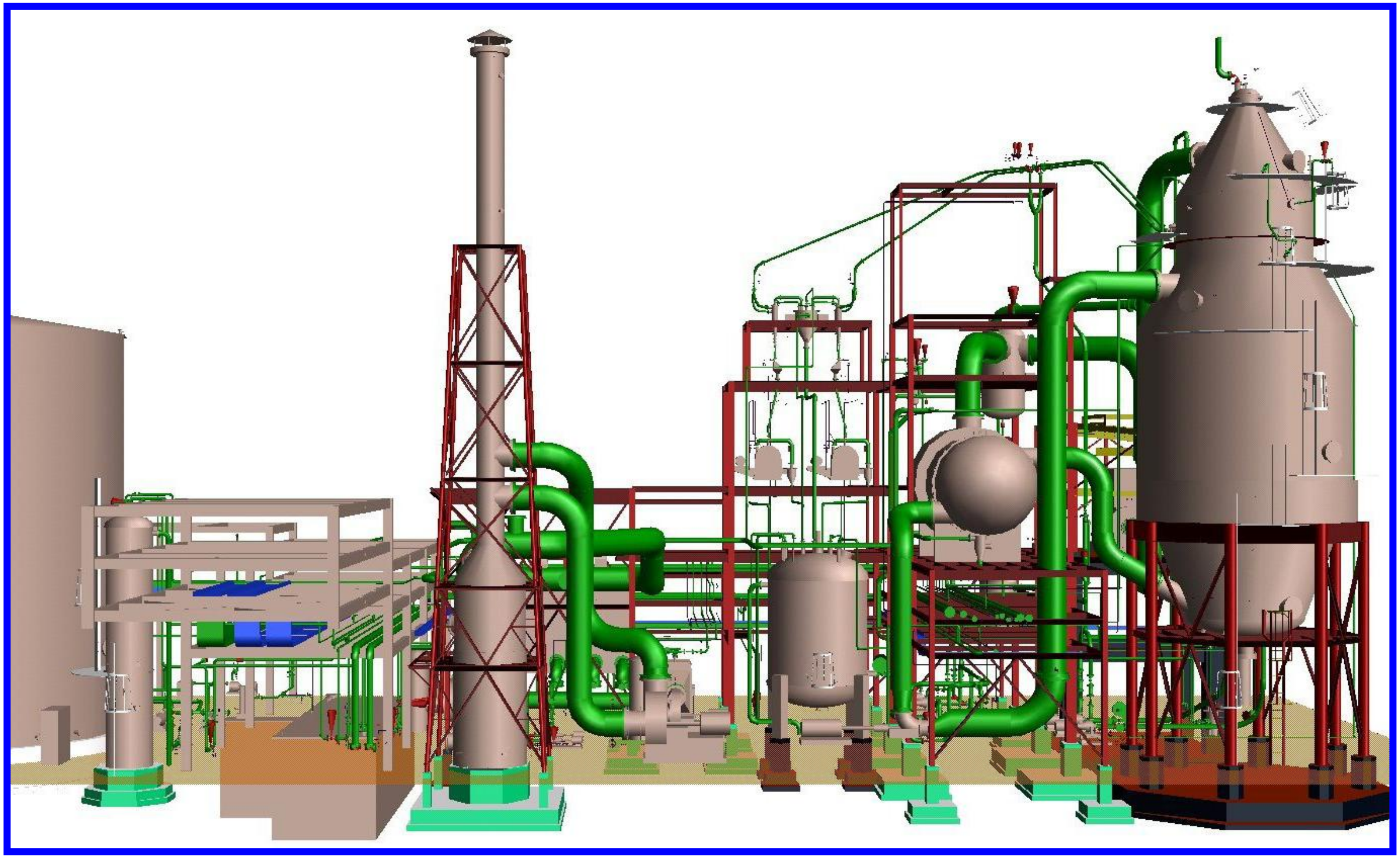
Crystallization



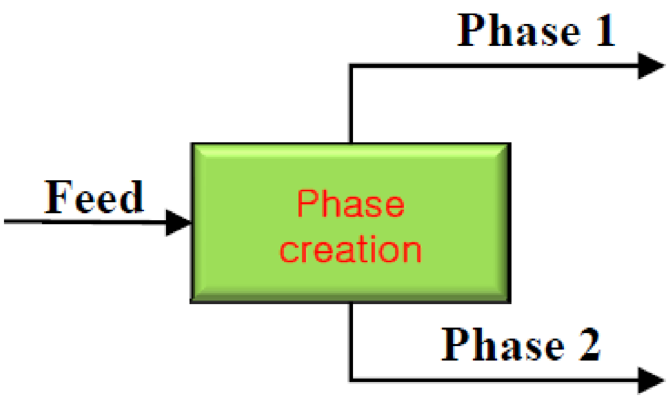
Principal references: Chapter 12 in C.J. Geankoplis book and Chapter 17 in Henley, Seader & Roper book.

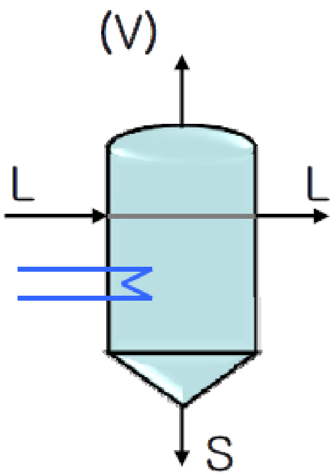
Overview and definitions

- Crystallization

Heat transfer (ESA)

▪Based on phase-creation:

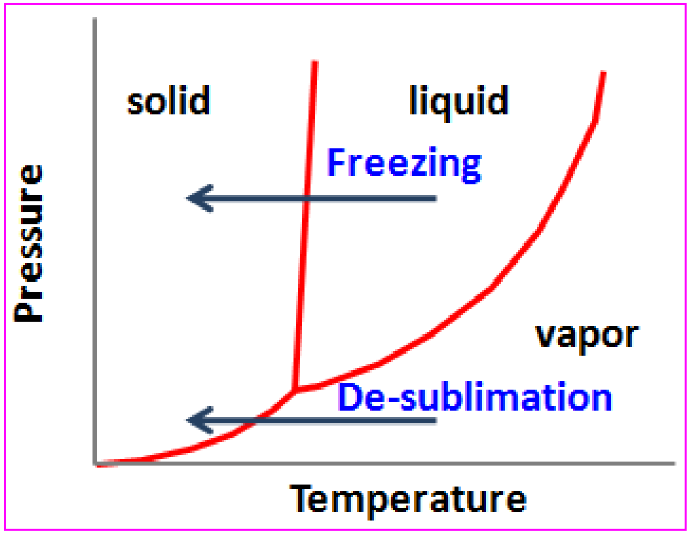


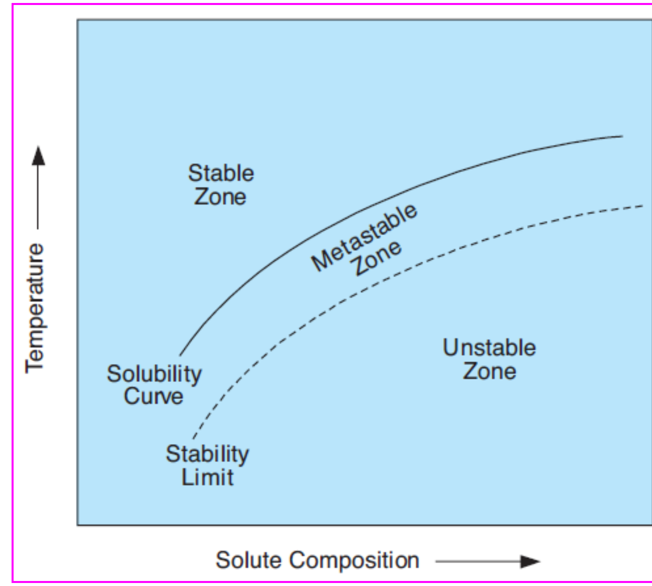


- Crystallization is **a solid-liquid operation.**
- Crystallization is a process where solid particles are formed from a homogeneous phase.
- **General principle of crystallization:** Solution is concentrated and usually cooled until the solute concentration becomes greater than its **solubility** at that temperature. Then, the solute comes out of the solution, forming crystals of approximately pure solute.

Overview and definitions

▪Common crystallization operations:





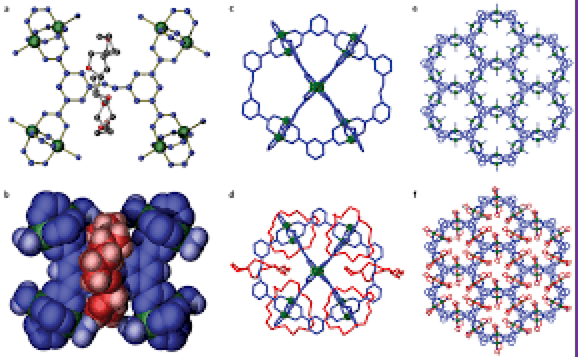
Crystallization Operations

- Formation of ice by freezing of water
- Formation of snow particles from a vapor
- Formation of solid particles from melt
- Separation of solid crystals from liquid solution

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

Overview and definitions

- **In commercial crystallization, the most important properties are:**
  - ☐ **Yield**
  - ☐ **Purity**
  - ☐ **Shape: needles, cubes, flakes,..**
  - ☐ **Size**
  - ☐ **Uniformity**



- **What is crystal?**

• A solid composed of atoms, ions, or molecules, that are arranged in an orderly and repetitive manner.

• Such atoms, ions, or molecules, are located in 3D arrays or space lattices.

• The interatomic distances are measured by **X-Ray diffraction**.

Overview and definitions

- **X-ray diffraction**

BRAGG LAW

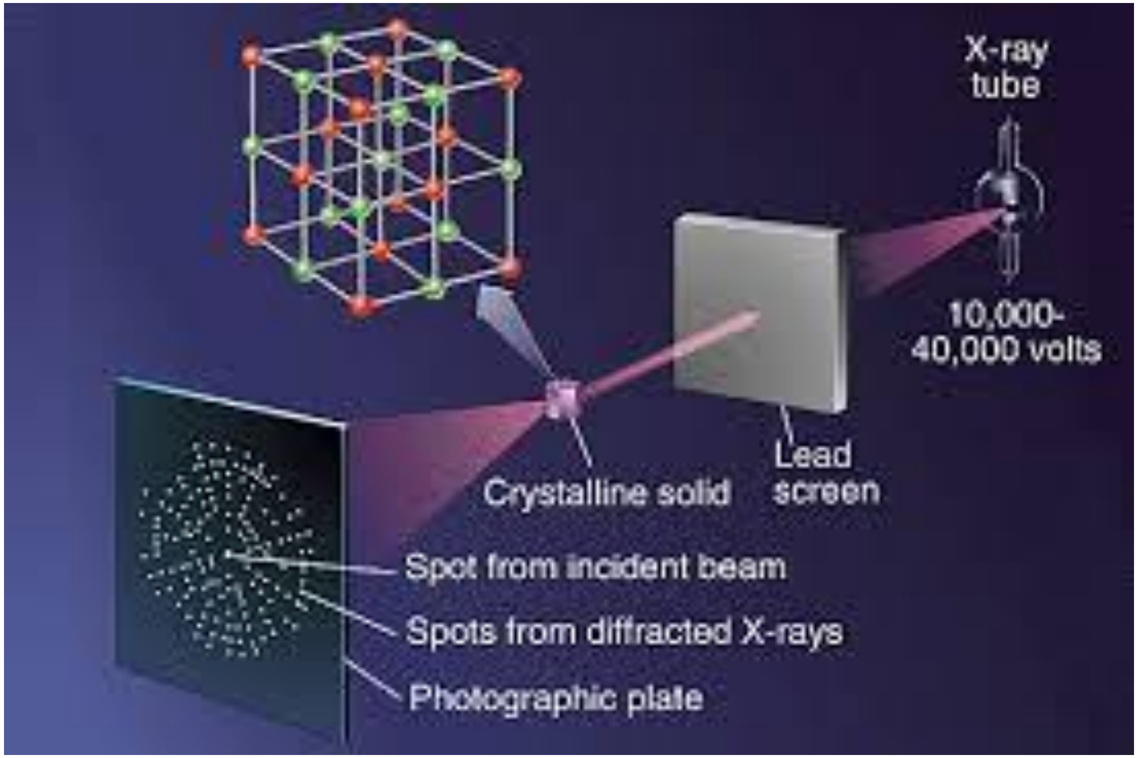
$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal

θ = x-ray incidence angle (Bragg angle)

λ = wavelength of the characteristic x-rays



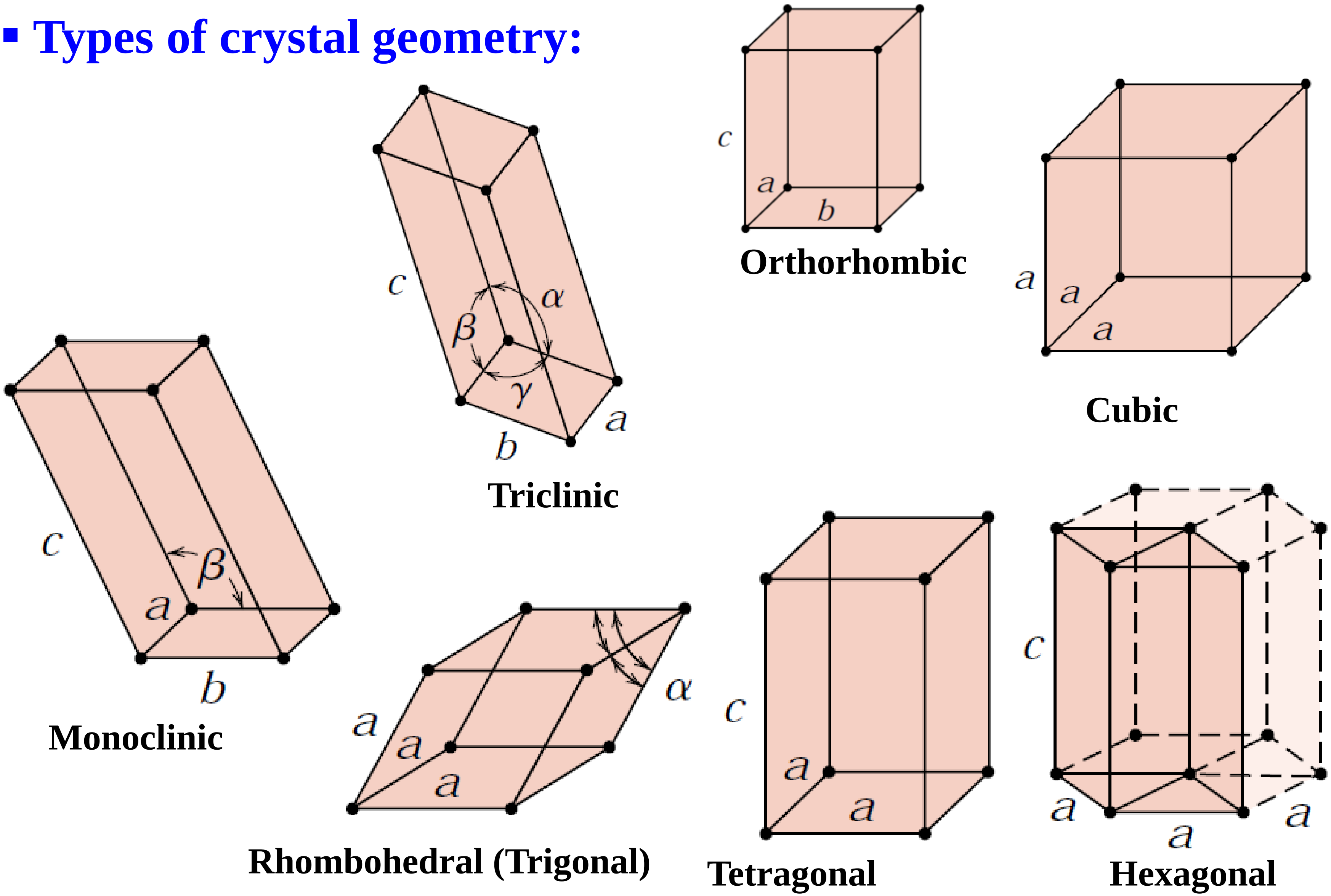
Overview and definitions

▪ Types of crystal geometry:

- Crystals appear as polyhedrons having flat faces and sharp corners.
- However, the shape of crystal particles has no relation to the crystal system and usually depends upon the process conditions of crystal growth.
- There are **7 classes of crystal systems**:
    1. **Cubic**
    2. **Tetragonal**
    3. **Hexagonal**
    4. **Rhombohedral (Trigonal)**
    5. **Orthorhombic**
    6. **Monoclinic**
    7. **Triclinic**

Overview and definitions

- **Types of crystal geometry:**



Overview and definitions

- **Examples of inorganic salts recovered from aqueous solution**

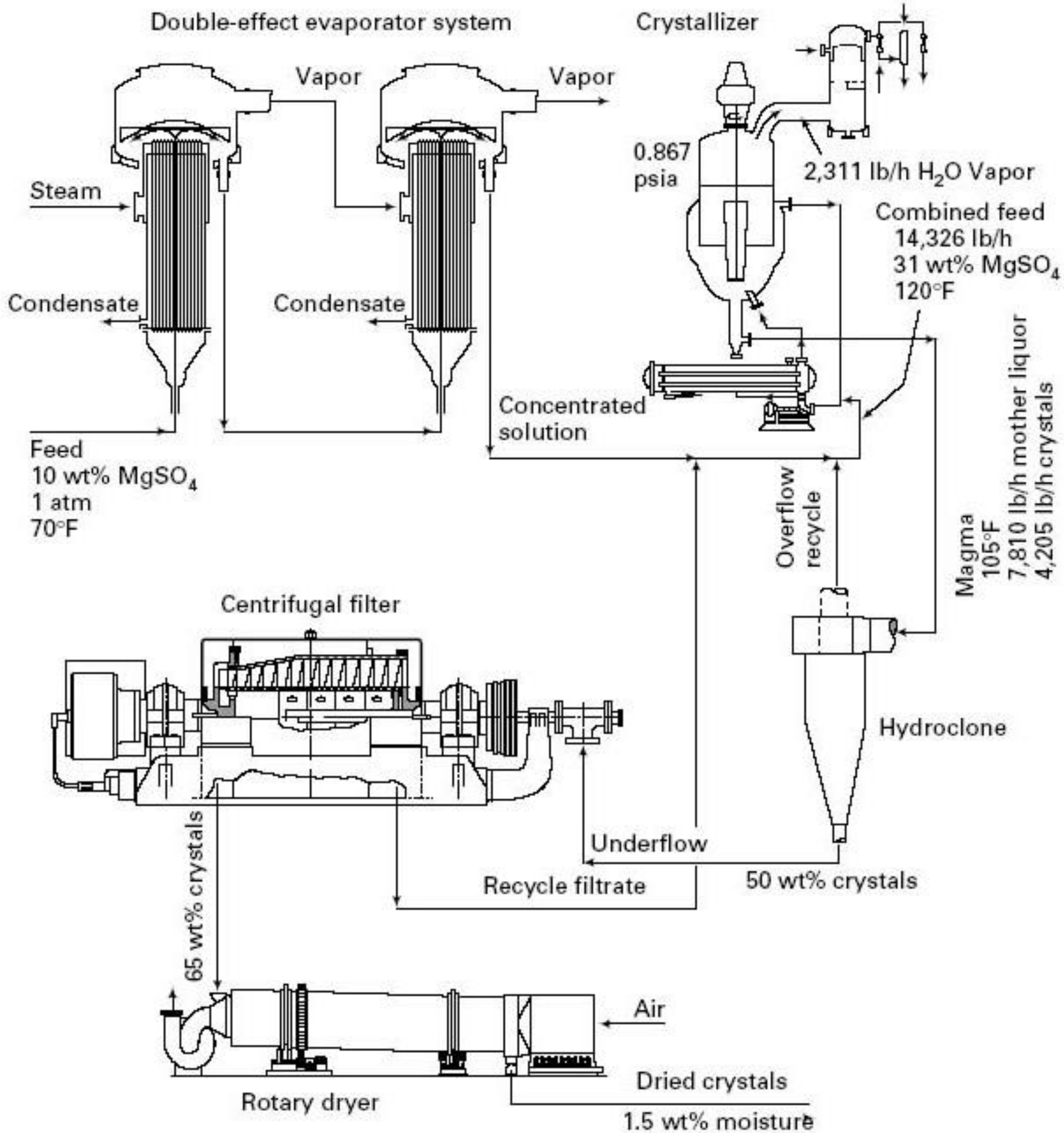
Table 17.1 Some Inorganic Salts Recovered from Aqueous Solutions

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

Overview and definitions

Industrial example:

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

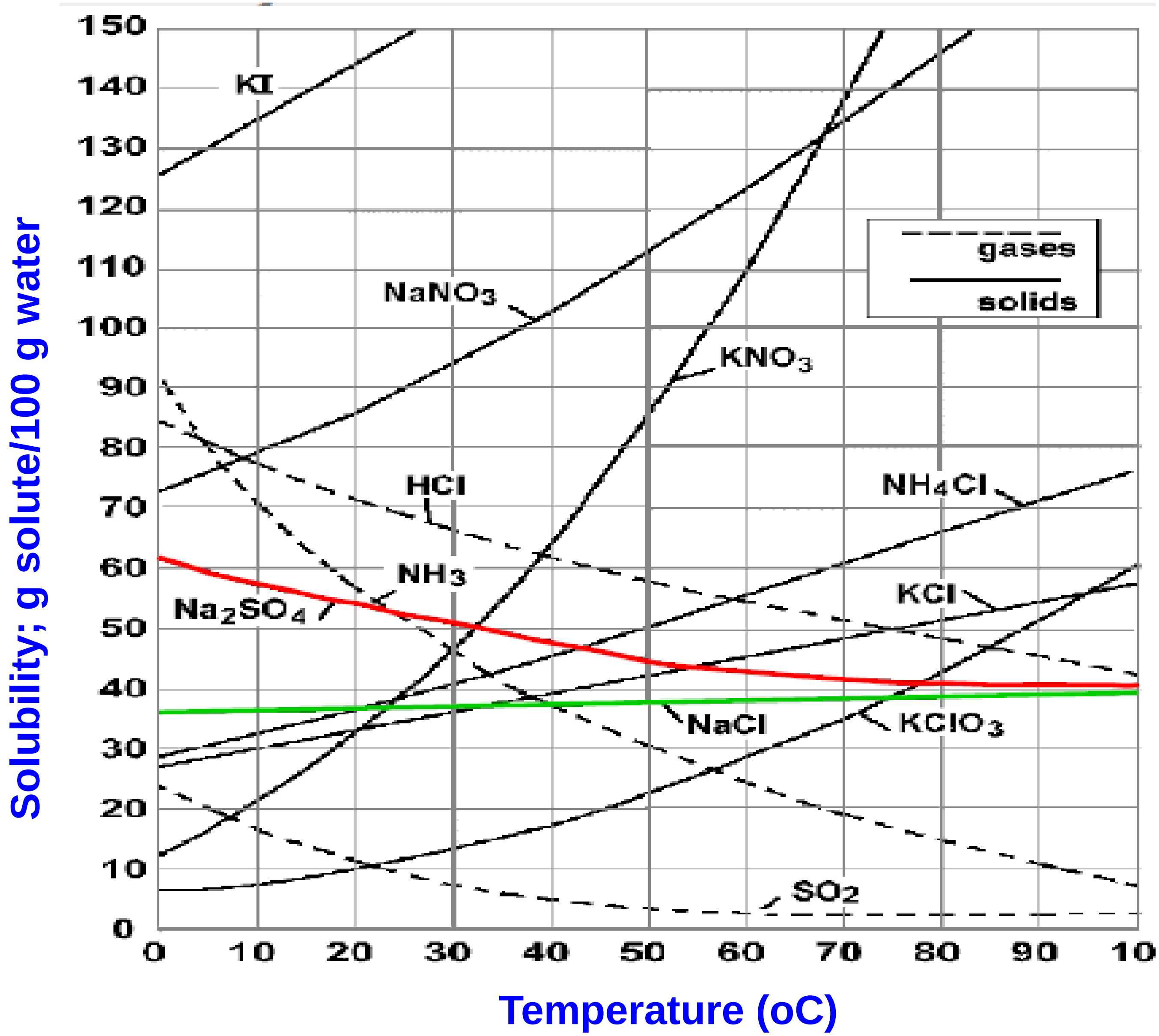


Equilibrium solubility in crystallization

- 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.
- For some salts, the solubility curve that definite breaks that indicates different hydrates; see the solubility curve of Sodium thiosulfate, $Na_2S_2O_3$).

