

Lecture 18

- Chemical reactions: basic concepts
 - extent of reaction
 - heat effects: standard heat of reaction, standard heat of formation
 - how to include reaction heat effects in first and second law
- Chemical equilibrium
 - gas phase
 - liquid phase I: reacting liquids
 - liquid phase II: reaction in common solvent
 - multiphase reactions
- Effects of temperature, pressure, inert gas
- Simultaneous equilibrium
- Coupled reactions – free energy transduction

Read Chs. 13 and 15 Sandler

Objectives

- Know the definition of basic properties
 - extent of reaction
 - heat effects: standard heat of reaction, standard heat of formation
 - standard Gibbs free energy of formation
 - standard states for gas, liquids (both solvent and solutes), solid
- Know how to include reaction heat effects in first and second law type problems
- Be able to derive specific chemical equilibrium conditions from the most general condition using chemical potential
- Effects of temperature, pressure, inert gas

Extent of Reaction

$$\nu_1 C_1 + \nu_2 C_2 + \dots + \nu_r C_r = 0$$

$$t = 0, \xi = 0 \qquad n_1^0 \qquad n_2^0 \qquad n_r^0$$

$$t = t, \xi = \xi \qquad n_1 \qquad n_2 \qquad n_r$$

$$\xi = \frac{n_i - n_i^0}{\nu_i} = \frac{\Delta n_1}{\nu_1} = \frac{\Delta n_2}{\nu_2} = \dots = \frac{\Delta n_r}{\nu_r}$$

$$d\xi = \frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_r}{\nu_r}$$

Depends on how reaction equation is written

Heat of Reaction

$$\nu_1 C_1 + \nu_2 C_2 + \dots + \nu_r C_r = 0$$

Constant V

$$\Delta_{rxn} U = \sum_i n_i u_i - \sum_i n_i^0 u_i = \xi \sum_i \nu_i u_i$$

Constant P

$$\Delta_{rxn} H = \sum_i n_i h_i - \sum_i n_i^0 h_i = \xi \sum_i \nu_i h_i(T, P)$$

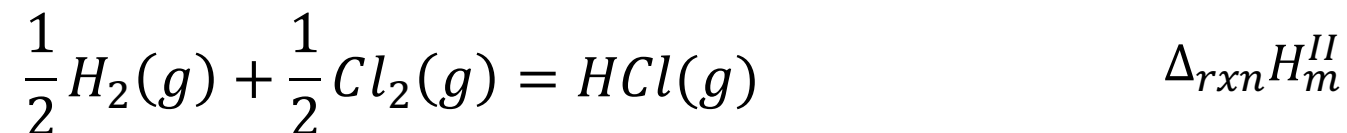
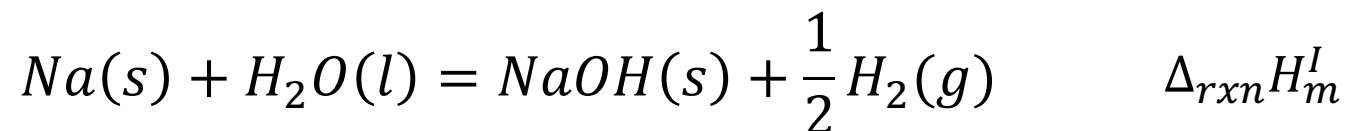
$$\Delta_{rxn} H_m = \frac{1}{\xi} \Delta_{rxn} H \quad \text{Molar heat of reaction}$$

Standard state: P=1 bar, any temperature

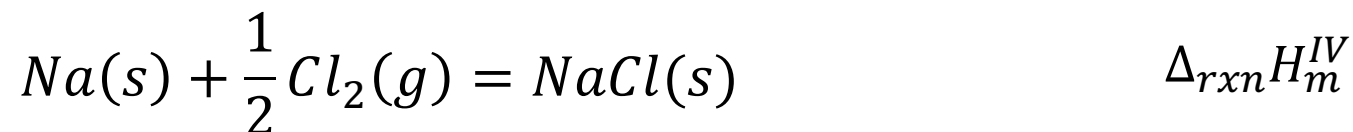
Special standard state: P= 1 bar, T=298.15 K

Hess's Law

$\Delta_{\text{rxn}}U$, $\Delta_{\text{rxn}}H$ etc. depend only on initial and final states and are independent of path



