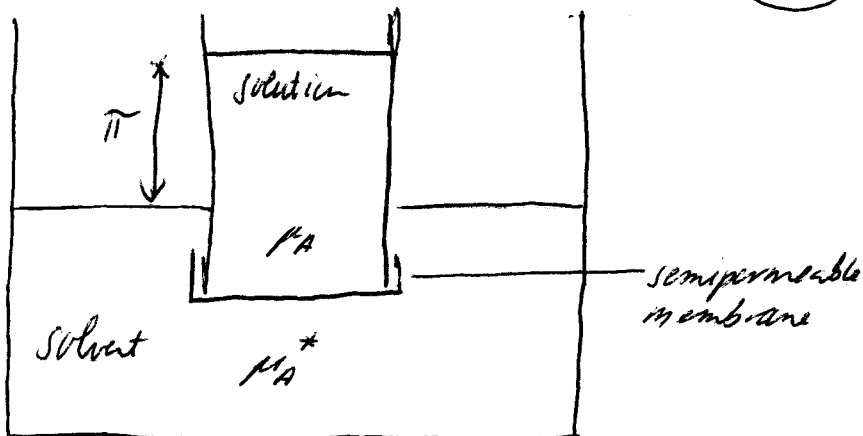


Osmotic pressure π

ideal solutions

mole fraction of the solvent $1 \rightarrow X_A$



solvent A:

$$\mu_A^*(p) = \mu_A(X_A, p + \pi) =$$

$$= \mu_A^*(p + \pi) + RT \ln X_A$$

$$\mu_A^*(p + \pi) = \mu_A^*(p) + \int_p^{p + \pi} V_m dp$$

$$\Rightarrow -RT \ln X_A = \int_p^{p + \pi} V_m dp$$

$\ln(1 - X_B) \approx -X_B$ for dilute
 $\int_p^{p + \pi} V_m dp \approx V_m \pi$ for dilute

$$\Rightarrow RT X_B = \pi V_m$$

$$\approx \frac{n_B}{n_A} \quad \rightarrow \quad n_A V_m = V$$

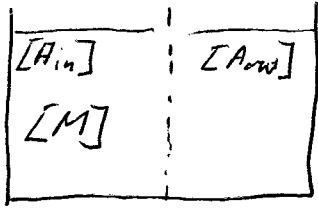
$$\Rightarrow \boxed{\pi = \frac{n_B}{V} RT}$$

(equal to an ideal gas law)

Binding of small reagents to proteins

[M] = concentration of a protein or other macromolecule
= solute which cannot pass membrane

[A] = concentration of small solute which can pass membrane and binds to M:



$$[A_{in}] = [A_{free}] + [A_{bound}]$$

$$[A_{free}] = [A_{out}]$$

average number \bar{c} of molecules A bound to M:

$$\bar{c} = \frac{[A_{bound}]}{[M]} = \frac{[A_{in}] - [A_{out}]}{[M]}$$

⇒ Dialysis: small molecule A can be removed in a dialysis tube when A_{out} is removed!

$$K = \frac{[MA]}{[M_{free}][A_{free}]} = \frac{[A_{bound}]}{([M] - [A_{bound}])[A_{free}]}$$

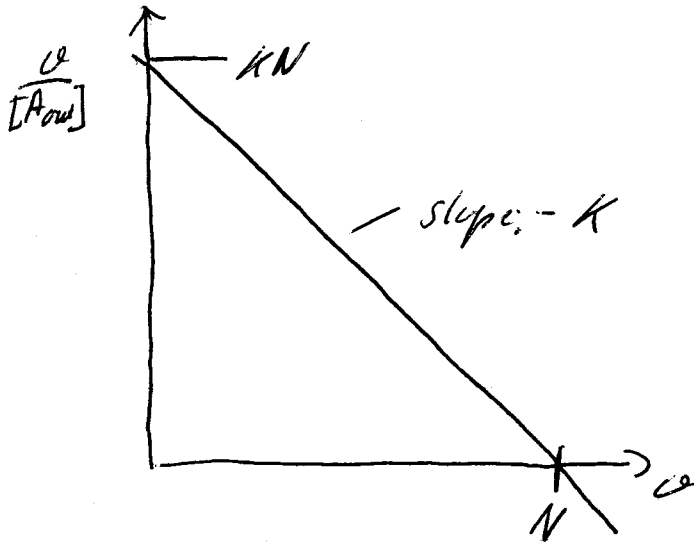
\bar{c}
divided by [M] $(1 - \bar{c}) [A_{out}]$

