

# Gibbs's Phase Rule:

Phase P: uniform state of matter

e.g. miscible liquids  $\Rightarrow$  1 phase  
dispersion  $\Rightarrow$  2 phases

constituent C: present chemical species

e.g. a solution of sodium chloride  
 $H_2O, Na^+, Cl^- \Rightarrow 2$

component C: chemically independent constituent

e.g.  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$   
Phase 1                      Phase 2                      Phase 3  
 $\Rightarrow$  2 components, 3 constituents

variance (= degrees of freedom) F:

number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium

- e.g. • in a single component and single phase system temperature and pressure can be changed independently  $\Rightarrow F = 2$
- if two phases are in equilibrium in a single component system, the temperature (or pressure) can be changed at will, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve phases

(63)

## Gibb's Phase rule

$$F = C - P + 2$$

Proof:

Counting the total number of intensive variables

$$P, T \Rightarrow 2$$

+ specify the composition of a phase by giving the mole fraction of  $C-1$  components ( $x_1 + x_2 + \dots + x_C = 1$ )

\* there are  $P$  phases

$\Rightarrow$  total number of intensive variables:  $P(C-1) + 2$

at equilibrium:  $\mu_j(\alpha) = \mu_j(\beta) = \dots$  for  $p$ -phases

$\Rightarrow$   $P-1$  equations for each component  $J$

\*  $C$  components

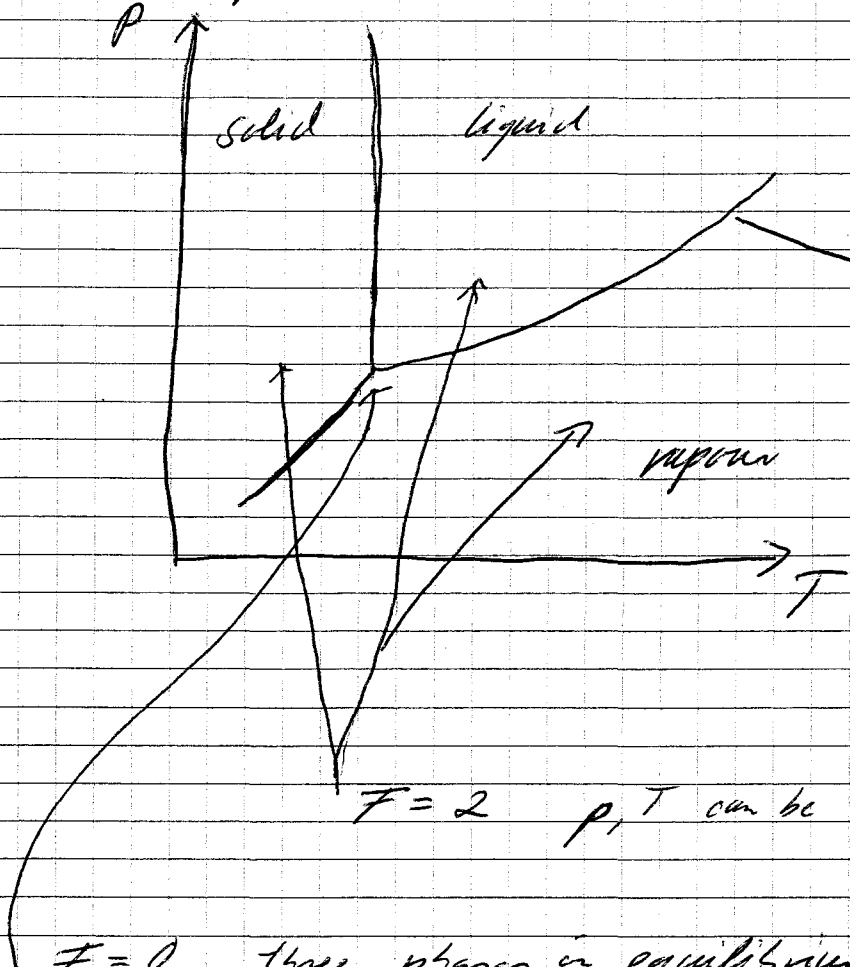
$\Rightarrow$  total number of equations:  $C(P-1)$

