Topic 6. Crystallization

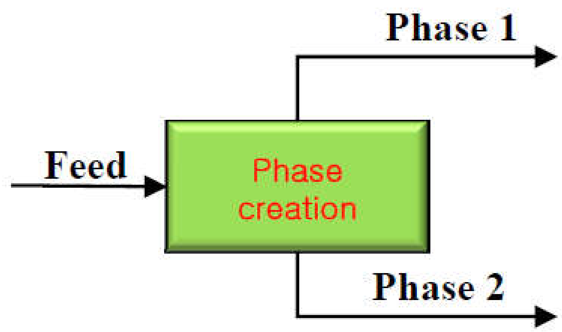
This lecture

- ✓ Describe the crystallization process
- ✓ Industrial examples of crystallization processes
- ✓

This lecture was obtained from notes of professor Zayed Hamamreh, ChE-University of Jordan

Definitions

Crystallization is a process where solid particles are formed from a homogeneous phase

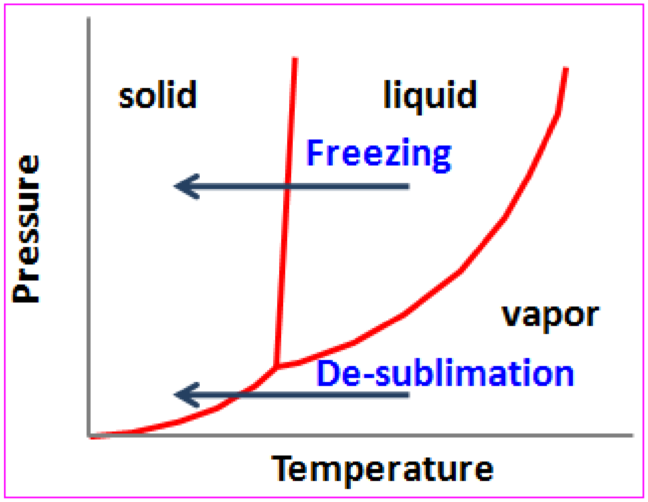


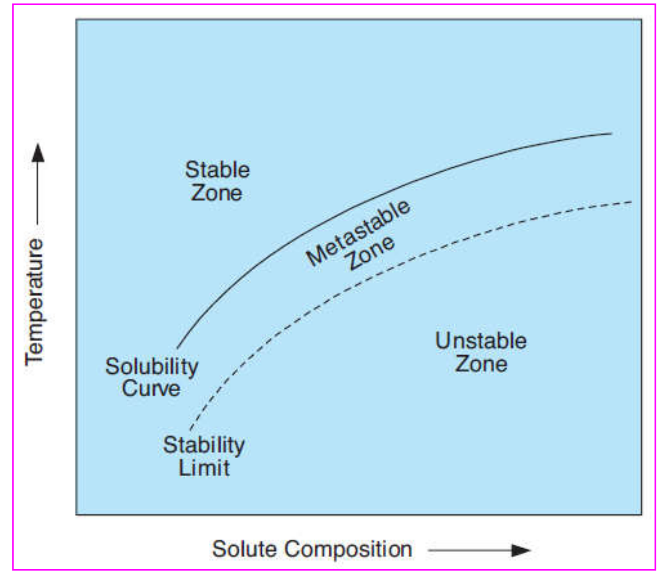
General principle of crystallization:

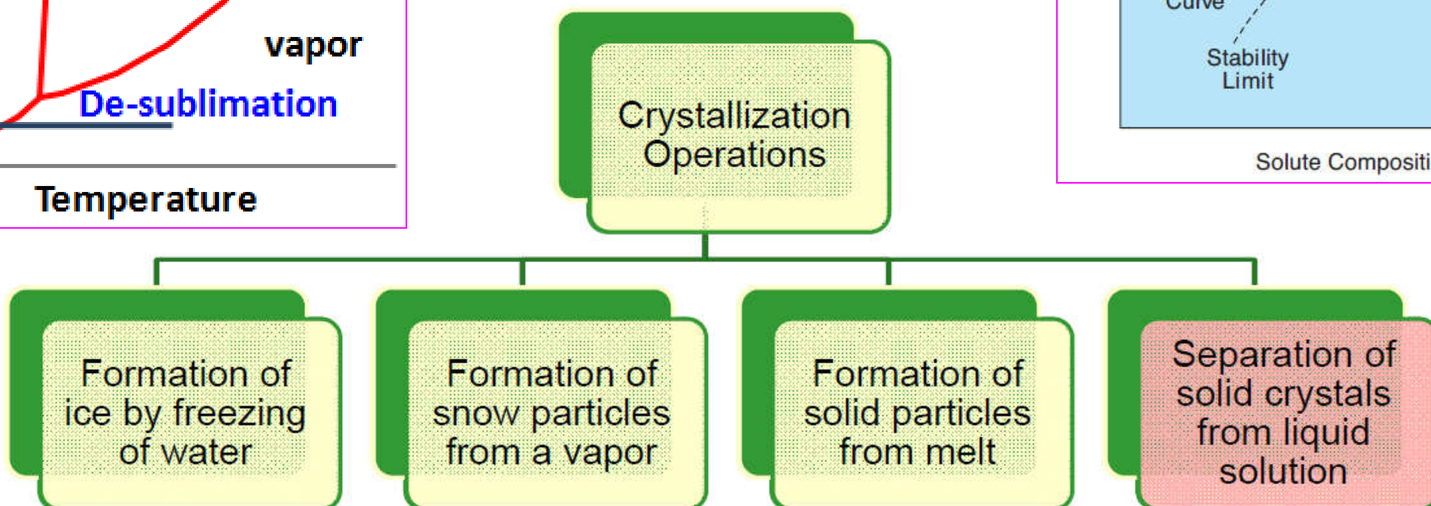
Solution is concentrated and usually cooled until the solute concentration becomes greater than its solubility at that temperature.

