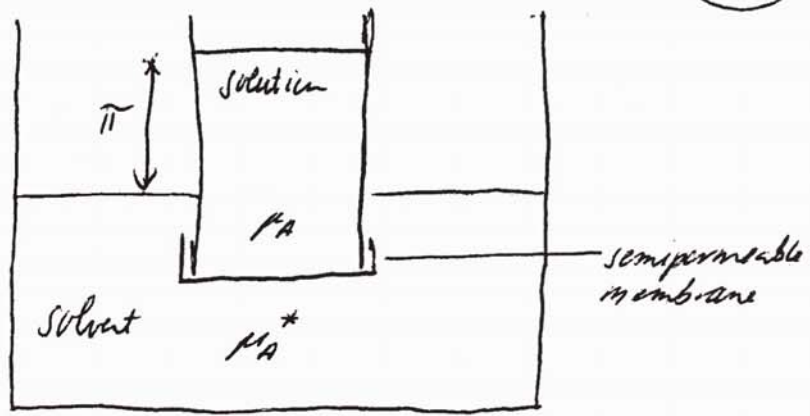


Osmotic pressure π

ideal solutions

mole fraction of the solvent $\rightarrow X_A$



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

\approx const. for dilute

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

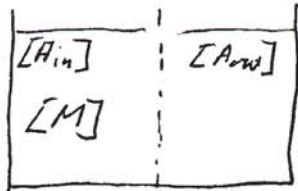
$$\approx \frac{n_B}{n_A} \rightarrow n_A V_m = V$$

$$\Rightarrow \boxed{\pi = \frac{n_B}{V} RT} \quad (\text{equal to an ideal gas law})$$

Binding of small ligands 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 θ of molecules A bound to M :

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

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

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

~~$$= \frac{\theta}{(1 - \theta)[A_{out}]}$$

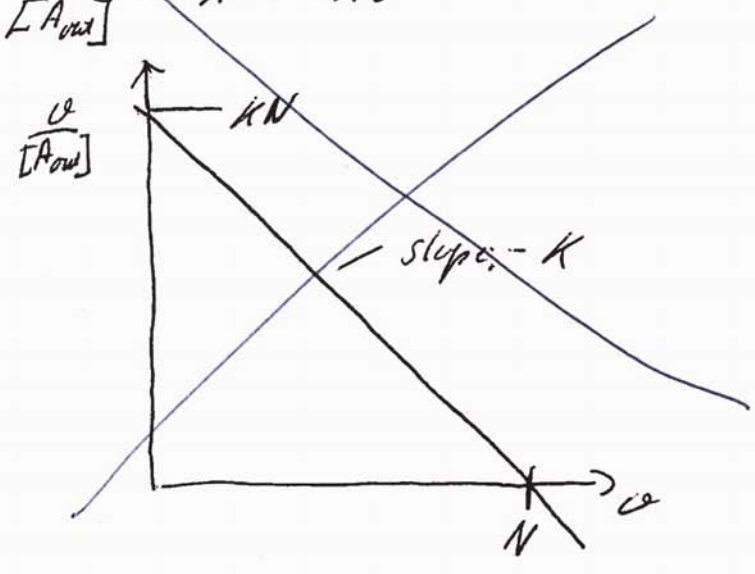
division by $[M]$~~

N identical and independent binding sites on each macromolecule

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

Scatchard plot:

$$\frac{c}{[A_{out}]} = KN - Kc$$



Molecular mass of a macromolecules:

for non-ideal solutions:

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

Taylor expansion

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

molecular weight

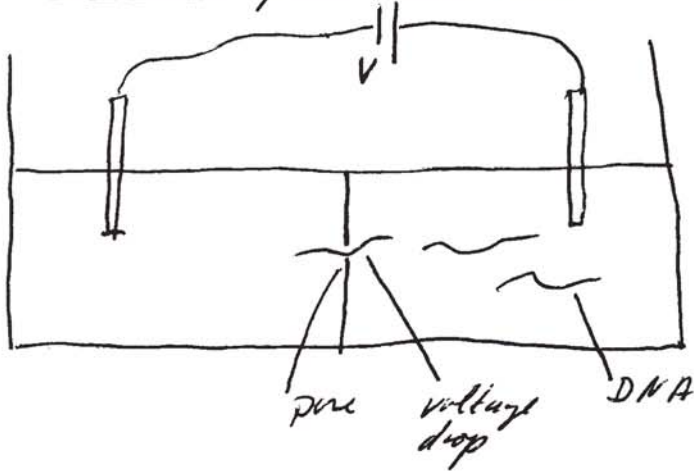
$$\Rightarrow \frac{h}{c} = \frac{RT}{\rho g M} \left(1 + B \frac{c}{M} + \dots \right)$$

