Lecture 15.
Crystallization – Crystal Geometry and Thermodynamics

- Type of Crystallization
- Industrial Example: Production of $MgSO_4 \cdot 7H_2O$
- Crystal Geometry
  - Crystal habit
  - Crystal-size distributions
  - Mean particle sizes
- Thermodynamics
  - Solubility and mass balances
  - Energy balances

Crystallization

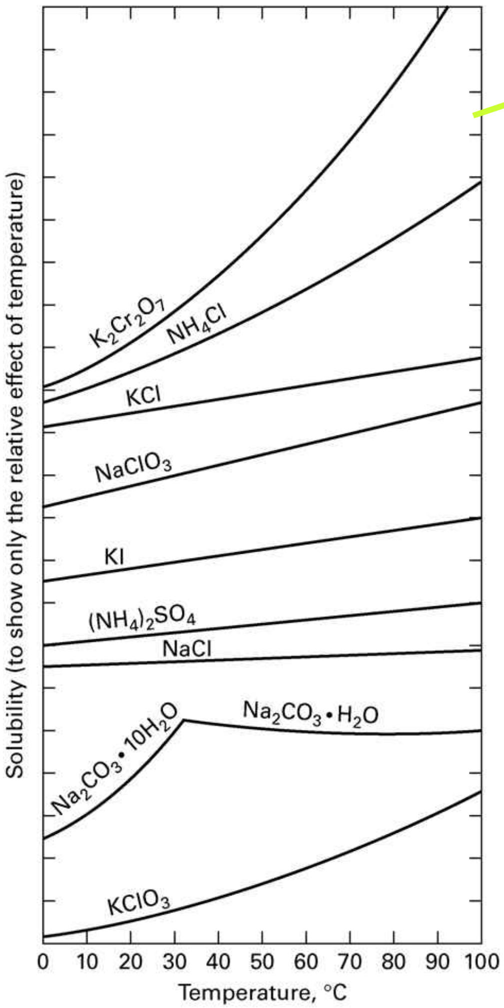
- A solid-fluid separation operation in which crystalline particles are formed from a homogeneous fluid phase
- One of the oldest separation operations: recovery of NaCl as salt crystals from seawater

- Factors for crystallization
  - Cooling the solution
  - Evaporating the solvent
  - Addition of a second solvent
    - when water is the additional solvent: watering-out
    - when an organic solvent is added to an aqueous salt solution: salting-out
    - fast crystallization called precipitation can occur

Type of Crystallization

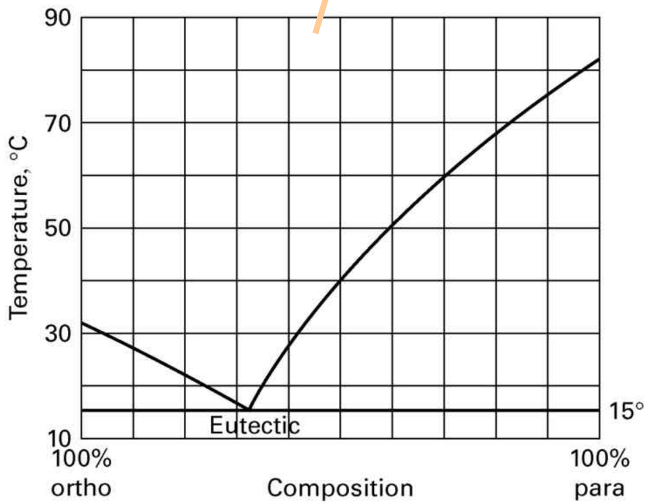
- Solubility curves

Solution crystallization
- Solute: inorganic salt → crystallized
- Solvent: water → remains in liquid phase



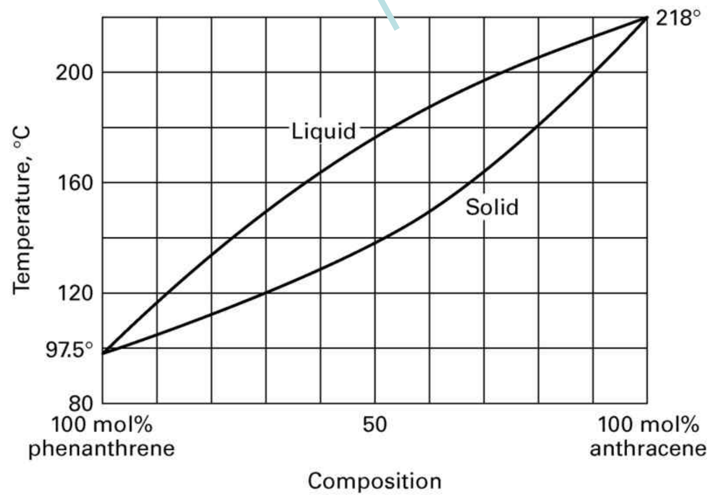
(a) Aqueous systems suitable for solution crystallization