Then, the solute comes out of the solution, forming crystals of approximately pure solute.

Common crystallization operations







Commercially, the most important one and will be discussed in this topic

Crystallization Steps: Nucleation and Crystal Growth

i. Nucleation

- The birth of a new crystals, which is called nucleation, refers to the beginning of the phase separation process.
- Molecules gather together in clusters in a defined manner.
- Clusters need to be stable under current experimental conditions to reach the "critical cluster size" or they will re-dissolve.

➢ The process of nucleation is the sum of contributions by

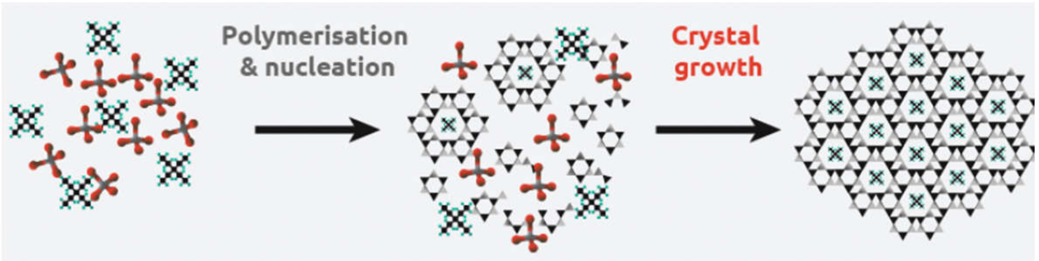
- ✓ Primary nucleation: occurs in the absence of crystals.
- ✓ Secondary nucleation: is attributed to the influence of existing crystals.

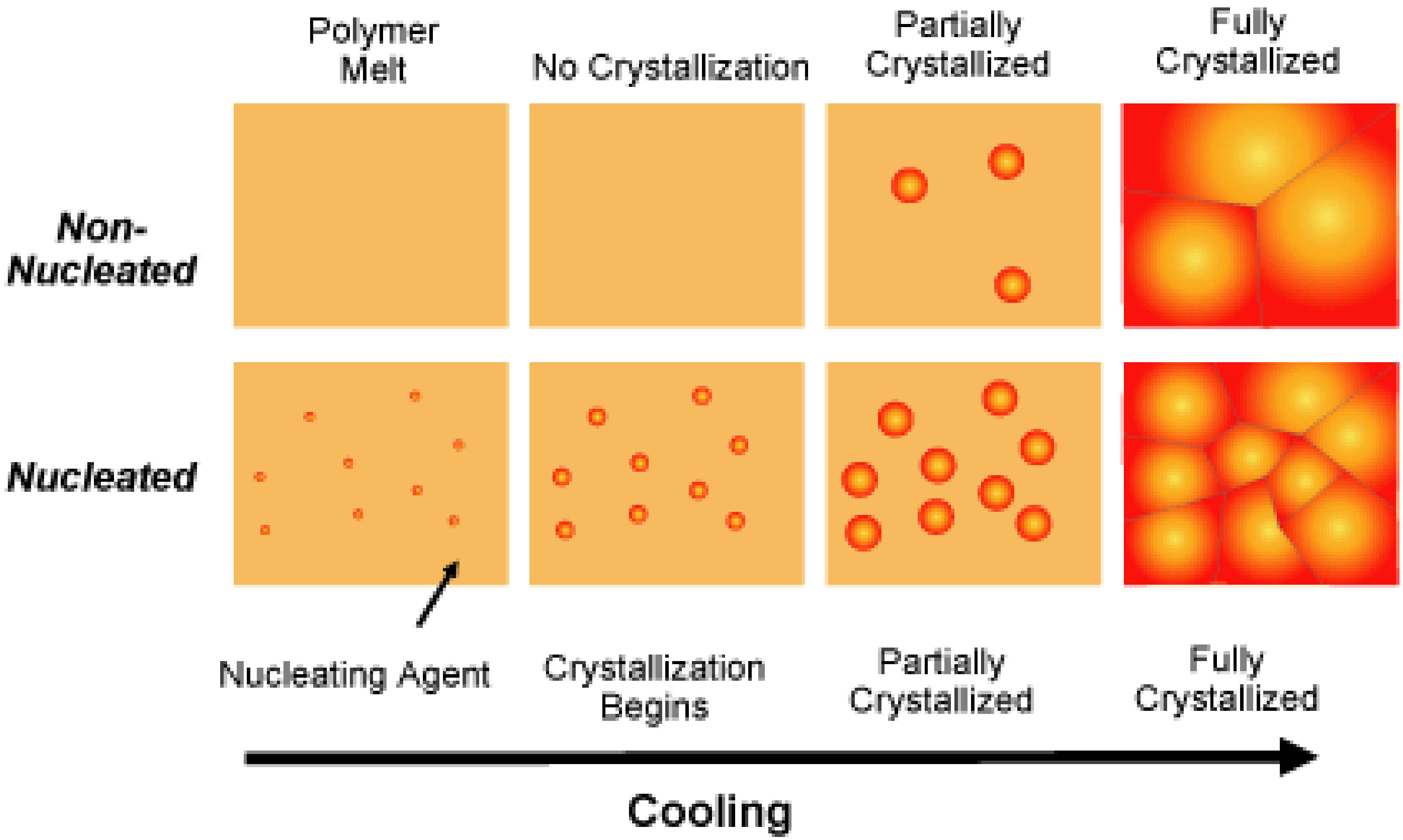
ii. Crystal Growth:

- Nuclei that have successfully achieved the "critical cluster size" begin to increase in size.
- Crystal growth is a dynamic process, with atoms precipitating from solution and becoming re-dissolved: Super-saturation and super-cooling are two of the most common driving forces behind crystal formation.