Equilibrium solubility in crystallization

Solubility curves:



Equilibrium solubility in crystallization

Solubility curves with different hydrates:

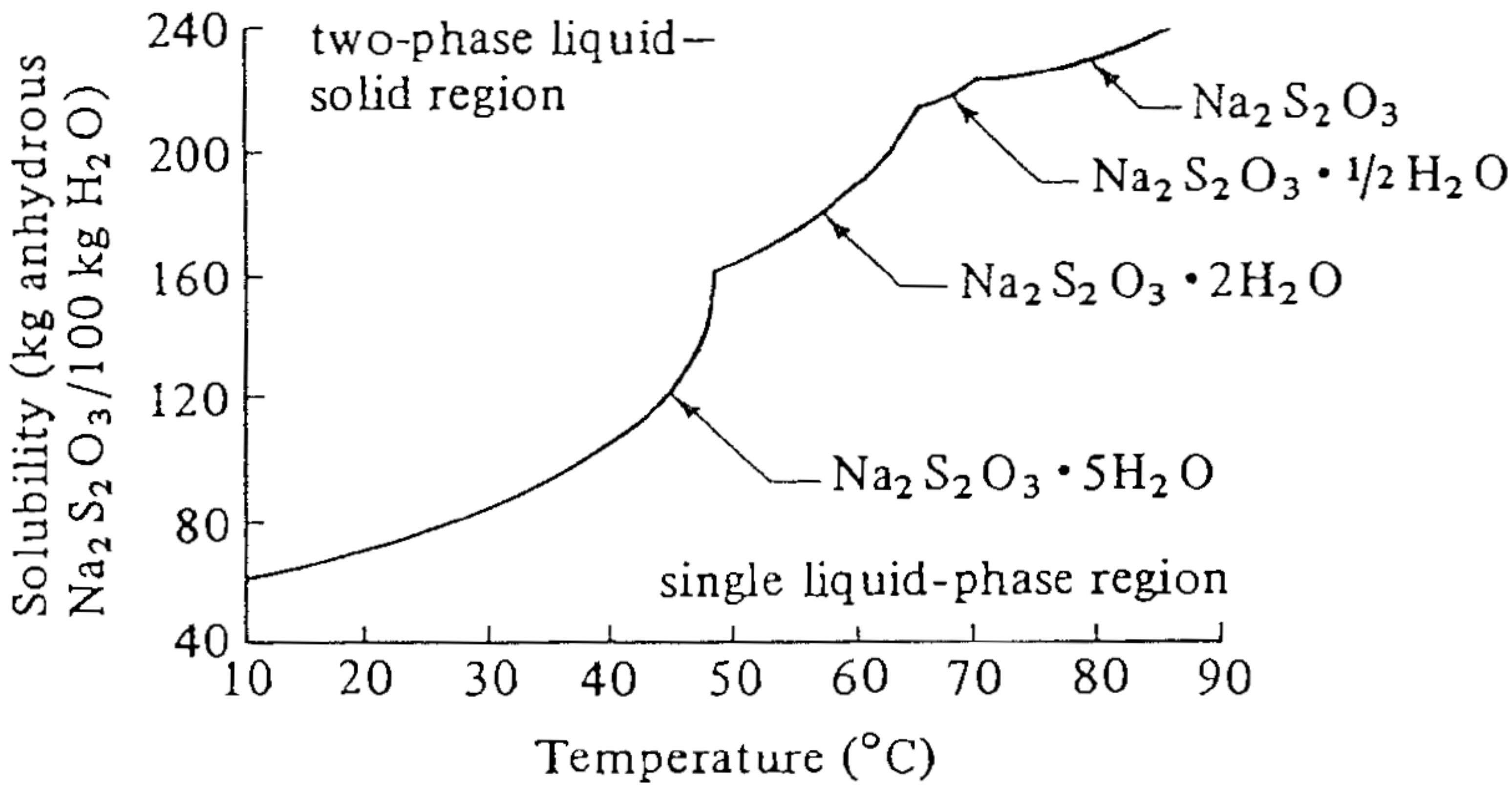


FIGURE 12.11-1. *Solubility of sodium thiosulfate, $Na_2S_2O_3$, in water.*

Equilibrium solubility in crystallization

Solubility tables (inorganic solutes):

Table 17.5 Solubility and Heat of Solution at Infinite Dilution of Some Inorganic Compounds in Water (A Positive Heat of Solution Is Endothermic)

Compound	Heat of Solution of Stable Hydrate (at Room Temperature) kcal/mole Compound	Solubility (Hydrate-free Basis) g/100 g H_2O at T, °C								Stable Hydrate at Room Temperature
		0	10	20	30	40	60	80	100	
NH_4Cl	+3.8	29.7	33.4	37.2	41.4	45.8	55.2	65.6	77.3	0
$(NH_4)_2SO_4$	+1.5	71.0	73.0	75.4	78.0	81.0	88.0	95.3	103.3	0
$BaCl_2$	+4.5	31.6	33.2	35.7	38.2	40.7	46.4	52.4	58.3	2
$CuSO_4$	+2.86	14.3	17.4	20.7	25.0	28.5	40.0	55.0	75.4	5
$MgSO_4$	+3.18	22.3	27.8	33.5	39.6	44.8	55.3	56.0	50.0	7
$MgCl_2$	−3.1	52.8	53.5	54.5	56.0	57.5	61.0	66.0	73.0	6
$NiSO_4$	+4.2	26	32	37	43	47	55	63	—	7
KCl	+4.4	27.6	31.0	34.0	37.0	40.0	45.5	51.1	56.7	0
KNO_3	+8.6	13.3	20.9	31.6	45.8	63.9	110	169	247	0
K_2SO_4	+6.3	7.4	9.3	11.1	13.1	14.9	18.3	21.4	24.2	0
$AgNO_3$	+5.4	122	170	222	300	376	525	669	952	0
$NaClO_3$	+5.4	80	89	101	113	126	155	189	233	0
$NaCl$	+0.93	35.6	35.7	35.8	36.1	36.4	37.1	38.1	39.8	0
$NaNO_3$	+5.0	72	78	85	92	98	—	133	163	0
Na_2SO_4	+18.7	4.8	9.0	19.4	40.8	48.8	45.3	43.7	42.5	10
$Na_2S_2O_3$	+11.4	52	61	70	84	103	207	250	266	5
Na_3PO_4	+15.0	1.5	4	11	20	31	55	81	108	12

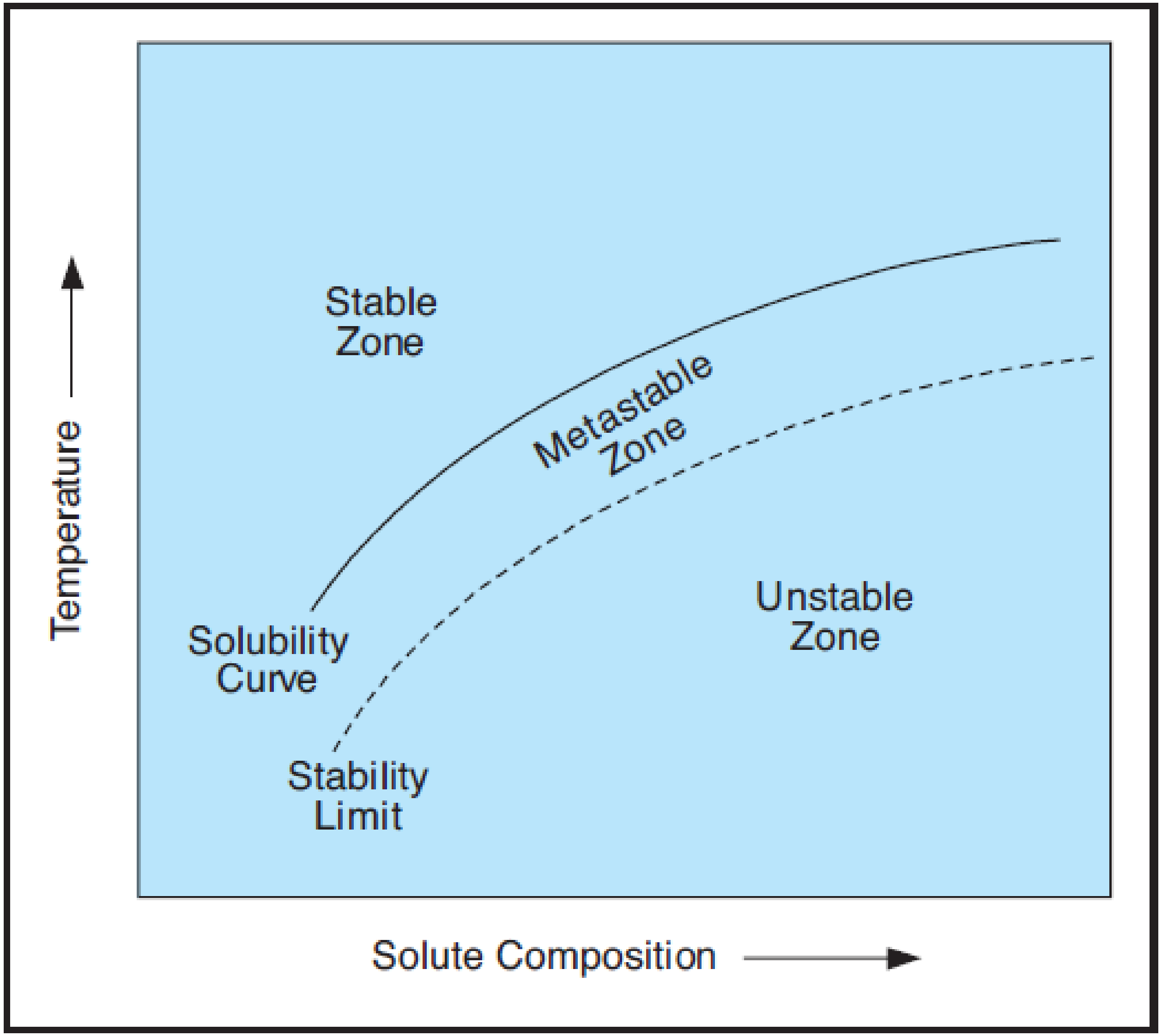
Equilibrium solubility in crystallization

Solubility tables (organic solutes):

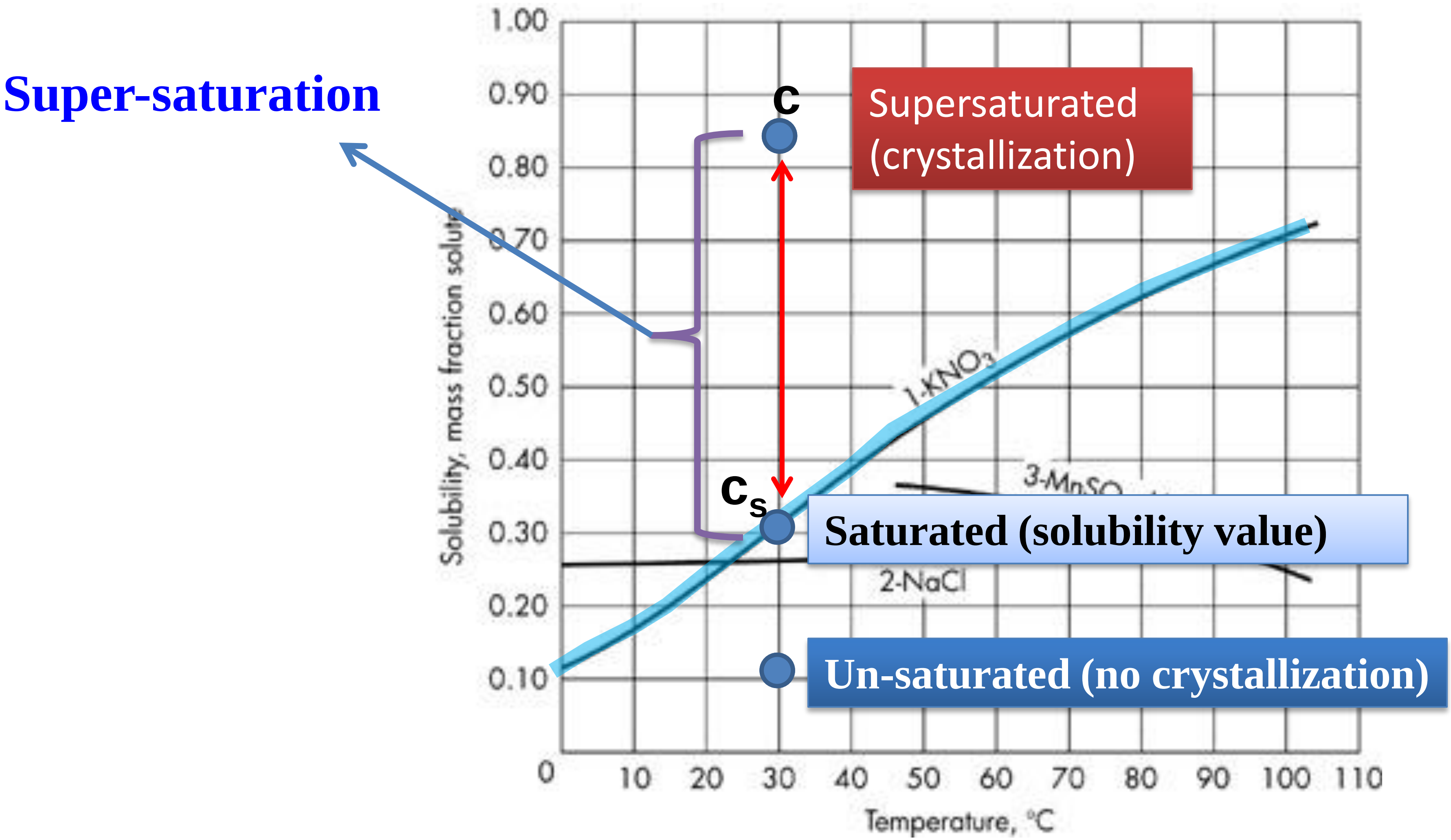
Table 17.7 Solubility and Melting Point of Some Organic Compounds in Water

Compound	Melting Point, °C	Solubility, g/100 g H_2O at T, °C							
		0	10	20	30	40	60	80	100
Adipic acid	153	0.8	1.0	1.9	3.0	5.0	18	70	160
Benzoic acid	122	0.17	0.20	0.29	0.40	0.56	1.16	2.72	5.88
Fumaric acid (trans)	287	0.23	0.35	0.50	0.72	1.1	2.3	5.2	9.8
Maleic acid	130	39.3	50	70	90	115	178	283	—
Oxalic acid	189	3.5	6.0	9.5	14.5	21.6	44.3	84.4	—
o-phthalic acid	208	0.23	0.36	0.56	0.8	1.2	2.8	6.3	18.0
Succinic acid	183	2.8	4.4	6.9	10.5	16.2	35.8	70.8	127
Sucrose	d	179	190	204	219	238	287	362	487
Urea	133	67	85	105	135	165	250	400	730
Uric acid	d	0.002	0.004	0.006	0.009	0.012	0.023	0.039	0.062

Mechanism of crystallization



Mechanism of crystallization



- Supersaturated solution (**mother liquor)** will transformed to a mixture of crystals and saturated solution. This mixtures is called **Magma.**

Mechanism of crystallization

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

Mechanism of crystallization

- **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.

Mechanism of crystallization

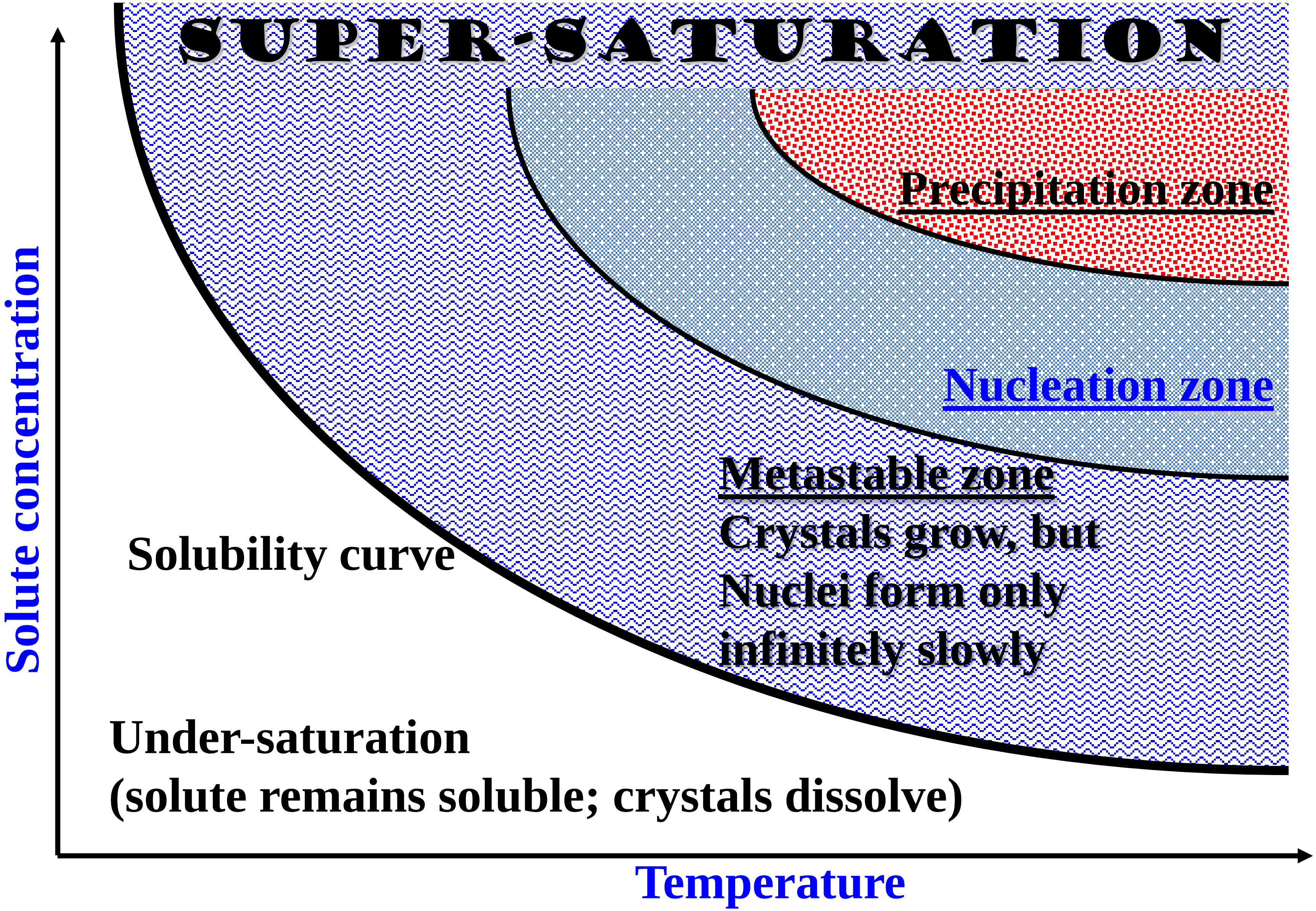
e) Watering: addition of a second solvent (water) to reduce solubility of the solute causing precipitation.