N identical and independent binding sites on each macromolecule

$$K = \frac{\bar{c}/N}{(1 - \bar{c}/N)[A_{out}]}$$

Scatchard plot:

$$\frac{v}{[A_{out}]} = KN - Kv$$



Molecular mass of a macromolecules:

for non-ideal solutions:

Taylor expansion

$$\pi = RT \left(\frac{n_B}{V} + B \frac{n_B^2}{V} + \dots \right)$$

$$\pi = \rho g h \quad \frac{n_B}{V} = \frac{C}{M} \quad [C] = \frac{mg}{ml}$$

molecular weight

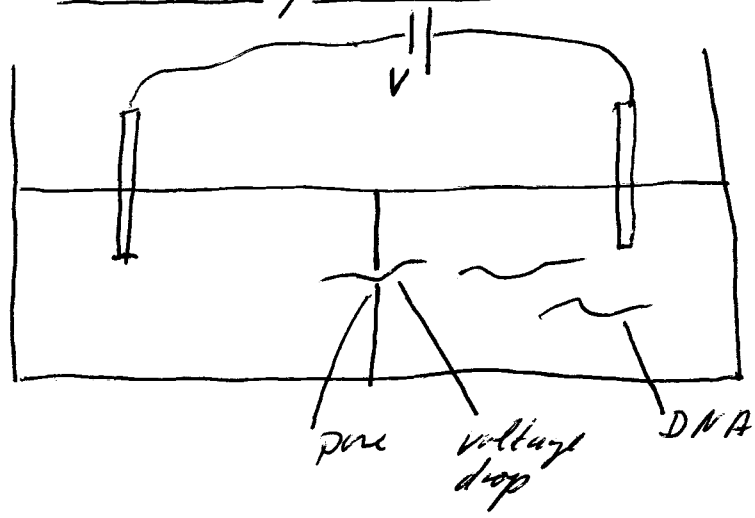
$$\Rightarrow \frac{h}{C} = \frac{RT}{\rho g M} \left(1 + B \frac{C}{M} + \dots \right)$$

$$= \frac{RT}{\rho g M} + \left(\frac{RTB}{\rho g M^2} \right) \cdot C + \dots$$

\Rightarrow Plot h/c against C intercepts ~~for~~
~~start~~ with C -Axis for $C=0$
 at $\frac{RT}{\rho g M}$

\Rightarrow M can be determined

Pores Molecular pores and DNA



osmotic pressure pushes
DNA through pore

Activities and non-ideal solutions

solvent: ideal + non-ideal: $\mu_A = \mu_A^* + RT \ln \frac{P_A}{P_A^*}$
 ideal : $\mu_A = \mu_A^* + RT \ln X_A$
 non-ideal : $\mu_A = \mu_A^* + RT \ln a_A$ with $a_A = \frac{P_A}{P_A^*}$
 activity

solute: ideal + non-ideal: $\mu_B = \mu_B^* + RT \ln \frac{P_B}{P_B^*}$
 ideal : $\mu_B = \mu_B^* + RT \ln \frac{K_B X_B}{P_B^0} + RT \ln X_B$
 $\quad \quad \quad = \mu_B^0$
 $\quad \quad \quad P_B = K_B X_B$
 $\quad \quad \quad \text{constant}$
 real : $\mu_B = \mu_B^0 + RT \ln a_B$ with $a_B = \frac{P_B}{K_B}$

4. Phase Diagrams:

4.1. Gibb's Phase Rule:

phase P: uniform state of matter

e.g. miscible liquids \Rightarrow 1 phase, water + ethanol
emulsion
~~dispersion~~ \Rightarrow 2 phases, water + oil

constituent: present chemical species

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

component c: chemically ~~the~~ independent constituent

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

variance F: number of intensive variables that can be
(= degrees of freedom) 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 freely, but the change in temperature (or pressure) demands a conform change in pressure (or temperature) $\Rightarrow F = 1$

Gibb's Phase Rule

$$F = C - P + 2$$

proof:total number of intensive variables $(p, T) = 2$ + specify the composition of a phase by giving the mole fraction of $C-1$ components $(x_1 + x_2 + \dots + x_c = 1)$ × P number of phase

$$= \boxed{\text{total number of intensive variables: } P(C-1) + 2}$$

At equilibrium: $\mu_i(\alpha) = \mu_i(\beta) = \dots$ for p -phase $\Rightarrow p-1$ equations for each component i × C components