Melt crystallization
- Eutetic point



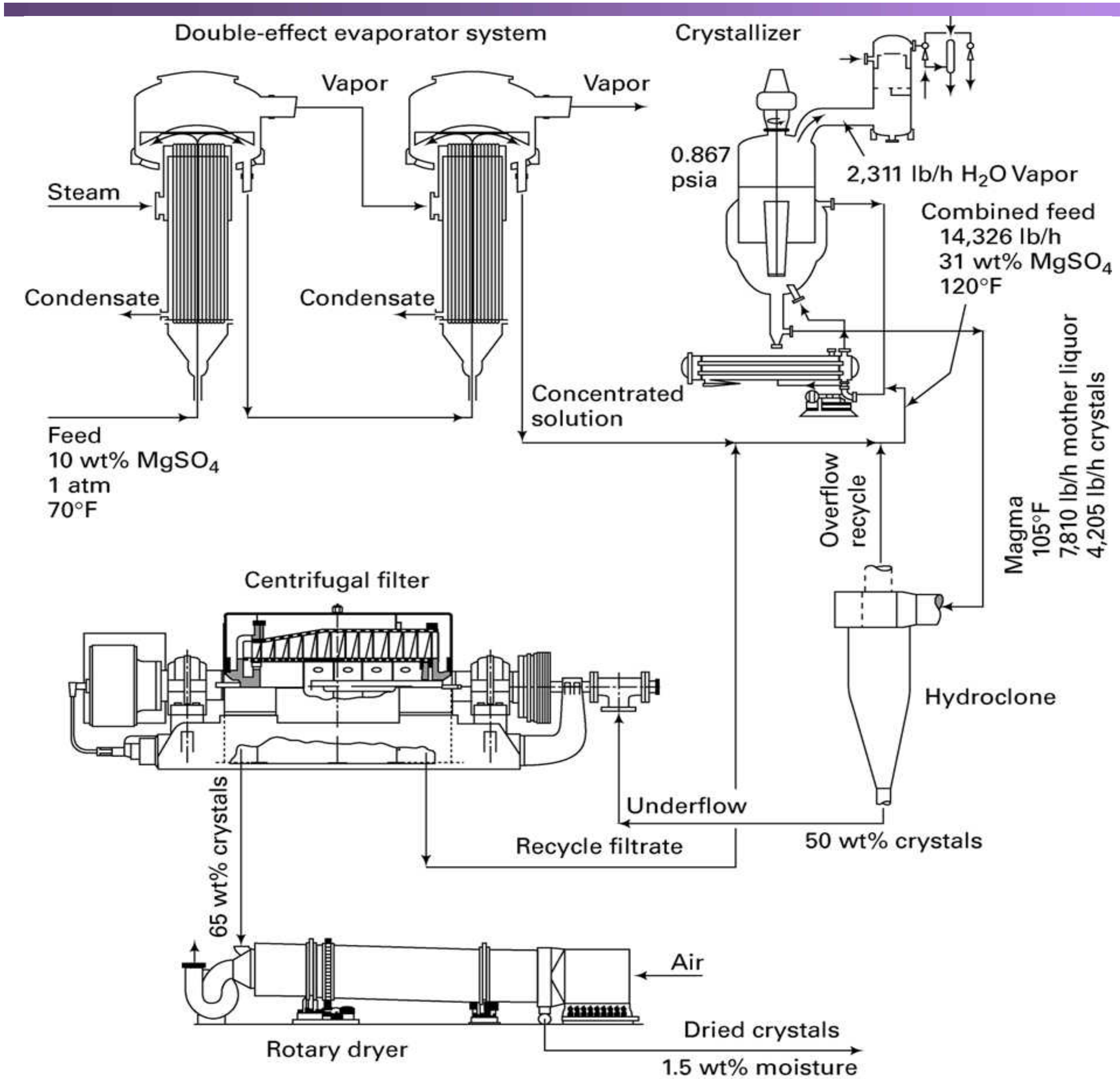
(b) Eutectic-forming system of ortho- and parachloro-nitrobenzene system suitable for melt crystallization

