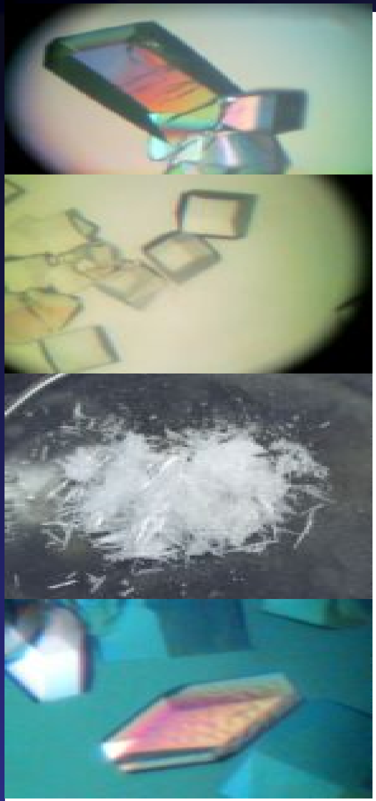


결정화 공정의 상평형의 원리와 이해

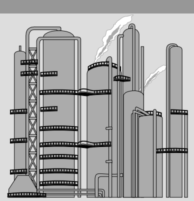
2007년 8월 20일

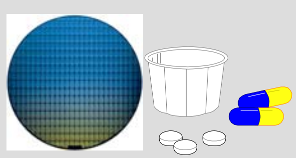
결정화 분리기술 사업단
고려대학교 화공생명공학과 강정원

1. 서론 – 상평형과 결정화 공정

21세기 한국 화학공업의 패러다임의 변화

산업의 성격	에너지 소모형	→	에너지 절약형
	소품종 대량생산		다품종 소량생산
	저부가가치 상품		고부가가치 상품
응용 분야	에너지 (정유,가스)	→	정밀화학
	석유화학 (고분자)		생명/의약/환경
	비료화학		전자재료
Phase	기체, 액체	→	고체





현 문제점

- 과다한 에너지 사용으로 이윤창출
- 전자재료, 정밀화학 등 주요 핵심 원료의 선진국 (특히 일본) 수입의존
- 주요 산업에서 화합물의 물성 (크기, 입도, 형상) 미달로 블루 오션을 창출하지 못함.

비전

고순도, 고부가가치 고체 생산을 위한 에너지 절약형 공정인 <u>결정화 공정 기술이 화학산업의 경쟁력 좌우</u>

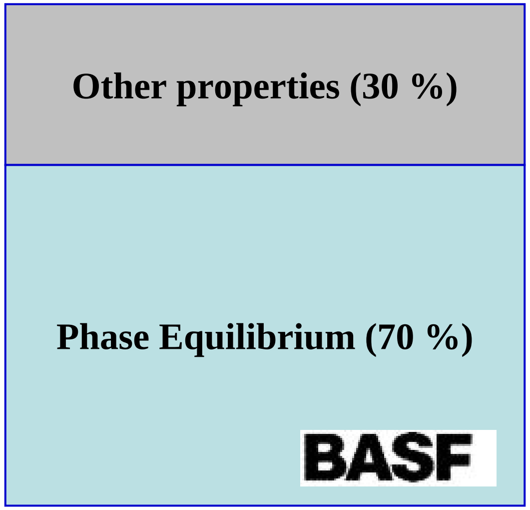
Importance of Thermophysical Properties

- Statistics says …
  - Separation process account for 40-70 % of capital and operating cost in chemical industries
  - Physical property errors are costly …
    - 20 % error in density $\rightarrow$ 16 % error in equipment size and cost
    - 20 % error in diffusivity $\rightarrow$ 4 % error in equipment size and cost
    - 10 % error in phase equilibrium
      - Easy-to-separate mixtures : 10 % error in equipment size and cost
      - Hard-to-separate mixtures : 200 % or more error