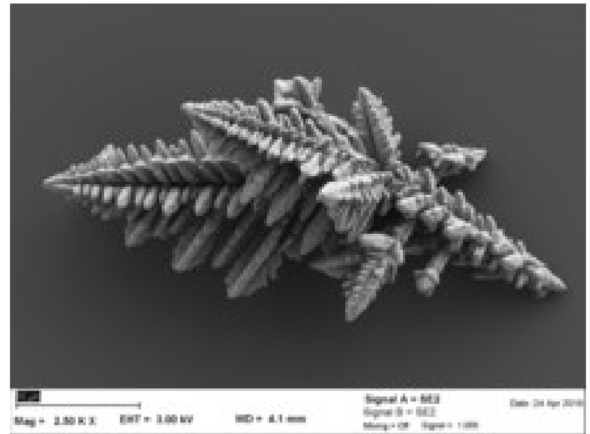
➢ The growth process in supersaturated solution includes two steps:

- Diffusion of solute from bulk solution to crystal surface and
- Surface integration (or reaction) of solute on the crystal surface.




Polymer Melt
No Crystallization
Partially Crystallized
Fully Crystallized
Non-Nucleated
Nucleated
Nucleating Agent
Crystallization Begins
Partially Crystallized
Fully Crystallized
Cooling

- **In summary, three aspects to the growth of a crystal are**
  - Nucleation: formation of a stable nucleus
  - Diffusion of material to the nucleus
  - Growth of the crystal by adding atoms
- The slowest of these three aspects generally controls the shape and size



Skeletal (Hollow) crystal

Dendrite crystal (branched)

well formed crystals

Types of crystal geometry

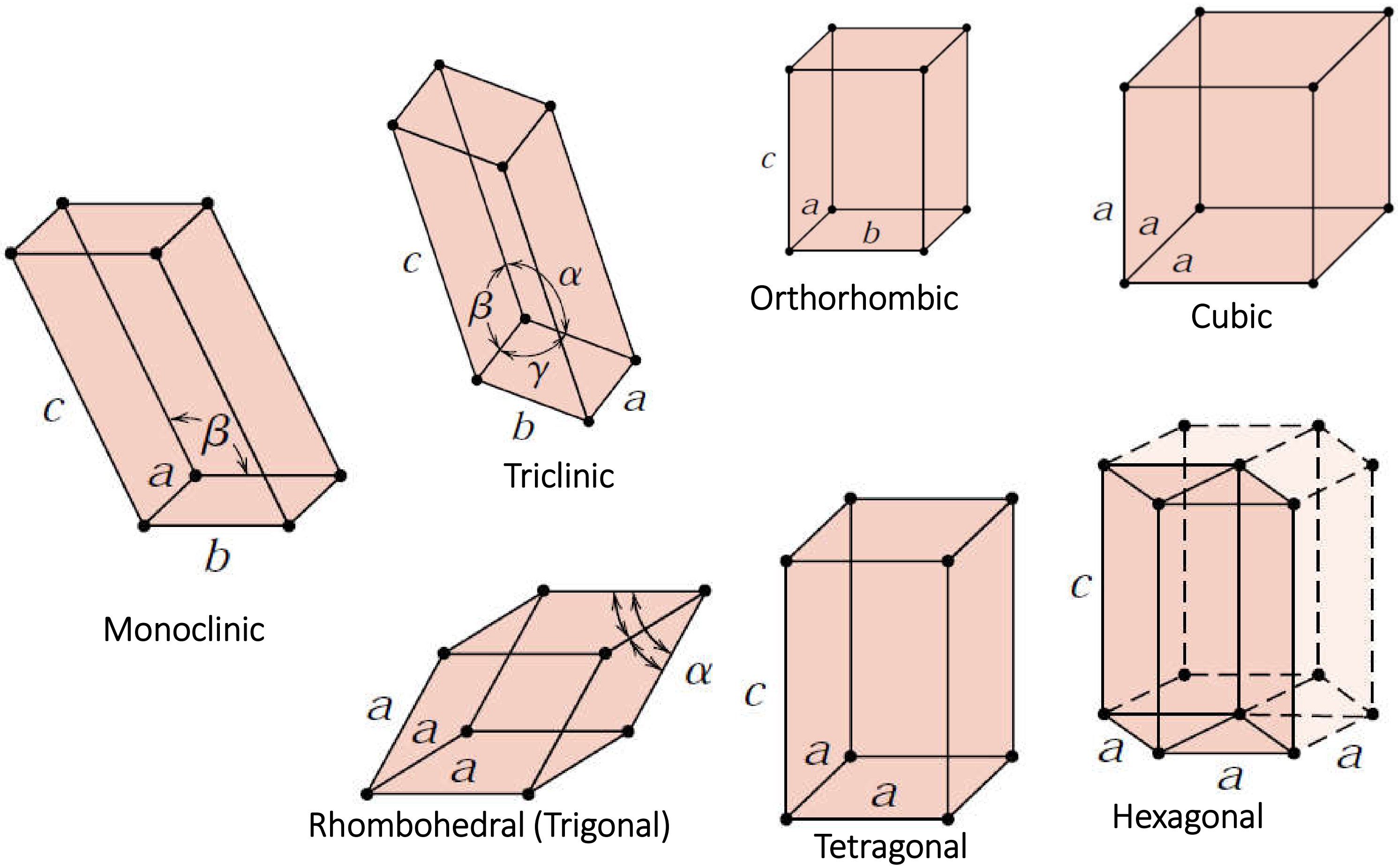
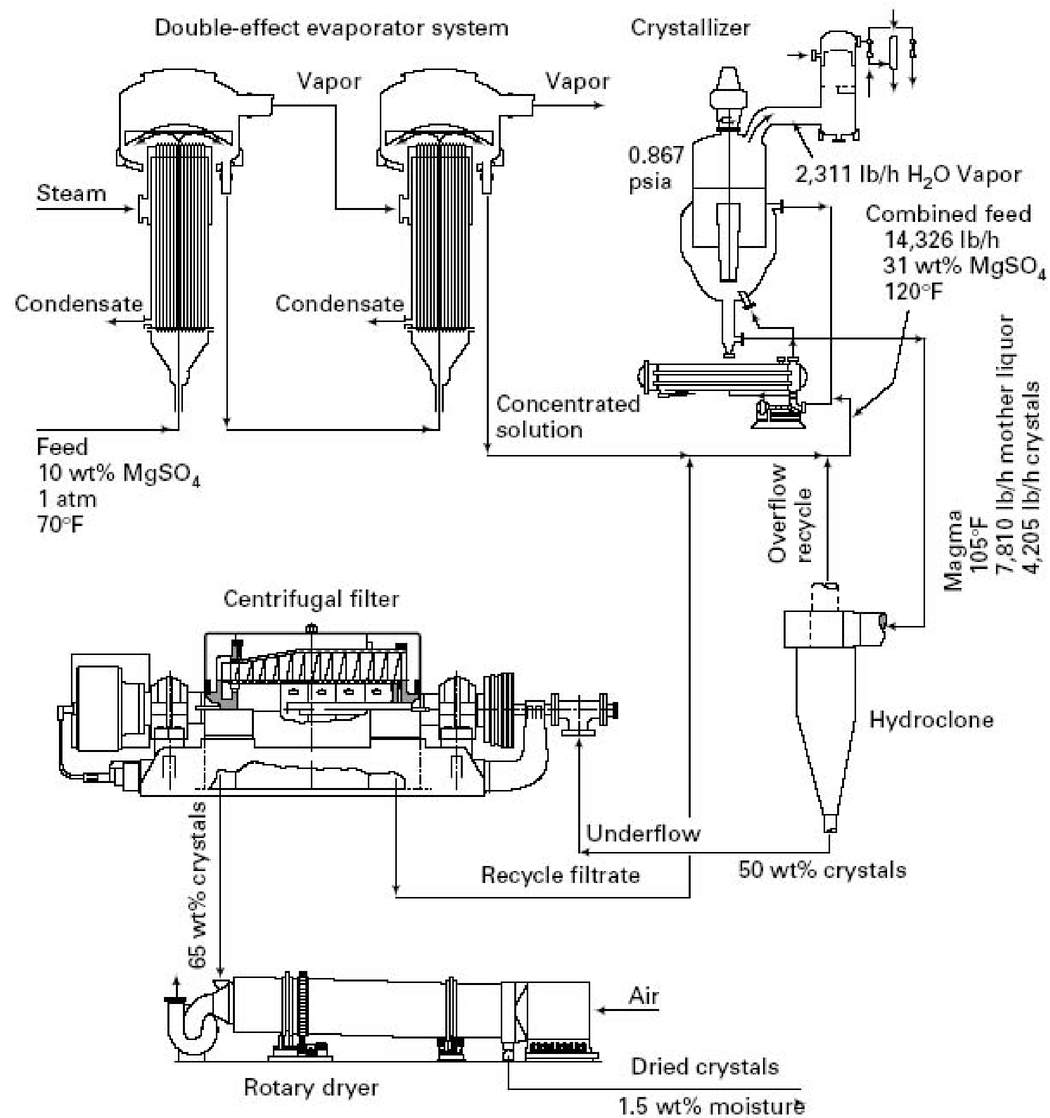