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:**

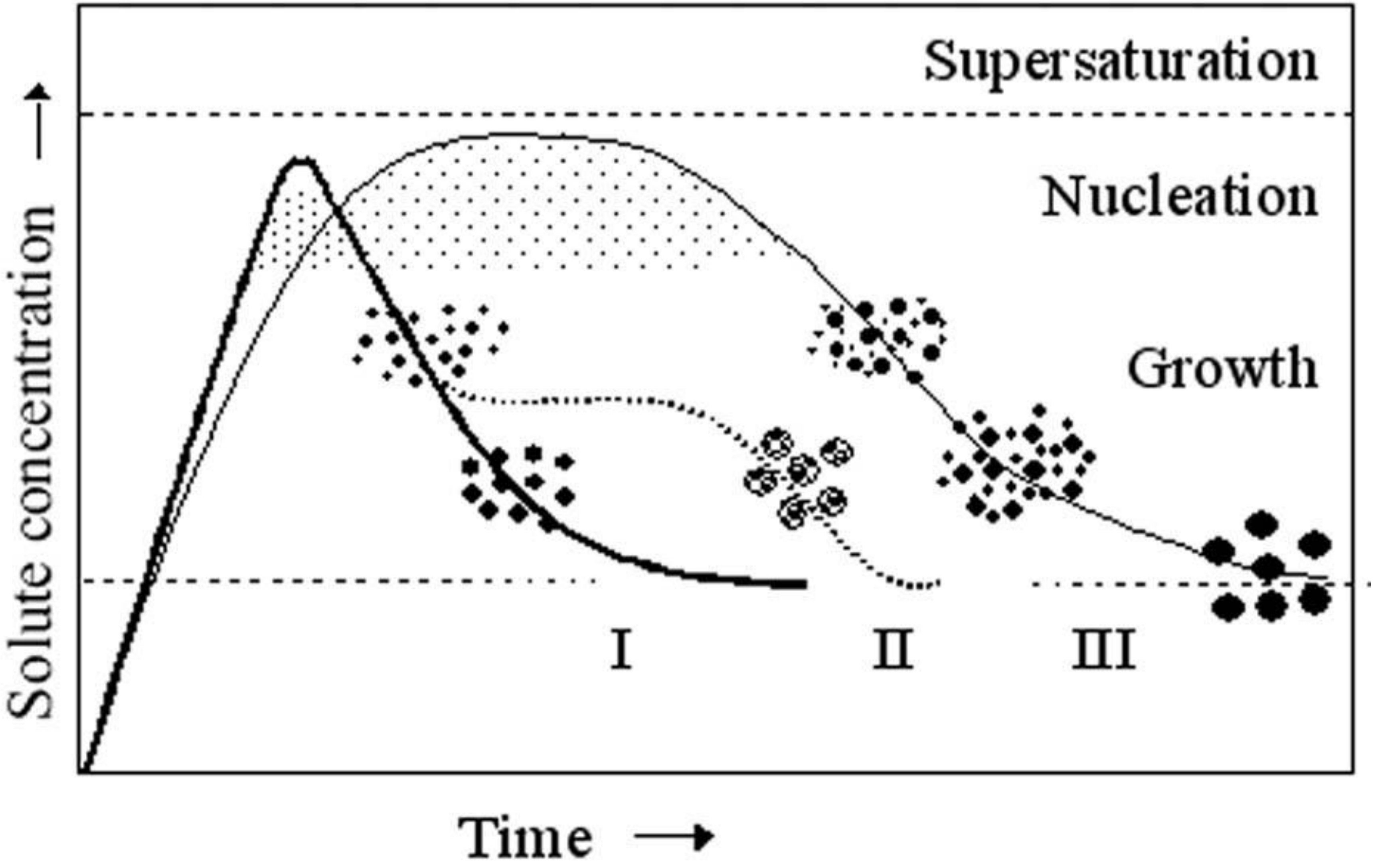
1. Degree of mixing
2. Presence of any solids (dust, rust, etc.)
3. Rate of cooling (if high $\rightarrow$easy nucleation)
4. Presence of ultrasonic waves, electric or magnetic fields, etc.

Mechanism of crystallization



Mechanism of crystallization

Nucleation



Yields and material balances in crystallization

- The **solution (mother liquor)** and the solid crystals are in contact for enough time to reach equilibrium.
- Hence, the mother liquor is saturated at the final temperature of the process.
- 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.**

Yields and material balances in crystallization

Example. A salt solution weighing 10000 kg with 30 wt% Na_2CO_3 is cooled to 293 K (20 °C). The salt crystallizes as the decahydrate. What will be the yield of $Na_2CO_3{\bullet}10H_2O$ crystals if the solubility is 21.5 kg anhydrous Na_2CO_3/100 kg of total water? Do this for the following cases:

(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.

Solution:

Molecular weights:

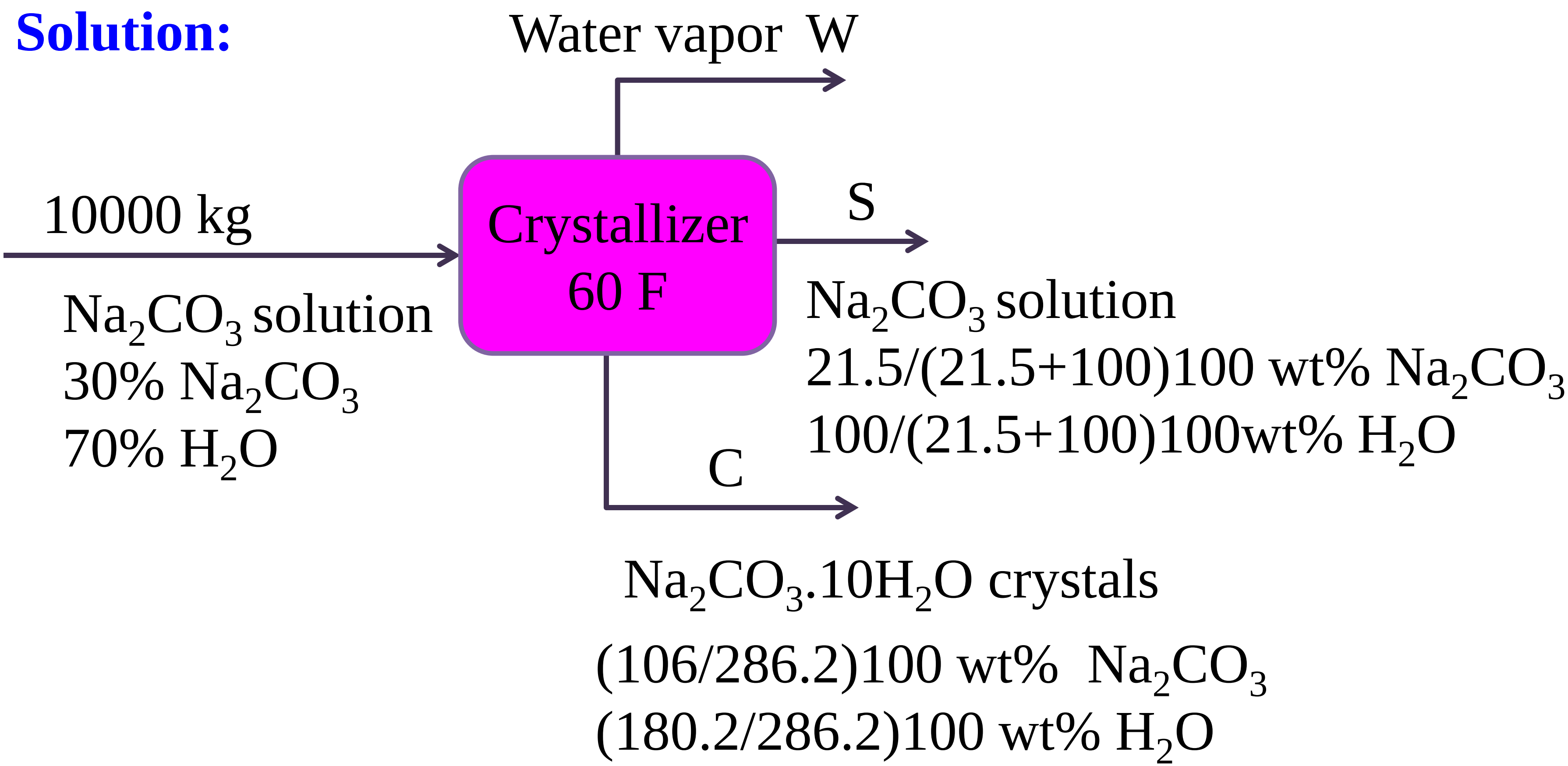
Na_2CO_3 = 106.0

$Na_2CO_3 .10H_2O$ = 286.2

$10H_2O$ = 180.2

Yields and material balances in crystallization

Solution:



Yields and material balances in crystallization

a) W= 0

Water MB: $$0.70(10\,000) = \frac{100}{100 + 21.5}(S) + \frac{180.2}{286.2}(C) + 0 \quad \textbf{(1)}$$

Na_2CO_3 MB: $$0.30(10\,000) = \frac{21.5}{100 + 21.5}(S) + \frac{106.0}{286.2}(C) + 0 \quad \textbf{(2)}$$

Solving Eqn. (1) & (2) simultaneously to obtain:

C = 6370 kg of $Na_2CO_3.10H_2O$ crystals ; S = 3630 kg solution

b) W= 0.03(10000)=300 kg water evaporated

Water MB: $$0.70(10\,000) = \frac{100}{100 + 21.5}(S) + \frac{180.2}{286.2}(C) + 300 \quad \textbf{(1)}$$

Na_2CO_3 MB : $$0.30(10\,000) = \frac{21.5}{100 + 21.5}(S) + \frac{106.0}{286.2}(C) + 0 \quad \textbf{(2)}$$

Solving the two Eqns. simultaneously to obtain:

C = 6630 kg of $Na_2CO_3.10H_2O$ crystals ; S = 3070 kg solution

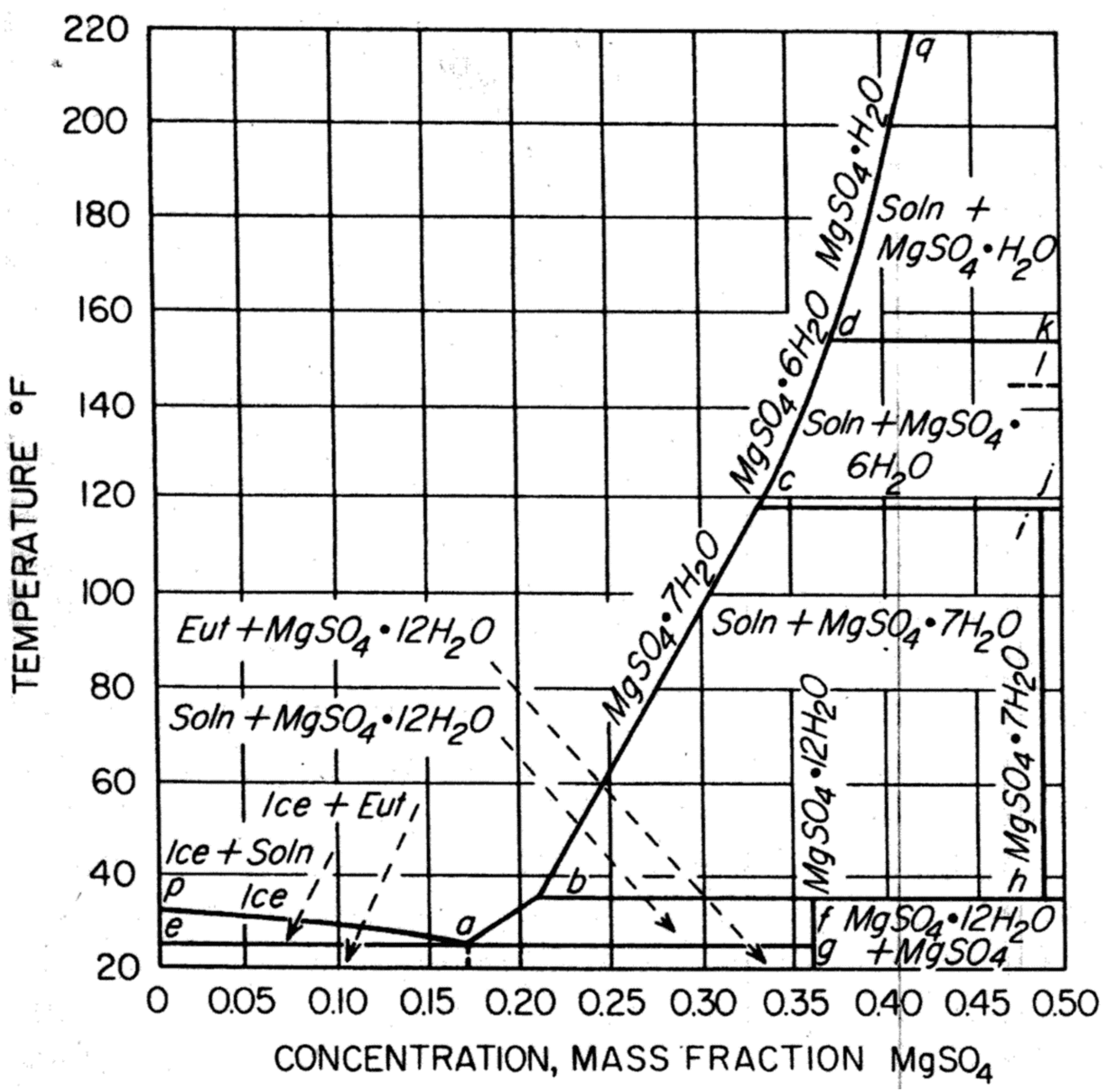
Yields and material balances in crystallization

Example. A solution consisting of 30% $MgSO_4$ and 70% H_2O is being crystallized at 60 °F. During this process, 5% of the total water in the system evaporates. Concentration-temperature phase diagram is given in the next slide.

a) Which type hydrated crystals is going to be produced at these conditions?

b) How many kilograms of crystals are obtained per 1000 kg of original mixture?

Yields material balances in crystallization

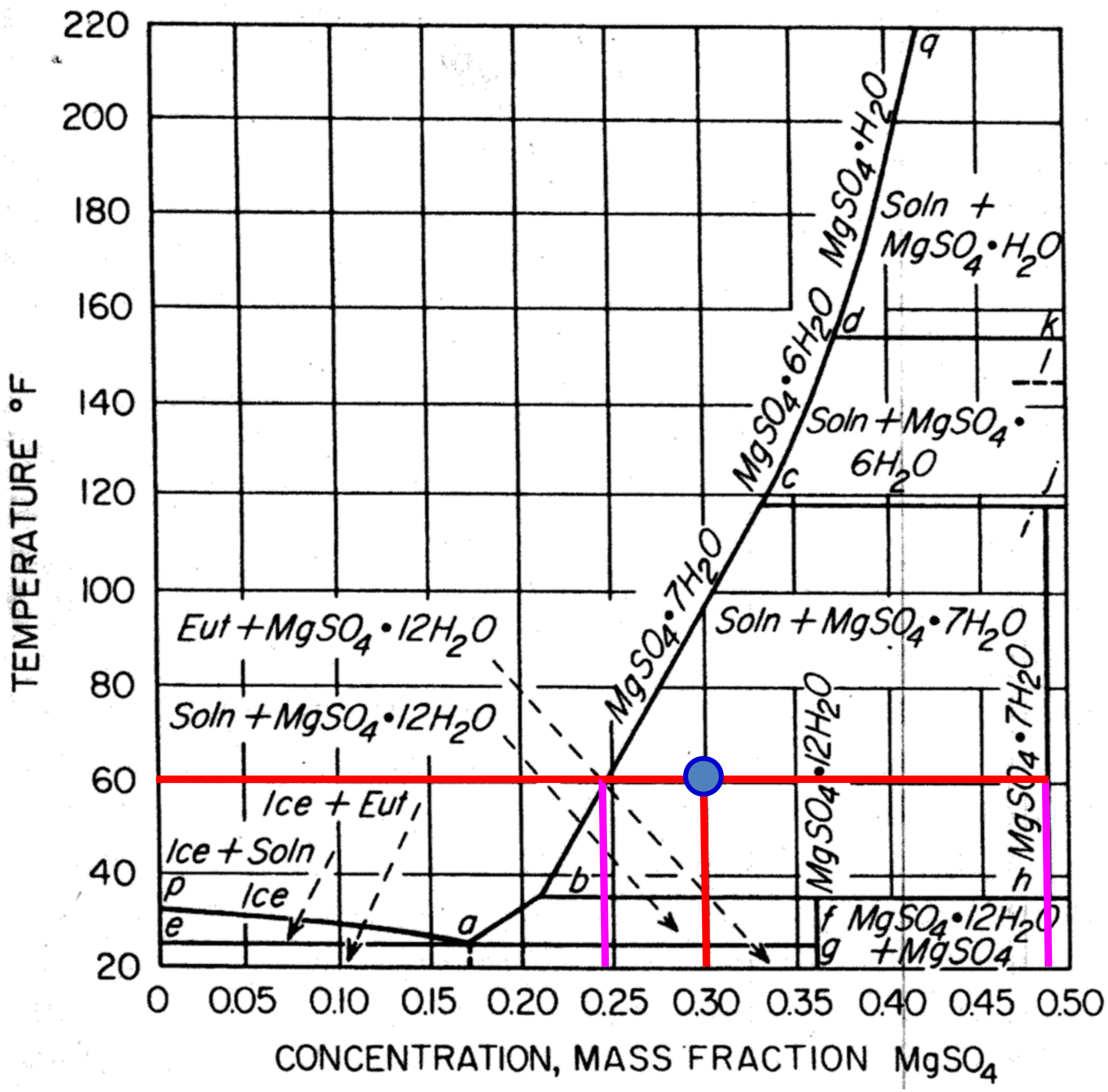


Yields material balances in crystallization

Solution:

a) Locate the point of T=60 °F and x_{MgSO4}= 0.3. The point is located in the region of $MgSO_4$ solution and heptahydrate crystal ($MgSO_4.7H_2O$)

From the phase diagram: the mass fraction of $MgSO_4$ solution is 0.24 and it is 0.488 for heptahydrate crystal

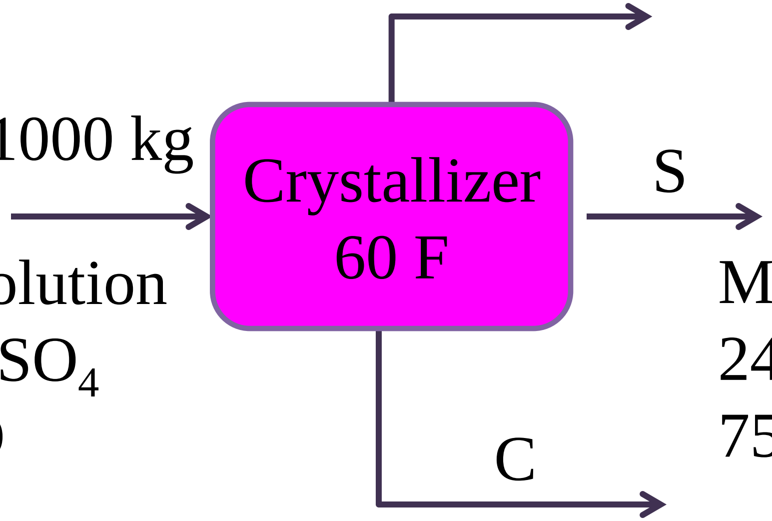


Yields material balances in crystallization

b)

Water vapor W=(0.05)(0.7)(1000) = 35 kg

Basis: F=1000 kg



$MgSO_4$ solution
30% $MgSO_4$
70% H_2O

S: $MgSO_4$ solution
24.5% $MgSO_4$
75.5% H_2O

C: $MgSO_4.7H_2O$ crystals
48.8% $MgSO_4$
51.2% H_2O

Molecular weights:
$MgSO_4$ = 120.4
$MgSO_4$ .7H_2O =246.5
7H_2O = 126.14

Water MB: $$(0.7)(1000) = 35 + (0.755)S + 0.512C \quad (1)$$

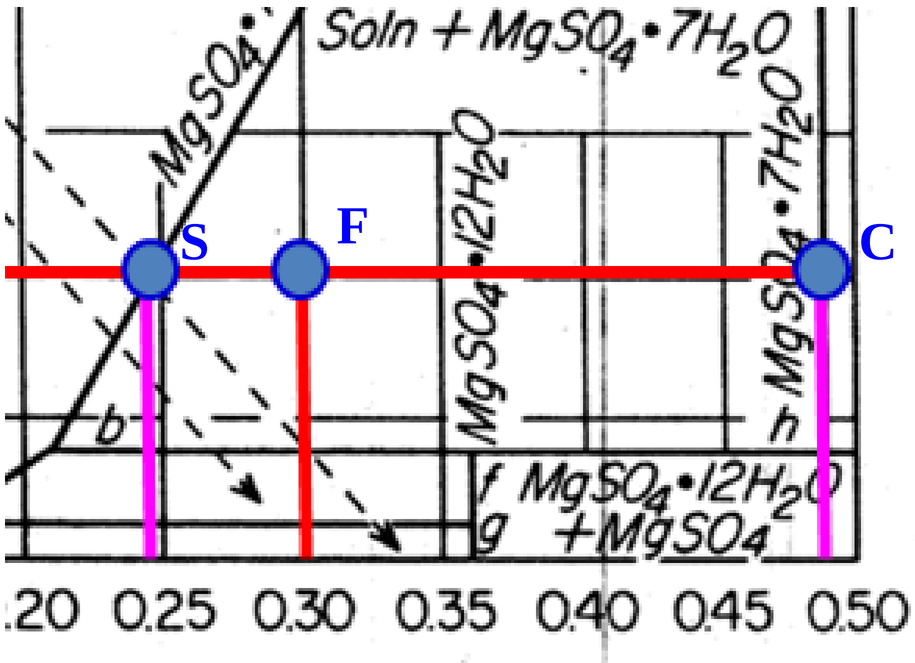
Total MB: $$1000 = 35 + S + C \quad (2)$$

Yields material balances in crystallization

Solving Eqn. (1) & (2) simultaneously to obtain:
C = 261 kg of $MgSO_4 .7H_2O$ crystals ; S = 704 kg solution