Important Thermophysical Properties

- Important Thermodynamic Properties in Crystallization Processes
  - Melting point
  - Heat of Fusion
  - Solubility (Phase Equilibrium)
  - Heat of Crystallization
  - Heat of Solution
  - Heat of Transition
  - Supersaturation

Annula total expenditure of BASF on Phase equilibria and themophysical Properties : 8,000,000 Euro p.a. (1993)



Basic Considerations …

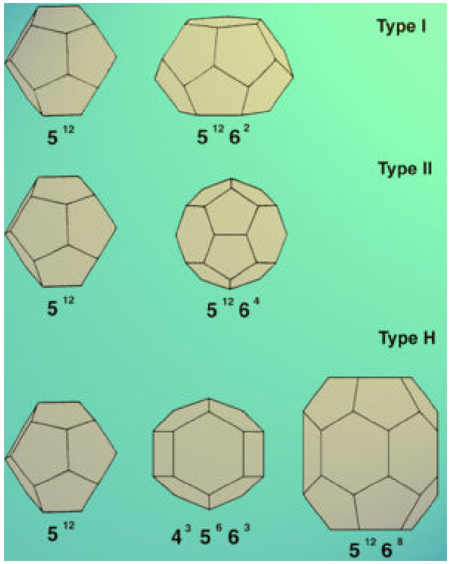
- Crystallization Process
  - Involves Solid-Liquid Equilibrium (SLE)
  - Solubility information
    - Most basic information required for the design of crystallization processes
    - Sometimes SLE exhibit complex phase behavior
      - Examples) hydrate formation, spinodal decomposition, ….
- Components involved in SLE
  - Solvents
    - Water
    - Nonelectrolytes (Organic compounds)
    - Electrolytes (Inorganic compounds), Ionic Liquids
  - Solutes
    - Electrolytes (Inorganic compounds)
    - Nonelectrolytes (Organic Compounds) , …

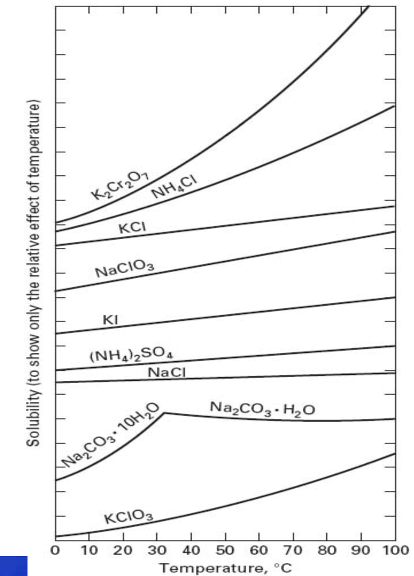
Complex Behavior – Hydrate Formation

- **Hydrate** : Solid state containing water
  - – Notation : (hydrous compound · *n*H_2O)
    - Example : $CuSO_4 \cdot 5H_2O$, $Na_2SO_4 \cdot 10H_2O$,…

(chalcanthite)

Gas Hydrate : Clathrate hydrate





(a) Aqueous systems suitable for solution crystallization

Characteristics of Molecules

- Intermolecular forces
  - Electrostatic forces
    - Coulomb's Law

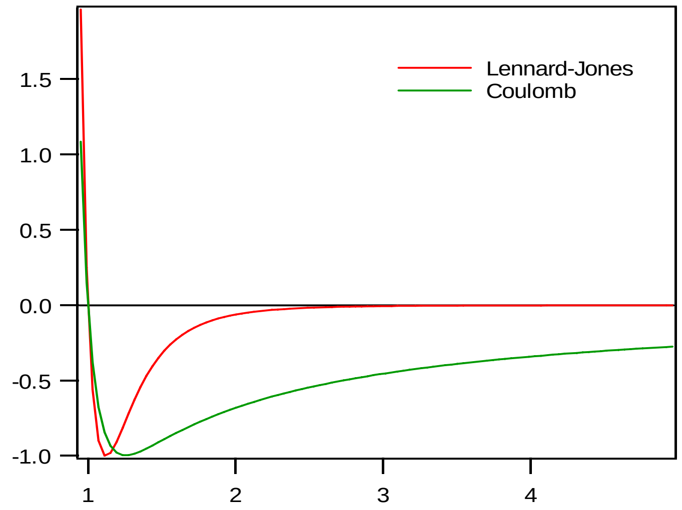
$$\Gamma_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r}$$

