CRYSTALLIZATION

• important industrially because:

  i) a crystal formed from an impure solution and itself pure

  ii) Practical method of obtaining pure chemical substances in a satisfactory condition for packaging and storing

• solid-liquid separation process

• yield, purity, sizes & shapes of crystals important

• crystals - uniform in size

• formation of 1,4-naphthoquinone crystals from a liquid solution
SOLUBILITY CURVE

- equilibrium is attained when the solution or mother liquor is saturated (represented by solubility curve)
- solubility dependent mainly on temperature
- solubilities of most salts increase slightly or markedly with temperature

**Solubility curve for some typical salts in water**

**Solubility curve for sodium thiosulfate**
Figure 27.3-Solubility curve for the MgSO₄-nH₂O system at 1 atm
YIELD & MATERIAL & HEAT BALANCES

- **yield** of crystals can be calculated by knowing:
  - initial concentration of solute
  - final temperature
  - solubility at this temperature

- **material balances**

  Mass balance:
  - Water balance: Input = Output
  - Solute balance: Input = Output

  \[ \text{F kg Hot solution} \]
  \[ \text{X}_1 \text{ kg solute/100 kg H}_2\text{O} \]
  \[ \text{C kg Crystal} \]
  \[ \text{S kg solution} \]
  \[ \text{X}_2 \text{ kg solute/100 kg H}_2\text{O} \]

Solute crystals are anhydrous - simple water & solute material balances

Crystals are hydrated - some water in the solution is removed with crystals
EXAMPLE 2

A salt solution weighing 10000 kg with 30 wt. % Na₂CO₃ is cooled from 333K to 293K. The salt crystallizes as the decahydrate. What will be the yield of Na₂CO₃·10H₂O crystals if the solubility is 21.5 kg anhydrous Na₂CO₃/100kg water?

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.
EXAMPLE 3

A solution consisting of 30 wt% MgSO$_4$ and 70% water is cooled to 60°F. During cooling 5% of the total water in the system evaporates. How many kilograms of crystals are obtained per 1000 kg of the original mixture?
SOLID-LIQUID PHASE DIAGRAM

Solubility curve for the MgSO₄-nH₂O system at 1 atm
EXAMPLE 4

A feed of 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$_4$.7H$_2$O crystals are removed. The solubility of the salt is 35.5 kg MgSO$_4$/100 kg total water. The average heat capacity of the feed solution can be assumed as 2.93 kJ/kg.K. The heat of solution at 291.2 K (18°C) is $13.31 \times 10^3$ kJ/kg mol MgSO$_4$.7H$_2$O.

Calculate the yield of crystals.
HEAT BALANCES IN CRYSTALLIZATION

normally, crystallization is exothermic

\[ F \cdot h_F + q = (S + C) \cdot h_M + W \cdot h_{V} \]

Total heat absorbed, \( q \) (kJ):

When \( T_{\text{datum}} = 32^\circ F = 0^\circ C \),

\[ F \cdot h_F + q = (S + C) \cdot h_M + W \cdot h_{V} \]

or

\[ F \cdot h_F + q = S \cdot h_S + C \cdot h_C + W \cdot h_{V} \]
HEAT BALANCES IN CRYSTALLIZATION

normally, crystallization is exothermic

\[ \Delta H_{\text{crys}} = - \Delta H_{\text{soln}} \]  

When \( T_{\text{datum}} = T_{\text{equil./sat.}} \),  
\[
F h_F + q = W \lambda + C h_C = W \lambda + C \Delta H_{\text{crys}}^\infty
\]

heat of crystallization, \( \Delta H_{\text{crys}} = - \) heat of solution at infinite dilution, \( \Delta H_{\text{soln}}^\infty \)

Heat absorbed, \( q = +'ve \), Heat given off, \( q = -'ve \)
EXAMPLE 4

A feed of solution of 2268 kg at 327.6 K (54.4°C) containing 48.2 kg MgSO₄/100 kg total water is cooled to 293.2 K (20°C), where MgSO₄·7H₂O crystals are removed. The solubility of the salt is 35.5 kg MgSO₄/100 kg total water. The average heat capacity of the feed solution can be assumed as 2.93 kJ/kg.K. The heat of solution at 291.2 K (18°C) is 13.31 x 10³ kJ/kg mol MgSO₄·7H₂O.

Calculate the yield of crystals and make a heat balance to determine the total heat absorbed/released, q, assuming that no water is vaporized.
a, b, c, d – saturation line, use to find enthalpy of solution

i, h – complete crystallization, use to find enthalpy of crystallization

Fig 27.4-Enthalpy-concentration diagram for the MgSO₄-nH₂O system at 1 atm
EXAMPLE 5

A 32.5% solution of MgSO$_4$ at 120°F (48.9°C) is cooled, without appreciable evaporation to 70°F (21.1°C) in a batch-cooled crystallizer. How much heat must be removed from the solution per 100 Ib of the feed solution?

The average heat capacity of the feed solution is 0.72 Btu/Ib °F and the heat of solution at 18°C is 23.2 Btu/Ib of MgSO$_4$.7H$_2$O.