Fractional melt crystallization
- Repeated melting and freezing steps



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

Industrial Example



- Production of $MgSO_4 \cdot 7H_2O$

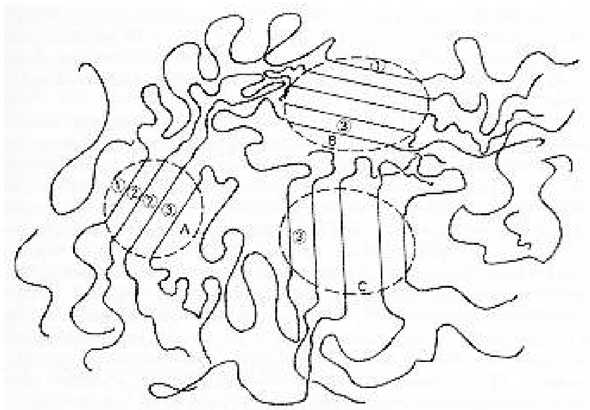
Evaporation in one or more vessels (effects) to concentrate solution

Partial separation and washing of the crystals from the resulting slurry (magma) by centrifugation or filtration

Drying the crystals to a specified moisture content

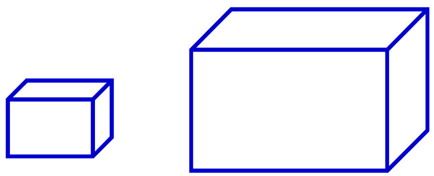
Crystal Geometry

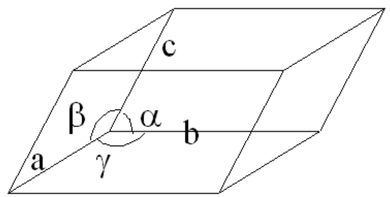
- Crystalline and amorphous states

Crystalline solid	Amorphous solid
– Regular arrangement of atoms – Physical properties depend on the direction of measurement (unless cubic in structure): anisotropic 	– Irregular arrangement of atoms – Physical properties are independent of the direction of measurement: isotropic 

Crystal Habit (1)

- When crystals grow, they form polyhedrons with flat sides and sharp corners (if unhindered by other surfaces such as container walls and other crystals)
- Crystals are never spherical in shape
- Law of constant interfacial angles (Hauy, 1784)
  - The angles between corresponding faces of all crystals are constant, even though the crystals vary in size and in the development of the various faces
  - Crystal habit
  - The interfacial angles and lattice dimensions can be measured by X-ray crystallography

