Lecture 14

Crystallization, Desublimation, and Evaporation

Crystallization is a solid-fluid separation operation in which crystalline particles are formed from a homogeneous fluid phase. Ideally, the crystals are a pure chemical, obtained in a high yield with a desirable shape and a reasonably uniform and desirable size. Crystallization is one of the oldest known separation operations, with the recovery of sodium chloride as salt crystals from water by evaporation dating back to antiquity. Even today, the most common applications are the crystallization from aqueous solution of various inorganic salts, a short list of which is given in Table 1. All these cases are referred to as solution crystallization because the inorganic salt is clearly the solute, which is crystallized, and water is the solvent, which remains in the liquid phase. The phase diagram for systems suitable for solution crystallization is a solubility curve, such as shown in Figure la.

For the formation of organic crystals, organic solvents such as acetic acid, ethyl acetate, methanol, ethanol, acetone, ethyl ether, chlorinated hydrocarbons, benzene, and petroleum fractions may be preferred choices, but they must be used with great care when they are toxic or flammable with a low flash point and a wide range of explosive limits.

For either aqueous or organic solutions, crystallization is effected by cooling the solution, evaporating the solvent, or a combination of the two. In some cases, a mixture of two or more solvents may be best, examples of which include water with the lower alcohols, and normal paraffins with chlorinated solvents. Also, the addition of a second solvent is sometimes used to reduce the solubility of the solute. When water is the additional solvent, the process is called watering-out; when an organic solvent is added to an aqueous salt solution, the process is called salting-out. For both of these cases of solvent addition, fast crystallization called precipitation can occur, resulting in large numbers of very small crystals. Precipitation also occurs when one product of two reacting solutions is a solid with low solubility. For example, when aqueous solutions of silver nitrate and sodium chloride are mixed together, insoluble silver chloride is precipitated leaving an aqueous solution of mainly soluble sodium nitrate.

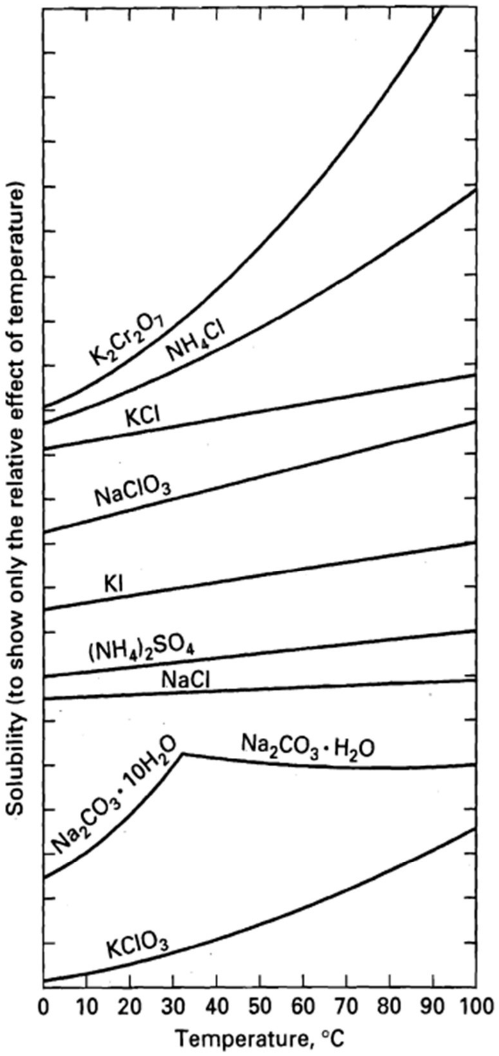
When both components of a homogeneous, binary solution have melting (freezing) points not far removed from each other, the solution is referred to as a melt. If, as in Figure lb, the phase diagram for the melt exhibits a eutectic point, it is possible to obtain, in one step called melt crystallization, pure crystals of one component or the other, depending on whether the composition of the melt is to the left or right of the eutectic composition. If, however, solid solutions form, as shown in Figure lc, a process of repeated melting and freezing steps, called fractional melt crystallization, is required to obtain nearly pure crystalline products. A higher degree of purity can be achieved by a technique called zone melting or rejining. Examples of binary organic systems that form eutectics include metaxylene-paraxylene and benzene-naphthalene. Binary systems of naphthalene-beta naphthol and naphthalene-P naphthylamine, which form solid solutions, are not as common.