  - Hydrogen bond , Specific (Chemical forces)
    - Not easily explained : Type specific
    - Systems involving –OH, -COOH, ….
  - Van der Waals Forces : Nonpolar Intermolecular forces
    - London force
    - Lennard Jones Potential

$$\Gamma = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Intermolecular Forces of Molecules

- Short range forces
  - Dispersion and Repulsion
- Long range forces
  - Ion-Ion and Dipole-Dipole Interaction



Interaction Type	Dependence	Typical E (kJ/mol)	Comment
Ion-Ion	$1/r$	250	
Ion-Dipole	$1/r^2$	15	
Dipole-Dipole	$1/r^3$	2	Stationary
London	$1/r^6$	2	

Basic Considerations….

- Electrolytes vs. Nonelectrolytes

- Electrolytes
  - Electrostatic force
  - High Melting Point
  - Ionization in Water
  - Crystallize in Water
- Nonelectrolytes
  - Van der Waals
Hydrogen Bond,….
  - Low Melting Point
  - No ionization
  - Not easily crystallize
Only crystallize when HB

⇨ Electrolytes are normally appear in Crystalline Structure

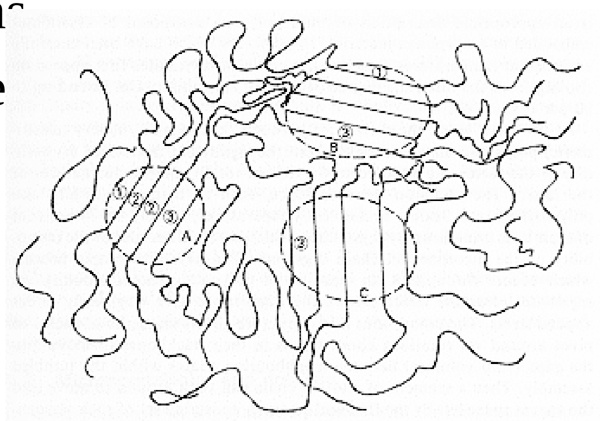
⇨ For nonlectrolyte molecules, specific forces are required to form a crystal