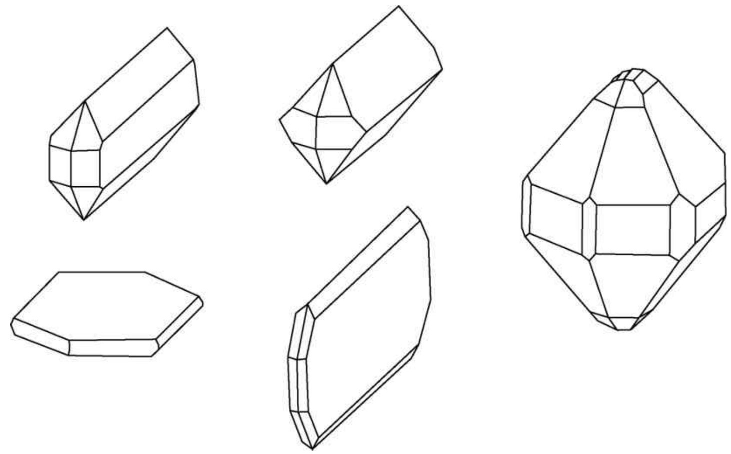




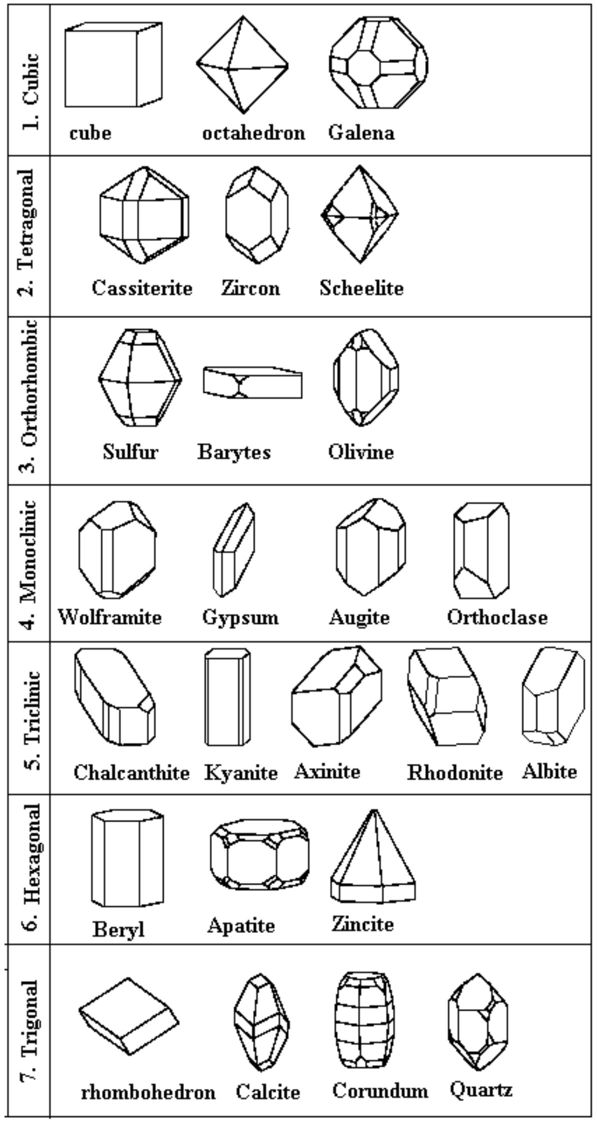
Crystal Habit (2)

- Crystals of a given substance and a given system exhibit markedly different appearances when the faces grow at different rates, particularly when these rates vary greatly, from stunted growth in one direction to give plates, to exaggerated growth in another direction to give needles

Some crystal habits of orthorhombic potassium-sulfate crystals



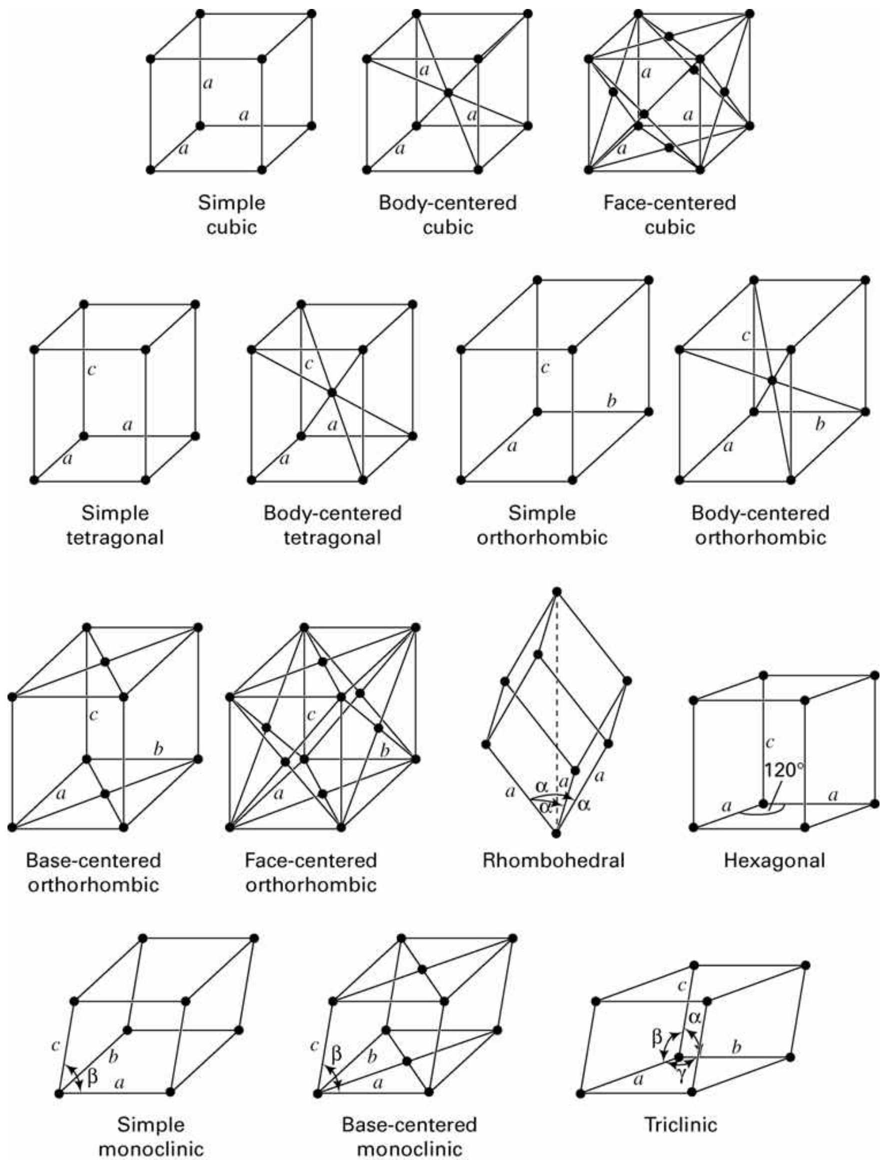
Crystal form of the seven crystal systems