Crystallization can also occur from a vapor mixture by a process more properly called desublimation. A number of pure compounds, including phthalic anhydride and benzoic acid, are produced in this manner. When two or more compounds tend to desublime, a fractional desublimation process can be employed to obtain near-pure products.

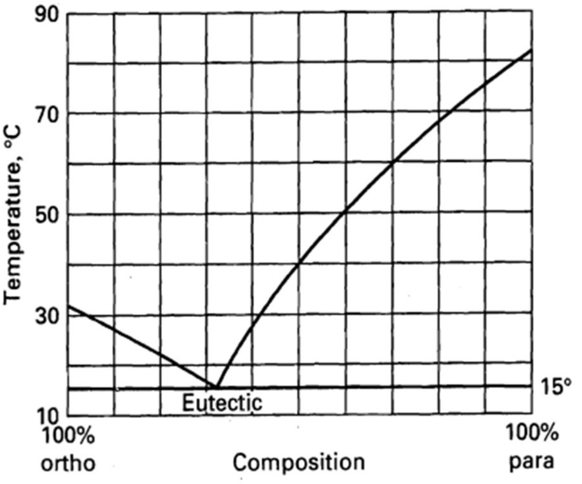
Crystallization of a compound from a dilute solution is often preceded by evaporation in one or more vessels, called effects, to concentrate the solution, and followed by partial separation and washing of the crystals from the resulting slurry, called the magma, by centrifugation or filtration. The process is completed by drying the crystals to specified moisture content.

Table 1 - Some inorganic salts recovered from aqueous solutions

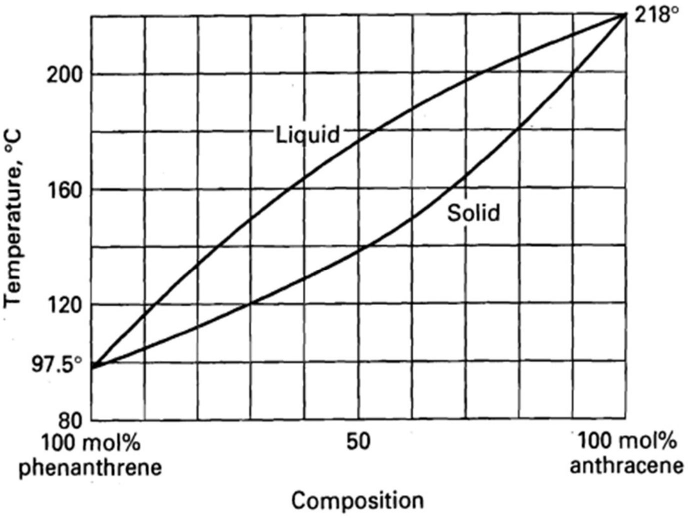
Chemical Name	Formula	Common Name	Crystal System
Ammonium chloride	NH_4Cl	sal-ammoniac	cubic
Ammonium sulfate	$(NH_4)_2SO_4$	mascagnite	orthorhombic
Barium chloride	$BaCl_2 \cdot 2H_2O$		monoclinic
Calcium carbonate	$CaCO_3$	calcite	rhombohedral
Copper sulfate	$CuSO_4 \cdot 5H_2O$	blue vitriol	triclinic
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	Epsom salt	orthorhombic
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	bischofite	monoclinic
Nickel sulfate	$NiSO_4 \cdot 6H_2O$	single nickel salt	tetragonal
Potassium chloride	KCl	muriate of potash	cubic
Potassium nitrate	KNO_3	nitre	hexagonal
Potassium sulfate	K_2SO_4	arcanite	orthorhombic
Silver nitrate	$AgNO_3$	lunar caustic	orthorhombic
Sodium chlorate	$NaClO_3$		cubic
Sodium chloride	$NaCl$	salt, halite	cubic
Sodium nitrate	$NaNO_3$	chile salt petre	rhombohedral
Sodium sulfate	$Na_2SO_4 \cdot 10H_2O$	glauber's salt	monoclinic
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	hypo	monoclinic
Zinc sulfate	$ZnSO_4 \cdot 7H_2O$	white vitriol	orthorhombic



(a) Aqueous systems suitable for solution crystallization



(b) Eutectic-forming system of ortho- and parachloronitrobenzene system suitable for melt crystallization



(c) Solid-solution system suitable for fractional melt crystallization

Figure 1 - Different types of solubility curves