Crystal vs. Amorphous State

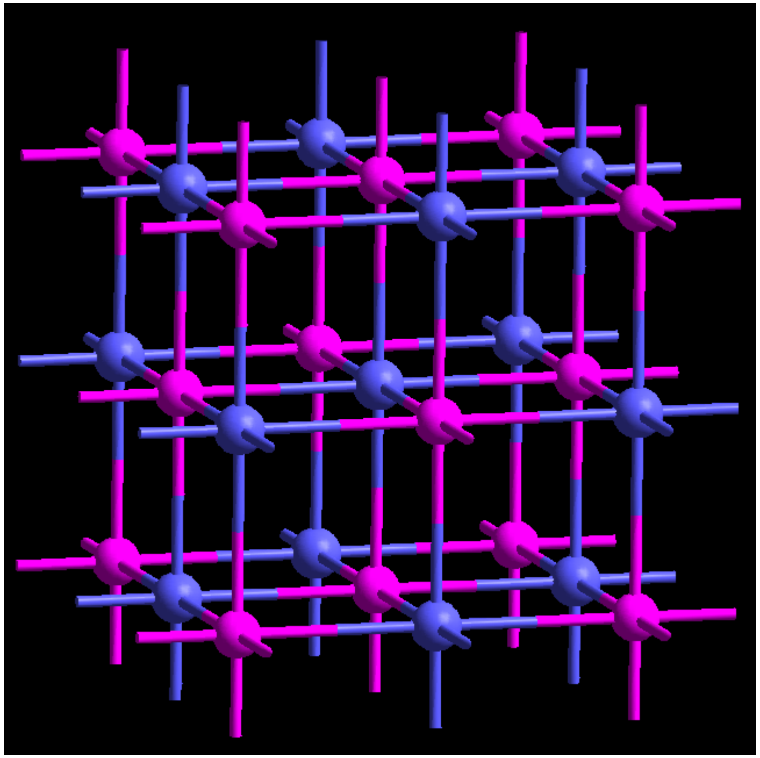
- Crystal and Amorphous State

  - Crystal
    - Regular arrangement of atoms
    - Physical properties depend on the direction of measurement → anisotropic
  - Amorphous
    - Irregular arrangement of atom
    - Physical Properties are indepe