Remark. For W=0, the problem can be also solved using lever-arm rule:

$$\frac{C}{F} = \frac{\overline{SF}}{\overline{SC}}$$



Heat effects and heat balances in crystallization

- When a compound, whose solubility increases as temperature increases, dissolves, there is an absorption of heat, called the ***heat of solution.***
- An evolution of heat occurs when the solubility decreases as the temperature increases.
- For compound dissolving whose solubility does NOT change with temperature, there is neither absorption nor evolution of heat; **See Table 17.5 in slide 13.**
- **In crystallization, the opposite to dissolution occurs**, at **equilibrium** the heat of crystallization is equal to the negative of the heat of solution at the same concentration in solution:

$$\Delta h_{crys} = -\Delta h_{sol}^{sat}$$

Heat effects and heat balances in crystallization

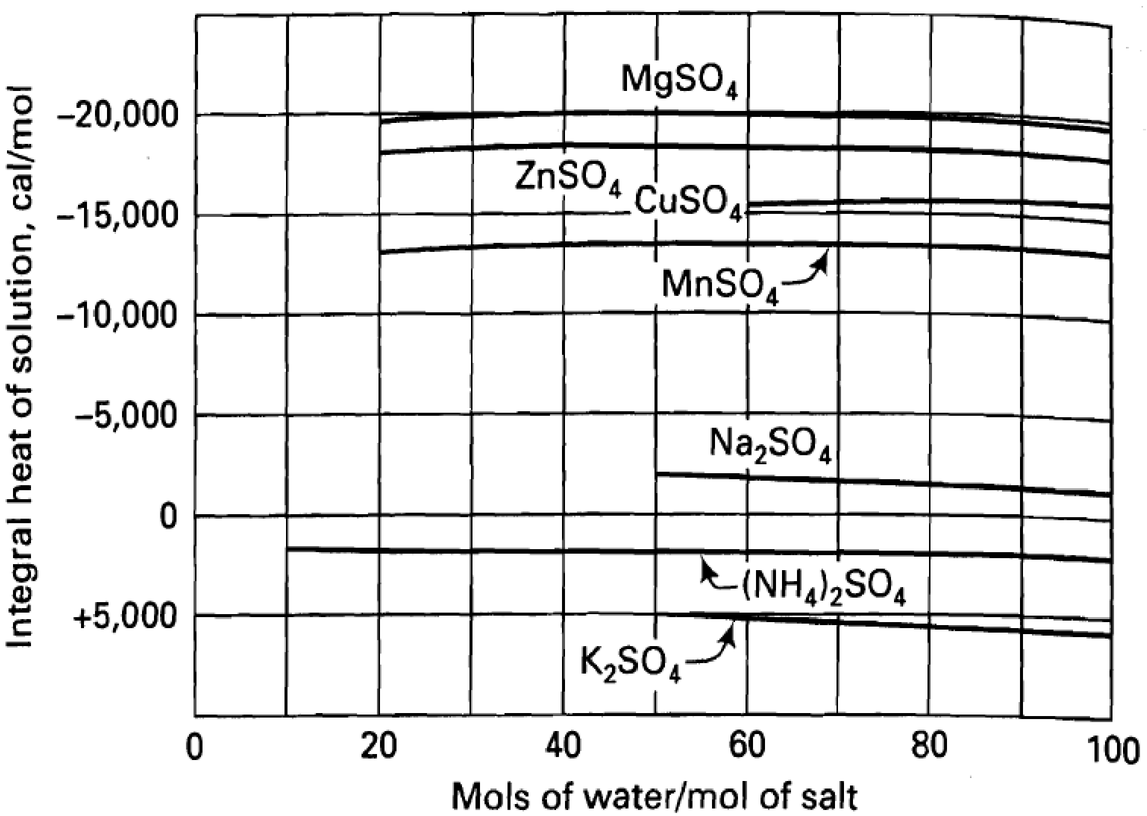
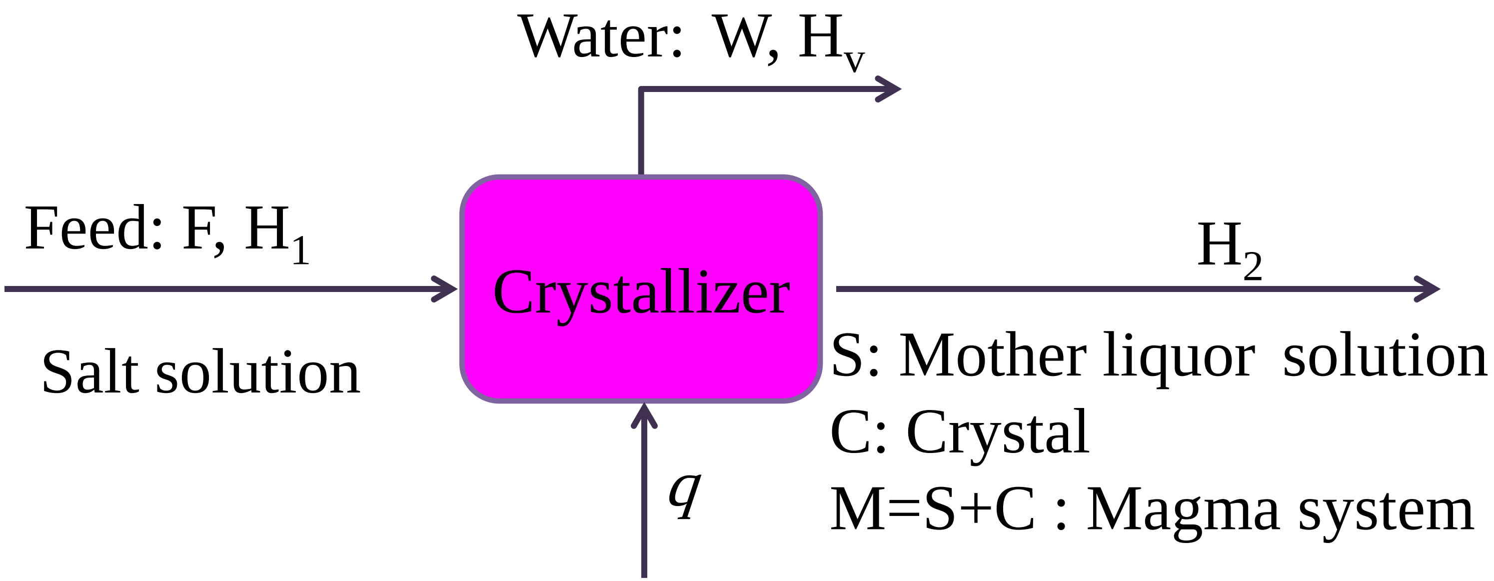


Figure 17.9 Integral heats of solution for sulfates in water at 25°C.

Heat effects and heat balances in crystallization



- By applying energy balance, the total heat is:

$$q = (S + C)h_2 + Wh_v - Fh_1 = (H_2 + H_v) - H_1$$

If q is **positive, heat must be added to the crystallizer**. If it is **negative, heat is evolved or given off**. Where H_1, H_2, and H_v are total enthalpies in kJ. While h_1,h_2, and h_v are specific enthalpies at the corresponding temperatures.

Heat effects and heat balances in crystallization

- **If enthalpy-concentration diagrams are used an in evaporation:**
  - The specific enthalpy h_1 of the entering solution at the initial temperature can be read off the enthalpy-concentration chart , where.
  - The enthalpy h_2 of the final mixture of crystals and mother liquor at the final temperature is also read off.

- **If some evaporation occurs, the specific enthalpy, h_v of the water vapor is obtained from the steam tables.**

- When average heat capacity of solution is used, the energy balance becomes:

$$q = F\overline{C}_{p,sol}(T_2 - T_1) - C\Delta h_{\text{crys}} - Wh_v$$

Heat effects and heat balances in crystallization

$MgSO_4 + H_2O$ system
Reference (datum) = liquid water at 32 °F (°0C)

Region	Temperature Range, °F	Phases
pae	25–32	ice and aqueous solution of $MgSO_4$
ea	25	ice and eutectic mixture
ag	25	eutectic and $MgSO_4 \cdot 12H_2O$
abfg	25–37.5	saturated solution and $MgSO_4 \cdot 12H_2O$
bcih	37.5–118.8	saturated solution and $MgSO_4 \cdot 7H_2O$
cdlj	118.8–154.4	saturated solution and $MgSO_4 \cdot 6H_2O$
dqrk	154.4–	saturated solution and $MgSO_4 \cdot H_2O$

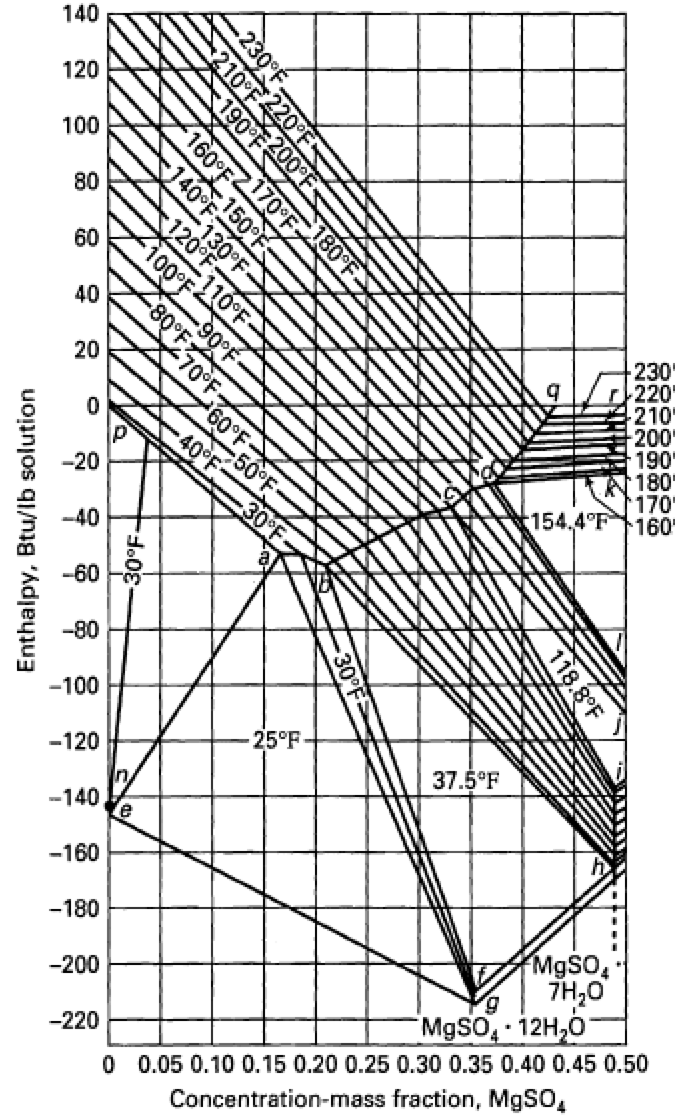


Figure 17.10 Enthalpy-concentration diagram for the $MgSO_4$-H_2O system at 1 atm.

Heat effects and heat balances in crystallization

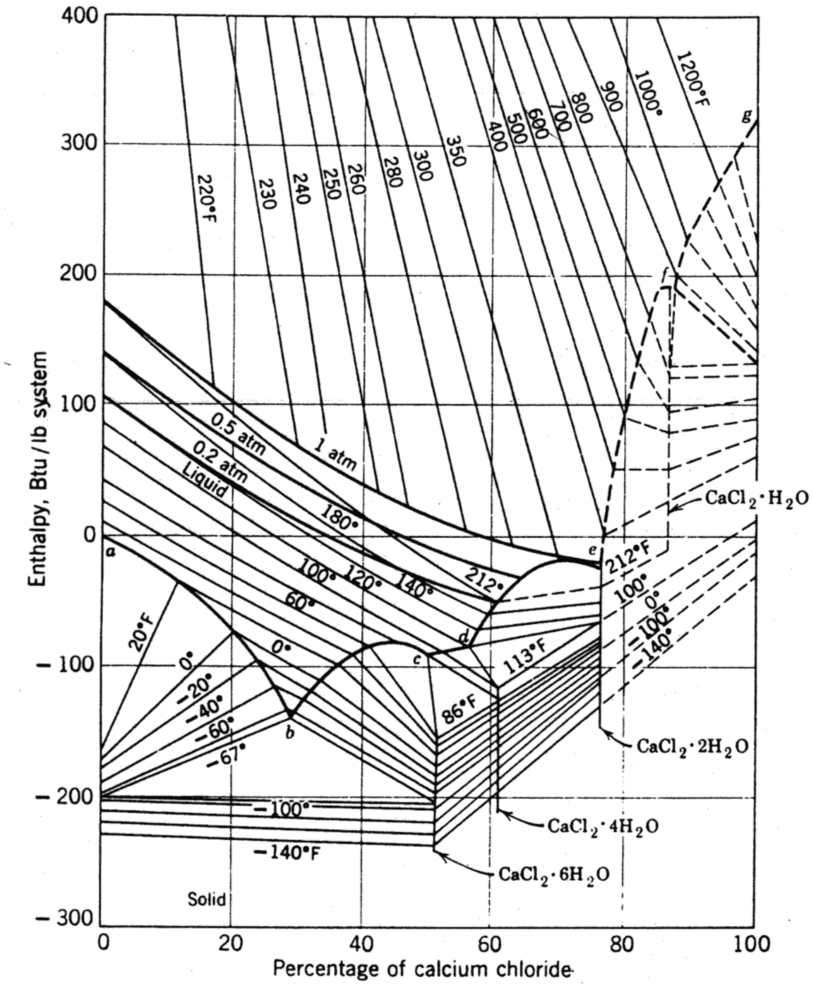


Figure 19.29. Enthalpy-concentration diagram for the $CaCl_2$—H_2O system. [Hougen, Watson, Ragatz, *Chemical Process Principles*, Part I, 2nd ed., John Wiley & Sons, New York, (1954).]

Heat effects and heat balances in crystallization

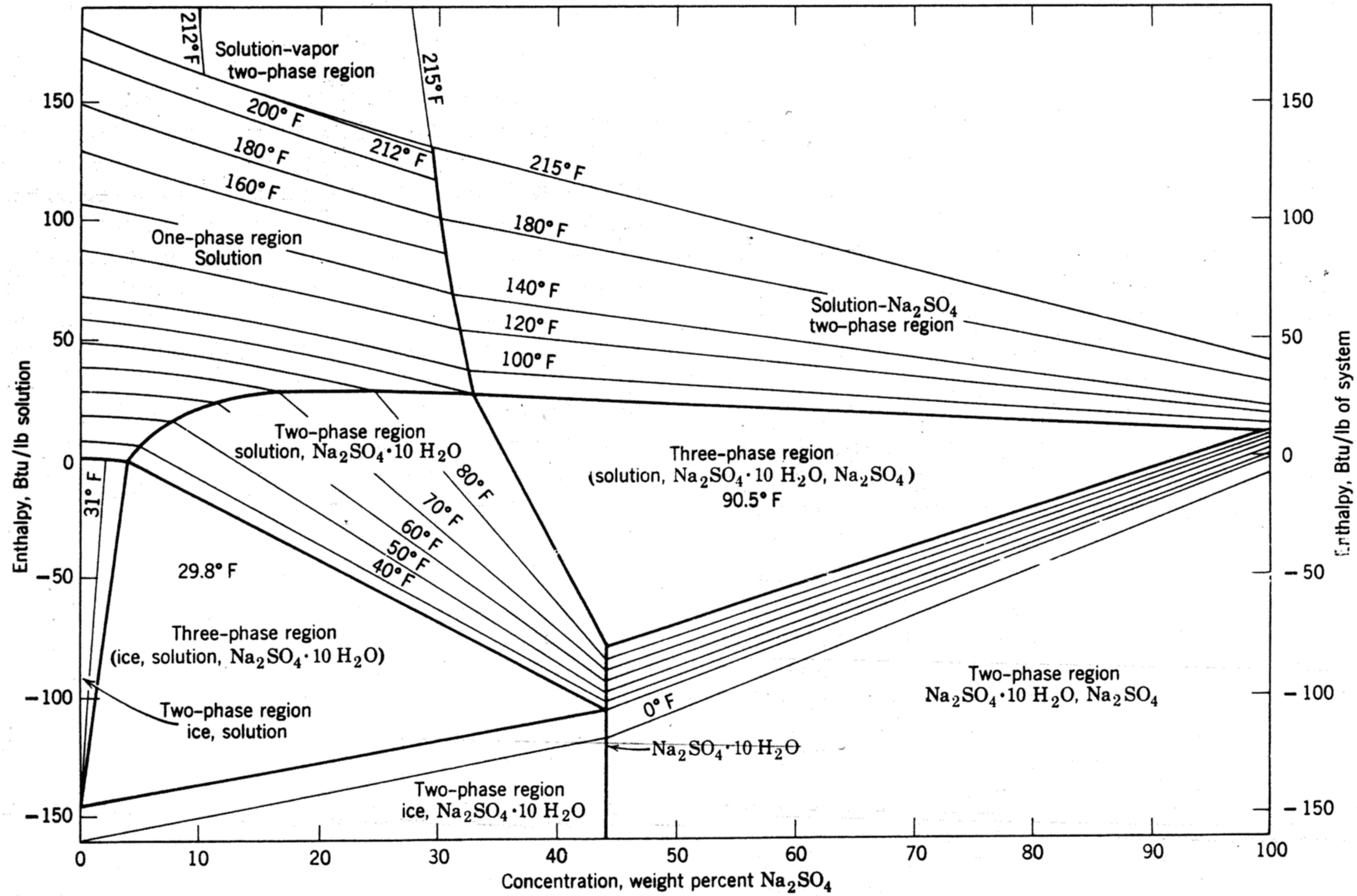


Figure 19.28. Enthalpy-concentration diagram for the Na_2SO_4—H_2O system at 1 atm total pressure. Bases: $H = 0$ for water at 32°F and the triple point pressure, $H = 0$ for Na_2SO_4 solid at 32°F and at 1 atm pressure.

Heat effects and heat balances in crystallization

Example. 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 $MgSO_4 \cdot 7H_2O$ 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 -13.31×10^3 kJ/kg mol $MgSO_4 \cdot 7H_2O$. **Calculate the yield of crystals and make a heat balance to determine the total heat absorbed, *q*, assuming that no water is vaporized.**

Solution:

Making a water balance and a balance for $MgSO_4$ as in previous examples gives:

C = 616.9 kg $MgSO_4 \cdot 7H_2O$ crystals
S = 1651.1 kg solution.

Heat effects and heat balances in crystallization

- The molecular weight of $MgSO_4 \cdot 7H_20$ is 246.49.
- The heat of solution (at 18 ºC) is:

$$\Delta h^{sat}{}_{sol} = \text{-}(13.31 \times 10^3 / 246.49 = \text{-}54.0 \text{ KJ/kg crystal}$$

- Then, the heat of crystallization is (at 18 ºC) is:

$$\Delta h_{crys} = -\Delta h^{sat}{}_{sol} = 54.0 \text{ KJ/kg crystal}$$

- Assuming that the heat of solution at 18 ºC is the same as the saturated temperature T_2= 20 ºC. The total heat absorbed, *q*, is

$$q = F\overline{C}_{p,sol}(T_2 - T_1) - C\Delta h_{crys} - Wh_v$$

$$= (2268)(2.93)(20 - 54.4) - (516.9)(54) - 0 = -261909 \text{ kJ}$$

Since *q* is negative, heat is given off and must be removed.

Heat effects and heat balances in crystallization

Using Enthalpy-concentration diagram

$$q = (S + C)h_2 + Wh_v - Fh_1 = F(h_2 - h_1)$$

- $MgSO_4$ mass fraction= 48.2/(48.2+100) = 0.325.
- From the diagram at x_1= 0.325, at T_1=54.4 ×1.8+32=129.9 °F: h_1=-26 Btu/lb sol
- From the diagram at x_1= 0.325, at T_1=20 ×1.8+32=68.0 °F: h_2=-77 Btu/lb sol
- F=2268 kg=5000 lbm

$$q = 5000(-77 - -26)$$

$$= -255000\,\text{Btu} = -269\,\text{kJ}$$

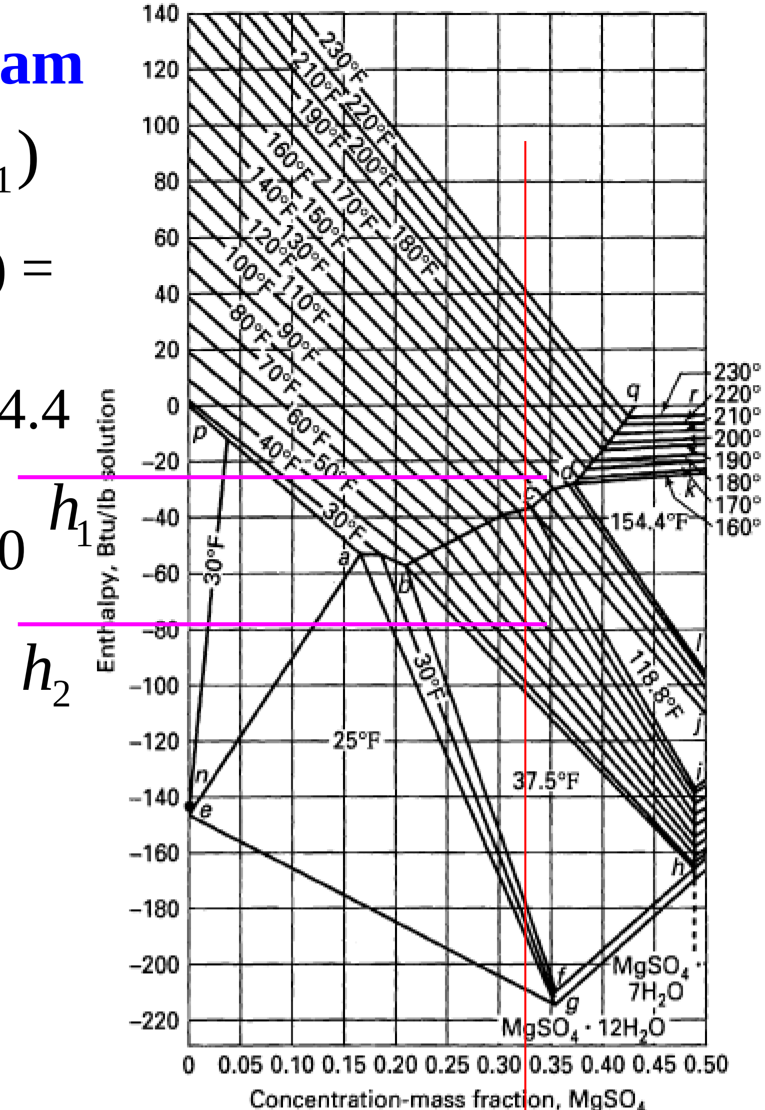


Figure 17.10 Enthalpy-concentration diagram for the $MgSO_4$-H_2O system at 1 atm.