Table 17.1 Some Inorganic Salts Recovered from Aqueous Solutions

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

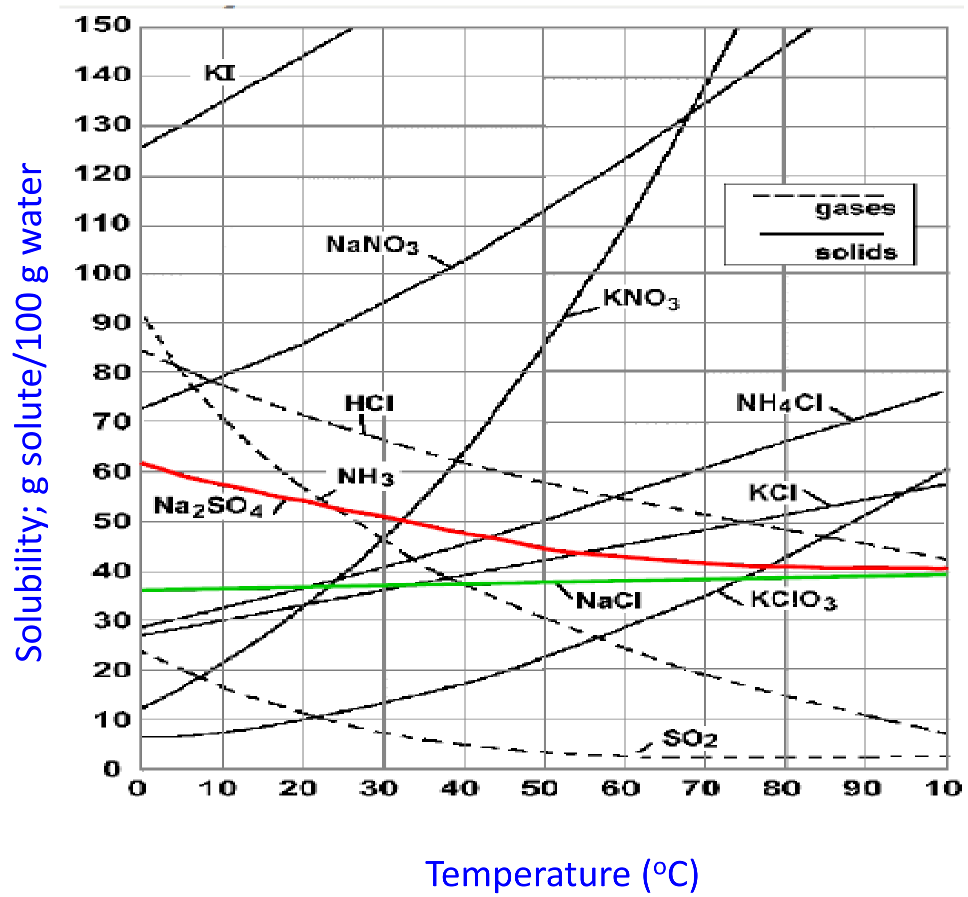
Industrial example

Production of $MgSO_4.7H_2O$
(Epsom salt)