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

\Rightarrow Plot h/c against c intercepts ~~for~~
~~at~~ 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

solvent: ideal + non-ideal: $\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*}$

ideal: $\mu_B = \mu_B^* + RT \ln \frac{K_B X_B}{p_B^0} + RT \ln X_B$
 $= \mu_B^0$
 $p_B = K_B X_B$
 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
 (= degree 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 $(X_1 + X_2 + \dots + X_C = 1)$

x P number of phase

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

At equilibrium: $\mu_i(\alpha) = \mu_i(\beta) = \dots$ for p -phase

$\Rightarrow p-1$ equations for each component i

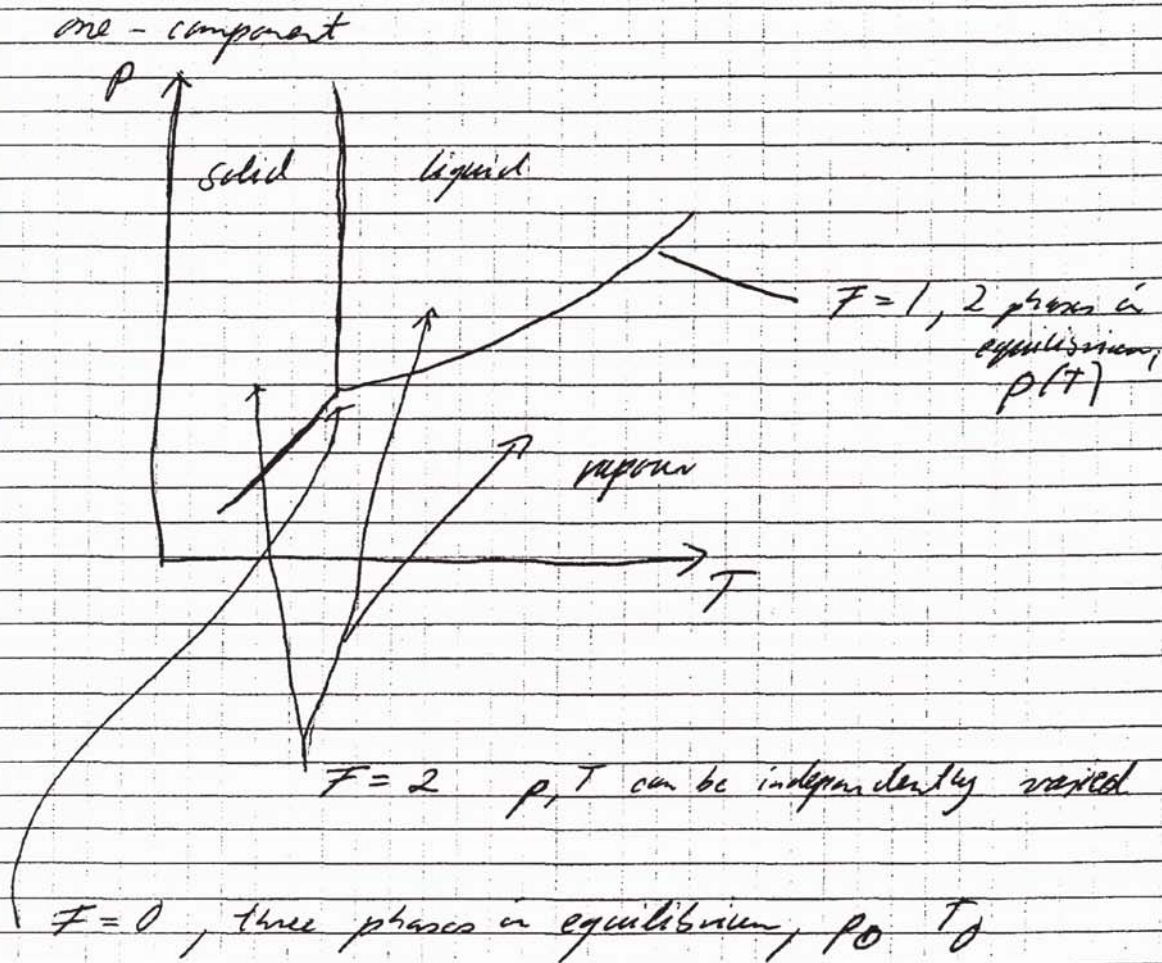
x C components

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

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

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

Gibb's rule helped to predict phase diagrams:



four phases in equilibrium? \Rightarrow not possible

experimental procedures:

thermal analysis \Rightarrow enthalpy change during a first order transition

\Rightarrow • differential scanning calorimetry

• DSC with cell

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

$P_A = \chi_A P_A^*$, $P_B = \chi_B P_B^*$ 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