Heat effects and heat balances in crystallization

Using Enthalpy-concentration diagram

- Also you can use enthalpy for crystal and saturated solution as:

$h_{2,satuaredsol}$

h_2

$h_{2,crystal}$

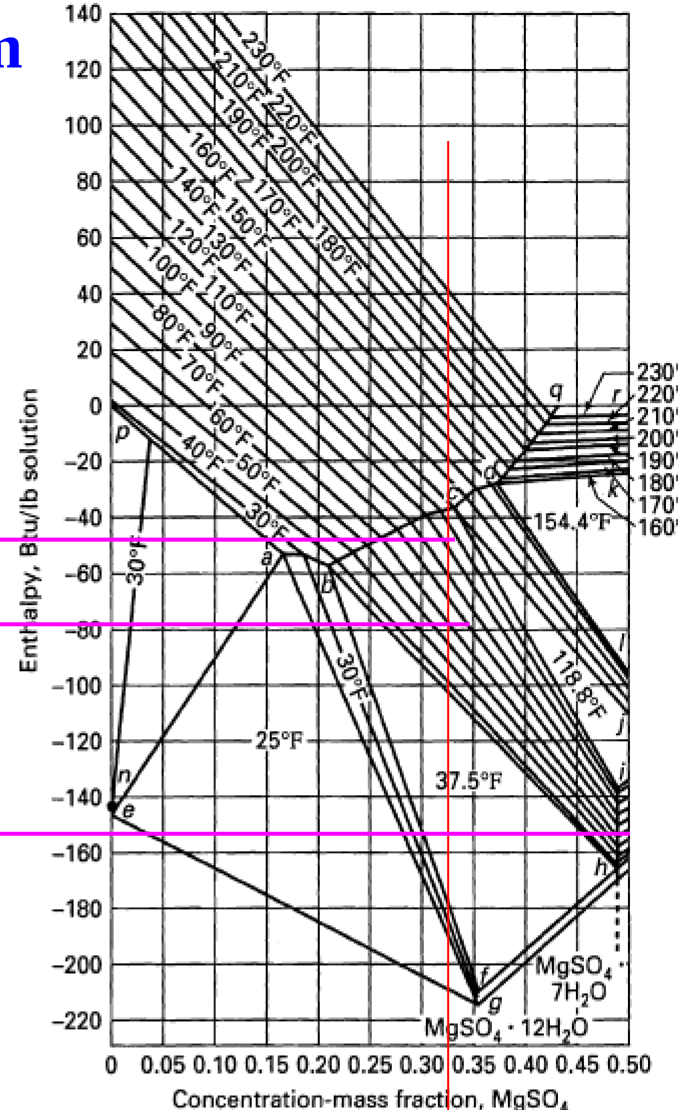


Figure 17.10 Enthalpy-concentration diagram for the $MgSO_4$-H_2O system at 1 atm.

$$(S+C)h_2 = Mh_2$$

$$= Sh_{2,satuaredsol}S + Ch_{2,crystal}$$

Heat effects and heat balances in crystallization

Example. A continuous adiabatic vacuum crystallizer is fed with 31% $MgSO_4$ solution. The equilibrium temperature of the magma in crystallizer is 86 F (30 ^oC), and the boiling point elevation of the solution is 2 ^oF (1.11 ^oC). A product magma containing 10000 lbm of $MgSO_4.7H_2O$ per hour is obtained. The volume ratio of solid to magma is 0.15; the densities of the crystals and mother liquor (sat solution) are 105 and 82.5 lbm/ft^3 respectively. Find the temperature of the feed, the feed rate, the rate of evaporation.

Solution: F=?, S=44524 lbm/h, W=? lbm/h, T_f =?

$$C = 1000\,\text{lbm/h} \qquad \rho_c = 105\ \text{lbm/ft}^3 \qquad \rho_S = 82.5\ \text{lbm/ft}^3$$

Volume ratio Eq.:

$$0.15 = \frac{C/\rho_c}{C/\rho_c + S/\rho_{ML}} = \frac{10000/105}{10000/105 + S/82.5}$$

$$\Rightarrow S = 44524\ \text{lbm/h}$$

$MgSO_4$MB:

$$(0.31)(F) = (x_S)S + x_C C = 44524 x_S + 10000\, x_C$$

Heat effects and heat balances in crystallization

- From phase diagram at 86 °F:

$$x_S = 0.28 \qquad x_C = 0.488$$

$$(0.31)(F) = 44524(0.28) + 10000(0.488)$$

$$\Rightarrow F = 55957 \text{ lbm/s}$$

Total MB: $F = S + C + W$

$$55957 = 10000 + 44524 + W$$

$$\Rightarrow W = 1433 \text{ lbm/h}$$

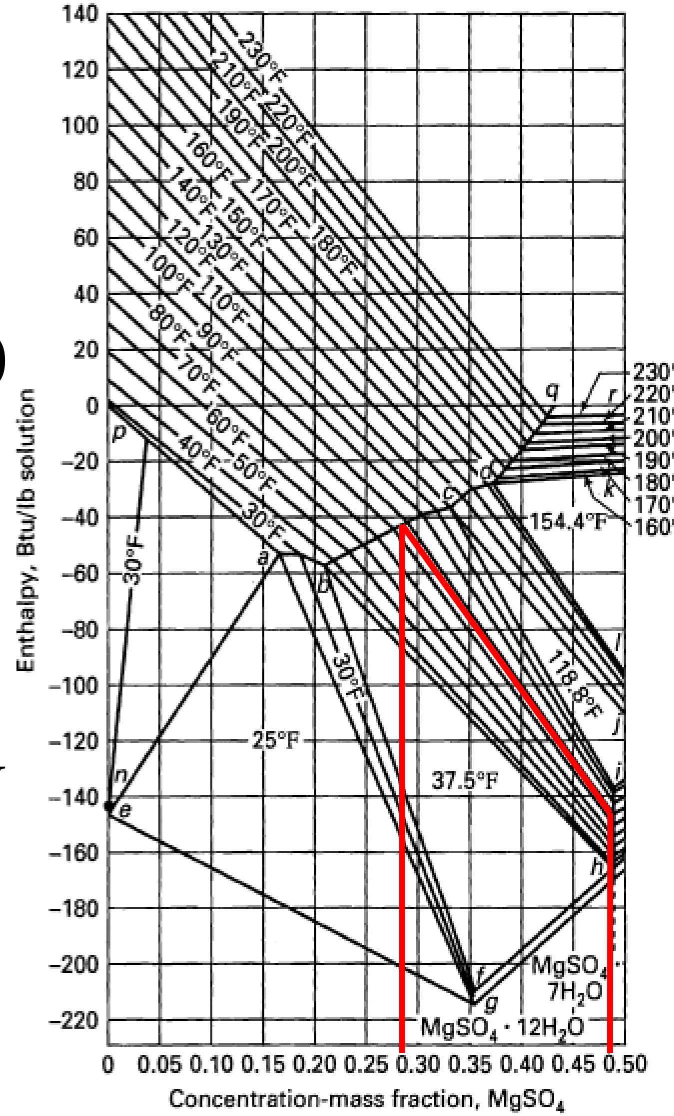


Figure 17.10 Enthalpy-concentration diagram for the $MgSO_4$-H_2O system at 1 atm.

Heat effects and heat balances in crystallization

Energy Balance:

$$q = (S + C)h_2 + Wh_v - Fh_1$$

$$\text{Adiabatic} \rightarrow q = 0$$

$$0 = (54524)h_2 + 1433h_v - 55957h_f$$

h_v :

- From steam tables:

• At saturation temperature of 86 ^oF: the saturated pressure is 0.617 psia.

•From superheated steam tables at T=86+BPE=86+2=88 ^oF and 0.617 psia: **h_v =1100 Btu/lbm**.

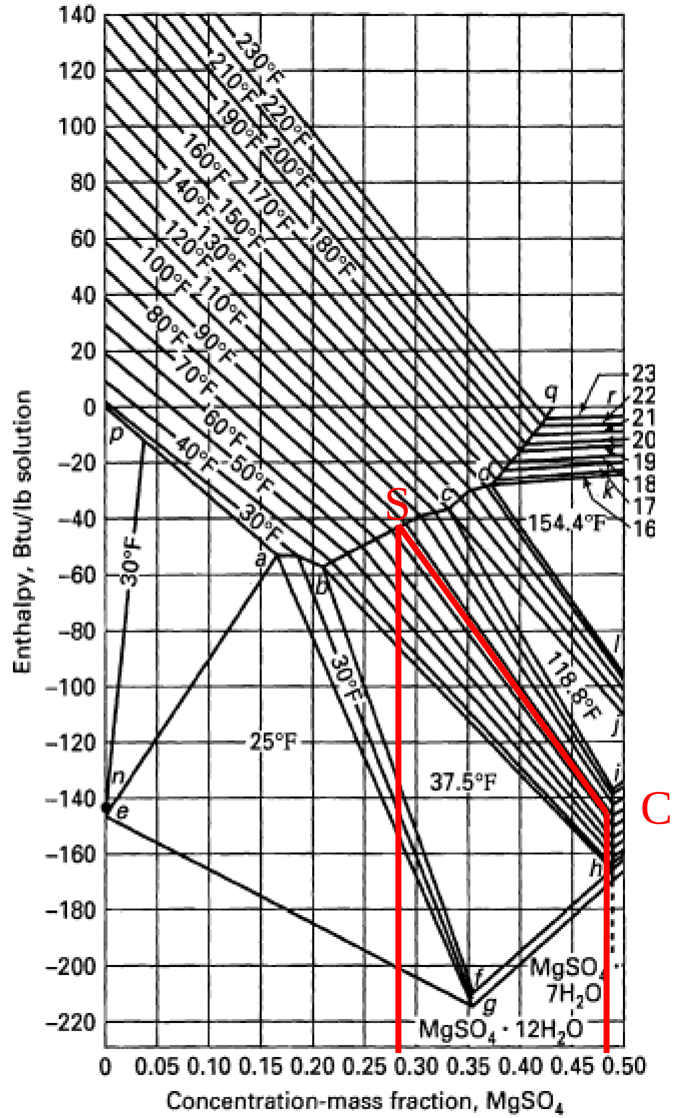


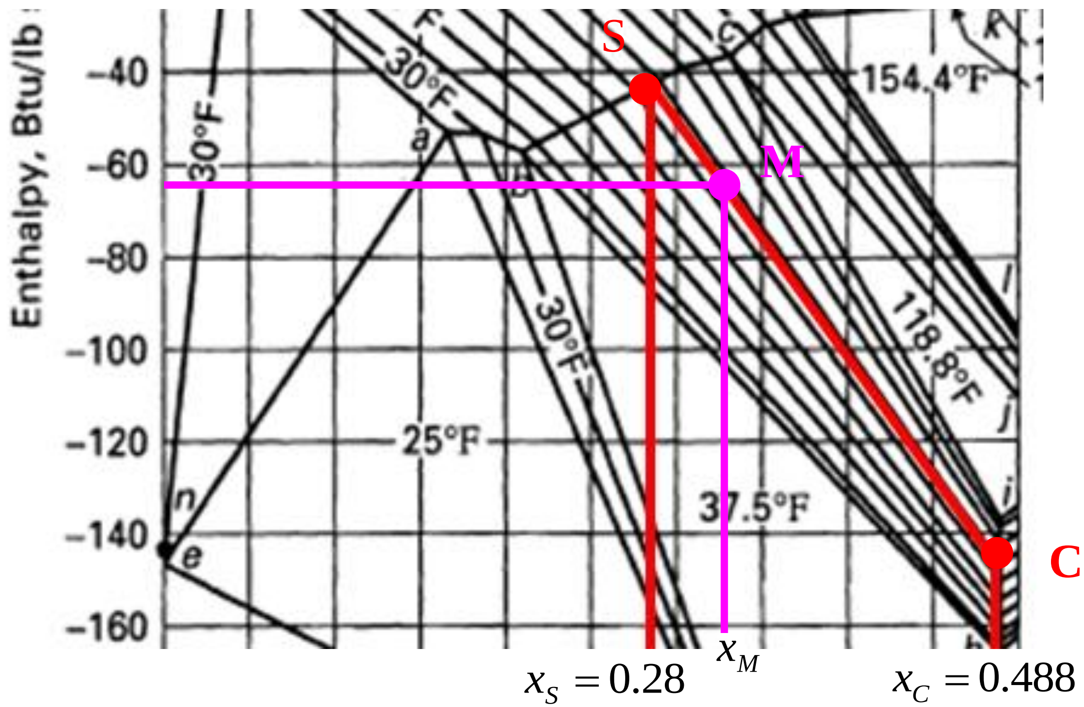
Figure 17.10 Enthalpy-concentration diagram for the $MgSO_4$-H_2O system at 1 atm.

Heat effects and heat balances in crystallization

h_2 : specific enthalpy of magma

- Apply lever-rule or mass balances to locate the M point :

$$\frac{S}{M} = \frac{S}{S+C} = \frac{44524}{54524} = 0.8166 = \frac{\overline{CM}}{\overline{SC}}$$



Measure $\overline{SC}$ to calculate $\overline{CM}$. Then M is located as shown above. At magma point M: **h_2= -64 Btu/lbm solution**.

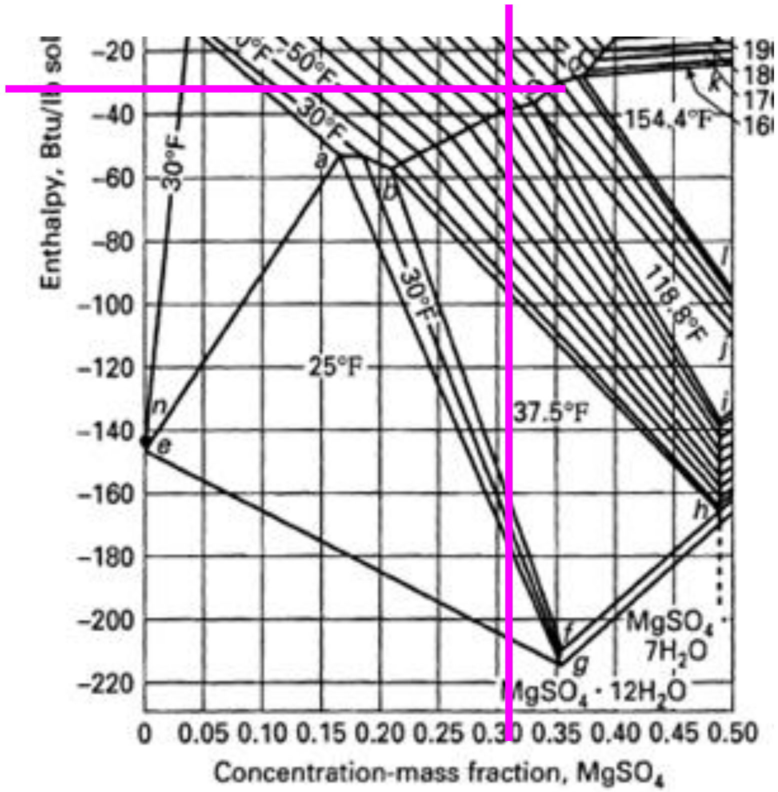
Heat effects and heat balances in crystallization

- Substitute specific enthalpies in the energy balance to get h_1:

$$0 = (54524)(-64) + 1433(1100) - 55957h_1 \Rightarrow h_1 = -34\,\text{Btu/lbm}$$

- Now from phase diagram at:

h_1 = -34 Btu/lbm and x1=0.31, the isotherm can be found to have feed temperature, T_1= 110 ^{o}F



Common equipments for crystallization

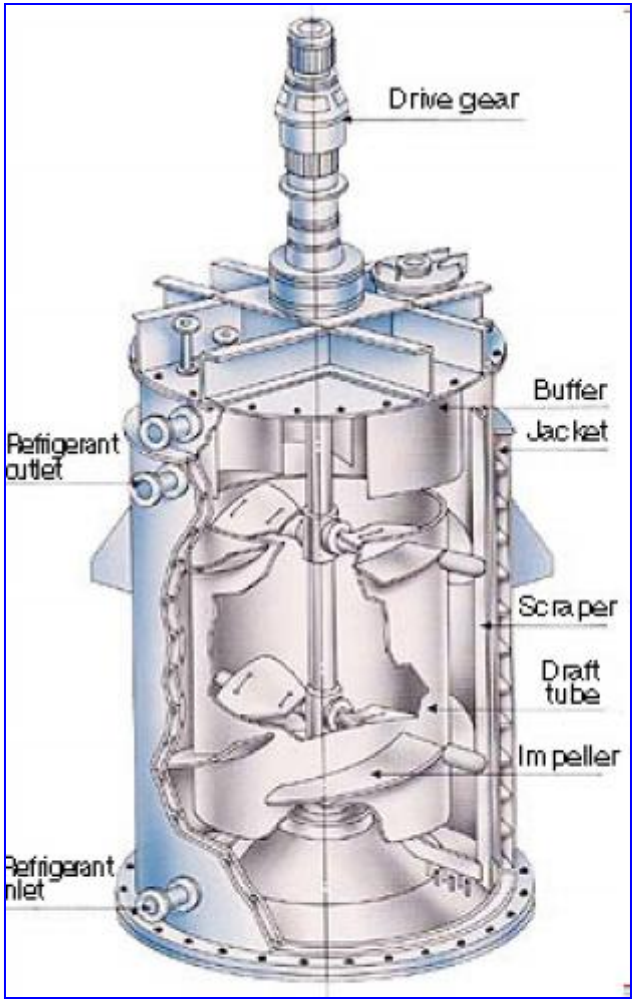
Tank Crystallizer

- Hot saturated solutions are allowed to cool in open tank.
- After a period of time, the mother liquor is drained and the crystals removed.
- Nucleation and the size of crystals are difficult to control.
- In some cases, the tank is cooled by coils or a jacket.
- agitator with moderated mixing speed is used to improve the heat transfer
- Labor costs are very high.
- It has limited application. It is sometimes used to produce certain fine chemicals and pharmaceutical products

Common equipments for crystallization

Scraped Surface Crystallizer

- One type of scraped surface crystallizer is the **Swenson-Walker crystallizer**, which consists of an open trough **0.6 m wide** with a semicircular bottom having a cooling jacket inside.
- **Slow-speed spiral agitator** rotates and suspends the growing crystals on turning.
- Blades pass close to the wall and break off any deposits of crystals on the cooled wall.
- Used in **crystallizing ice cream** and **plasticizing margarine**.
- Also called ***Votator*.**



Common equipments for crystallization

Scraped Surface Crystallizer

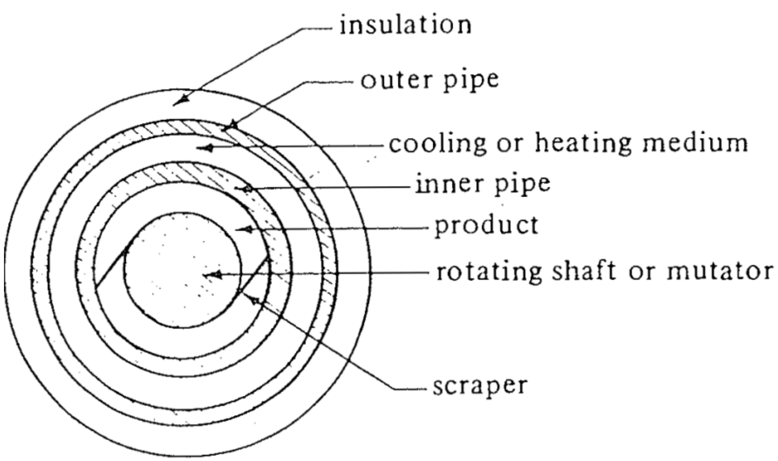


FIGURE 4.13-2. *Scraped surface heat exchanger.*

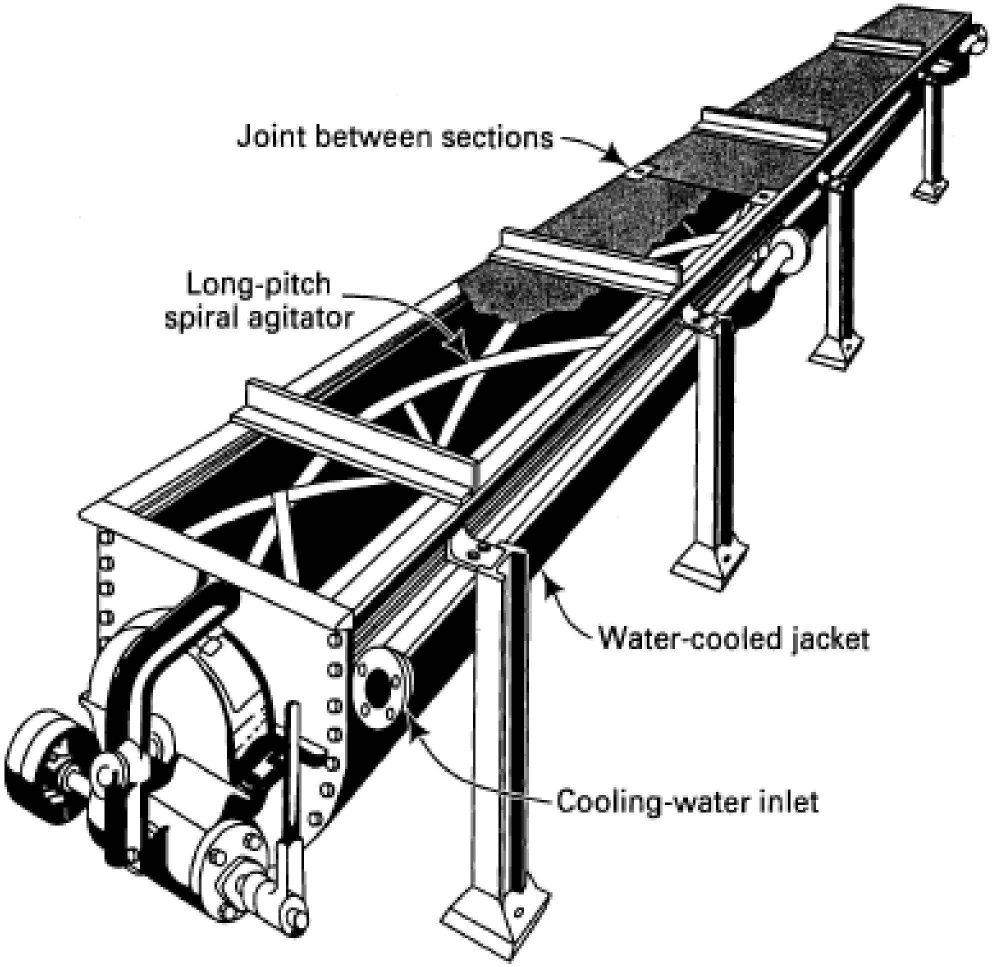
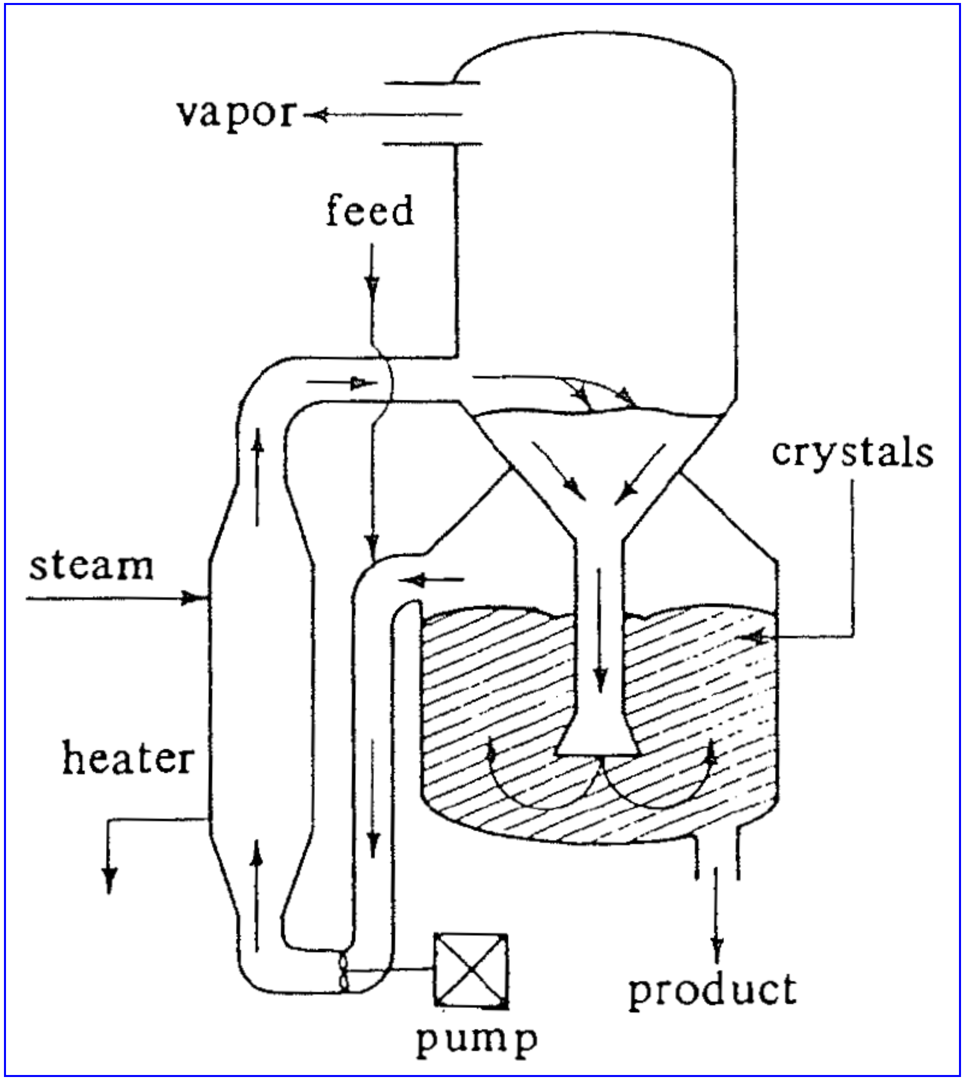


Figure 17.15 Swenson–Walker continuous, cooling crystallizer.