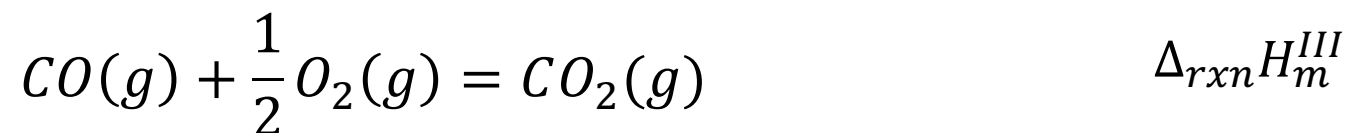
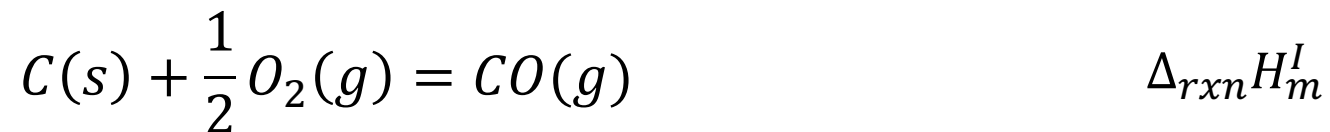
Net reaction



$$\Delta_{\text{rxn}}H_m^{IV} = \Delta_{\text{rxn}}H_m^I + \Delta_{\text{rxn}}H_m^{II} + \Delta_{\text{rxn}}H_m^{III}$$

Application of Hess's Law

Allows calculating $\Delta_{\text{rxn}}H$ for reactions that are difficult to realize or control



Clearly

$$\Delta_{\text{rxn}}H^I = \Delta_{\text{rxn}}H^{II} - \Delta_{\text{rxn}}H^{III}$$

Standard Heat of Formation

At standard pressure, and any specified temperature, the standard heat of formation (or standard enthalpy of formation) is defined as the molar enthalpy of reaction to form the compound from the most stable form of the element

By definition, standard heat of formation for all stable elements is zero

For gas, standard state is a hypothetical state when the gas is ideal

Similar considerations for Standard Gibbs Free Energy of Formation

Kirchhoff's Law

$$\Delta_{rxn}H_m(T) = \Delta_{rxn}H_m(T_0) + \int_{T_0}^T \Delta_{rxn}C_P dT$$

$$\Delta_{rxn}C_P = \sum_i v_i C_{p,i}$$

Reaction Heat in Energy and Entropy Balance

No separate terms involving reaction heat in energy and entropy balance

Heat of reaction enters in the appropriate internal energy and enthalpy terms in the energy balance

Entropy of reaction enters in entropy balance

Chemical Equilibrium – General Condition

$$\sum_i \nu_i \mu_i = 0$$

$$\sum_i v_i \mu_i = 0$$

Gas Phase Reaction

$$\mu_i = \mu_i^\ominus(T) + RT \ln \left(\frac{f_i}{P^\ominus} \right)$$

$$\sum_i v_i \mu_i^\ominus(T) + RT \sum_i \ln \left(\frac{f_i}{P^\ominus} \right)^{v_i} = 0$$

$$\prod_i \left(\frac{f_i}{P^\ominus} \right)^{v_i} = \exp \left[-\frac{\Delta_{rxn} G_m^\ominus}{RT} \right] = K_f^\ominus(T)$$

chemical equilibrium isotherm

$$\Delta_{rxn} G_m^\ominus \equiv \sum_i v_i \mu_i^\ominus$$

Standard Gibbs free
energy of reaction

$$\sum_i \nu_i \mu_i = 0$$

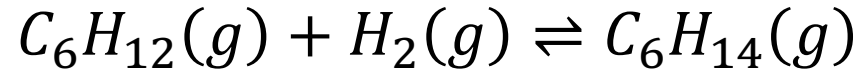
Ideal Gases

$$\prod_i x_i^{\nu_i} = K_x(T, P) = K_f^{\ominus}(T) \left(\frac{P}{P^{\ominus}} \right)^{-\sum_i \nu_i}$$

$$\prod_i P_i^{\nu_i} = K_P(T) = K_f^{\ominus}(T) (P^{\ominus})^{-\sum_i \nu_i}$$