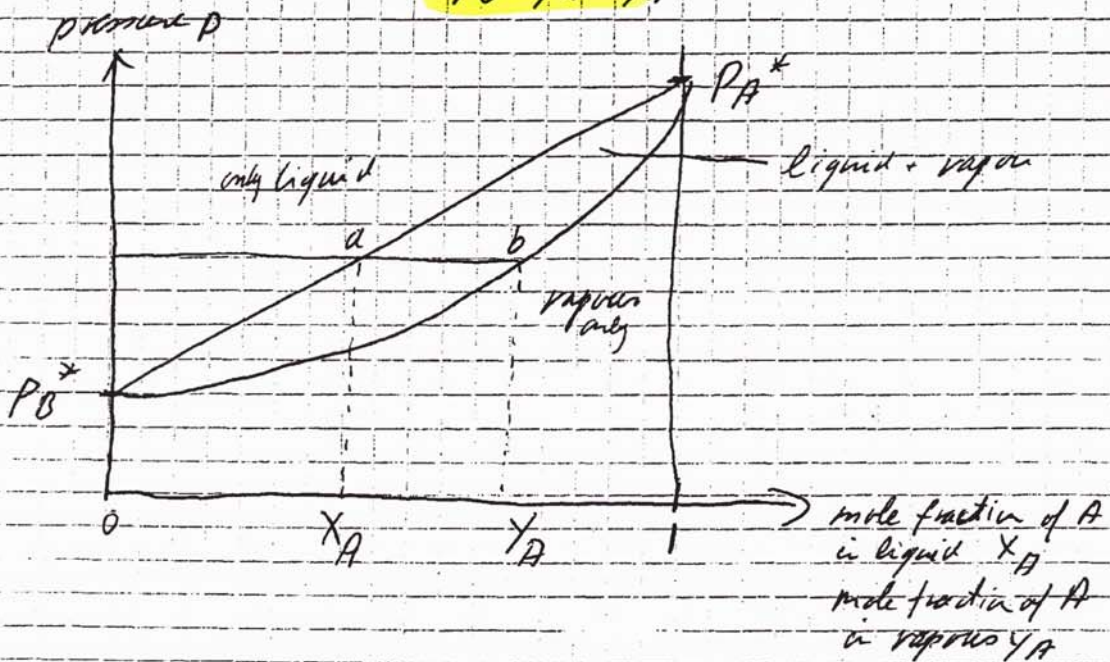
$\chi_A = \frac{P_A}{P}$

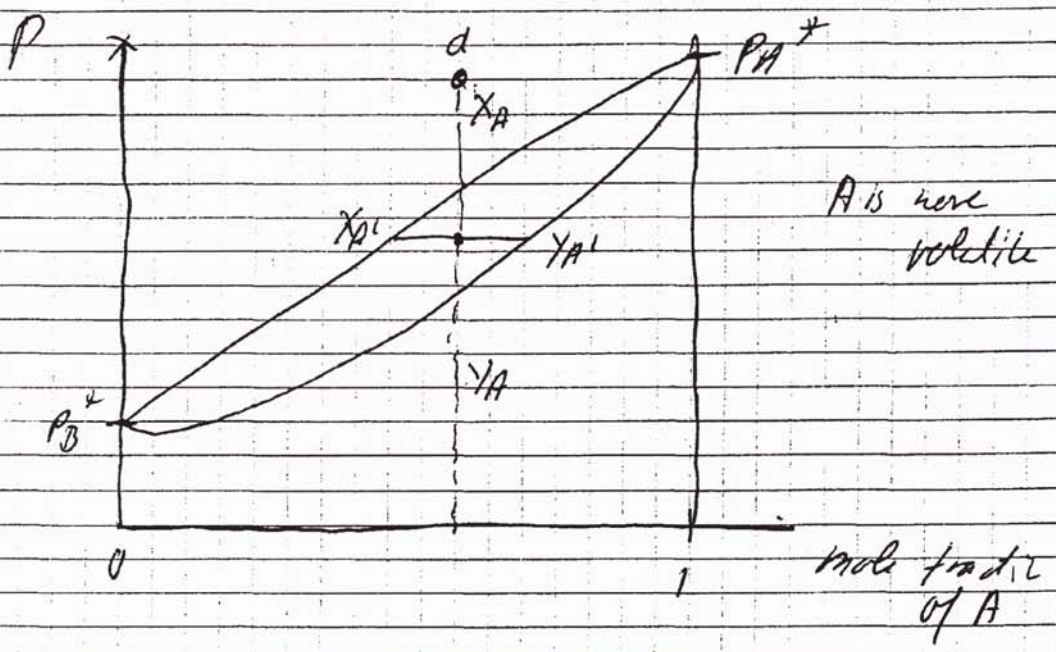
$\chi_B = \frac{P_B}{P}$

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

$\chi_B = 1 - \chi_A$

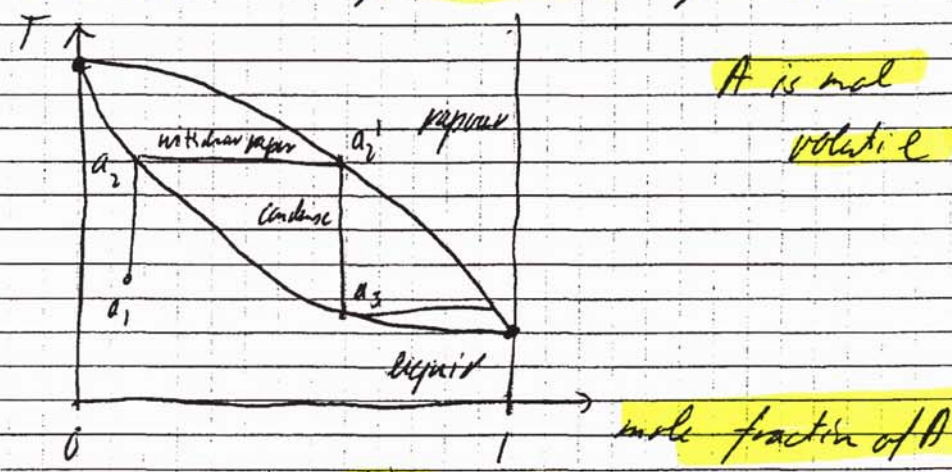
gas $P = \frac{P_A^* P_B^*}{P_A^* + (P_B^* - P_A^*) \chi_A}$





Temperature-composition diagrams

T variable p = const p = latm



simple distillation

fractional distillation

Ques 12.11.07
Answer

Liquid crystals

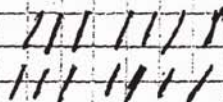
- mesophase: intermediate between solid and liquid