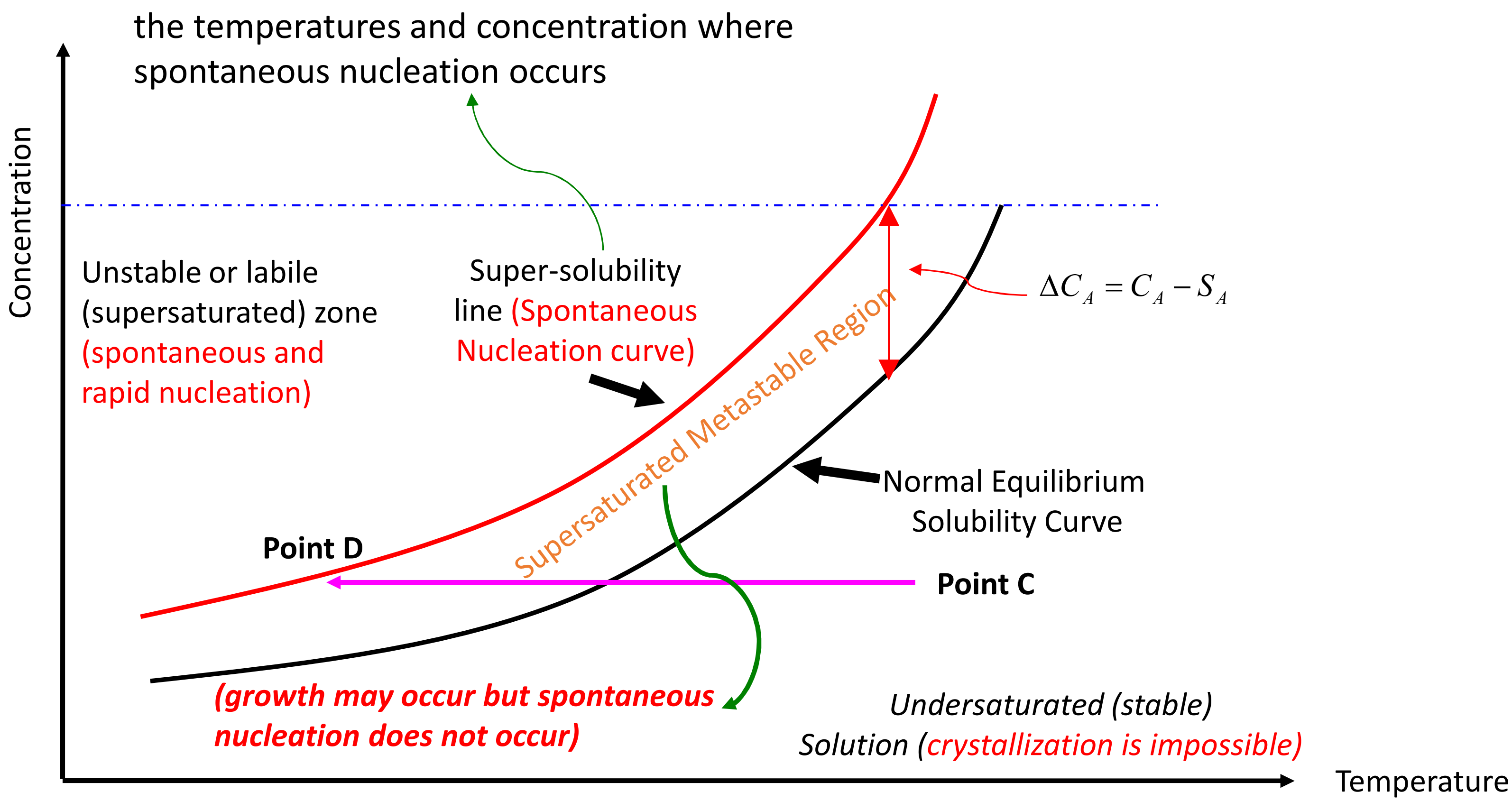


Equilibrium solubility in crystallization

- Usually solubility of salts increases with temperature. Temperature has negligible effects on the solubility of some salts such as NaCl.
- Solubility of some salts decreases with temperature increase such as sodium sulfate (Na_2SO_4) and some other sulfates.
- Generally, the presence of more than one solute, in the solution, decreases the solubility of both solutes.
- Pressure has negligible effect on solubility of salts.