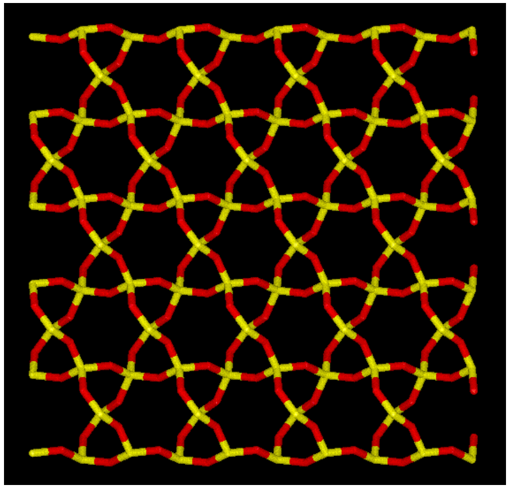
      measurements → isotropic



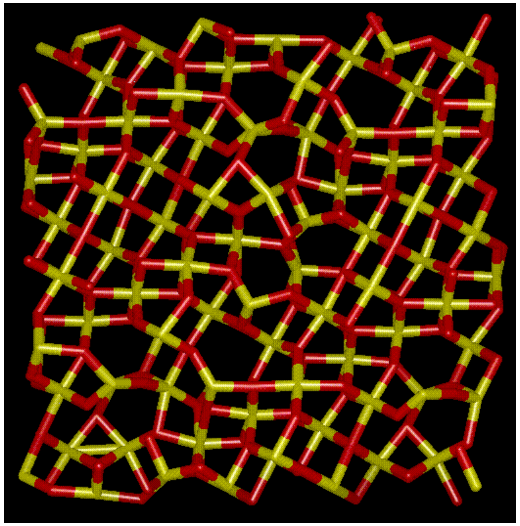
Crystal vs. Amorphous State…



Crystal Structure of NaCl (Sodium Chloride)
Fcc lattice structure

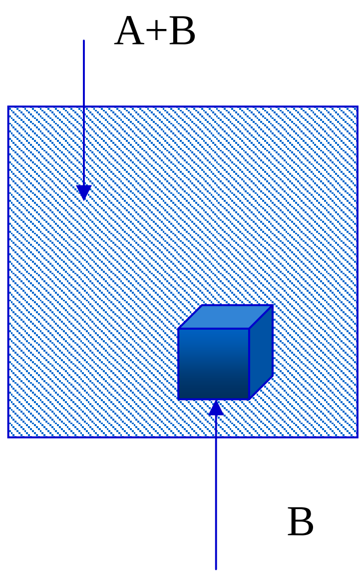


SiO_2 : An ordered crystal



SiO_2 : An armophous glass

Basic Consideration … Solubility



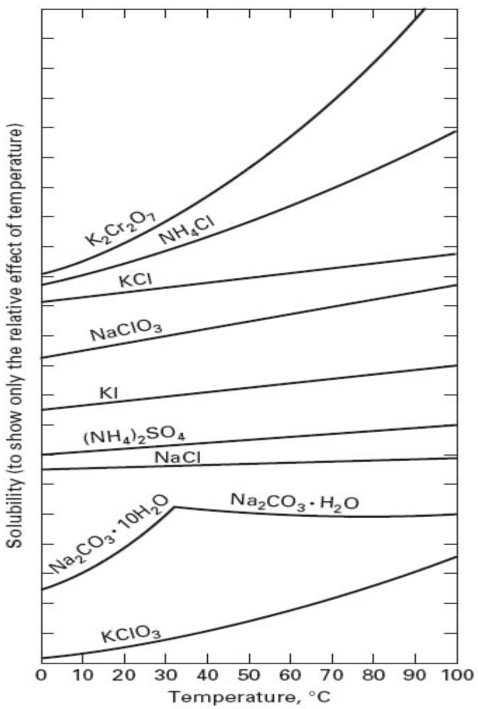
- Basic Principles to Calculate Solubility
  - Solid + Liquid Equilibrium
    - Solids normally exists in pure form
  - Equality of Chemical Potential

$$\mu_B^{solid}(T,P) = \mu_B^{solution}(T,P,x)$$

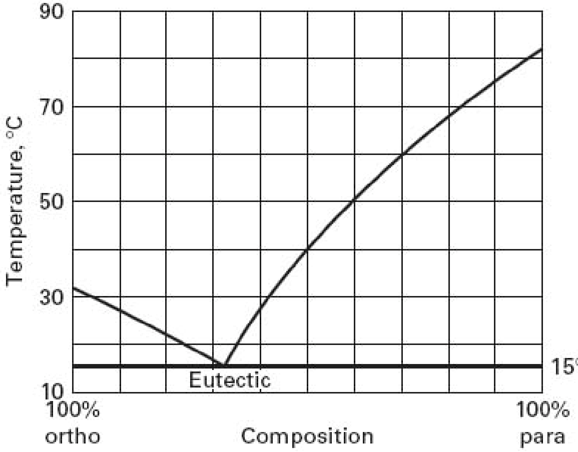
  - When the meaning of chemical potential is not so clear, fugacity can be used instead (units in pressure)

$$f_B^{solid}(T,P) = f_B^{solution}(T,P,x)$$

A Typical SLE Diagrams …



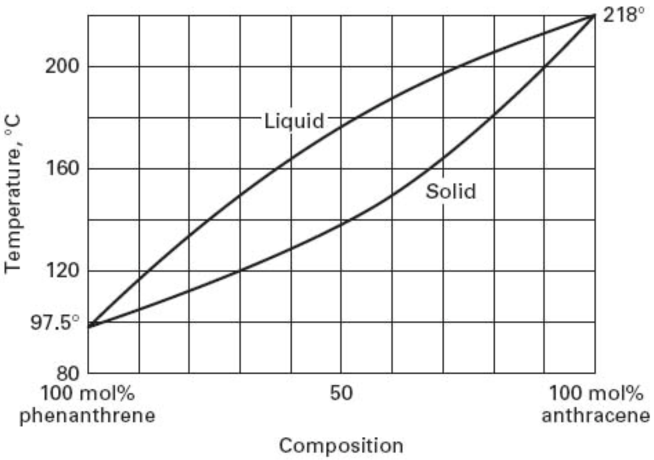
(a) Aqueous systems suitable for solution crystallization



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

Melt

Solution



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

Far away from melting point of solute
Near M.P of solute solvent is in gas state

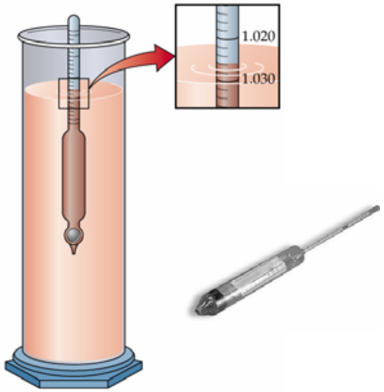
2. 물성과 용해도 측정

Density

- Measurement of density
  - Measurements of weight of substances with known volume
    - Pycnometer
    - Hydrometer
    - Insertion Density Transmitters