- molecules have highly anisotropic shape

nematic

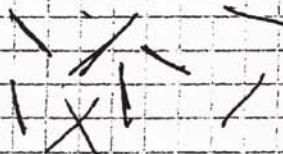


ordered in one
direction parallel
in all other direction

smectic



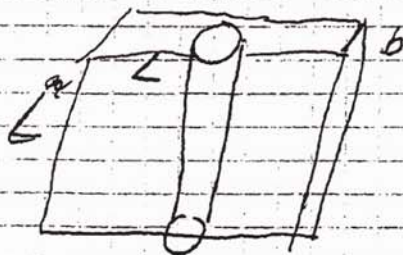
discordered



- 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

Ohsuga criterion: ~~isotropic phase~~

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

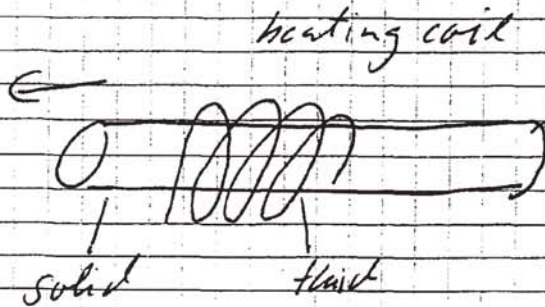


• LCD display:

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

Fine refining:

\Rightarrow pure silicon or germanium



impurities like to stay in fluid phase

potential exercises:

8.2, 8.3, 8.7

potential problems

8.5, 8.10

5. Chemical Equilibrium

1. Spontaneous chemical reactions



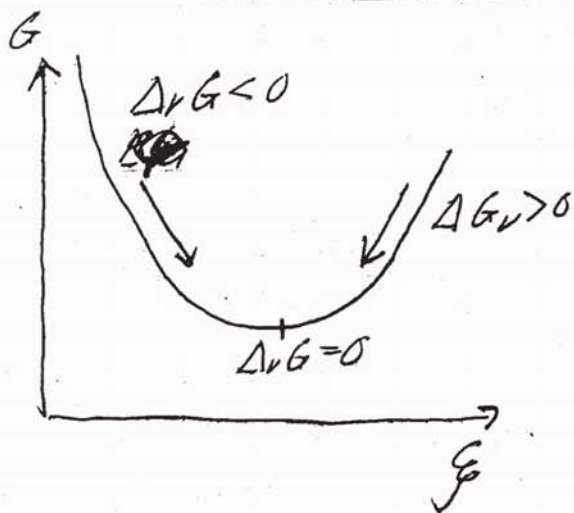
ξ : extent of reaction

$$dn_A = -d\xi = dn_B$$

$$dG = \mu_A dn_A + \mu_B dn_B = (\mu_B - \mu_A) d\xi$$

Def.: reaction Gibbs energy

$$\Delta_r G = \left. \frac{\partial G}{\partial \xi} \right|_{P,T} = \mu_B - \mu_A$$



$\Delta_r G < 0$:

reaction is spontaneous

\Rightarrow exergonic

$\Delta_r G > 0$:

reverse reaction is

spontaneous \Rightarrow endergonic

$\Delta_r G = 0$: equilibrium

2. Description of equilibrium



$$\Delta_r G = \mu_B - \mu_A = (\mu_B^\circ + RT \ln p_B) - (\mu_A^\circ + RT \ln p_A)$$

$$= \Delta_r G^\circ + RT \ln \frac{p_A}{p_B} = \Delta_r G + RT \ln Q$$

= Q reaction quotient

~~$\Delta_r G^\circ$~~ $\Delta_r G^\circ = G_{B,m}^\circ - G_{A,m}^\circ = \mu_B^\circ - \mu_A^\circ =$
 $= \Delta_{\text{formation}} G^\circ(B) - \Delta_{\text{formation}} G^\circ(A)$

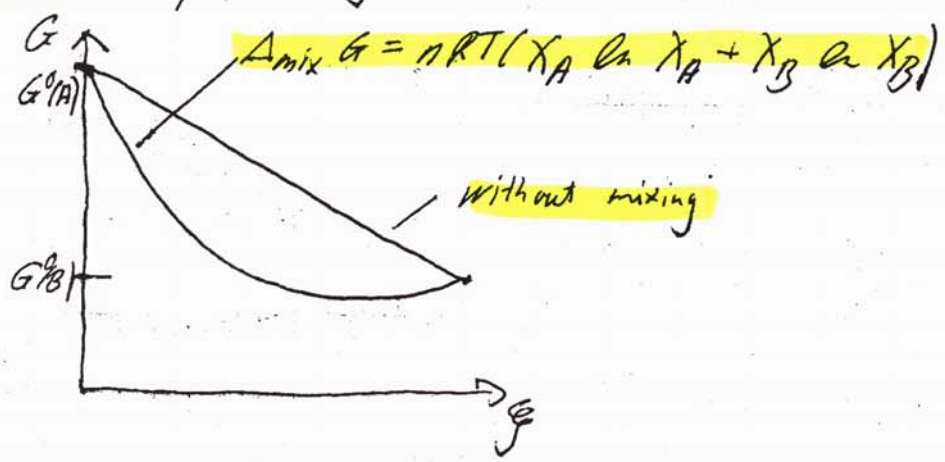
At equilibrium:

$\Delta_r G = 0 \Rightarrow 0 = \Delta_r G^\circ + RT \ln K$

$$\Rightarrow K = \frac{p_B}{p_A} \Big|_{\text{equilibrium}}$$

equilibrium constant

relevance of mixing:



2. Description of equilibrium



$$\Delta_r G = \mu_B - \mu_A = (\mu_B^\circ + RT \ln p_B) - (\mu_A^\circ + RT \ln p_A)$$

$$= \Delta_r G^\circ + RT \ln \frac{p_A}{p_B} = \Delta_r G + RT \ln Q$$

= Q reaction quotient

~~$$\Delta_r G^\circ = G_{B,m}^\circ - G_{A,m}^\circ = \mu_B^\circ - \mu_A^\circ =$$~~