each equation reduces our freedom to vary one of the intensive variables

$$\Rightarrow F = P(C-1) + 2 - C(P-1) = C - P + 2$$

Gibbs's rule helps to predict phase diagrams:

one-component



$F = 1$ , 2 phases in equilibrium,  $p(T)$

$F = 2$   $p, T$  can be independently varied

$F = 0$ , three phases in equilibrium,  $p_0, T_0$

four phases in equilibrium?  $\Rightarrow$  not possible

experimental procedures:

thermal analysis  $\Rightarrow$  enthalpy change during a first order transition

- $\Rightarrow$  • Differential scanning calorimetry
- DSC
- DSC

# 2-component systems

• vapour pressure diagrams:

2 components  $\Rightarrow C=2 \quad F=4-P$

$T = \text{const} \Rightarrow F' = 3-P$

$\Rightarrow$  remaining degrees of freedom:  
pressure, composition

liquid mole fraction

$P_A = \chi_A P_A^*, \quad P_B = \chi_B P_B^*$  Raoult's law

$P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^* = P_B^* + (P_A^* - P_B^*) \chi_B$

gas mole fraction

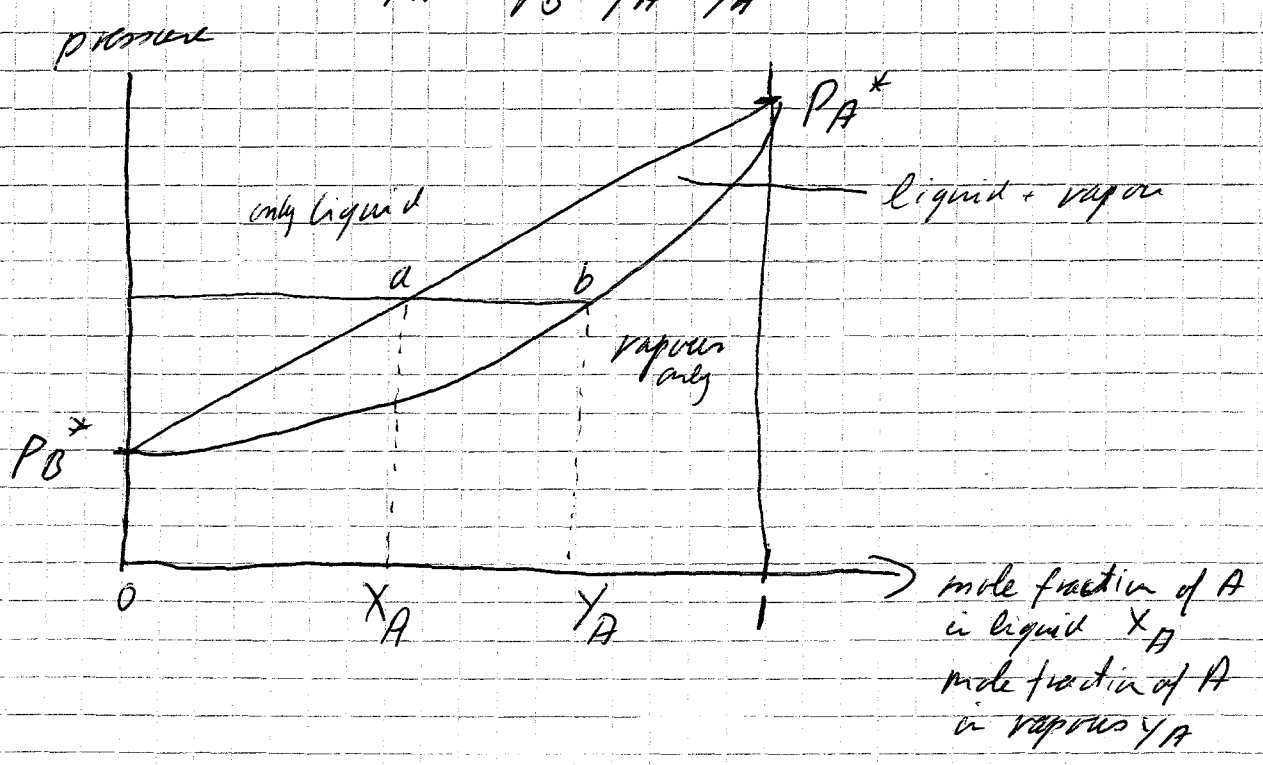
$\chi_A = \frac{P_A}{P}$

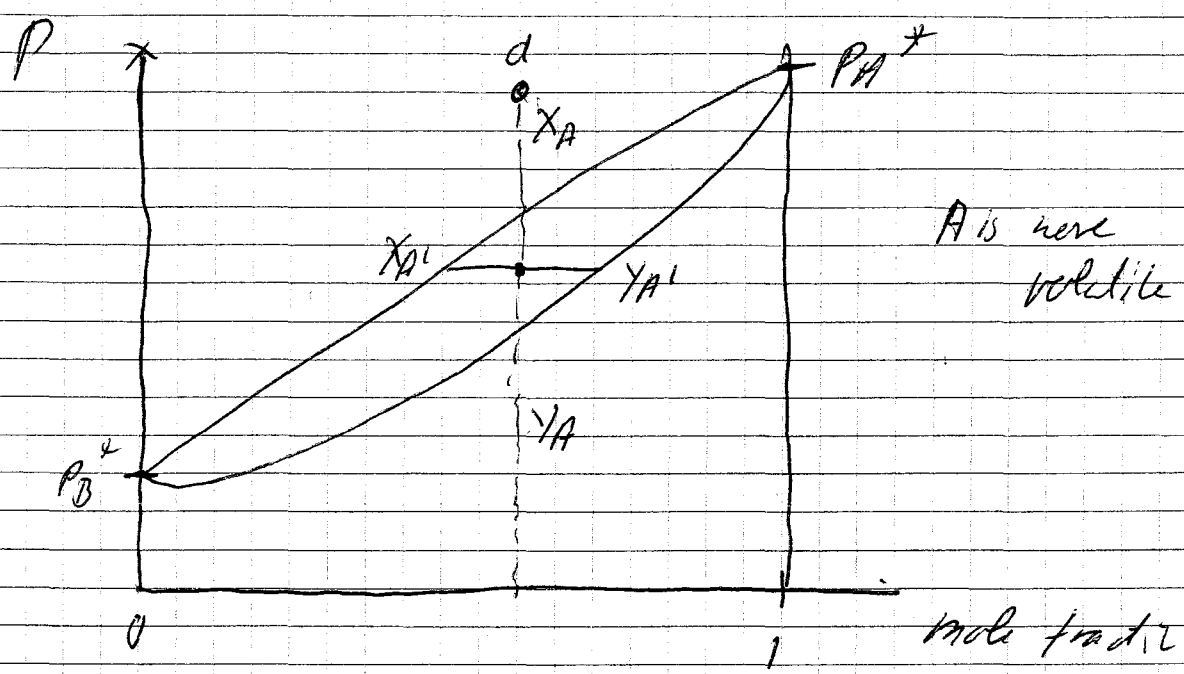
$\chi_B = \frac{P_B}{P}$

$\chi_A = \frac{\chi_A P_A^*}{P_B^* + (P_A^* - P_B^*) \chi_A}$

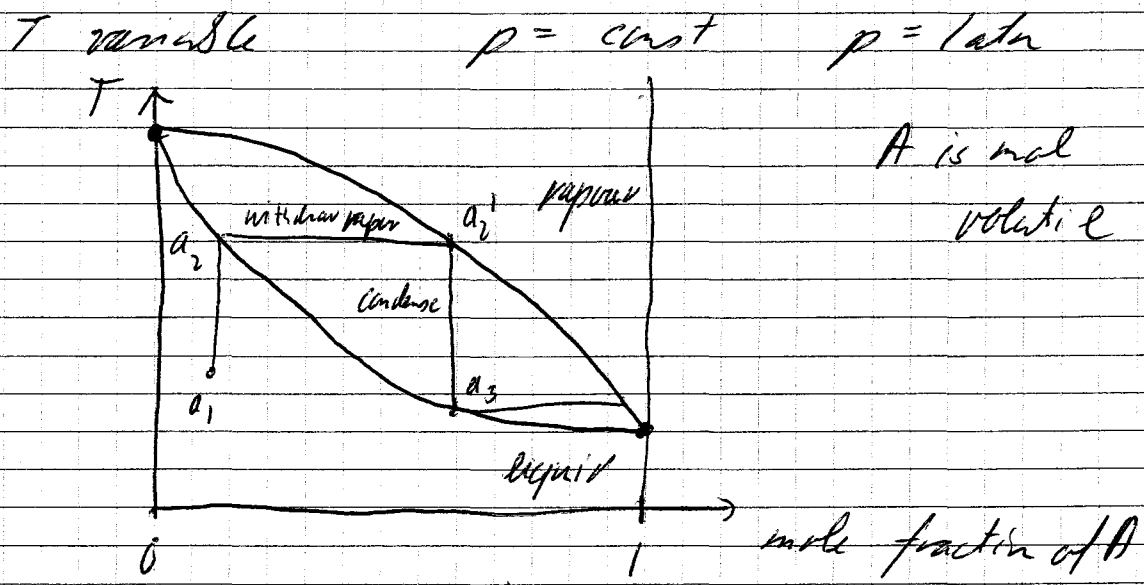
$\chi_B = 1 - \chi_A$

$P = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) \chi_A}$





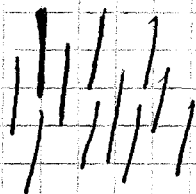
Temperature composition diagrams



# Liquid crystals

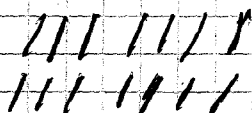
- mesophase: intermediate between solid and liquid
- molecules have highly anisotropic shape

nematic

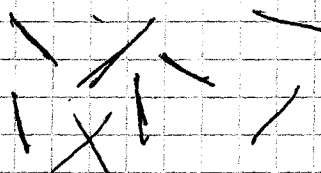


ordered in one direction fluid in all other direction

smectic



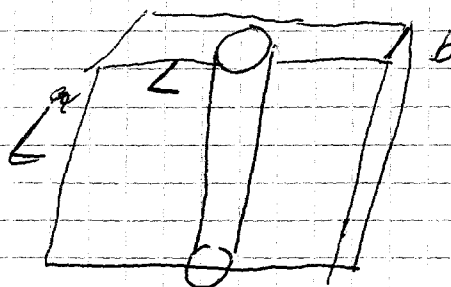
disordered



- thermotropic liquid crystal displays a transition to the liquid crystalline phase as the temperature is varied