Has dimensions

Example



at $P^\ominus, T = 298.15K$

$\Delta_f H^\ominus$ (kJ/mol)	-123.1	0	-166.9
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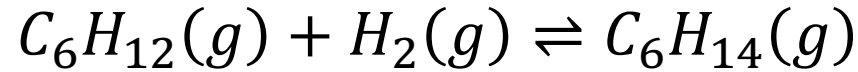
$\Delta_f G^\ominus$ (kJ/mol)	31.9	0	0.2
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$$\Delta_{rxn} H_m^\ominus = -43.8 \text{ kJ/mol} \quad \text{exothermic}$$

$$\Delta_{rxn} G_m^\ominus = -31.7 \text{ kJ/mol} \quad \text{favorable in forward direction}$$

$$K_f^\ominus(298.15) = \exp \left[-\frac{\Delta_{rxn} G_m^\ominus}{RT} \right] = e^{12.788} = 3.58 \times 10^5$$

Example



at $P^\ominus, T = 298.15K$

$$n^0 \qquad \qquad 1 \qquad \qquad 1 \qquad \qquad 0$$

$$n \qquad \qquad y \qquad \qquad y \qquad \qquad 1-y$$

$$K_f^\ominus(298.15) = 3.58 \times 10^5$$

If reaction takes place at ambient pressure

$$\prod_i x_i^{v_i} = K_x(T, P) = K_f^\ominus(T) \left(\frac{P}{P^\ominus} \right)^{-\sum_i v_i}$$

$$\frac{(1-y)/(1+y)}{y^2/(1+y)^2} = 3.58 \times 10^5$$

Since expect $y \ll 1$, to good approximation

$$\frac{1}{y^2} = 3.58 \times 10^5 \qquad y = 1.67 \times 10^{-3}$$

$$\sum_i \nu_i \mu_i = 0$$

Liquid Phase I: Reacting Liquids

$$\mu_i(T, P, x_i) = \mu_i^{(0)}(T, P) + RT \ln a_i$$

$$\prod_i a_i^{\nu_i} = \exp \left[-\frac{\Delta_{rxn} G_m^{(0)}}{RT} \right] = \exp \left[-\frac{\Delta_{rxn} G_m^{\ominus}}{RT} \right] = K_a^{\ominus}(T)$$

chemical equilibrium isotherm

neglecting Poynting factor correction

$$\sum_i \nu_i \mu_i = 0$$

Liquid Phase II: Solutes Reacting in Common Solvent

$$\mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln a_i$$

$$\prod_i a_i^{\nu_i} = \exp \left[-\frac{\Delta_{rxn} G_m^*}{RT} \right] = K_a^*(T)$$

often use concentration in unit of M

$$\mu_i(T, P, x_i) = \mu_i^{**}(T, P) + RT \ln(\gamma_i c_i)$$

$\mu_i^{**}(T, P)$ hypothetical state at 1M concentration

$$\sum_i \nu_i \mu_i = 0$$

Multiphase Reactions

Need to be careful about standard state for each phase



$$\mu_{NH_3} = \mu_{NH_3}^\ominus(T) + RT \ln \frac{f_{NH_3}}{P^\ominus}$$

$$\mu_{HCl} = \mu_{HCl}^\ominus(T) + RT \ln \frac{f_{HCl}}{P^\ominus}$$

$$\mu_{NH_4Cl}(P) = \mu_{NH_4Cl}^\ominus(T) + \nu_{NH_4Cl}(P - P^\ominus) \approx \mu_{NH_4Cl}^\ominus(T)$$

$$\frac{f_{NH_3}}{P^\ominus} \cdot \frac{f_{HCl}}{P^\ominus} = \exp \left[-\frac{\Delta_{rxn} G_m^\ominus}{RT} \right] = K(T)$$

Activity of pure liquid or solid is 1

Effects of Temperature

Gibbs-Helmholtz $\frac{d(G/T)}{dT} = -\frac{H}{T^2}$

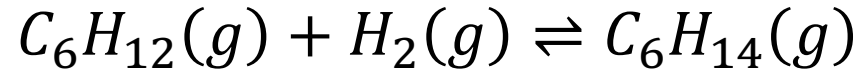
$$\Delta_{rxn} G_m^\ominus = -RT \ln K^\ominus(T)$$

$$\frac{d \ln K^\ominus(T)}{dT} = \frac{\Delta_{rxn} H_m^\ominus}{RT^2}$$

Endothermic $\Delta_{rxn} H_m^\ominus > 0$ K^\ominus increases with T

Exothermic $\Delta_{rxn} H_m^\ominus < 0$ K^\ominus decreases with T

Example



at $P^\ominus, T = 298.15K$

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$\Delta_f G^\ominus$ (kJ/mol)	31.9	0	0.2
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Increasing temperature shifts reaction to the left

