** The molecular weights are 106.0 for  $\text{Na}_2\text{CO}_3$ , 180.2 for  $10\text{H}_2\text{O}$ , and 286.2 for  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . The process flow diagram is shown in Fig. 12.11-2, with  $W$  being kg  $\text{H}_2\text{O}$  evaporated,  $S$  kg solution (mother liquor), and  $C$  kg crystals of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . Making a material balance around the dashed-line box for water for part (a), where  $W = 0$ ,

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

where  $(180.2)/(286.2)$  is wt fraction of water in the crystals. Making a balance for  $\text{Na}_2\text{CO}_3$ ,

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

Solving the two equations simultaneously,  $C = 6370$  kg of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  crystals and  $S = 3630$  kg solution.

For part (b),  $W = 0.03(10\,000) = 300$  kg  $\text{H}_2\text{O}$ . Equation (12.11-1) becomes

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

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  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  crystals and  $S = 3070$  kg solution.