- Modifications of crystal habit are most often accomplished by addition of impurities

Crystal Systems and Space Lattices

Crystal system	Space lattices	Length of axes	Angles between axes
Cubic (regular)	Simple cubic Body-centered cubic Face-centered cubic	a = b = c	$\alpha = \beta = \gamma = 90^o$
Tetragonal	Square prism Body-centered square prism	a = b < c	$\alpha = \beta = \gamma = 90^o$
Orthorhombic	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90^o$
Monoclinic	Simple monoclinic Base-centered monoclinic	a ≠ b ≠ c	$\alpha = \beta = 90^o$ $\gamma \neq 90^o$
Rhombohedral (trigonal)	Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90^o$
Hexagonal	Hexagonal	a = b ≠ c	$\alpha = \beta = 90^o$ $\gamma = 120^o$
Triclinic	Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^o$



Sphericity

- Typical magmas from a crystallizer contain a distribution of crystal sizes and shapes
- Characteristic crystal dimension for irregular-shaped particle → sphericity, ψ

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

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

$$\left(\frac{s_p}{v_p}\right)_{\text{sphere}} = \frac{\pi D_p^2}{(\pi D_p^3/6)} = \frac{6}{D_p}$$

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

Crystal Size Distributions (1)

- Crystal-size distributions are most often determined with wire-mesh screens: crystal size is taken to be the screen aperture (opening) through which the crystal just passes

Mechanical shaking of a stack of ordered screens is used in sieving operations

- Screen analysis: particle-size-distribution data

Mesh number	Aperture, D_p, mm	Mass retained on screen, g	% 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

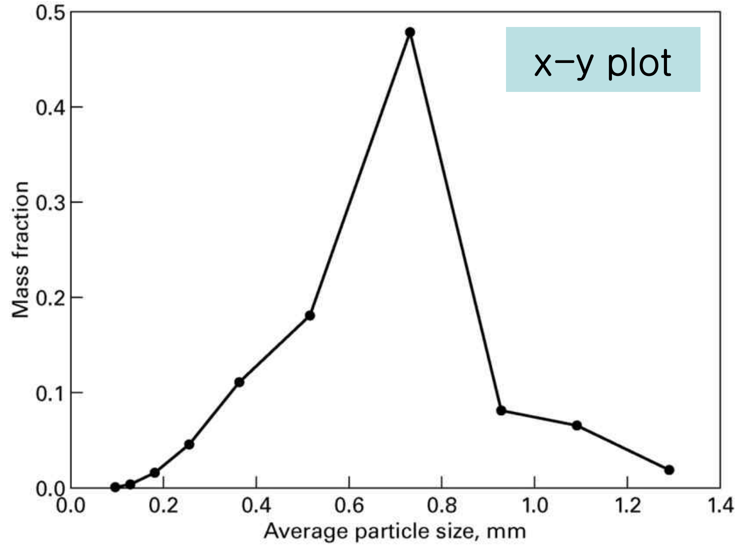
* Crystal of $Na_2SO_4 \cdot 10H_2O$ grown at 18°C during a residence time of 37.2 minutes in a well-mixed laboratory cooling crystallizer

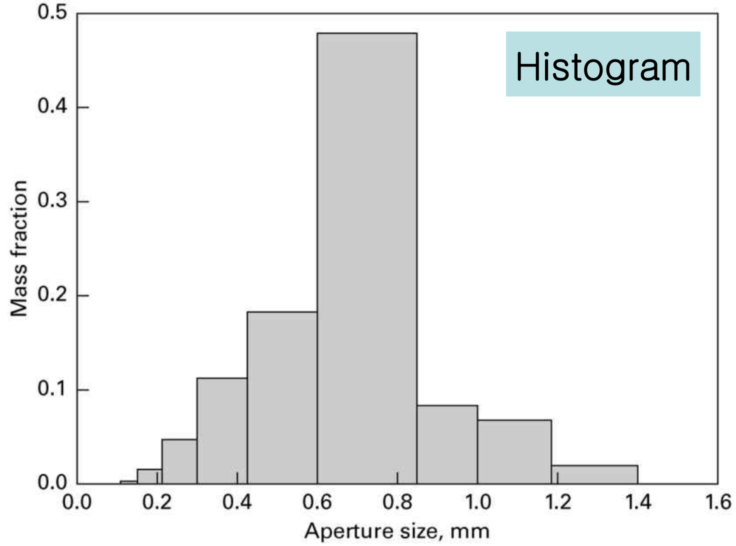
Crystal Size Distributions (2)