Effects of Pressure – Gas Phase

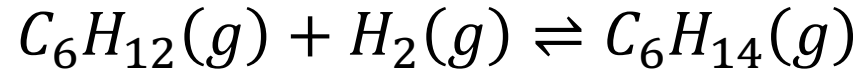
K_f^\ominus is unaffected, however K_x changes according to

$$K_x = K_f^\ominus(T) \left(\frac{P}{P^\ominus} \right)^{-\sum_i \nu_i}$$

$\sum_i \nu_i > 0$ Increases P shifts equilibrium to left

$\sum_i \nu_i < 0$ Increases P shifts equilibrium to right

Example



$$\nu: \quad \quad -1 \quad \quad -1 \quad \quad 1$$

$$\sum_i \nu_i = -1 \quad \quad \prod_i x_i^{\nu_i} = K_x(T, P) = K_f^\ominus(T) \left(\frac{P}{P^\ominus} \right)^{-\sum_i \nu_i}$$

Increases P shifts equilibrium to right

Effects of Pressure – Condensed Phase

Amounts to Poynting correction, usually negligible except at very high pressures

$$C(Di) = C(Gr)$$

conversion pressure

$$\mu^{\ominus}(Di) - \mu^{\ominus}(Gr) = (P^* - P^{\ominus})[v(Gr) - v(Di)]$$

$$\mu^{\ominus}(Di) - \mu^{\ominus}(Gr) = 2.9 \text{ kJ/mol}$$

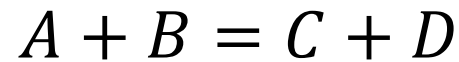
$$\rho(Di) = 3.52 \text{ g/cm}^3 \quad \rho(Gr) = 2.26 \text{ g/cm}^3$$

$$P^* \approx 1.5 \times 10^9 \text{ Pa} = 1.5 \text{ GPa}$$

Simultaneous Equilibrium

One or more reactants and products involved in several simultaneous reactions

Special case: product of one reaction becomes reactant of another: free energy transduction



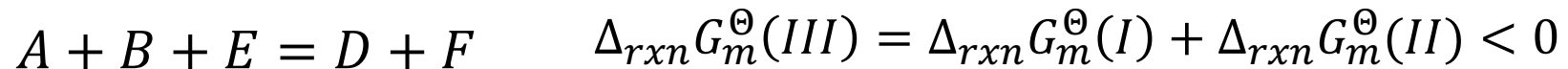
$$\Delta_{rxn} G_m^\ominus(I) > 0$$

couple with



$$\Delta_{rxn} G_m^\ominus(II) \ll 0$$

Net reaction



Questions to Think about

- Why the amount of pure liquid or solid does not appear in the chemical equilibrium isotherm?
- Work out the conversion pressure from graphite to diamond

Lecture 19

- Introduction to electrolyte and polyelectrolyte solutions
- Chemical potential for salt in solution
 - mean molality of salt
 - mean activity coefficient
 - Debye-Hückel limiting law for dilute electrolyte solution
- Ionic equilibrium
 - electrochemical potential
 - Donna equilibrium

Read Chs. 9 and 13

Objectives

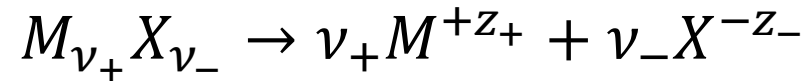
- Have appreciation for charge neutrality
- Know electrochemical potential
- Know Donnan equilibrium

Specialness of Electrolyte Solutions

- Charge neutrality $\int_V \rho_C(\vec{r}) d\vec{r} = 0$
- Charge interactions (Coulomb interactions) are long-ranged
- Charges (ions) respond to electric field (potential)

Basic Stoichiometry for Electrolytes

Consider strong electrolytes, i.e., salts dissociates fully in solution (usually aqueous due to strong solvation of ions by water)



z_+ (z_+) valence of cation (anion)

e.g. $CaCl_2$ $\nu_+ = 1$ $\nu_- = 2$ $z_+ = 2$ $z_- = 1$

Electroneutrality $\nu_+ z_+ = \nu_- z_-$

Salt Chemical Potential

Chemical potential for the ions

$$\mu_+(m_+) = \mu_+^* + RT \ln m_+ + RT \ln \gamma_+$$

$$\mu_-(m_-) = \mu_-^* + RT \ln m_- + RT \ln \gamma_-$$

m is concentration in molality
(can also use molarity)

molality: moles/kg of solvent
molarity: moles/liter of solution

Reference chemical potential and activity coefficients must be consistent with concentration unit