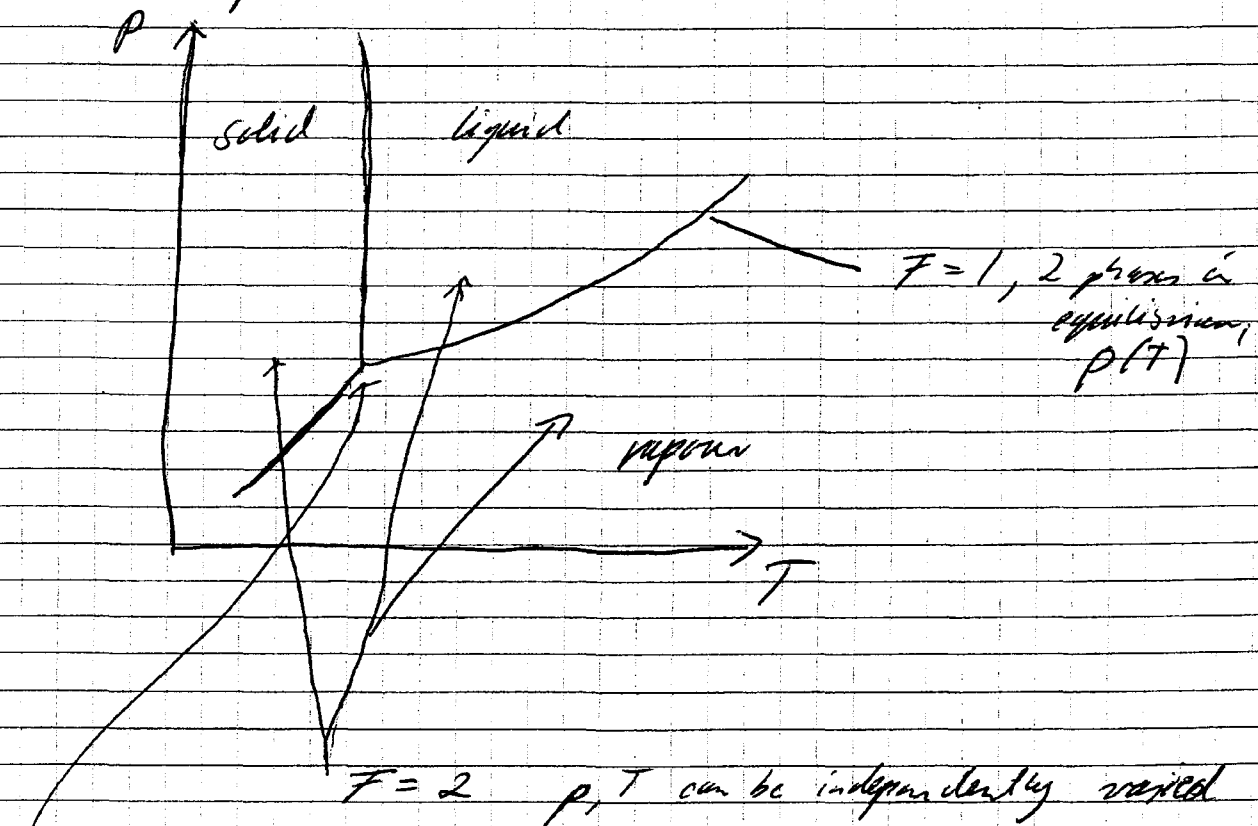
$$= \boxed{\text{total number of equations: } C(P-1) \text{ for equilibrium}}$$