- Differential screen analysis: made by determining the arithmetic-average aperture for each mass fraction that passes through one screen but not the next

Mesh range	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	0.4796
−30 +40	0.513	0.1816
−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

Nominal particle size for that mass fraction

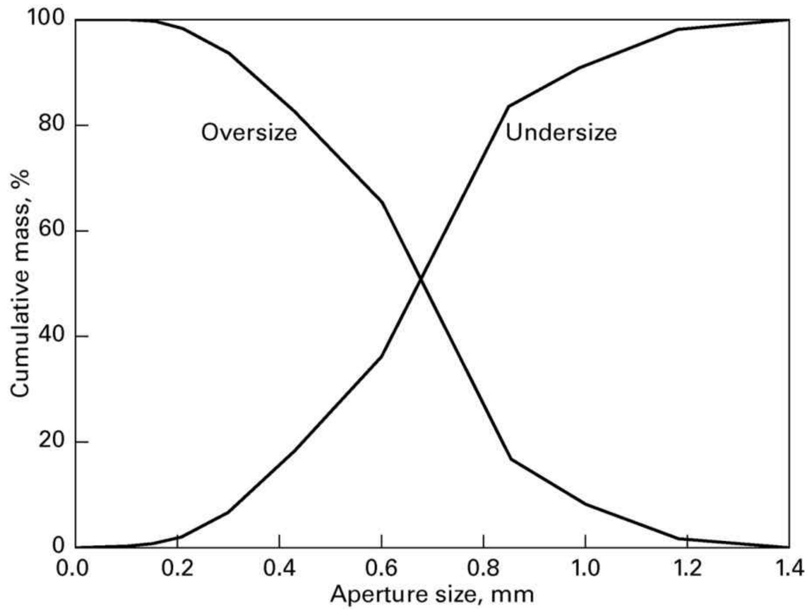




Crystal Size Distributions (3)

- Cumulative screen analysis: plot of cumulative-weight-percent oversize or undersize as a function of screen aperture

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



- The curves are mirror images of each other, crossing at a median size where 50 wt% is larger in size and 50 wt% is smaller
- If a wide range of screen aperture is covered, a log scale for aperture is preferred

Mean Particle Sizes (1)

- Specific surface area (area/mass) of a particle

$$A_w = s_p / m_p = s_p / v_p \rho_p$$

$$A_w = 6 / \psi \rho_p D_p$$

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

$$A_w = \sum_{i=1}^{n} \frac{6 x_i}{\psi \rho_p \bar{D}_{p_i}} = \frac{6}{\psi \rho_p} \sum_{i=1}^{n} \frac{x_i}{\bar{D}_{p_i}}$$

x_i : mass fraction
$\bar{D}_{p_i}$: average aperture

$$A_w = \frac{6}{\psi \rho_p \bar{D}_S}$$

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

- Weight or mass-mean diameter $$\bar{D}_W = \sum_{i=1}^{n} x_i \bar{D}_{p_i}$$

Mean Particle Sizes (2)

- Arithmetic-mean diameter

$$\bar{D}_N = \frac{\sum_{i=1}^{n} N_i \bar{D}_{p_i}}{\sum N_i}$$

N_i : number of particles in each size range

$$x_i = \frac{\text{mass of particles of average size } \bar{D}_{p_i}}{\text{total mass}} = \frac{N_i f_v (\bar{D}_{p_i})^3 \rho_p}{M_t}$$

M_t : total mass
f_v : volume shape factor defined by $v_p = f_v \bar{D}_{p_i}^3$
(for a spherical particles, $f_v = \pi/6$)

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

Mean Particle Sizes (3)

- Volume-mean diameter

$$\left(f_v \bar{D}_V^3\right)\sum_{i=1}^{n} N_i = \sum_{i=1}^{n}\left(f_v \bar{D}_{p_i}^3\right) N_i$$

For a constant value of f_v

$$\bar{D}_V = \left(\frac{\sum_{i=1}^{n} N_i \bar{D}_{p_i}^3}{\sum_{i=1}^{n} N_i}\right)^{1/3}$$