Salt Chemical Potential

Gibbs free energy of salt solution

$$G = n_w\mu_w + n_+\mu_+ + n_-\mu_-$$

But, salts are always added in cation-anion neutral pairs $M_{\nu_+}X_{\nu_-}$

Each mole of salt produces ν_+ moles of cations and ν_- moles of anions

$$n_+ = \nu_+ n_s \quad n_- = \nu_- n_s$$

$$G = n_w\mu_w + n_s\nu_+\mu_+ + n_s\nu_-\mu_-$$

Salt Chemical Potential

Salt chemical potential

$$\mu_s = \nu_+ \mu_+ + \nu_- \mu_- = \nu_+ \mu_+^* + \nu_- \mu_-^* + RT \ln(m_+^{\nu_+} m_-^{\nu_-}) + RT \ln(\gamma_+^{\nu_+} \gamma_-^{\nu_-})$$

Define mean ionic molality m_{\pm}

$$m_{\pm}^{\nu} = m_+^{\nu_+} m_-^{\nu_-} \qquad \nu = \nu_+ + \nu_-$$

And mean ionic activity coefficient γ_{\pm}

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

weighted geometric average between cation and anion

Debye-Hückel Limiting Law

$$\ln \gamma_{\pm} = -\alpha z_+ z_- \sqrt{I}$$

$$I = \frac{1}{2} \sum_i z_i^2 m_i$$

ionic strength

semi-empirical

$$\ln \gamma_{\pm} = -\frac{\alpha z_+ z_- \sqrt{I}}{1 + \beta a \sqrt{I}}$$

$$\alpha = 1.129 - 1.379 (mol/kg)^{-1/2} \quad \text{for } T = 0 - 100^\circ\text{C}$$

$$\beta \approx 3.3 [(mol/kg)^{-1/2} nm]^{-1}$$

$$a = 0.4 nm$$

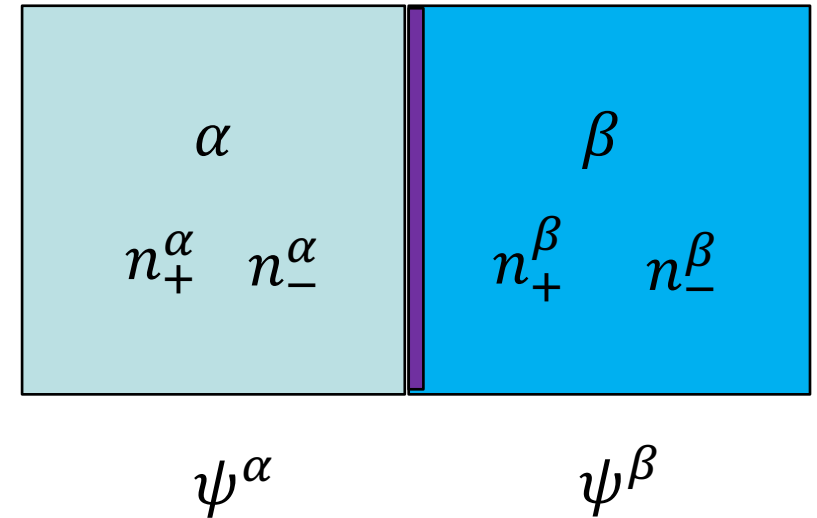
hydrated ion radius

Electrochemical Potential

$$\psi^\alpha \neq \psi^\beta$$

(e.g, one side contains a polyanion gel)

Electric work $\delta W_{ele} = \psi \delta Q$



At constant T, V, equilibrium requires Helmholtz free energy to be minimized with respect to real or virtual changes in the number of ions across the two compartments (unconstrained internal variable)

$$\delta F = \delta F^\alpha + \delta F^\beta = 0$$

Electrochemical Potential

$$\delta F = \delta F^\alpha + \delta F^\beta = 0$$

$$\delta F^\alpha = \mu_+^\alpha \delta n_+^\alpha + \mu_-^\alpha \delta n_-^\alpha + \underbrace{\psi^\alpha N_{av} e_0 (z_+ \delta n_+^\alpha - z_- \delta n_-^\alpha)}_{\delta W_{ele} = \psi \delta Q} \quad \delta Q = N_{av} e_0 (z_+ \delta n_+ - z_- \delta n_-)$$

$$\delta F^\beta = \mu_+^\beta \delta n_+^\beta + \mu_-^\beta \delta n_-^\beta + \psi^\beta N_{av} e_0 (z_+ \delta n_+^\beta - z_- \delta n_-^\beta)$$