Insertion Density Transmitter

Pycnometer



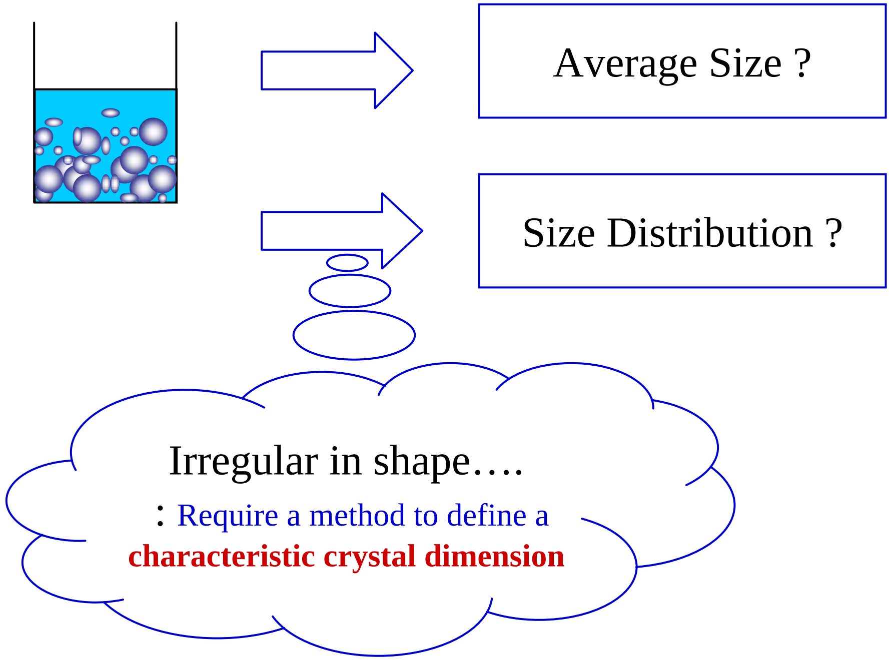
Hydrometer

Anton Paar Density Meter
: Oscillating U-tube method

Size Classification of Crystals

- Crystallizers are often operated in batch mode
- How to characterize a batch of crystals (particles) ?

Characterization



Sphericity

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

$$\psi = 1 : \text{sphere}$$
$$\psi < 1 : \text{all other particles}$$

For a sphere particle of diameter ***D_p***

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

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

Methods of Measuring Particle Size

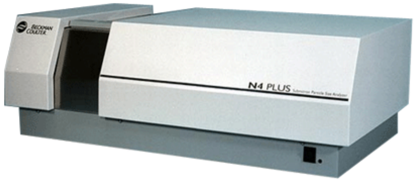
Method	Size Range (micron)	Size Range (nm)
Woven-wire screen	32-5600	
Coulter electrical sensor	1-200	
Gravity sedimentation	0.5-1-50	
Optical microscopy	0.5-150	
Laser-light scattering	0.04-2000	40-2000000
Centrifugal sedimentation	0.01-5	10-5000
Electron microscopy	0.001-5	1-5000

Result may differ by **50 %** depending on measurement methods

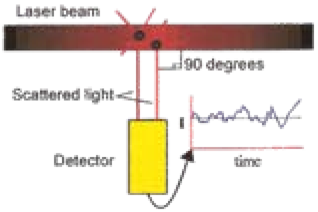
Standard Sieve

Automatic Sieve Analyzer

Coulter Image Analysis System



Laser-light Scattering



Particle Size Distribution using Wire-Mesh Screen (Sieve)