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

Solubility and Mass Balances (1)

- Important thermodynamic properties for crystallization: melting point, heat of fusion, solubility, heat of crystallization, heat of solution, heat of transition, specific heat, and supersaturation
- Solubility of just slightly or sparingly soluble or almost insoluble compounds is expressed as an equilibrium constant, called the solubility product for dissolution, by the law of mass action in terms of ion concentration

$$\mathrm{Al(OH)_{3(s)}} \Leftrightarrow \mathrm{Al^{3+}_{(aq)}} + \mathrm{3OH^{-}_{(aq)}}$$

$$K_c = \frac{(c_{\mathrm{Al^{3+}}})(c_{\mathrm{OH^-}})^3}{a_{\mathrm{Al(OH)_3}}} = (c_{\mathrm{Al^{3+}}})(c_{\mathrm{OH^-}})^3$$

- For less sparingly soluble compounds, the equilibrium constant, K_a, is the more rigorous form

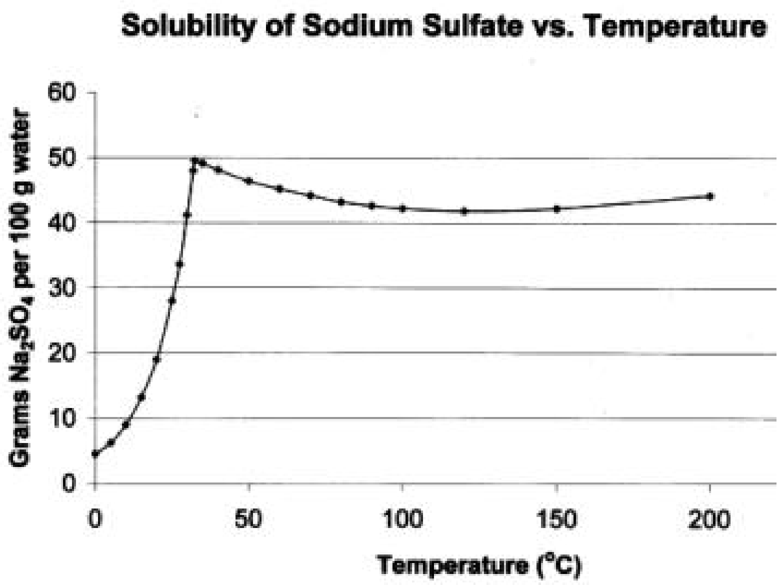
$$K_a = \frac{(a_{\mathrm{Al^{3+}}})(a_{\mathrm{OH^-}})^3}{a_{\mathrm{Al(OH)_3}}} = (\gamma_{\mathrm{Al^{3+}}})(c_{\mathrm{Al^{3+}}})(\gamma_{\mathrm{OH^-}})^3(c_{\mathrm{OH^-}})^3$$

Solubility and Mass Balances (2)

- Solubility of most inorganic compounds increases with temperature, but a few common compounds (hard salts) exhibit a negative or inverted solubility in certain ranges of temperature, where solubility decreases with increasing temperature
- A change in the solubility curve can occur when a phase transition from one stable hydrate to another takes place

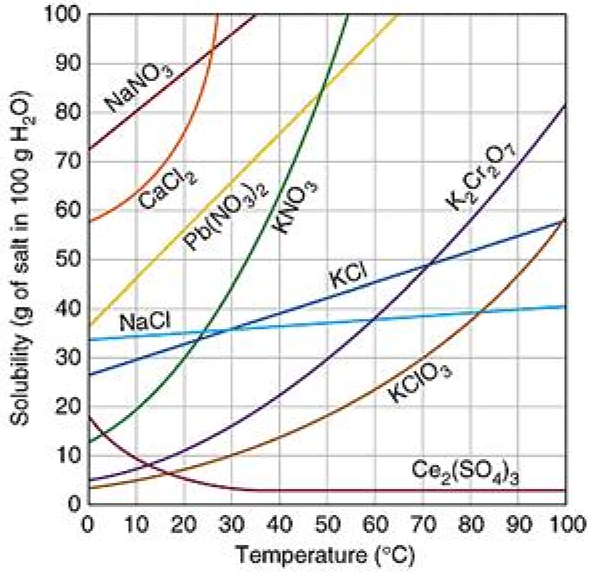
Example of sodium sulfate

- From 0°C to 32.4°C, $Na_2SO_4 \cdot 10H_2O$ is the stable form and the solubility increases from 4.8 to 49.5 g (hydrate-free basis)/100 g H_2O
- From 32.4°C to 100°C, Na_2SO_4 is the stable form and the solubility decreases from 49.5 to 42.5 g/100 g H_2O