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



$F=0$, 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

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

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

gas mole fraction

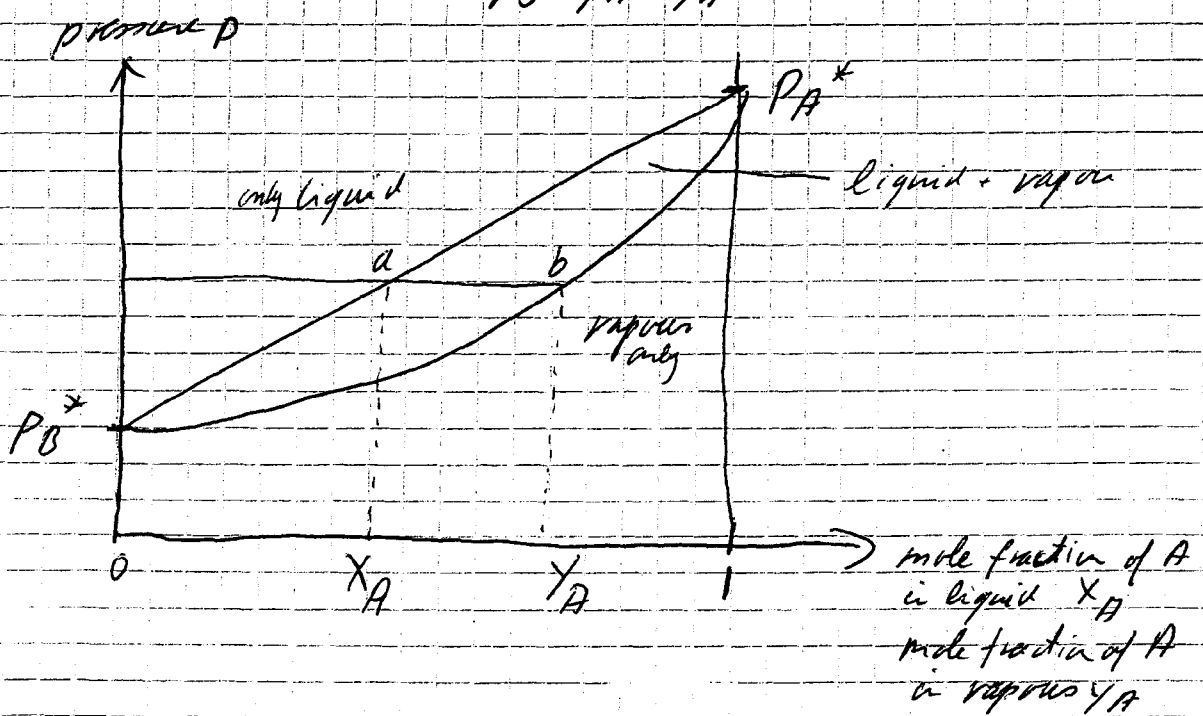
$\chi_A = \frac{P_A}{P}$

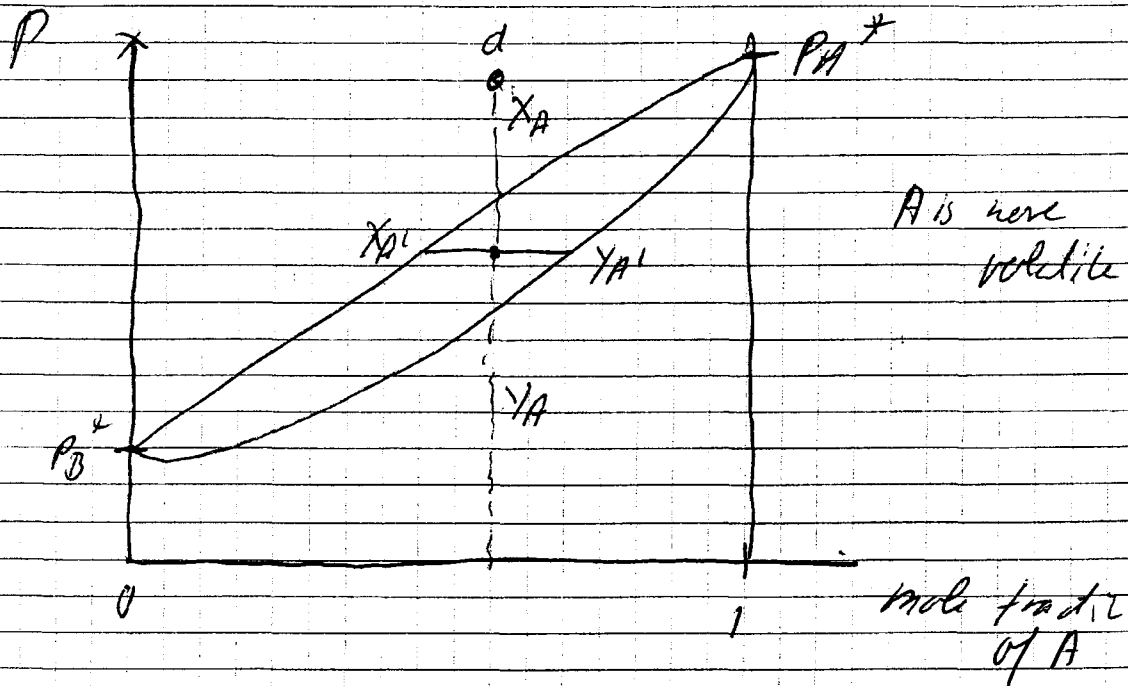
$\chi_B = \frac{P_B}{P}$

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

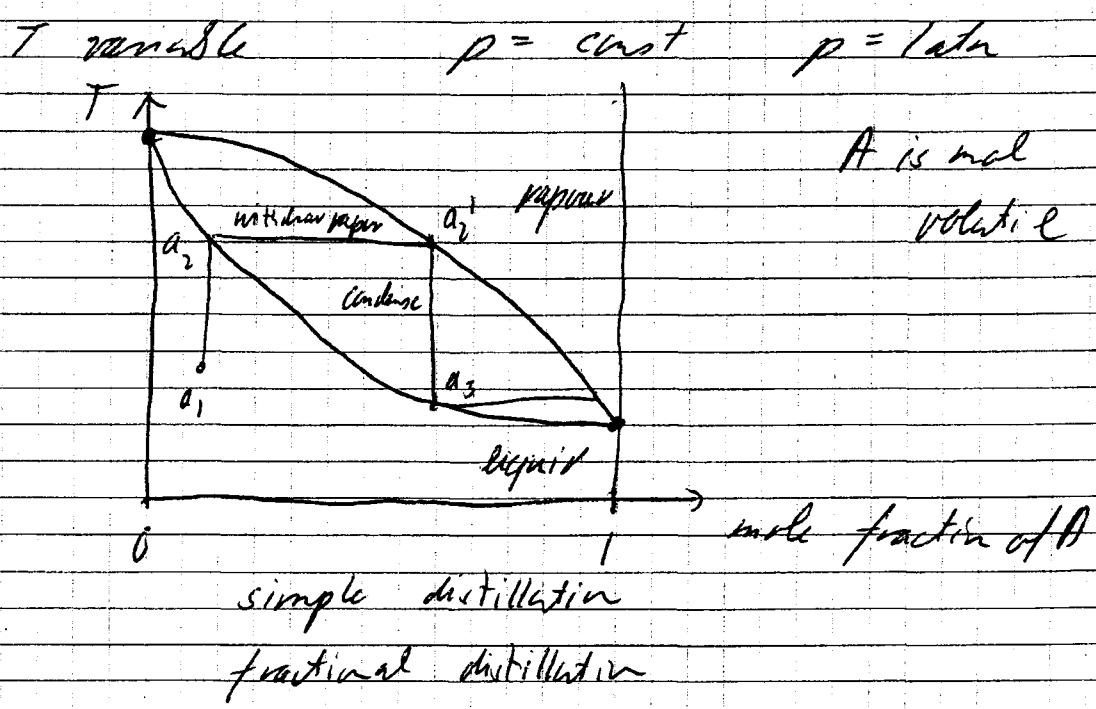
$\chi_B = 1 - \chi_A$

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





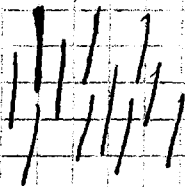
Temperature composition diagrams



Liquid crystals

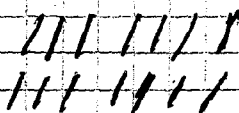
- mesophase: intermediate between solid and liquid
- molecules have highly anisotropic shape

nematic

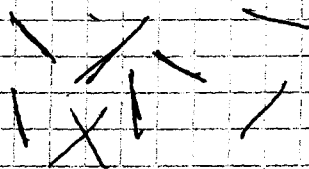


ordered in one
