PHEN 612

SPRING 2008

WEEK 13

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Crystallization

- ✓ ***Crystallization is a common separation process in***
- • Commodity inorganic industry (e.g., salts)
- • Food industry (e.g., sugars)
- • Pharmaceutical manufacturing (e.g., drugs)

- In crystallization: differences in composition of liquid and solid phases

- The desired product is usually a pure solid

- Two ways to crystallize:
- • Cool the solution if the solubility of desired product decreases with temperature
- • Evaporate the volatile component, if the crystallizable material is non-volatile

- ✓ Addition or removal of energy is usually is usually required to shift the equilibrium toward the two-phase region

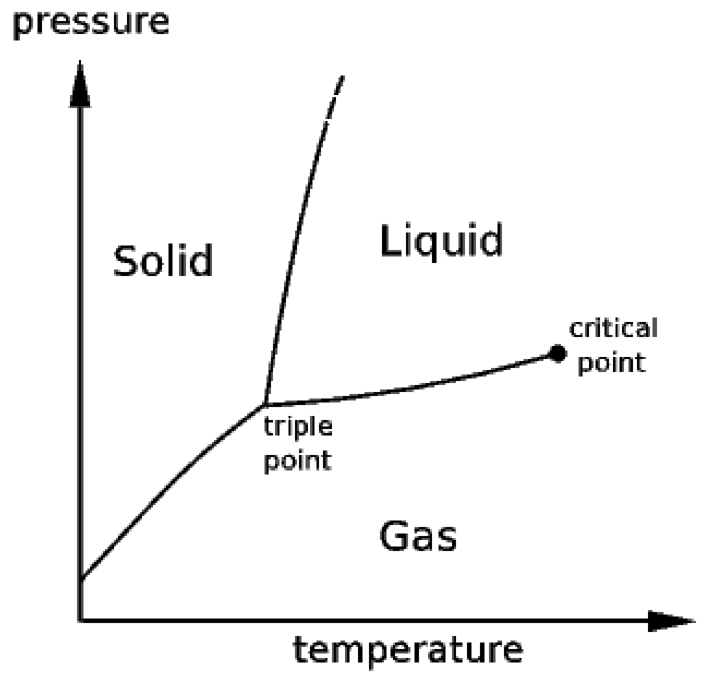
Murphy, 2007

Crystallization

Phase diagram

• Diagram of a pure substance is a plot of one system variable against another

• The condition at which the substance exists as a solid, liquid, a gas is shown



Phase diagram

Introduction and Equipment for Crystallization (Geankoplis, 2003)

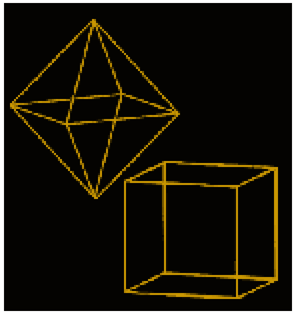
- Crystallization and types of crystals
  - In commercial crystallization, the yield, purity, size and shape of the crystals are important
  - Crystals need to be uniform in size
  - Reason for uniformity:
    - minimize cracking in the package
    - ease of pouring
    - Ease in washing and filtering
    - Uniform behavior

Shapes of Crystals

<u>Crystals</u>: Solid composed of atoms, ions, or molecules arranged in an orderly and repetitive manner.

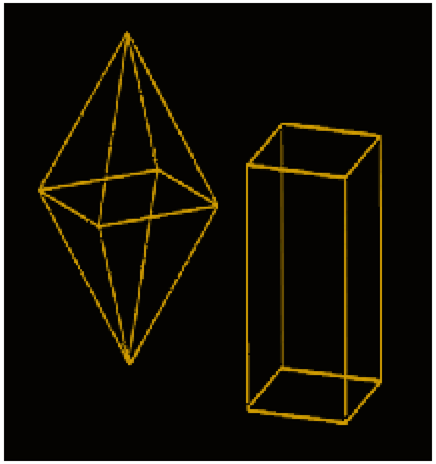
- The atoms, ions, or molecules are arranged in thre-dimensional arrays and space lattices
-Interatomic distances between planes or space lattices are measured by X-ray diffraction

Cubic crystals: 3 equal axes at right angles to each other



Tetragonal crystals: 3 equal axes at right angles to each other, one axis longer than the other two

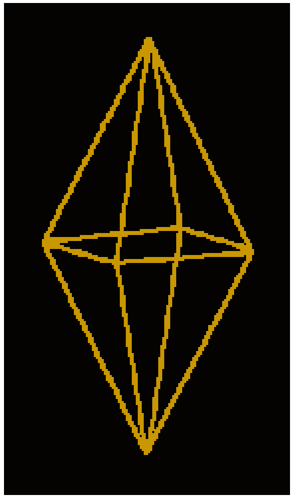
(Geankoplis, 2003)