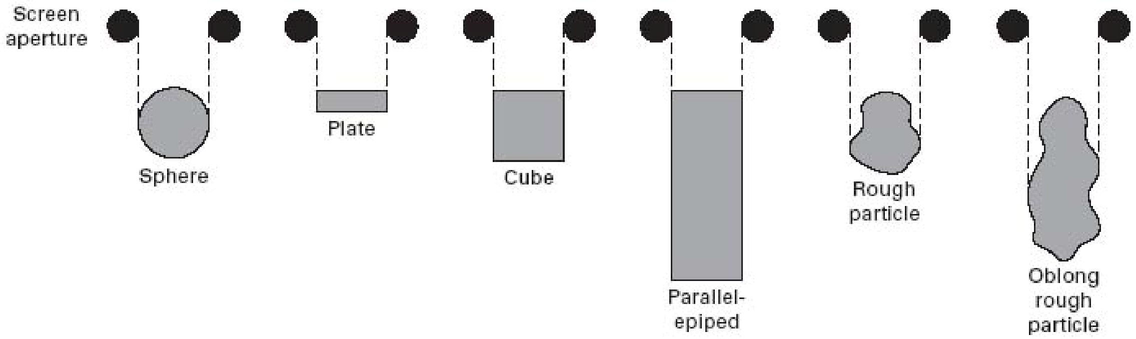
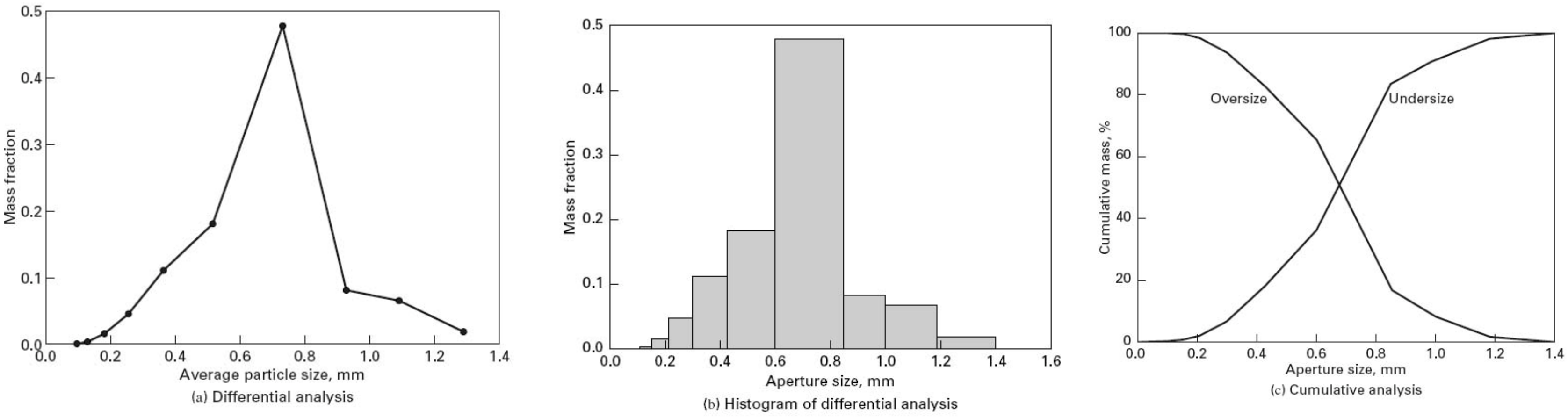


Figure 17.7 Different particle shapes that just pass through the same screen.



Mean Particle Size

- Surface-mean diameter
- Mass-mean diameter
- Volume-mean diameter

Measurement of Solubility

- Elements for Solubility Measurement
  - Temperature Control
  - Agitation of Solution
  - Sampling
  - Achievement of Equilibrium
- Measurement Technique
  - Polythermal Method
  - Isothermal Method

Solubility Data Source

- Dortmund Databank (SLE Database)
- IUPAC Solubility Data Series