Chapter 4

Crystallization
<table>
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<tr>
<th>Topic</th>
<th>Learning Outcome</th>
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<tr>
<td>Crystallization</td>
<td><em>It is expected that students will be able to:</em></td>
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<tr>
<td>☐ Principle of Crystallization</td>
<td>☐ Explain the principle of crystallization in chemical engineering</td>
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<td>☐ Purity and Yields</td>
<td>☐ Explain the importance and effect of solubility in crystallization</td>
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<td>☐ Solubility and Solubility Curves</td>
<td>☐ Apply mass and energy balances to determine the yield in crystallization</td>
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<td>☐ Mass and Energy Balances in Crystallization</td>
<td>☐ Identify types of crystallization equipments and know their basic operations</td>
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Crystallization

- A solid – liquid separation
- Mass transfer occurs of a solute from the liquid solution to a pure solid crystalline phase.
- Solid particles formed from a homogeneous phase eg:
  - Water to form ice
  - Formation of snow particles from a vapor
  - Formation of solid particles from a liquid melt
  - Formation of solid crystals from a liquid solution
Crystallizer
Crystallization Process

H$_2$O, $T_c$

Hot Solution, $T_f$

Solute/solvent

Cooling $T_c$

Solution, $T_c$

Solute/solvent

Crystal, $T_c$
Mass Balances in Crystallization

The solution (mother liquor) and 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.

The yield can be calculated using the initial concentration of solute, the final temperature and the solubility at this temperature.

The crystals can be anhydrous or hydrate.

Mass balance:

Water balance: Input = Output
Solute balance: Input = Output
Heat Balance in Crystallization

- Heat of Solution – absorption heat; when a compound whose solubility increases as temperature increases dissolves.

- 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.

- The most satisfactory method of calculating heat effects during a crystallization process is to use the enthalpy-concentration chat. However only a few charts are available.

\[
Q = (H_2 + H_3 + H_v) - H_1
\]
**Terminology**

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**Clue:**
- The two phase mixture of mother-liquor and solid crystals is known as M _ G __
- Two of crystal shapes. C _ _ _ C and H _ _ _ _ O _ _ _ L
- One example of crystallization process. Water F _ _ _ _ I _ G
- The solution of dissolved solid must be super-S _ U _ _ _ _ D in order for crystallization to initiate.
- The first step of crystallization growth is known as N _ _ _ _ AT _ _
- _Y _ _ _ _ T _ is a term to show that a compound has one or more water molecules attached to it, whereas A _ H _ _ _ _ U _ is another term for a compound without water molecules.
- The solute-solvent mixture (dissolved solid solution) is usually referred as mother- _ _ Q _ _ R.
A saturated solution containing 400 kg of KCl at 360 K is cooled to 290 K in an open tank. The solubility of KCl at 360 K and 290 K are 43.55 kg KCl/100 kg H₂O and 34.5 kg KCl/100 kg H₂O, respectively. The specific gravity of the solution is 1.17. Calculate

- Volume of the tank (in m³).
- Amount of crystals formed if 22% of the total water is vaporized.
A saturated solution containing 1500 kg of MgSO₄ at 550 K is cooled to 293 K in an open tank. The cooling process will crystallize the salt as decahydrate, (MgSO₄·10H₂O) and then be separated from the tank. If the solubility at 550 K is 35.5 kg MgSO₄/100 kg H₂O and at 293 K is 21.5 kg MgSO₄/100 kg H₂O, calculate the weight of crystals formed if only 5% of the total water is lost by evaporation during cooling process.

If the crystallization process was conducted in a closed tank but not insulated, calculate the heat lost to the surrounding if:

- Average heat capacity of feed = 2.85 kJ/kg.K
- Heat of solution = – 13.3 x 10³ kJ/kgmol
- MgSO₄·10H₂O
- Latent heat of vaporization (H₂O, 293K) = 2453 kJ/kg
- Molecular weight: Mg 24; S 32; O 16; H 1.
Tutorial

1. A hot solution of \( \text{Ba(NO}_3\text{)}_2 \) from an evaporator contains 30.6 kg \( \text{Ba(NO}_3\text{)}_2/100 \text{ kg H}_2\text{O} \) and goes to a crystallizer where the solution is cooled and \( \text{Ba(NO}_3\text{)}_2 \) crystallizes. On cooling, 10 % of the original water present evaporates. For a feed solution of 100 kg total, calculate:

   a) The yield of crystals if the solution is cooled to 290 K, where the solubility is 8.6 kg \( \text{Ba(NO}_3\text{)}_2/100 \text{ kg total water} \).

   b) The yield if cooled instead to 283 K, where the solubility is 7.0 kg \( \text{Ba(NO}_3\text{)}_2/100 \text{ kg total water} \).

2. A batch of 100 KCl is dissolved in sufficient water to make a saturated 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 wt. % of the original water evaporates on cooling?

3. A hot solution containing 100 kg of MgSO\(_4\) and water having a concentration of 30 wt% MgSO\(_4\) is cooled to 288.8 K, where crystals of MgSO\(_4\).7H\(_2\)O are precipitated. 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.
4. 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$_4$.7H$_2$O crystals are formed. 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 $-13.3 \times 10^3$ kJ/kg mol MgSO$_4$.7H$_2$O.

Calculate the yield of crystals and make a heat balance to determine the total heat absorbed, q, assuming that no water is vaporized.

5. 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$_4$.7H$_2$O crystals are removed. The solubility of the feed solution is 0.70 btu/lbm.°F. The heat of solution at 18 °C is $-4.4$ kcal/gmol (-18.4 kJ/gmol) FeSO$_4$.7H$_2$O.

Calculate the yield of crystals and make a heat balance. Assume that no water is vaporized.