- lyotropic liquid crystals is a solution that displays a transition to the liquid crystalline phase as the concentration is increased

Onsager criterion: ~~isotropic, nematic~~

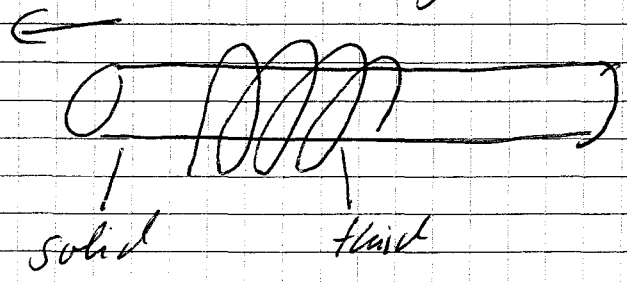
$$k_{onset, nematic} = \frac{1}{bL^2}$$



- LCD display:
  - twisted nematic between two flat plates  $\approx 10 \mu m$
  - plates are coated with conducting material
  - between two polarizing filter
  - nematic is twisted by  $270^\circ$ 
    - $\Rightarrow$  linear polarized becomes spherical polarized
    - $\Rightarrow$  gets through polarizer
  - additional E-field destroys twist and orients  $\Rightarrow$  no more light through since linear polarized in wrong direction

Zone refining:

$\Rightarrow$  pure silicon or germanium  
heating coil



impurities like to stay in liquid phase

potential exercises:

8.2, 8.3, 8.7

potential problems

8.3, 8.10