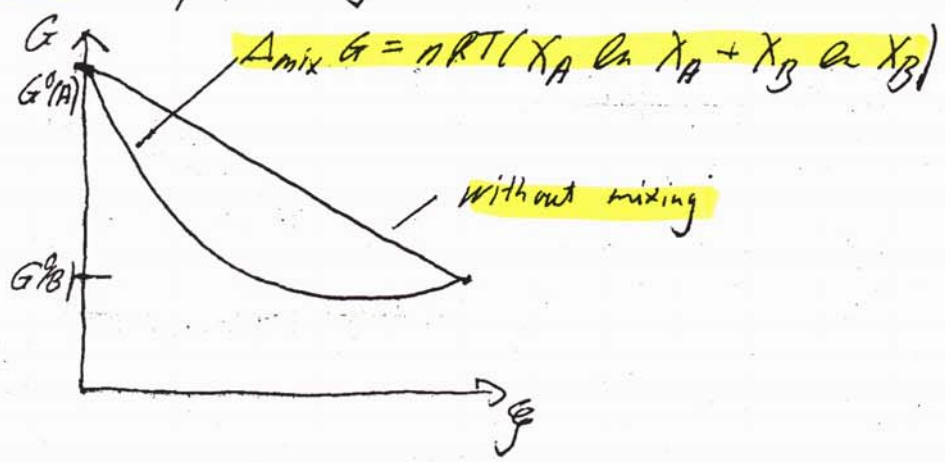
$$= \Delta_{\text{formation}} G^\circ(B) - \Delta_{\text{formation}} G^\circ(A)$$

At equilibrium:

$\Delta_r G = 0 \Rightarrow 0 = \Delta_r G^\circ + RT \ln K$

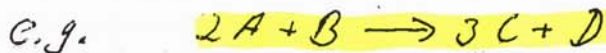
$$\Rightarrow K = \frac{p_B}{p_A} \Big|_{\text{equilibrium}} \text{ equilibrium constant}$$

relevance of mixing:



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general reactions:



$\Rightarrow 0 = 3C + D - 2A - B$ products positive
 $\quad \quad \quad = \nu_C \quad \nu_D \quad -\nu_A \quad -\nu_B$ reactants negative

general: $0 = \sum_j \nu_j J$

stoichiometric
numbers

$$dG = \sum_j \mu_j da_j = \left(\sum_j \nu_j \mu_j \right) d\xi$$

$$\Delta_r G = \frac{\partial G}{\partial \xi} \Big|_{P,T} = \sum_j \nu_j \mu_j \quad \text{and} \quad \mu_j = \mu_j^\circ + RT \ln a_j$$

activity
↓

$$\Delta_r G = \underbrace{\sum_j \nu_j \mu_j^\circ}_{=\Delta_r G^\circ} + RT \sum_j \nu_j \ln a_j$$

$$= \Delta_r G^\circ + RT \ln \underbrace{\prod_j a_j^{\nu_j}}_{=Q} = \Delta_r G^\circ + RT \ln Q$$

$$Q = \prod_j a_j^{\nu_j} = \frac{\text{activities of products}}{\text{activities of reactants}}$$

$$K = \prod_j a_j^{\nu_j} \Big|_{\text{equilibrium}}$$

usually activities are
approximated by molar concentrations!



$$K = \frac{a_C a_D}{a_A a_B} \quad = \frac{K_C K_D}{K_A K_B} \quad = K_X$$

$a_j = \gamma_j X_j$

Molecular interpretation:

$$K = e^{-\Delta_r G^\circ / RT} = e^{-\Delta_r H / RT} e^{\Delta_r S / R}$$

3. Equilibria in biological systems

- ATP:
- fuel of molecular motors and polymerization
 - provides phosphate for phosphorylation

⇒ ATP hydrolysis at 37 °C:

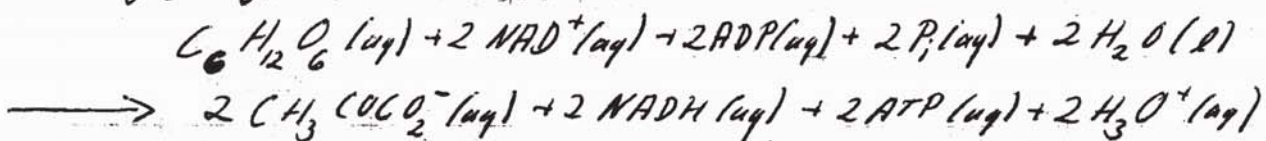


$$\Delta_r G = -30 \frac{\text{kJ}}{\text{mol}} \Rightarrow \text{exergonic}$$

↑
inorganic phosphate group

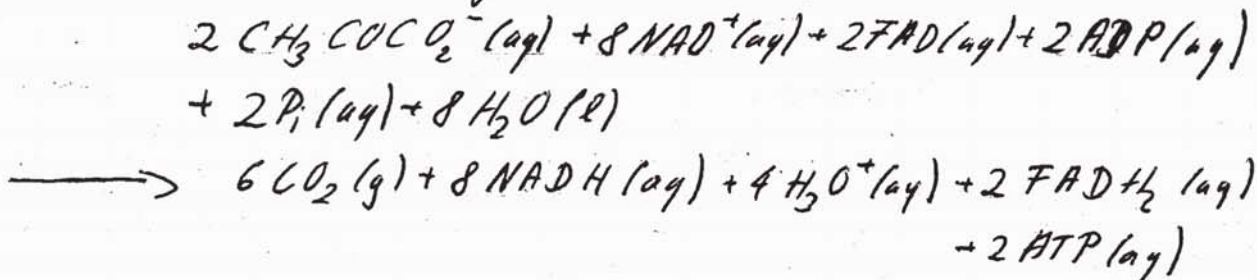
Production of ATP:

- glycolysis in the cytosol:



$$\Delta_r G = -87 \frac{\text{kJ}}{\text{mol}}$$

- citric acid cycle in mitochondria



(70)

4. Temperature and Pressure Dependence

4.1. pressure

• by definition $\left. \frac{\partial K}{\partial P} \right|_T = 0$



$$K = \frac{P_B^2}{P_A P^0} \Rightarrow \text{shift to } A \leftarrow 2B$$

• Le Chatelier's principle:

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance



amount of A at equilib: $(1-\alpha)n$

" of B " " : $2\alpha n$

$$X_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \quad X_B = \frac{2\alpha}{1+\alpha}$$

$$\Rightarrow K = \frac{P_B^2}{P_A P^0} = \frac{X_B^2 P}{X_A P^0} = \frac{4\alpha^2 P}{(1-\alpha^2) P^0}$$

$$\alpha = \left(\frac{1}{1 + 4 P/P^0 \cdot 1/K} \right)^{1/2}$$

4.2. Temperature

(71)

The van't Hoff equation:

$$\ln K = - \frac{\Delta_r G^\circ}{RT}$$

$$\boxed{\frac{d \ln K}{dT} = - \frac{1}{R} \frac{d(\Delta_r G^\circ / T)}{dT} = - \frac{\Delta_r H^\circ}{RT^2}}$$

standard reaction enthalpy

$$\frac{d(1/T)}{dT} = - \frac{1}{T^2} \Rightarrow dT = -T^2 d(1/T)$$

$$\Rightarrow \boxed{\frac{d \ln K}{d(1/T)} = - \frac{\Delta_r H^\circ}{R}}$$

\Rightarrow K at different temperatures:

$$\ln K_2 - \ln K_1 = \frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^\circ d(1/T)$$

$\approx T$ independent

$$\Rightarrow \boxed{\ln K_2 - \ln K_1 = - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

4.3 The pH

$$pH = -\log a_{H_3O^+}$$

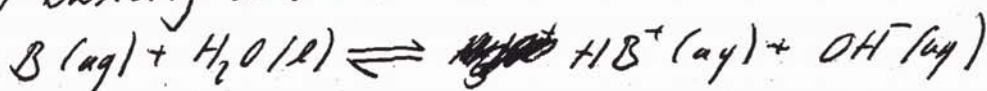
acid-base equilibria in water:

~~KA~~ (i) acidity constant



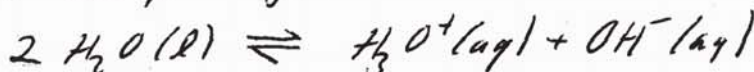
$$K_A = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} \Rightarrow pK_A = -\log K_A$$