Common equipments for crystallization

Circulating-liquid evaporator-crystallizer

- **Supersaturation** is generated by evaporation.
- Circulating liquid is drawn by the screw pump down inside the tube side of condensing steam heater.
- **Heated liquid** then flows into the vapor space, where flash evaporation occurs, giving some supersaturation.
- The vapor leaving is condensed.
- Also called **Oslo crystallizer**.



Common equipments for crystallization

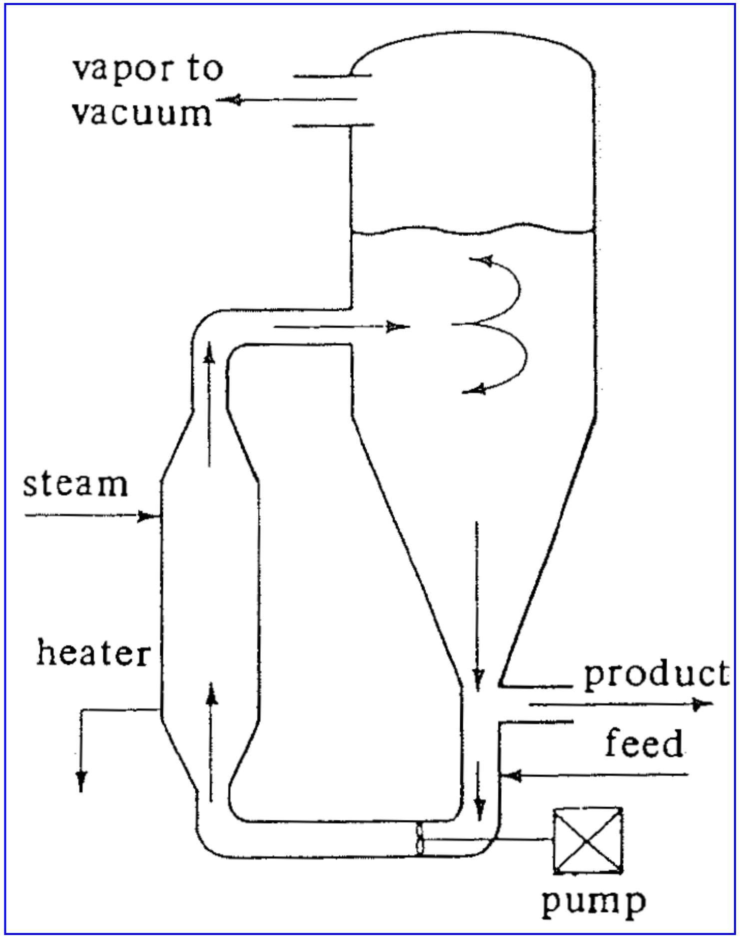
Circulating-liquid evaporator-crystallizer

- The supersaturated liquid flows down the downflow tube and then up through the bed fluidized and agitated crystals, which are growing in size.
- The leaving saturated liquid then goes back as a recycle stream to the heater, where it is joined by the entering feed.
- The larger crystals settle out and a slurry of crystals and mother liquor is withdrawn as product.

Common equipments for crystallization

Circulating-magma vacuum crystallizer

- The magma or suspension of crystals is circulated out the main body through a circulating pipe by a screw pump
- Magma flows through a heater, where its temperature is raised 2-6 K.
- The heated liquor then mixes with body slurry and boiling occurs at liquid surface
- This cause supersaturation in the swirling liquid near the surface, which results in deposits on the swirling suspended crystals until they leave again via the circulating pipe
- The vapors leave through the top
- A steam-jet ejector provides the vacuum



Selection of crystallizers

Crystalliser type	Applications	Typical uses
Tank	Batch operation, small-scale production	Fatty acids, vegetable oils, sugars
Scraped surface	Organic compounds, where fouling is a problem, viscous materials	Chlorobenzenes, organic acids, paraffin waxes, naphthalene, urea
Circulating magma	Production of large-sized crystals. High throughputs	Ammonium and other inorganic salts, sodium and potassium chlorides
Circulating liquor	Production of uniform crystals (smaller size than circulating magma). High throughputs.	Gypsum, inorganic salts, sodium and potassium nitrates, silver nitrates

Crystal-size distribution

- Typical magmas from a crystallizer contain a distribution of crystal sizes and shapes.
- Dried crystals are screened to determine the particle sizes using:
  - **- Tyler standard screen**
  - **- U.S. standard screens ASTM EII**
- The most common methods for measuring particle size are listed in the table below:

Table 17.3 Methods of Measuring Particle Size

Method	Size Range, Microns
Woven-wire screen	32–5600
Coulter electrical sensor	1–200
Gravity sedimentation	1–50
Optical microscopy	0.5–150
Laser-light scattering	0.04–2000
Centrifugal sedimentation	0.01–5
Electron microscopy	0.001–5

Crystal-size distribution

Table 17.4 U.S. Standard Screens ASTM EII

	Opening of Square Aperture		
Mesh Number	in.	mm	µm
3-1/2	0.220	5.60	5600
4	0.187	4.75	4750
5	0.157	4.00	4000
6	0.132	3.35	3350
7	0.110	2.80	2800
8	0.0929	2.36	2360
10	0.0787	2.00	2000
12	0.0669	1.70	1700
14	0.0551	1.40	1400
16	0.0465	1.18	1180
18	0.0394	1.000	1000
20	0.0335	0.850	850
25	0.0280	0.710	710
30	0.0236	0.600	600
35	0.0197	0.500	500
40	0.0167	0.425	425
45	0.0140	0.355	355
50	0.0118	0.300	300
60	0.00984	0.250	250
70	0.00835	0.212	212
80	0.00709	0.180	180
100	0.00591	0.150	150
120	0.00492	0.125	125
140	0.00417	0.106	106
170	0.00354	0.090	90
200	0.00295	0.075	75
230	0.00248	0.063	63
270	0.00209	0.053	53
325	0.00177	0.045	45
400	0.00150	0.038	38
450	0.00126	0.032	32

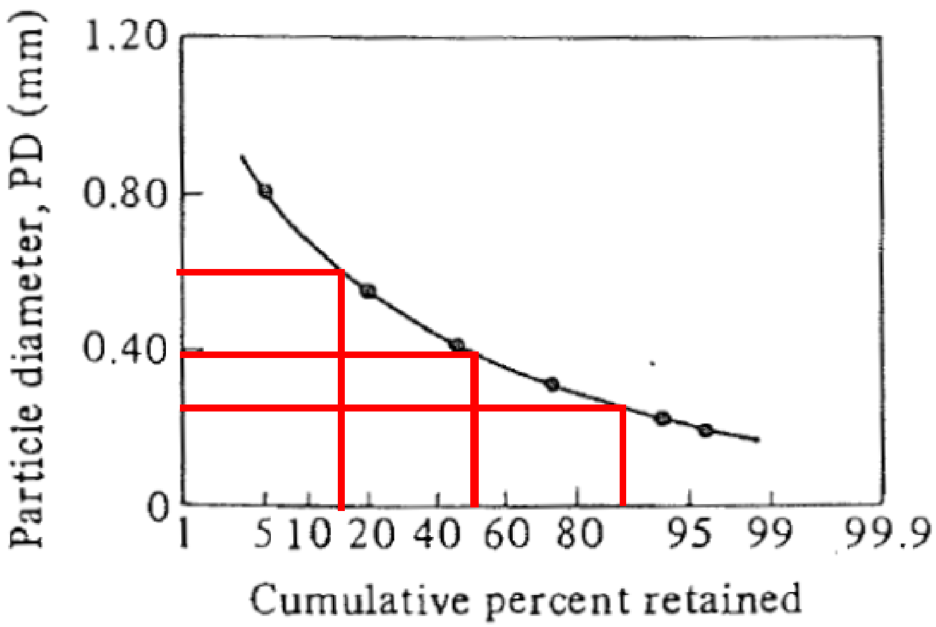
A.5-3 Tyler Standard Screen Scale

Sieve Opening		Nominal Wire Diameter		
mm	in. (approx. equivalents)	mm	in. (approx. equivalents)	Tyler Equivalent Designation
26.9	1.06	3.90	0.1535	1.050 in.
25.4	1.00	3.80	0.1496	
22.6	0.875	3.50	0.1378	0.883 in.
19.0	0.750	3.30	0.1299	0.742 in.
16.0	0.625	3.00	0.1181	0.624 in.
13.5	0.530	2.75	0.1083	0.525 in.
12.7	0.500	2.67	0.1051	
11.2	0.438	2.45	0.0965	0.441 in.
9.51	0.375	2.27	0.0894	0.371 in.
8.00	0.312	2.07	0.0815	$2\frac{1}{2}$ mesh
6.73	0.265	1.87	0.0736	3 mesh
6.35	0.250	1.82	0.0717	
5.66	0.223	1.68	0.0661	$3\frac{1}{2}$ mesh
4.76	0.187	1.54	0.0606	4 mesh
4.00	0.157	1.37	0.0539	5 mesh
3.36	0.132	1.23	0.0484	6 mesh
2.83	0.111	1.10	0.0430	7 mesh
2.38	0.0937	1.00	0.0394	8 mesh
2.00	0.0787	0.900	0.0354	9 mesh
1.68	0.0661	0.810	0.0319	10 mesh
1.41	0.0555	0.725	0.0285	12 mesh
1.19	0.0469	0.650	0.0256	14 mesh
1.00	0.0394	0.580	0.0228	16 mesh
0.841	0.0331	0.510	0.0201	20 mesh
0.707	0.0278	0.450	0.0177	24 mesh
0.595	0.0234	0.390	0.0154	28 mesh
0.500	0.0197	0.340	0.0134	32 mesh
0.420	0.0165	0.290	0.0114	35 mesh
0.354	0.0139	0.247	0.0097	42 mesh
0.297	0.0117	0.215	0.0085	48 mesh
0.250	0.0098	0.180	0.0071	60 mesh
0.210	0.0083	0.152	0.0060	65 mesh
0.177	0.0070	0.131	0.0052	80 mesh
0.149	0.0059	0.110	0.0043	100 mesh
0.125	0.0049	0.091	0.0036	115 mesh
0.105	0.0041	0.076	0.0030	150 mesh
0.088	0.0035	0.064	0.0025	170 mesh
0.074	0.0029	0.053	0.0021	200 mesh
0.063	0.0025	0.044	0.0017	250 mesh
0.053	0.0021	0.037	0.0015	270 mesh
0.044	0.0017	0.030	0.0012	325 mesh
0.037	0.0015	0.025	0.0010	400 mesh

Crystal-size distribution

- It is common to characterize the particle size distribution by the mean particle diameter and the coefficient of variation (CV), as percent:

$$CV = 100\frac{PD_{16\%} - PD_{84\%}}{2PD_{50\%}}$$



Crystal-size distribution

- Some crystal shapes might require two characteristic dimensions, while one might suffice for others.
- One solution to this problem, which is particularly applicable to the correlation of transport rates involving particles, is to relate the irregular-shaped particle to a sphere by the sphericity *defined as*.

$$\psi = \frac{\text{surface area of a sphere with the same volume as the particle}}{\text{surface area of the particle}}$$

For a sphere, $\psi = 1$, while for all other particles, $\psi < 1$

For a spherical particle of diameter, D_p, the surface area, s_p, to volume, υ_p, ratio is

$$(s_p/\upsilon_p)_{\text{sphere}} = (\pi D_p^2)/(\pi D_p^3/6) = 6/D_p$$

Therefore, ψ becomes

$$\psi = \frac{6}{D_p}\left(\frac{\upsilon_p}{s_p}\right)_{\text{particle}}$$

Crystal-size distribution

Example. Estimate the sphericity of a cube of dimension **a** on each side.

Solution:

$$\psi = \frac{6}{D_p}\left(\frac{a^3}{6a^2}\right) = \frac{a}{D_p}$$

Because the volumes of the sphere and the cube must be equal,

$$\pi D_p^3/6 = a^3$$

Solving,

$$D_p = 1.241\,a$$

Then,

$$\psi = a/(1.241\ a) = 0.806$$

Crystal-size distribution

- Particle size-distribution data are analyzed in two ways:
  - **Differential screen Analysis**
  - **Cumulative screen Analysis**

Example. Consider the following laboratory screen-analysis data presented by Graber and Taboada for crystals $Na_2SO_4.10H_2O$ (Glauber's salt) grown at about 18 °C:

Mesh Number	Aperture, D_p, mm	Mass Retained on Screen, Grams	% Mass Retained
14	1.400	0.00	0.00
16	1.180	9.12	1.86
18	1.000	32.12	6.54
20	0.850	39.82	8.11
30	0.600	235.42	47.95
40	0.425	89.14	18.15
50	0.300	54.42	11.08
70	0.212	22.02	4.48
100	0.150	7.22	1.47
140	0.106	1.22	0.25
Pan	—	0.50	0.11
		491.00	100.00

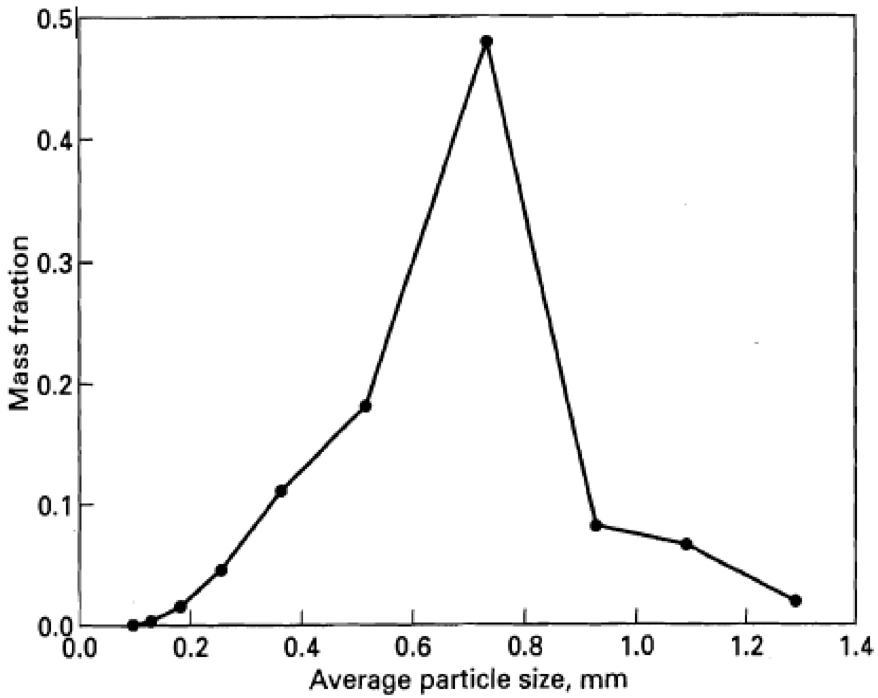
Crystal-size distribution

Differential screen-analysis of $Na_2SO_4.10H_2O$ crystals

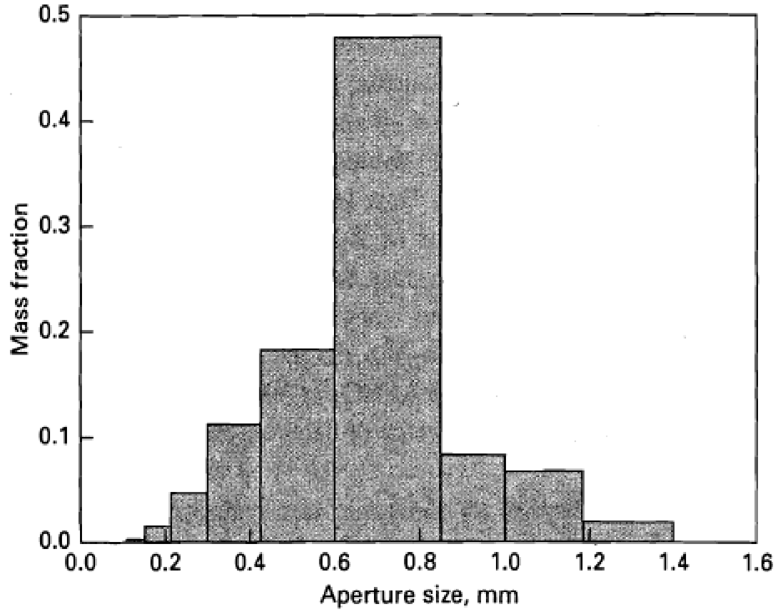
Mesh Range	$\bar{D}_p$, Average Particle Size, mm	Mass Fraction, x_i
−14 + 16	1.290	0.0186
−16 + 18	1.090	0.0654
−18 + 20	0.925	0.0811
−20 + 30	0.725	0.4795
−30 + 40	0.513	0.1815
−40 + 50	0.363	0.1108
−50 + 70	0.256	0.0448
−70 + 100	0.181	0.0147
−100 + 140	0.128	0.0025
−140 + (170)	0.098	0.0011
		1.0000

Crystal-size distribution

Differential screen-analysis of $Na_2SO_4.10H_2O$ Crystals:



(a) Differential analysis



(b) Histogram of differential analysis

Crystal-size distribution

Cumulative screen-analysis of $Na_2SO_4.10H_2O$ Crystals

Aperture, D_p, mm	Cumulative wt% Undersize	Cumulative wt% Oversize
1.400	100.00	0.00
1.180	98.14	1.86
1.000	91.60	8.40
0.850	83.49	16.51
0.600	35.54	64.46
0.425	17.39	82.61
0.300	6.31	93.69
0.212	1.83	98.17
0.150	0.36	99.64
0.106	0.11	99.89

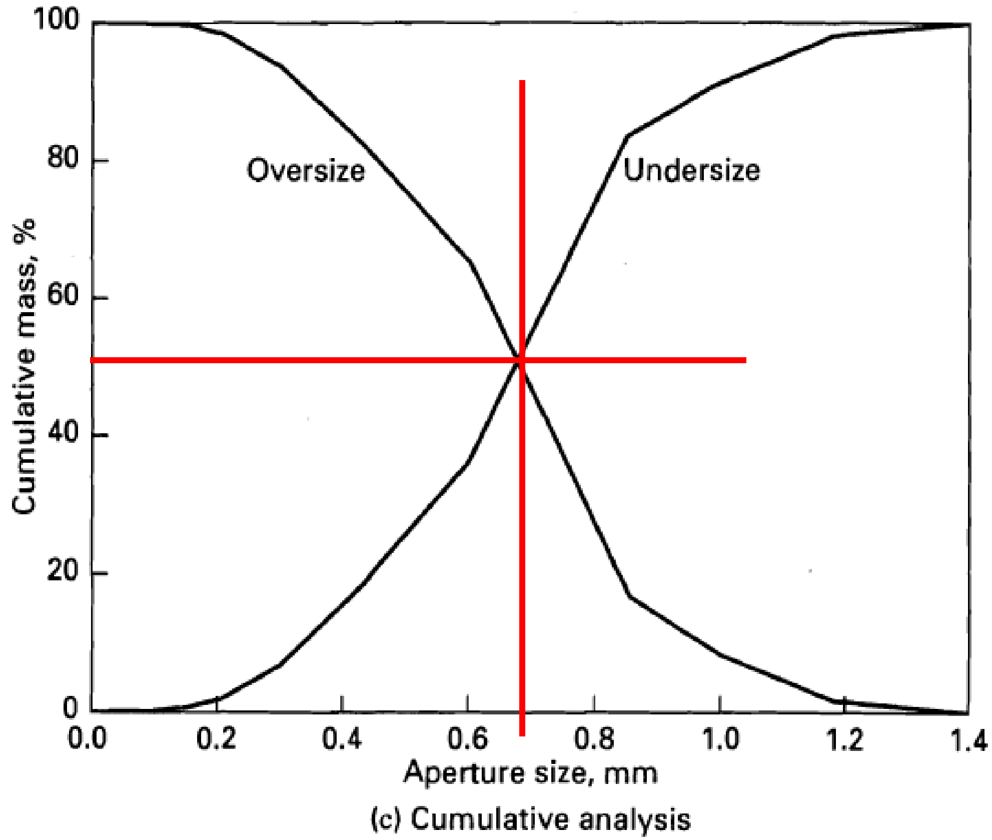


Figure 17.8 Screen analyses for data of Graber and Taboada [2].