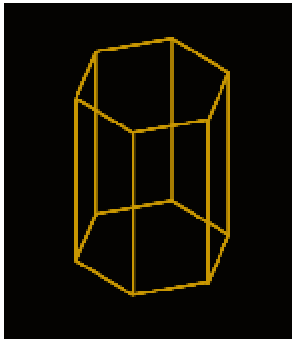
http://www.windows.ucar.edu/tour/link=/earth/geology/crystal_shapes2.html

Shapes of Crystals (Geankoplis, 2003)

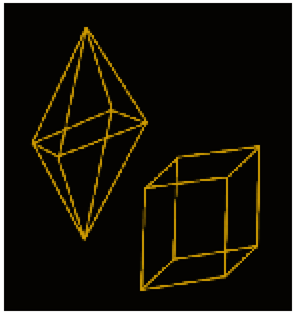
Orthorhombic crystals: 3 axes at right angles
to each other, all of different lengths



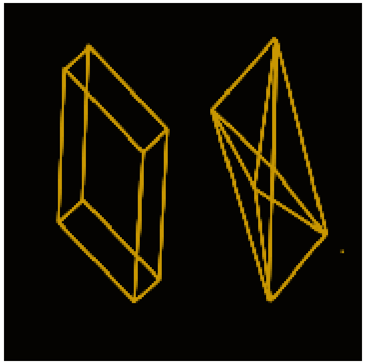
Hexagonal crystals: three equal axes
in one plane at 60^{o} to each other, and
a fourth axis at right angle to this plane
And not necessarily the same length



Monoclinic crystals: 3 unequal axes, two
at right angles in a plane and a third at some angle
to this plane



Triclinic crystals: 3 unequal axes at unequal
angles to each other and not 30, 60, 90^{o}



http://www.windows.ucar.edu/tour/link=/earth/geology/crystal_shapes2.html

Equilibrium Solubility in Crystallization

- Equilibrium is achieved when the solution or mother liquor is saturated

- Solubility is mainly a function of temperature

- Solubility curve for some typical salts in water are given (see handout: Fig 8.1-1)

- The solubility of NaCl is marked by its small change with temperature (see handout: Fig 8.1-1)

- For KNO_3, the solubility increases markedly with temperature (see handout: Fig 8.1-1)

Yields, Heat and Material Balances in Crystallization

- In most of the industrial crystallization processes, the solution (mother liquid) and the solid crystals are in contact enough time to reach equilibrium

- The mother liquid is saturated at the final temperature of the process

- The final concentration of the solute in solution is given by the solubility curve

- The yield can be obtained from the initial concentration of solute, the final temperature, and the solubility at this temperature

Problems: **Example 12.11-1**

(Geankoplis, 2003)

Heat Effects and Heat Balances in Crystallization

- *Heat of solution*: absorption of heat during dissolution as the temperature of a compound increases. Solubility increases with temperature in this case.
- Evolution of heat occurs when a compound dissolves whose solubility decreases as temperature increases.
- Some compounds dissolve while the solubility does not change as temperature increases. No heat evolution in this cases.

(Geankoplis, 2003)

- In crystallization, the opposite of dissolution occurs.
- At equilibrium, the heat of crystallization is the negative of the heat of solution at the same concentration in solution.

$$q = \left(H_2 + H_v\right) - H_1$$

H_1: enthalpy of entering solution at the initial at final T

H_v: enthalpy of the water vapor obtained from steam table

H_2: enthalpy of mixture of crystals and mother liquor at final T

Problems: **Example 12.11-2**

Equipment for Crystallization

- Batch crystallizers
- Continuous crystallizers
- Crystallization cannot occur without supersatutation

✓ Equipment are classified based on the methods used to bring about supersaturation

  - ✓ Cool the solution with negligible evaporation: tank and batch-type crystallizers
  - ✓ Evaporate the solvent with little or no cooling: evaporator-crystallizers and crystallizing evaporators
  - ✓ Combine cooling and evaporation in an adiabatic evaporator: vacuum crystallizers

Equipment for Crystallization

- Equipment can be classified based on the method of suspending the growing product crystals
  - Suspension is agitated in a tank
  - Circulated by a heat exchanger

- Equipment can be classified based on how the supersatured liquid contacts the growing crystals
  - Circulating magma method: magma of crystals and supersaturated liquid in one steam
  - Circulating liquid method: a separate stream of supersaturated liquid is passed through a fluidized bed of crystals, where the crystals grow and new one form by nucleation

- Please download the following article for discussion (See link below): Understanding Crystallization and Crystallizers (CEP, 2006):

http://hood.eas.asu.edu/che211/crystalization.pdf