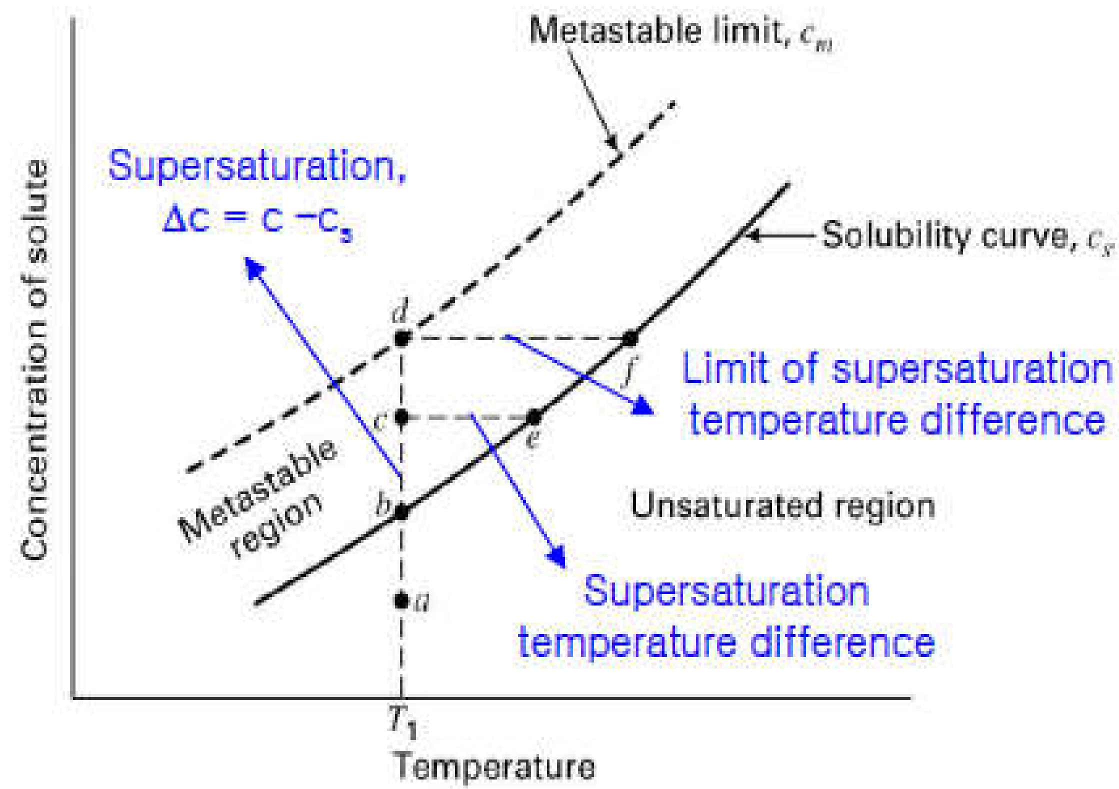
Mechanism of crystallization



- If a solution having the composition and temperature of point C is cooled in the direction of CD, it is first crosses the solubility curve and crystallization is expected.

Mechanism of crystallization

- ✓ Point a: the solution is undersaturated; crystals of all sizes dissolve
- ✓ Point b: equilibrium between a saturated solution and crystals that can be seen by naked eyes
- ✓ Point c: metastable region; crystals can grow but cannot nucleate
- ✓ Point d: spontaneous nucleation of very small crystals, that are invisible to the naked eyes, occurs



Limiting supersaturation: $\Delta c_{limit} = c_m - c_s$

Relative supersaturation: $$s = \frac{c - c_s}{c_s} = \frac{c}{c_s} - 1 = S - 1$$

In practice, s is usually less than 2%

Driving force for crystallization ≡ degree of super-saturation

- **Super-saturation**: the concentration difference between supersaturated solution in which the crystals are growing and that of a solution in equilibrium with the crystals.

- The degree of super-saturation is defined in different ways:

1) Mole fraction super-saturation : $\Delta y = y - y_s$
2) Molar super-saturation: $\Delta c = c - c_s$
3) Relative super-saturation: $s = (c - c_s)/c_s$
4) Super-saturation ratio: $S = c/c_s$

y = mole fraction of solute in solution
y_s = mole fraction of solute in saturated solution
c = molar concentration of solute in solution
c_s = molar concentration of solute in saturated solution

Crystallization mechanism can be summarized in two steps:

1. **Production of supersaturated solution (mother liquor) by one or a combination of the following:**
   a) **Cooling Crystallizers:** cooling of the solution if the solubility increases significantly with temperature and the original solution is near to the saturation state (this method is commonly used)
   b) **Evaporation Crystallizers:** concentrating the original solution by evaporation if the temperature effect on the solubility is small, or if the solubility decreases with temperature as NaCl salts.
   c) **Vacuum Crystallizers:** evaporation and cooling together hot solution is fed to a vacuum vessel, where the solvent flashes and the solution is cooled adiabatically. Used for large scale production.
   d) **Salting-out Crystallizers:** Salting out (decreasing of the solubility by adding of new more soluble solute) for thermally sensitive salts or low concentrated solutions with high solubility.

e) Watering: addition of a second solvent (water) to reduce solubility of the solute causing precipitation.

2. Nucleation:

- Formation of clusters of particles (or molecules) of solute due to rapid local fluctuations on a molecular scale in a homogeneous phase.
- **Mier's Theory: "Nucleation requires a certain degree of super-saturation to take place; this degree differs from solute to another."**
- **Super-saturation degree depends on:**

  1. Degree of mixing
  2. Presence of any solids (dust, rust, etc.)
  3. Rate of cooling (if high $\rightarrow$easy nucleation)
  4. Presence of ultrasonic waves, electric or magnetic fields, etc.

Yields and material balances in crystallization

- The **solution (mother liquor)** and the solid crystals are in contact for enough time to reach equilibrium.
- The final concentration of the solute in the solution can be obtained from the solubility curve.
- The yield can be calculated **knowing the initial concentration of solute, the final temperature, and the solubility at this temperature.**
- 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 crystallizations are hydrated, some of the water in solution is removed with the **crystals as a hydrate.**

Example 6.1. Percent recovery after crystaliization

Given solubility data for Phthalic acid as follows:

18 g / 100 mL water at 100 ºC

0.54 g / 100 mL water at 15 ºC

A student obtained 3.2 g of crude phthalic acid. After recrystallization and drying, 2.5 g of pure phthalic acid was obtained at 15 ºC. Calculate:

a) The percent recovery

2.5g/3.2gx100 =78%

b) Amount of water needed for recrystallization

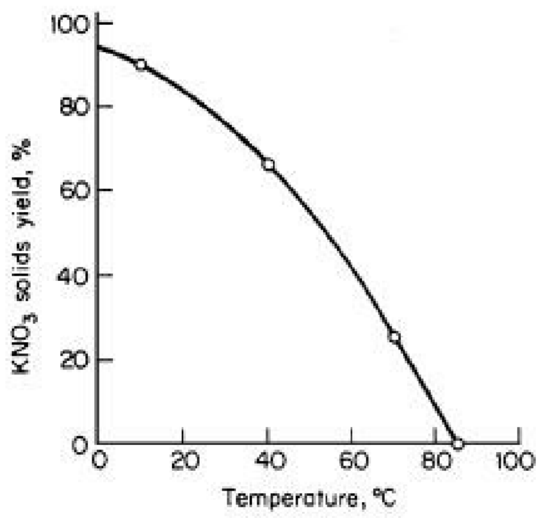
100mL/18gx3.2g = 17.7mL

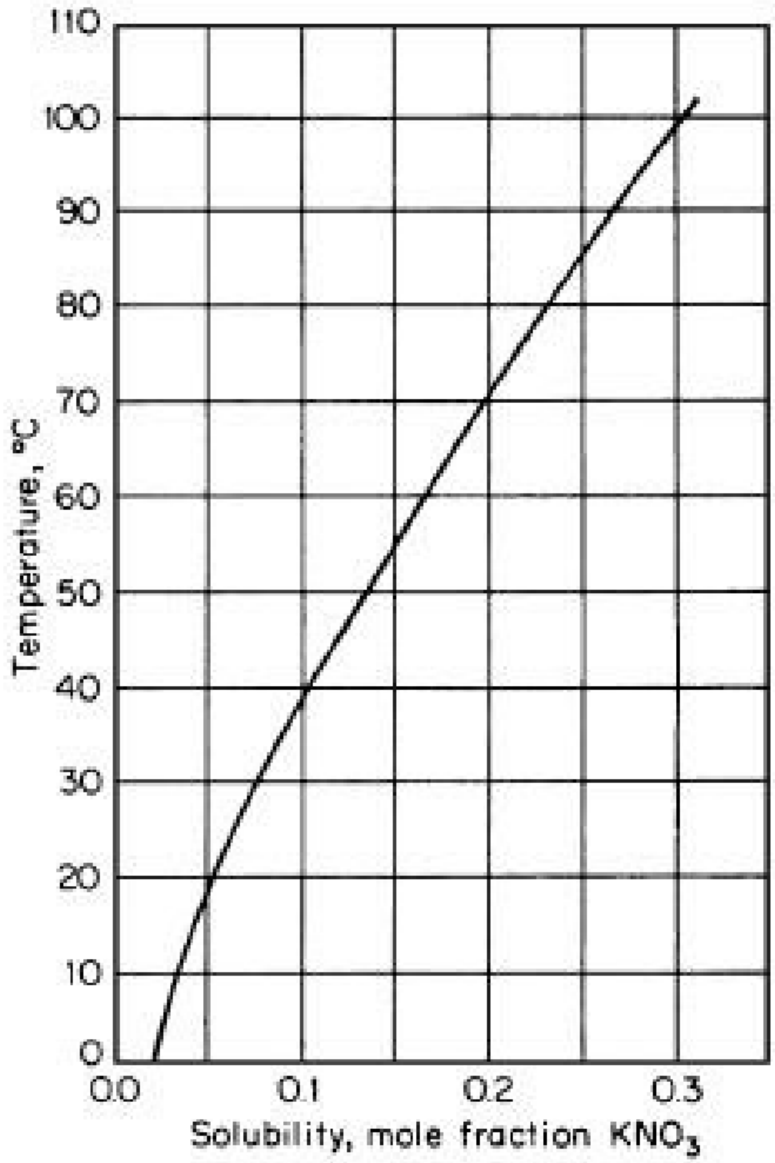
c) Amount of product lost to the filtrate.

0.54g/100mLx17.7mL=0.1g

Example 6.2. Yield vs. Temperature

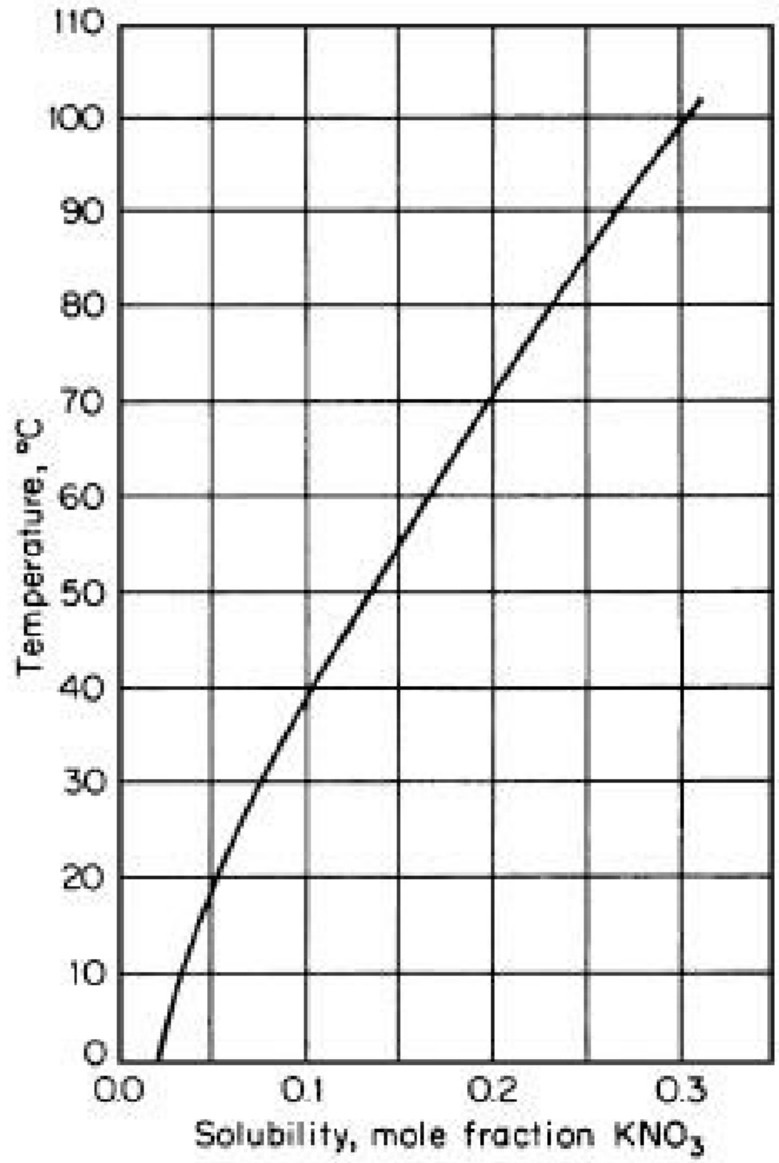
A 65.2 wt % aqueous solution of potassium nitrate originally at 100°C (212°F) is gradually cooled to 10°C (50°F). What is the yield of KNO3 solids as a function of temperature? How many pounds of KNO3 solids are produced at 10°C if the original solution weighed 50,000 lb (22,680 kg)?