- The two curves, which are mirror images of each other, cross at a median size where 50 wt% is larger in size and 50 wt% is smaller.

Crystal-size distribution

Mean particle size

- Different mean particle sizes are derived from screen analysis:

1. Surface-mean diameter (the specific surface area (area/mass) of a particle):

$$\bar{D}_S = \frac{1}{\sum_{i=1}^{n} \frac{x_i}{\bar{D}_{p_i}}}$$

2. Mass-mean diameter:

$$\bar{D}_W = \sum_{i=1}^{n} x_i \bar{D}_{p_i}$$

3. Arithmetic mean diameter:

$$\bar{D}_N = \frac{\sum_{i=1}^{n} \left(\frac{x_i}{\bar{D}_{p_i}^2} \right)}{\sum_{i=1}^{n} \left(\frac{x_i}{\bar{D}_{p_i}^3} \right)}$$

4. Volume-mean diameter:

$$\bar{D}_V = \left(\frac{1}{\sum \frac{x_i}{\bar{D}_{p_i}^3}} \right)^{1/3}$$

Crystal-size distribution

Example. Using the screen analysis data of $Na_2SO_4.10H_2O$ crystals, compute all four mean diameters.

$\bar{D}_p$, mm	x	$x/\bar{D}_p$	$x\bar{D}_p$	$x/\bar{D}_p^2$	$x/\bar{D}_p^3$
1.290	0.0186	0.0144	0.0240	0.0112	0.0087
1.090	0.0654	0.0600	0.0713	0.0550	0.0505
0.925	0.0811	0.0877	0.0750	0.0948	0.1025
0.725	0.4795	0.6614	0.3476	0.9122	1.2583
0.513	0.1815	0.3538	0.0931	0.6897	1.3444
0.363	0.1108	0.3052	0.0402	0.8409	2.3164
0.256	0.0448	0.1750	0.0115	0.6836	2.6703
0.181	0.0147	0.0812	0.0027	0.4487	2.4790
0.128	0.0025	0.0195	0.0003	0.1526	1.1921
0.098	0.0011	0.0112	0.0001	0.1145	1.1687
	1.0000	1.7695	0.6658	4.0032	12.5909

$$\bar{D}_S = \frac{1}{1.7695} = 0.565\ \text{mm}$$

$$\bar{D}_W = 0.666\ \text{mm}$$

$$\bar{D}_N = \frac{4.0032}{12.5909} = 0.318\ \text{mm}$$

$$\bar{D}_V = \left(\frac{1}{12.5909}\right)^{1/3} = 0.430\ \text{mm}$$

- Note that the mean diameters vary significantly.

Relationship between solubility and crystal size

- The relationship between solubility and crystal size is given quantitatively by the **Kelvin equation** (also known as the Gibbs Thompson and Ostwald equations):

$$\ln\left(\frac{c}{c_s}\right) = \left(\frac{4v_s\sigma_{s,L}}{vRT\,D_p}\right)$$

where

v_s = molar volume of the crystals

$\sigma_{s,L}$ = interfacial tension

v = number of ions/molecule of solute

c/c_s = supersaturation ratio = S

- Measured values of interfacial tension (also called surface energy) range from as low as 0.001 J/m^2 for very soluble compounds to 0.170 for compounds of low solubility.

Relationship between solubility and crystal size

Example. Determine the effect of crystal diameter on the solubility of KCl in water at 25 °C. The solution interfacial tension is 0.028 J/m^2. The density of KCl is 1980 kg/m^3.

- MW of KCl = 74.6 g/mol
- From Table 17.5, by interpolation, c_s = 35.5 g KCl/100 gH_2O
- Because KC1 dissociates into K^+ and $C1^-$, $v = 2$.

$$v_s = \frac{74.6}{1980} = 0.0376\ \mathrm{m^3/kmol}$$

$$T = 298\ \mathrm{K}$$

$$R = 8314\ \mathrm{J/kmol\text{-}K}$$

$$c = c_s \exp\left(\frac{4 v_s \sigma_{s,L}}{v R T D_p}\right)$$

$$= 35.5 \exp\left[\frac{4(0.0376)(0.028)}{2(8315)(298) D_p}\right] \text{ for } D_p \text{ in m, or}$$

$$= 35.5 \exp(0.00085/D_p, \mu\mathrm{m})$$

D_p, µm	c/c_s	c, g KCl/100 g H_2O
0.01	1.0887	38.65
0.10	1.0085	35.80
1.00	1.00085	35.53
10.00	1.000085	35.50
100.00	1.0000085	35.50

Crystallization kinetic

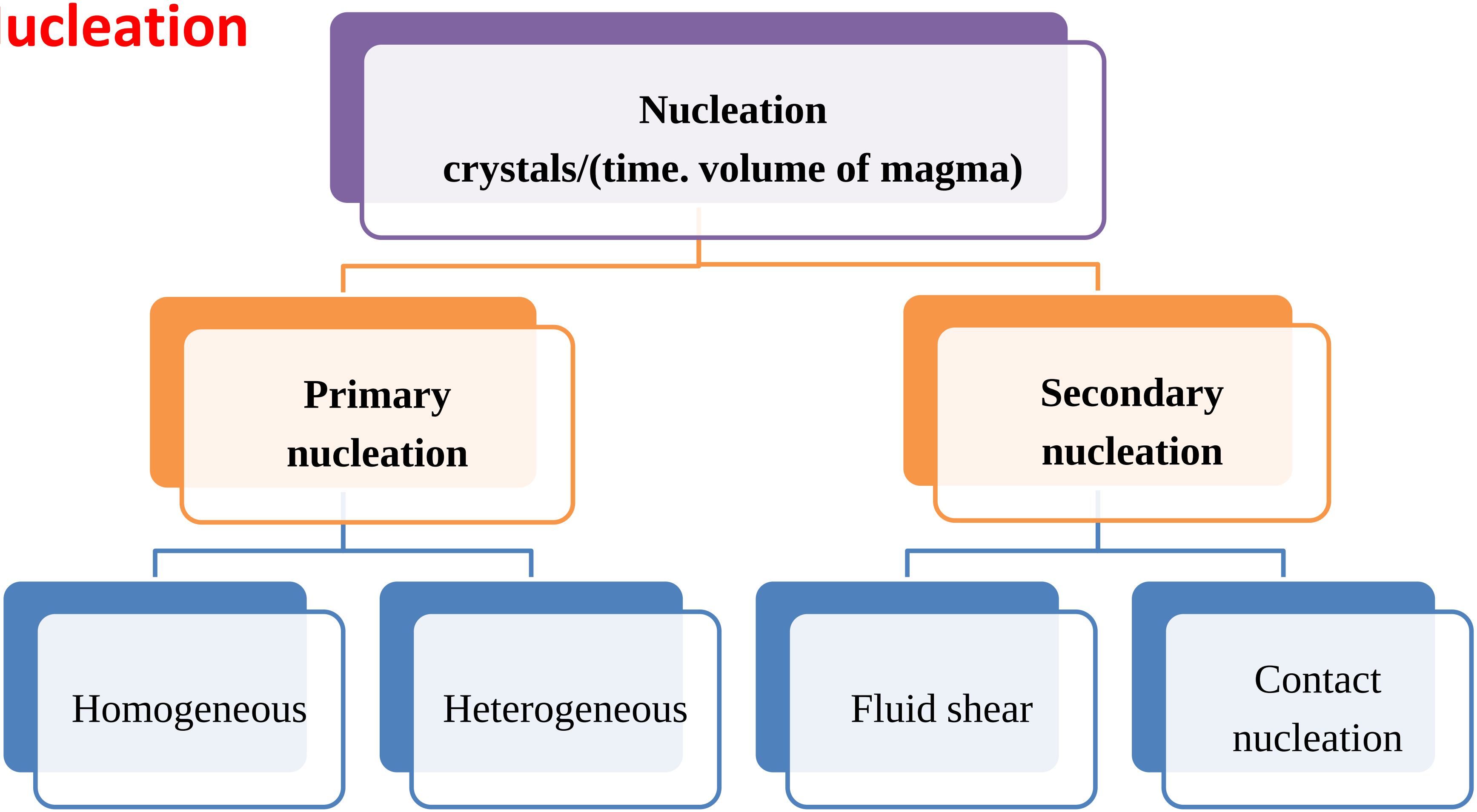
- Crystallization involves :

  1. **Nucleation (birth)**
  2. **Two-step theory of crystal growth**

- As mentioned before, driving force for crystallization is the super-saturation.

- Rates determine crystal size distribution (CSD).

Nucleation



- Homogeneous: in the absence of any foreign matter, such as dust.
- Fluid shear past crystal surfaces that sweeps away nuclei.
- Contact nucleation: Collisions of crystals with metal surfaces such as the crystallizer vessel wall or agitator blades.

Nucleation

Primary homogeneous nucleation

$$B^o = C\ Exp.\left(\frac{-16\sigma^3 v_s^{\ 2} Na}{3v^2 (RT)^3 [\ln(c/c_s)]^2}\right)$$

B^o = nucleation rate (nuclie/s.cm^3)

σ= surface energy or interfacial tension (J/m^2)

Na= Avogadro's number = 6.02×10^{26} molecule/kmol

v_s = molar volume of crystal (m^3 /kmol)

v= number of ions per molecule of solute, e.g., NaCl = 2

C = frequency factor = 10^{30} nuclei/cm^3.s for homogeneous nucleation

c/c_s = super-saturation ratio = S

- The rate of primary nucleation is extremely sensitive the supersaturation ratio (S).

Exercise. Does the nucleation of KCl crystal in water at 25 ^{o}C occurs by this method? Why?

Nucleation

Secondary nucleation

- Nucleation in industrial crystallizers occurs mainly by secondary nucleation caused by the presence of existing crystals in the supersaturated solution.
- Secondary nucleation can occur by:

1. Fluid shear past crystal surfaces that sweeps away nuclei.
2. Collisions of crystals with each other.
3. Collisions of crystals with metal surfaces such as the crystallizer vessel wall or agitator blades.

- The latter two mechanisms, which are referred to as **contact nucleation** are the **most common types since they can occur at the low values of relative supersaturation** that are typically encountered in industrial applications

Nucleation

Secondary nucleation

- **There is no theory about the complex phenomena of secondary nucleation rate**, however, the following empirical power-law is widely used:

$$B^o = k_N S^b M_T{}^j N^r$$

M^T = mass of crystals per volume of magma

N= agitation rate (e.g., rpm of an impeller)

k_N = constant determined experimentally; sensitive to crystallizer size

b = constant determined experimentally

j = constant determined experimentally

r = constant determined experimentally

S= super-saturation ratio = c/c_s

Crystal growth

- Diffusion-reaction theory (the two-step theory of crystal growth):

Step1. Mass transfer of solute from the bulk of the solution to the crystal-solution interface:

$$dm/dt = k_c A(c - c_i)$$

where

dm/dt = rate of mass deposited on the crystal surface

A = surface area of the crystal

kc = mass-transfer coefficient

c = mass solute concentration in the bulk supersaturated solution,

c_i = the supersaturated concentration at the interface.

Step 2. A first-order reaction is assumed to occur at the crystal-solution interface, in which solute molecules are integrated into the crystal-lattice structure:

$$dm/dt = k_i A(c_i - c_s)$$

Where k_i is the first-order reaction constant

Crystal growth

- Combining the previous two equations gives:

$$dm/dt = \frac{A(c - c_s)}{1/k_c + 1/k_i}$$

- Rewriting the above Eq.in terms of an overall coefficient (K_c)

$$dm/dt = K_c A(c - c_s)$$

$$1/K_c = 1/k_c + 1/k_i$$

- Typically k_c will depend on the velocity of the solution as determined by the degree of agitation (Re). At low velocities, the growth rate may be controlled by the mass-transfer step. The reaction step can be important, especially when the solution velocity past the crystal surface is high, such that k_c is very large compared to k_i.

Crystal growth

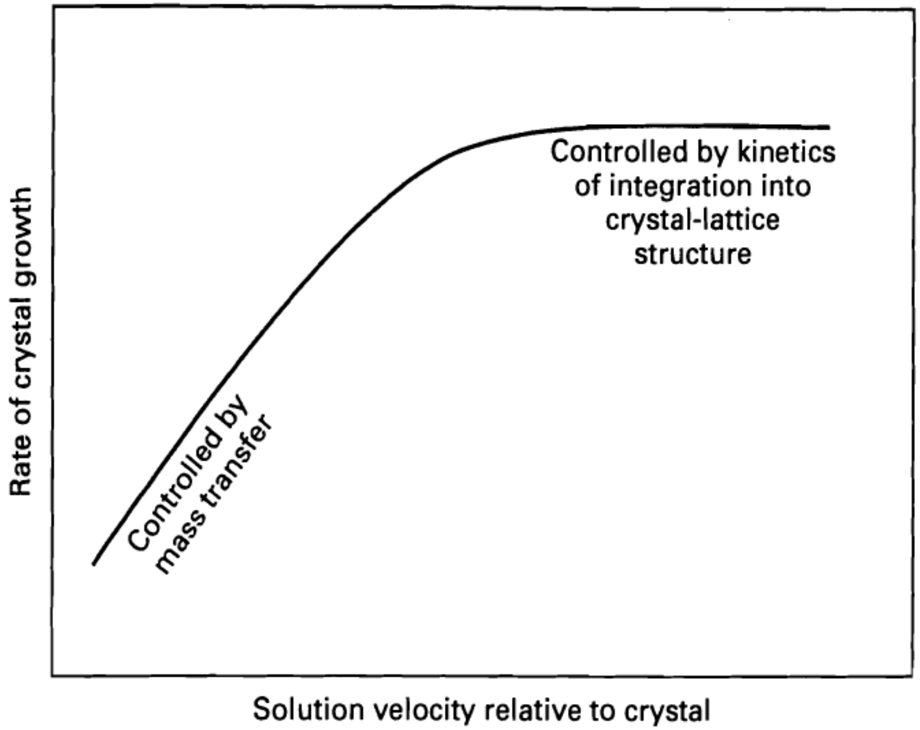


Figure 17.12 Effect of solution velocity past crystal on the rate of crystal growth.

- Many factors affects both resistances, such as:
  - Temperature (viscosity, both rates and solubility)
  - Presence of additives.
  - Mixing degree and method (mechanical agitation; fluidization circulation)

The ΔL law of crystal growth (McCabe law):

▪ **McCabe has shown that all geometrically similar crystals of the same material suspended in the same solution grow at the same rate. If growth rate is defined as:**

$$G = \frac{\Delta L}{\Delta t}$$

G = constant growth rate in time interval Δt (mm/s)
ΔL = growth of crystal length (mm)

- This law fails when surface defects or dislocations significantly alter the growth rate of a crystal face.
- This law is a reasonably accurate for many materials when the crystals are under 50 mesh in size (0.3 mm).
- It simplifies the mathematical treatment in modeling real crystallizers and is useful in predicting crystal-size distribution in many types of industrial crystallization equipment.

The ΔL law of crystal growth

- Published growth rates for some industrial and bench-scale crystallizers:

Material	G (mm/h)	T (°C)
$(NH_4)SO_4$	0.06012	70
$(NH_4)SO_4$	0.0072	20
$MgSO_4 \cdot 7H_2O$	0.11 – 0.25	25
KCl	0.07 – 0.43	32
KCl	0.119	37
KNO_3	0.293	20
K_2SO_4	0.07	10
K_2SO_4	0.216	50
NaCl	0.144 – 0.468	50

The MSMPR crystallization model

- This model is referred to as the **Mixed-Suspension, Mixed-Product-Removal** (MSMPR) model and is based on the following assumptions:

1. Continuous, steady-flow, steady-state operation.
2. Perfect mixing of the magma.
3. No classification of crystals.
4. Uniform degree of supersaturation throughout the magma.
5. Crystal growth rate independent of crystal size.
6. No crystals in the feed, but seeds are added initially.
7. No crystal breakage.
8. Uniform temperature.
9. Mother liquor in product magma in equilibrium with the crystals.
10. Nucleation rate is constant and uniform and due to secondary nucleation by crystal contact.
11. Crystal-size distribution (CSD) is uniform in the crystallizer and equal to that in the magma.
12. All crystals have the same shape, i.e, same shape factor (a).

The MSMPR crystallization model

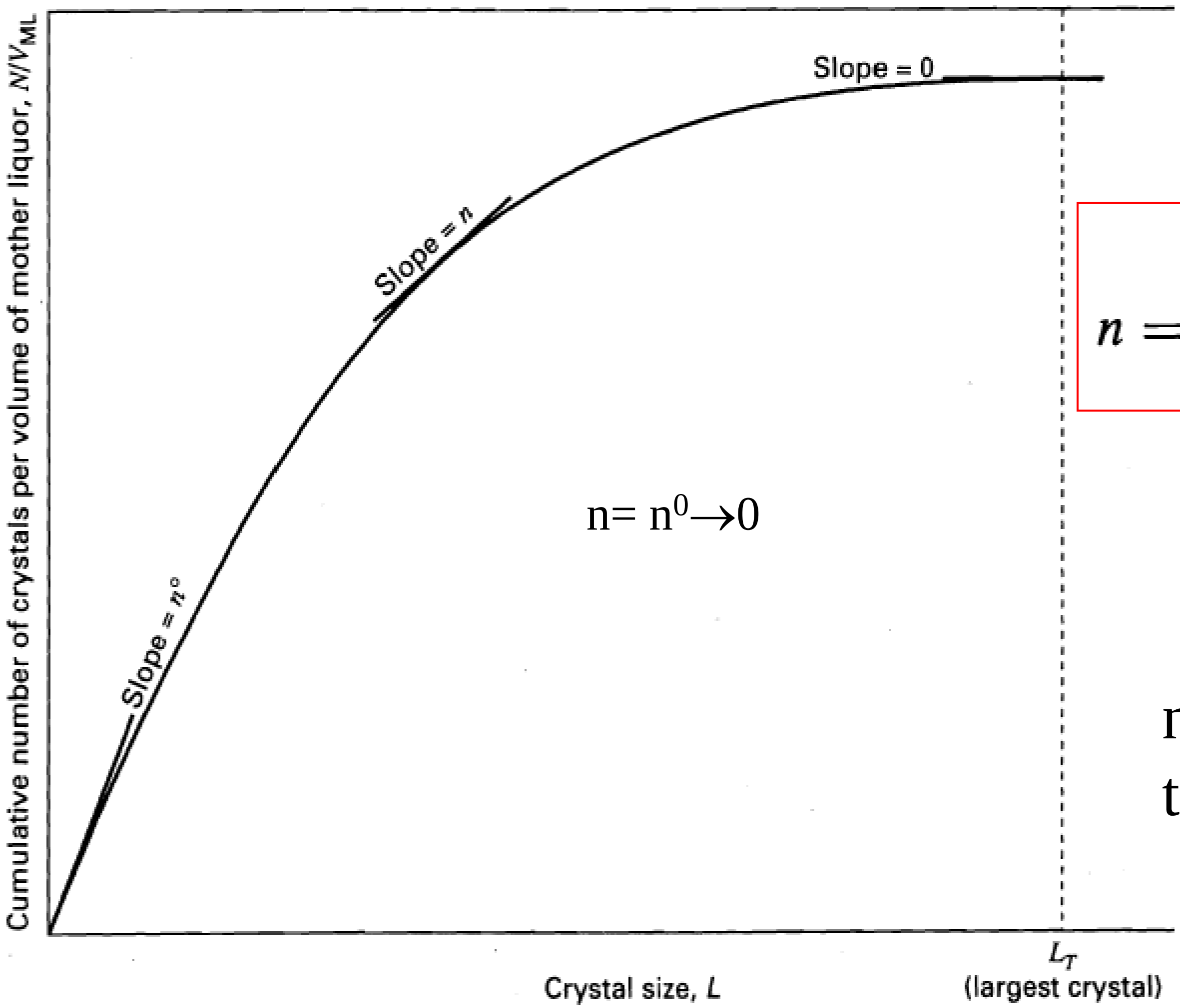
Crystal population density (*n*):

L = a characteristic crystal size (e.g., from a screen analysis)
N = cumulative number of crystals of size L and smaller in the magma in the crystallizer
V_{ML} = volume of mother liquor in the magma in the crystallizer.

n = number of crystals per unit size (L) per unit volume which is equal to the slope for plot of cumulative-numbers undersize per unit volume (N/V_{ML}) versus the crystal size L.

The MSMPR crystallization model

Crystal population density (n)



$$n = \frac{d(N/V_{ML})}{dL} = \frac{1}{V_{ML}}\frac{dN}{dL}$$

$$dN = nV_{ML}\,dL =$$

number of crystals in the size range *dL*

The MSMPR crystallization model

Crystal population balance

- **Because of the perfect mixing assumption for the magma:**

$$\frac{\text{number of crystals withdrawn}}{\text{mother-liquor volume withdrawn}} = \frac{\text{number of crystals in the crystallizer}}{\text{mother-liquor volume in the crystallizer}}$$

- **This gives:**

$$\frac{\text{number of crystals withdrawn}}{\text{number of crystals in crystallizer}} = \frac{\text{mother-liquor volume withdrawn}}{\text{mother-liquor volume in the crystallizer}}$$

number of crystals withdrawn = $\Delta n dL$

number of crystals in the crystallizer = $n dL$

mother-liquor volume withdrawn= $Q_{ML}\,\Delta t$

mother-liquor volume in the crystallizer= V_{ML}

where Q_{ML} is volumetric flow rate of mother liquor in the withdrawn product magma

The MSMPR crystallization model

Crystal population balance

- Substituting to have: $$\frac{\Delta n dL}{n dL} = -\frac{\Delta n}{n} = \frac{Q_{ML}\,\Delta t}{V_{ML}}$$
- With constant growth rate $(\Delta L = G\Delta t)$: $$-\frac{\Delta n}{\Delta L} = \frac{Q_{ML}\;n}{V_{ML}\,G}$$
- Taking the limit and rearranging as: $$-\frac{dn}{n} = \frac{dL}{G\tau}$$

Where $\tau = V_{ML}/Q_{ML}$ is the retention time of mother liquor in the crystallizer.