(ii) basicity constant



$$K_B = \frac{a_{HB^+} a_{OH^-}}{a_B} \Rightarrow pK_B = -\log K_B$$

(iii) autoprotolysis



$$K_W = a_{H_3O^+} a_{OH^-} \quad pK_W = -\log K_W$$

$$pK_W = pH + pOH \quad \text{with } pOH = -\log a_{OH^-}$$

$$K_W = K_A K_B$$

acids

weak acids and bases: minimum lies close to reactants

⇒ proton transfer small

⇒ HA or B ≈ unchanged

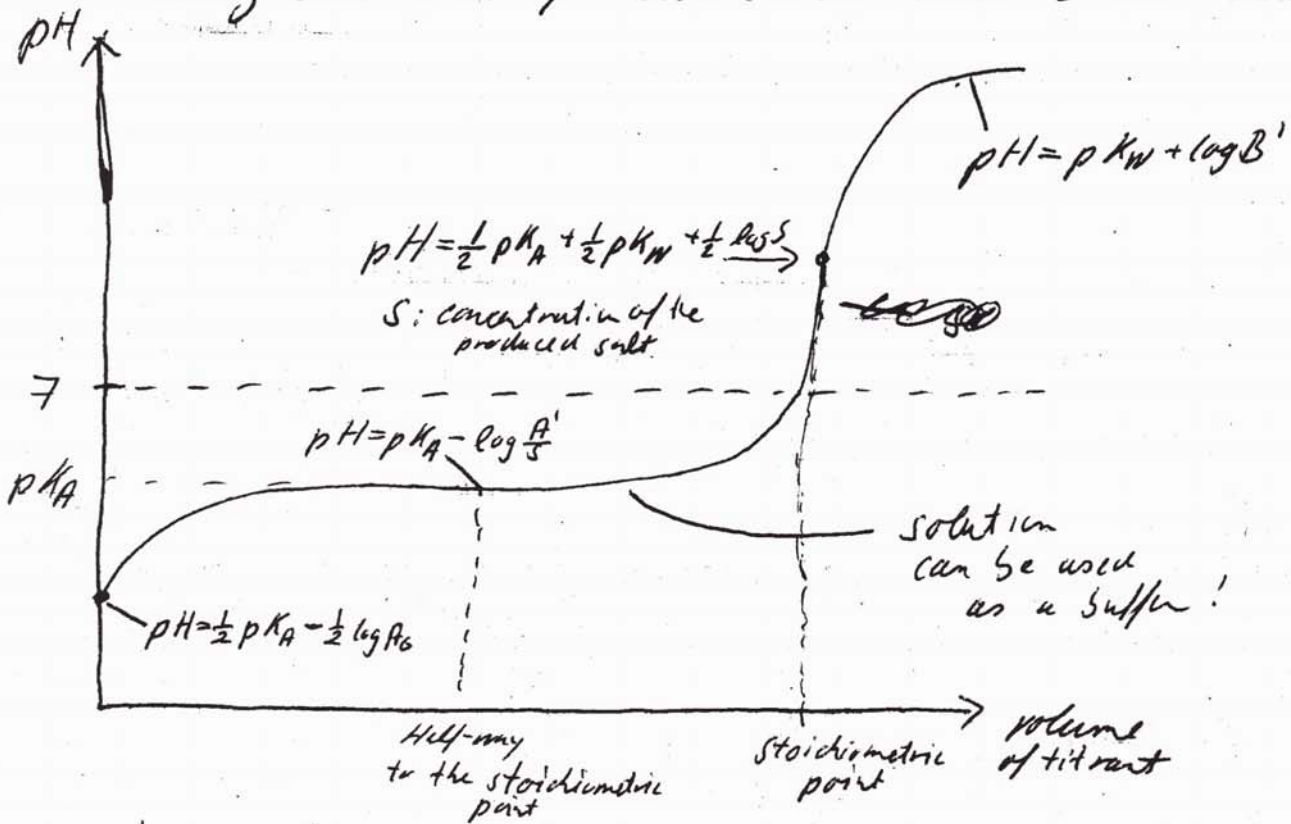
$$K_A \approx \frac{[H_3O^+]^2}{[HA]} \Rightarrow pH \approx \frac{1}{2} pK_A - \frac{1}{2} \log [HA]$$

$[H_3O^+] \approx [A^-]$

analog: $pH = pK_w - \frac{1}{2} pK_B + \frac{1}{2} \log [B]$

Titration:

titrating a volume V_A of a weak acid of molar concentration A_0 (the analyte) with a solution of a strong base MOH of molar concentration B (the titrant)



$$A' = A_0 \frac{V_A}{V} - S$$