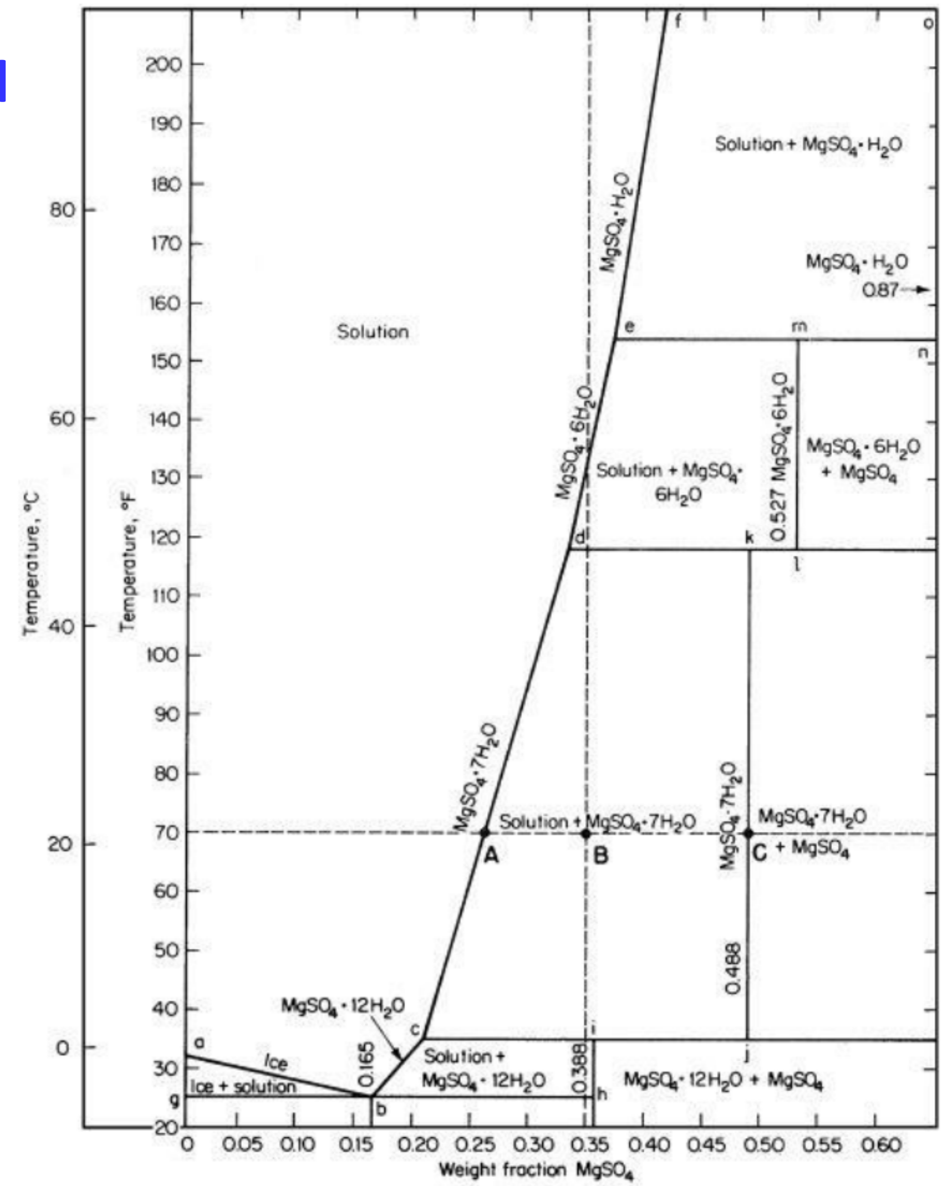
Example 6.3 Crystallization by boiling

A 70°C (158°F) aqueous solution initially containing 15 mol % KNO3 is to be boiled so as to give a final yield of solid KNO3 of 60 percent. How much of the initial water must be boiled off? What is the final liquid composition?



Example 6.4. Crystallization of hydrated solids ($MgSO_4.7H_2O$)

A 35 wt % aqueous $MgSO_4$ solution is originally present at 200°F(366 K). If the solution is cooled (with no evaporation) to 70°F (294 K), what solid-phase hydrate will form



The solution originally containing 35 wt % MgSO4

After cooling to 70°C, a saturated aqueous solution containing 27 wt % MgSO4 (point A) in equilibrium with MgSO4·7H2O hydrated solids (point B).

The molecular weights of MgSO4 and MgSO4·7H2O are 120 and 246, respectively.

The solid-phase hydrate is (120/246)(100) = 48.8 wt % MgSO4.

The rest of the solid phase is H2O in the crystal lattice structure.