Solubility and Mass Balances (3)

- The solubility curve is the most important property for determining the best method for causing crystallization and the ease or difficulty of growing crystals
  - Crystallization by cooling is attractive only for compounds having a solubility that decreases rapidly with decreasing temperature
  - For most inorganic compounds, crystallization by evaporation is the preferred technique



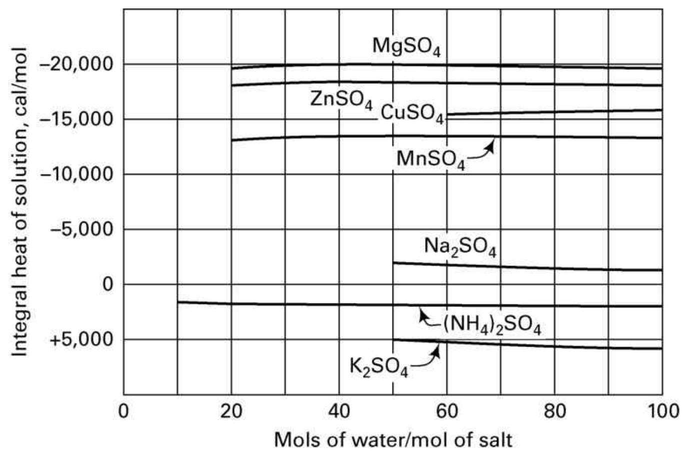
- Solid compounds with low solubility can be produced by reacting two soluble compounds

$$AlCl_{3(aq)} + 3NaOH_{(aq)} \Leftrightarrow Al(OH)_{3(ppt)} + 3NaCl_{(aq)}$$

  - The reaction is so fast that only very fine crystals, called a precipitate, are produced

Energy Balances (1)

- When an anhydrous solid compound, whose solubility increases with increasing temperature, dissolves isothermally in a solvent, heat is absorbed by the solution
- Heat of solution at infinite dilution, ΔH_{sol}^{∞}: the amount of heat per mole of compound in an infinite amount of solvent
- For compounds that form hydrates, heat of solution at infinite dilution may be exothermic (−) for the anhydrous form, but becomes less negative and often positive as higher hydrates are formed by $\mathbf{A \cdot \mathit{n}H_2O_{(s)} \rightarrow A_{(aq)} + \mathit{n}H_2O}$
- As crystals continue to dissolve in a solvent, the heat of solution (integral heat of solution) varies as a function of concentration
- {integral heat of solution at saturation} = −{heat of crystallization} $\Delta H_{sol}^{sat} = -\Delta H_{crys}$



Energy Balances (2)

- {integral heat of solution at saturation} – {heat of solution at infinite dilution} = {heat of dilution}

$$\Delta H_{sol}^{sat} - \Delta H_{sol}^{\infty} = \Delta H_{dil}$$

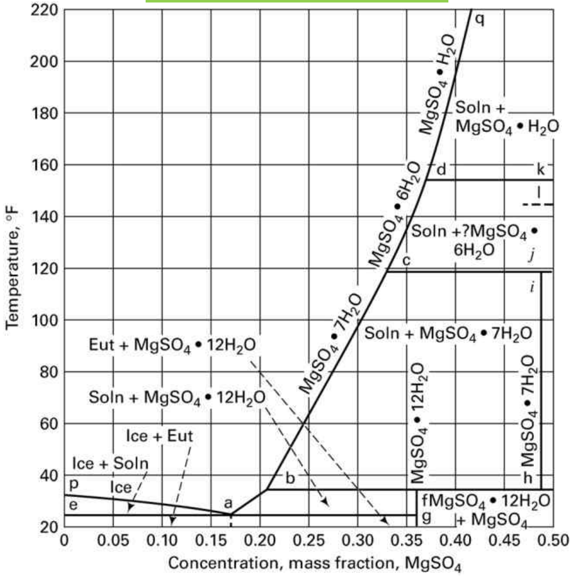
$$\Delta H_{crys} \approx -\Delta H_{sol}^{\infty}$$

Heats of dilution are relatively small

- An overall energy balance around the crystallizer

$$m_{feed} H_{feed} + Q_{in}$$
$$= m_{vapor} H_{vapor}$$
$$+ m_{liquid} H_{liquid}$$
$$+ m_{crystals} H_{crystals}$$

Solid–liquid phase diagram



Enthalpy–concentration diagram