direction parallel
in all other direction

smectic



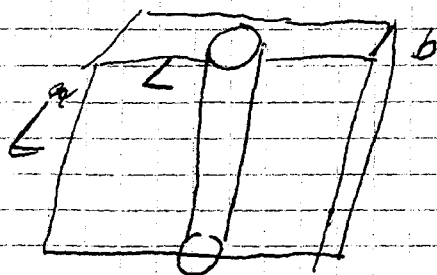
discoidal



- 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:

$$N_{\text{onset, nematic}} = \frac{1}{b L^2}$$



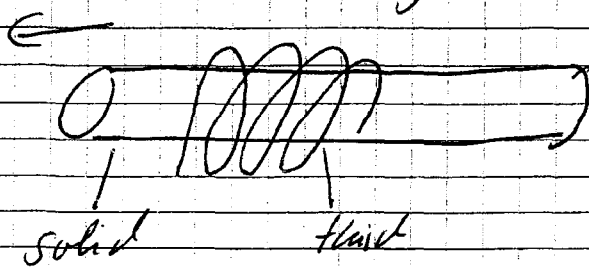
- LCD display:

- twisted nematic between two flat plates $\approx 120\mu\text{m}$
- plates are coated with conducting material
- between two polarizing filter
- nematic is twisted by 270°
 - \Rightarrow linear polarized becomes spherical polarized
 - \Rightarrow gets through polarizer
- additional E-field destroys twist and aligns \Rightarrow no more light through since linear polarized in wrong direction

Fibre refining:

\Rightarrow pure silicon or germanium

heating coil



impurities like to stay in fluid phase

potential exercises:

8.2, 8.3, 8.7

potential problems

8.5, 8.10