- Integrating the above Eq. to have: $$n = n^{o} \exp(-L/G\tau)$$

This equation is the starting point for determining **distribution curves** for crystal population, crystal size or length, crystal surface area, and crystal volume or mass.

The MSMPR crystallization model

Distribution curves for crystal population:

▪ To obtain crystal population, the number of crystals, N, per unit volume of mother liquor below size L is:

$$n = \frac{d(N/V_{ML})}{dL} = \frac{1}{V_{ML}}\frac{dN}{dL} \longrightarrow N/V_{ML} = \int_0^L n\,dL$$

▪ The total number of crystals, N_T, per unit volume of mother liquor is:

$$N_T/V_{ML} = \int_0^\infty n\,dL$$

▪ Using ($n = n^\circ \exp(-L/G\tau)$) and after integration, the cumulative number of crystals of size smaller than L, as a fraction of the total is:

$$x_n = \frac{\int_0^L n^\circ e^{-L/G\tau}\,dL}{\int_0^\infty n^\circ e^{-L/G\tau}\,dL} = 1 - \exp(-L/G\tau)$$

The MSMPR crystallization model

Distribution curves for crystal population:

- define a dimensionless crystal size as: $z = L/G\tau$

$$x_n = 1 - \exp(-L/G\tau)$$

$z = L/G\tau$

$$x_n = 1 - e^{-z}$$ **cumulative distribution of number of crystals**

$$\frac{dx_n}{dz} = e^{-z}$$ **Differential distribution of number of crystals**

The MSMPR crystallization model

Generalization for different distribution curves

- From statistics, the general moment equations is:

$$x_k = \frac{\int_0^z n z^k \, dz}{\int_0^\infty n z^k \, dz}$$

$$n = n^\circ \exp(-L/G\tau)$$

$$z = L/G\tau$$

where k is the order of the moment.

- Set k=0 (zero-order moment), for distribution of number of crystals.
- Set k=1 (first-order moment), for distribution of length or size.
- Set k=2 (second-order moment), for distribution of area.
- Set k=3 (third-order moment), for distribution of mass or volume.

The MSMPR crystallization model

Crystal distribution curves:

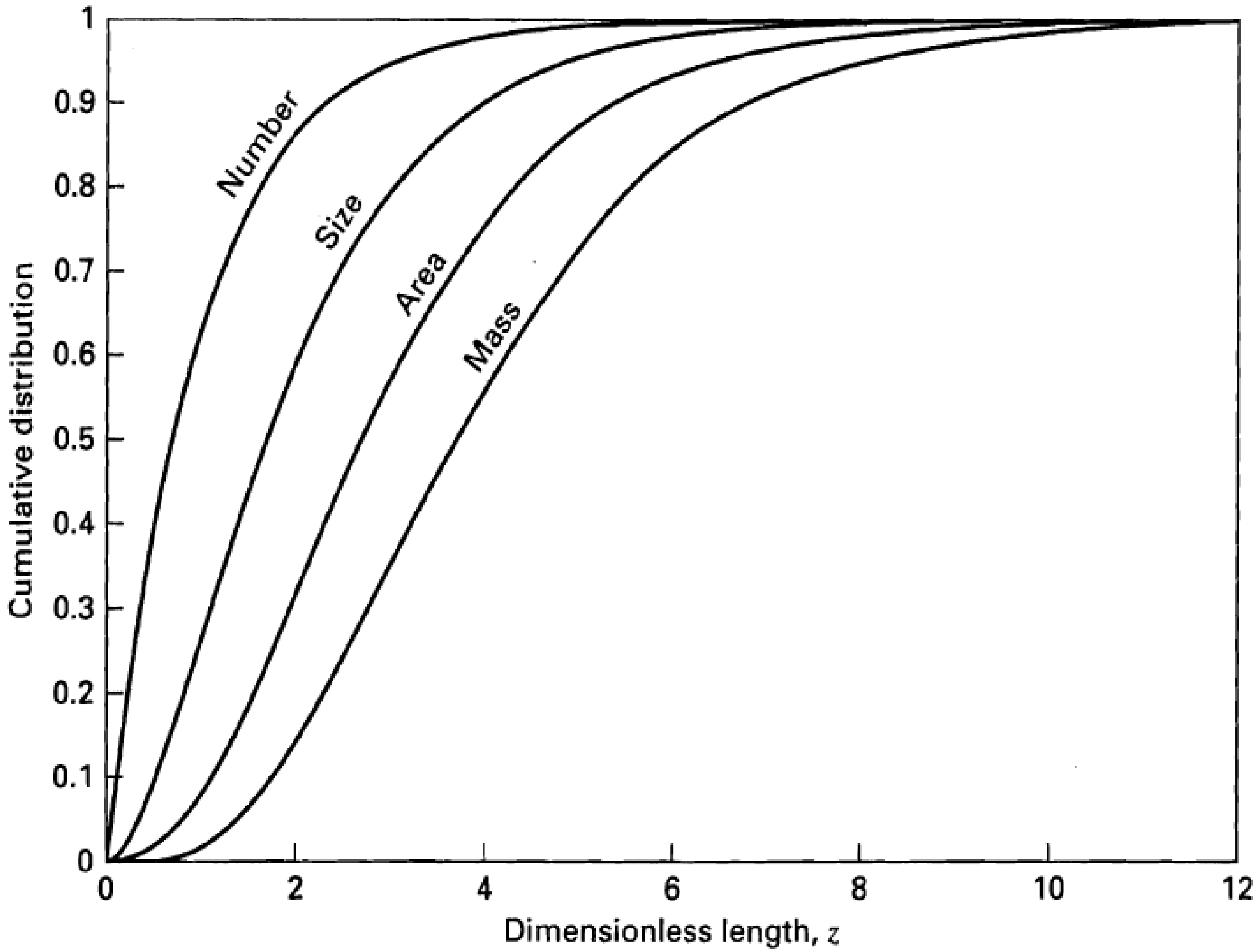
Table 17.9 Cumulative and Differential Plots for Moments of Crystal Distribution for Constant Growth Rate

Moment	Distribution Basis	Cumulative	Differential
Zeroth	Number	$x_n = 1 - e^{-z}$	$dx_n/dz = e^{-z}$
First	Size or length	$x_L = 1 - (1 + z)e^{-z}$	$dx_L/dz = ze^{-z}$
Second	Area	$x_a = 1 - \left(1 + z + \frac{z^2}{2}\right) e^{-z}$	$dx_a/dz = \frac{z^2}{2} e^{-z}$
Third	Volume or mass	$x_m = 1 - \left(1 + z + \frac{z^2}{2} + \frac{z^3}{6}\right) e^{-z}$	$dx_m/dz = \frac{z^3}{6} e^{-z}$

$z = L/G\tau$.

The MSMPR crystallization model

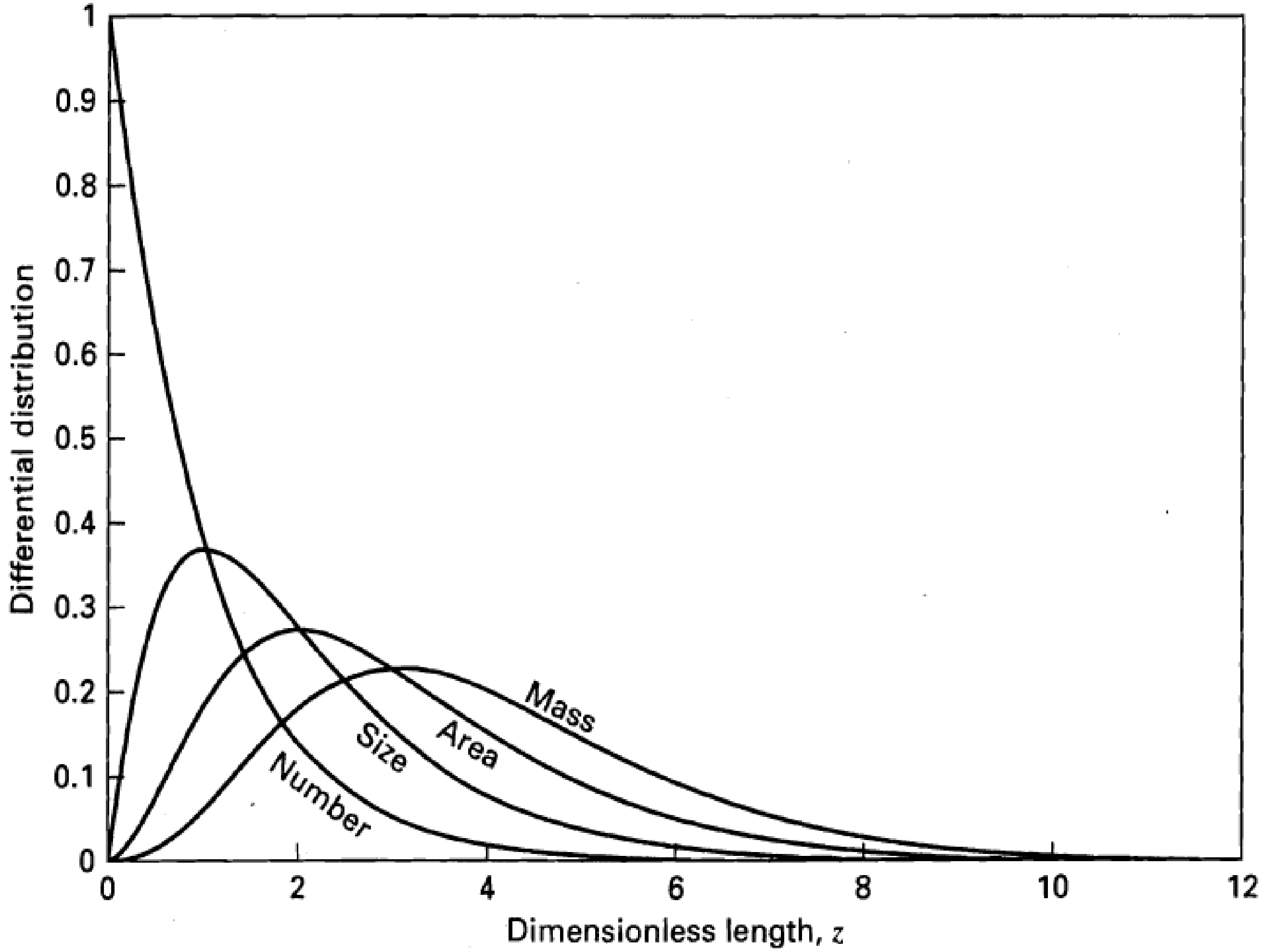
Distribution curves crystal population:



(a) Cumulative distributions

The MSMPR crystallization model

Distribution curves crystal population:



(b) Differential distributions

The MSMPR crystallization model

Average and predominant crystal size

- They are usually defined in terms of **volume or mass distribution**.

Predominant crystal size L_{pd}: it is size corresponds to the peak of the differential-mass.

Average crystal size (L_a): It is size at which 50% of the mass of product is small or larger in size than this value.

- They are of interest in the design and operation of crystallizer.

The MSMPR crystallization model

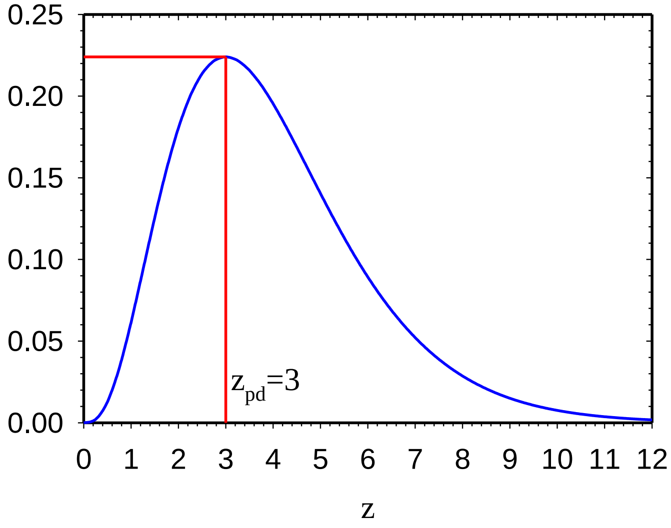
Average and predominant crystal size

Predominant crystal size L_{pd}

$$dx_m/dz = (z^3/6)e^{-z}$$

At the peak,

$$\frac{d\left(\frac{dx_m}{dz}\right)}{dz} = 0 = \frac{3z^2 e^{-z}}{6} - \frac{z^3 e^{-z}}{6}$$



$$z_{pd} = 3.00 \rightarrow L_{pd} = 3.00 G\tau$$

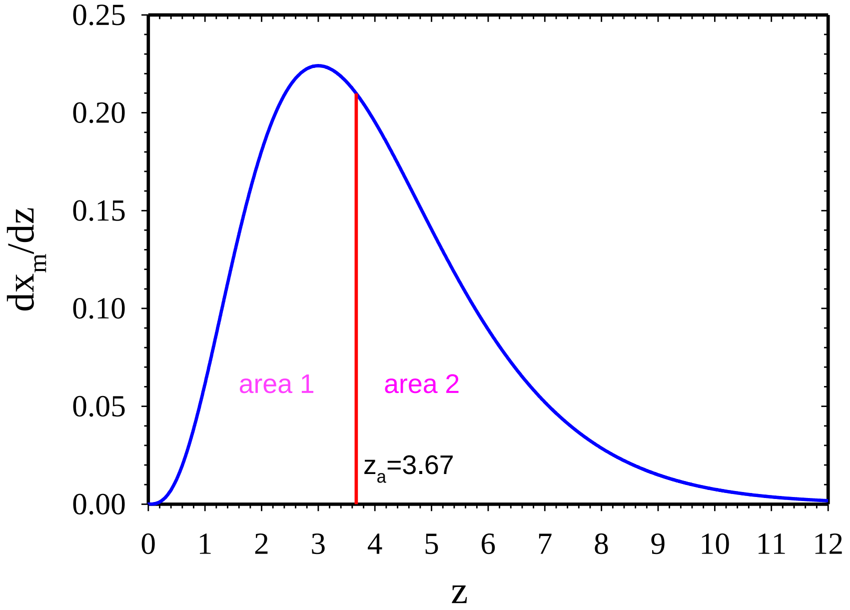
The MSMPR crystallization model

Average and predominant crystal size

Average crystal size L_a

$$dx_m/dz = (z^3/6)e^{-z}$$

$$\int_{z=0}^{Z_a} \frac{z^3}{6} e^{-z} dz = \int_{z=Z_a}^{\infty} \frac{z^3}{6} e^{-z} dz$$



- Solving the above equation by, for example, graphical method (to get area1=area 2) gives:

$$z_a = 3.67 = L_a/(G\tau) \rightarrow L_a = 3.67G\tau$$

The MSMPR crystallization model

Prediction of growth and nucleation rates using MSMPR model

- Using population density equation: $n = \dfrac{d(N/V_{ML})}{dL} = \dfrac{1}{V_{ML}}\dfrac{dN}{dL}$
- Multiplying by G=*dL*/*dt*: $\dfrac{1}{V_{ML}}\dfrac{dN}{dt} = \dfrac{1}{V_{ML}}\dfrac{dN}{dL}\left(\dfrac{dL}{dt}\right)$
- The nucleation rate is obtained for the limit when L→0:

$$\lim_{L\to 0}\frac{1}{V_{ML}}\frac{dN}{dt} = B^{o}$$

and the corresponding population density is : $\lim_{L\to 0}\dfrac{1}{V_{ML}}\dfrac{dN}{dL} = n^{o}$

- Therefore: $B^{o} = Gn^{o}$ → $n = \dfrac{B^{o}}{G}\exp\left(-L/G\tau\right)$

$$n = n^{o}\exp\left(-L/G\tau\right)$$

The MSMPR crystallization model

Example. Screen analysis (Tyler Standard Screen Scale) for crystal samples of urea is as follows:

Mesh	wt%
-14, +20	4.4
-20, +28	14.4
-28, +35	24.2
-35, +48	31.6
-48, +65	15.5
-65, +100	7.4
-100	2.5

The slurry density is ρ_s= 450 g crystal/L, the crystal shape factor is a=1.00. The crystal density, ρ_c, is 1.335 g/cm^3 and the residence time is τ=3.38 h. Calculate the growth rate (G), the nucleation rate (B^o), the average crystal size (L_a) , and the predominant crystal size (L_{pd}).

The MSMPR crystallization model

Prediction of growth and nucleation rate using MSMPR model

- Using Tyler Standard Screen Scale, calculate, L_{av} and ΔL:

Mesh	L (mm)	Mesh	L (mm)	L_{av} (mm)	ΔL (mm)	wt%
14	1.168	20	0.833	1.001	0.335	4.4
20	0.833	28	0.589	0.711	0.244	14.4
28	0.589	35	0.417	0.503	0.172	24.2
35	0.417	48	0.295	0.356	0.122	31.6
48	0.295	65	0.208	0.252	0.087	15.5
65	0.208	100	0.147	0.178	0.061	7.4

- The crystal volume, V_P, can be calculated using shape factor and volume of cube: $V_p = aL_{av}^3 = (1)(L_{av}^3)$

- Calculation the population density n:

$$n = \frac{dN}{V_{ML}dL} = \frac{\Delta N}{V_{ML}\Delta L} = \frac{\rho_s(mass\ fraction)}{\rho_c v_p \Delta L} = \frac{\rho_s(mass\ fraction)}{\rho_c L_{av}^3 \Delta L}$$

The MSMPR crystallization model

Prediction of growth and nucleation rate using MSMPR model

$$n = \frac{\rho_s (mass\ fraction)}{\rho_c L_{av}^3 \Delta L} = \frac{(450 g/L)(mass\ fraction)}{(1.335 g/1000 mm^3) L_{av}^3 \Delta L}$$

$$= \frac{3.371\times 10^5 (mass\ fraction)}{L_{av}^3 \Delta L} [=] \frac{crystals}{L.mm}$$

L_{av} (mm)	ΔL (mm)	wt%	n
1.001	0.335	4.4	4.414E+04
0.711	0.244	14.4	5.535E+05
0.503	0.172	24.2	3.727E+06
0.356	0.122	31.6	1.935E+07
0.252	0.087	15.5	3.753E+07
0.178	0.061	7.4	7.251E+07

The MSMPR crystallization model

Prediction of growth and nucleation rate using MSMPR model

- Linearizing Eq.: $n = \frac{B^o}{G} \exp(-L/G\tau)$

$$\ln(n) = \ln\left(\frac{B^o}{G}\right) - \frac{L}{G\tau}$$

- Plotting ln(n) versus L gives: Slope = $-1/(G\tau)$

  Intercept= $\ln(B^o/G)$

L (mm)	n	ln(n)
1.001	4.414E+04	10.695
0.711	5.535E+05	13.224
0.503	3.727E+06	15.131
0.356	1.935E+07	16.778
0.252	3.753E+07	17.441
0.178	7.251E+07	18.099

The MSMPR crystallization model

Prediction of growth and nucleation rate using MSMPR model

$$-9.12 = -\frac{1}{G\tau} = -\frac{1}{3.38G}$$

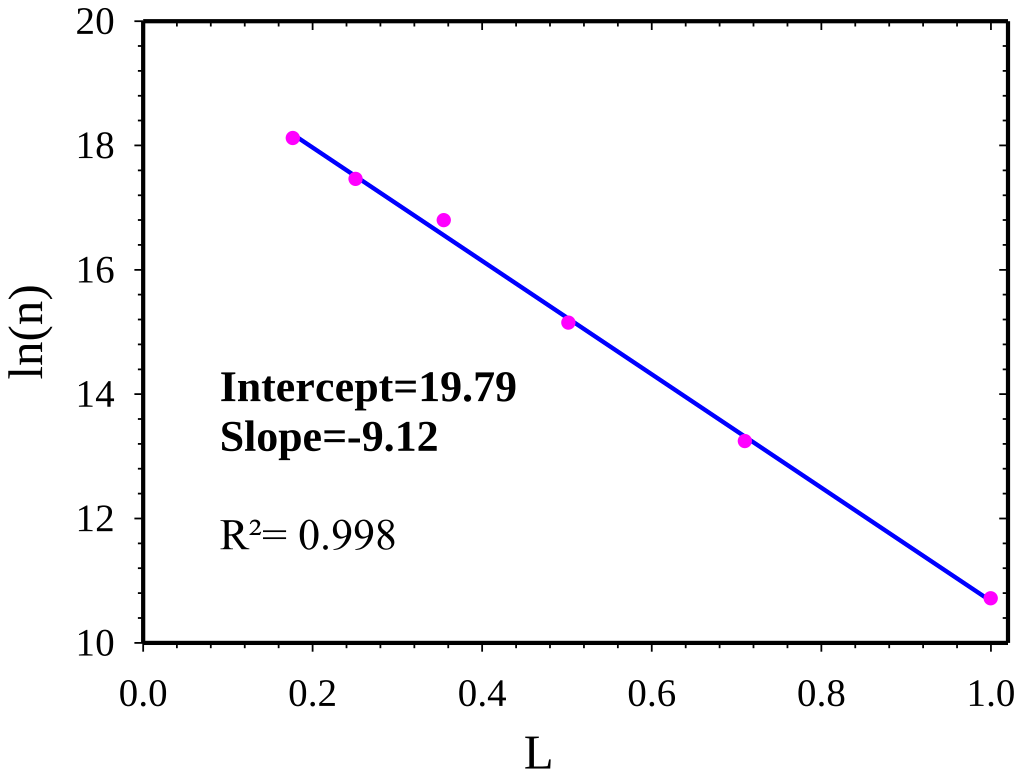
$$\Rightarrow G = 0.03244 \text{ mm/h}$$

$$19.79 = \ln(B^o / G)$$

$$19.79 = \ln(B^o / 0.03244)$$

$$\Rightarrow$$

$$B^o = 1.276 \times 10^7 \text{ nuclei/(h. L)}$$



$$L_a = 3.67G\tau = 3.67(0.03244)(3.38) = 0.402 \text{ mm}$$

$$L_{pd} = 3G\tau = 0.329 \text{ mm}$$