Due to arbitrariness of δn_+^α etc., and noting $\delta n_+^\beta = -\delta n_+^\alpha$

$$\mu_+^\alpha + \psi^\alpha \mathcal{F} z_+ = \mu_+^\beta + \psi^\beta \mathcal{F} z_+$$

$$\mu_-^\alpha - \psi^\alpha \mathcal{F} z_- = \mu_-^\beta - \psi^\beta \mathcal{F} z_-$$

$$\mathcal{F} = N_{av} e_0 \approx 96485 \text{ C/mol}$$

Faraday constant, amount of charge in 1 mole of electrons

Electrochemical Potential

$$\bar{\mu}_+ = \psi z_+ + \mu_+$$

$$\bar{\mu}_- = -\psi z_- + \mu_-$$

where for notational simplicity we have
absorbed the Faraday constant into the
electrostatic potential $\mathcal{F}\psi \rightarrow \psi$

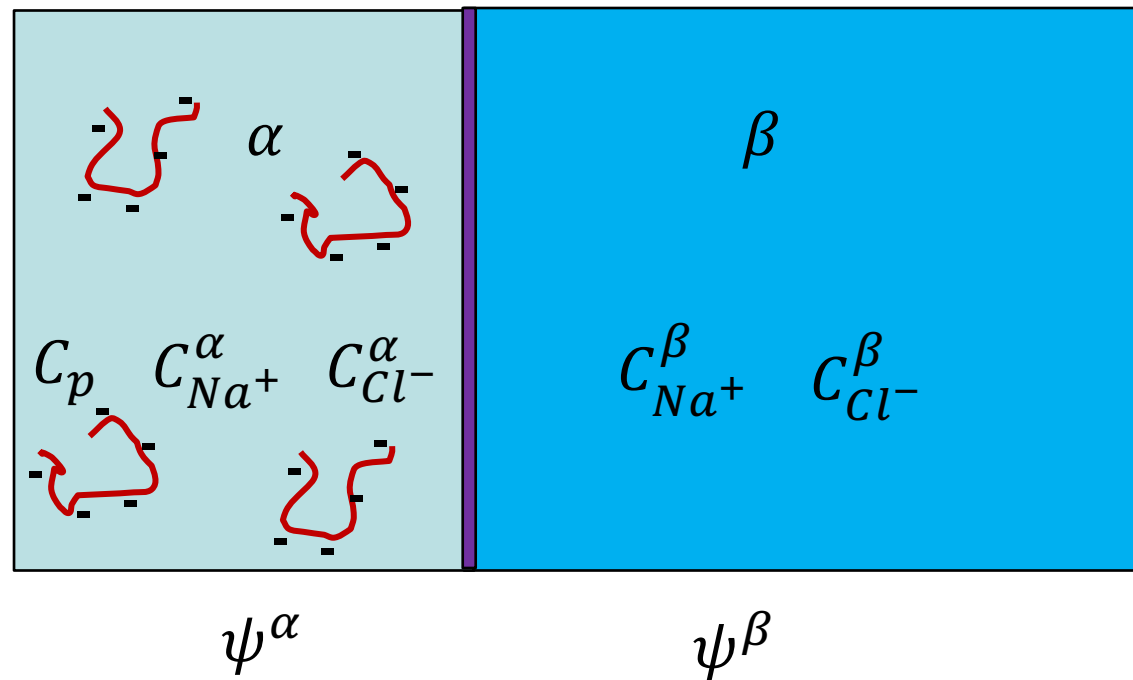
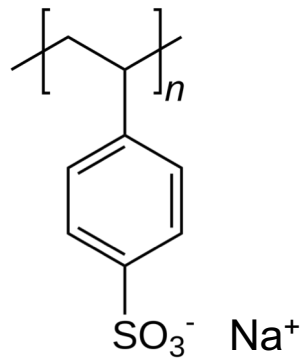
Ionic equilibrium requires equality of electrochemical potential

Can be generalized to include other external
potential effects, such as gravity

Donnan Equilibrium

Ionic equilibrium involving semipermeable membrane that does not allow certain ions (usually polyions) to pass through

e.g: sodium polystyrene sulfonate



Given polymer concentration, buffer salt concentration, determine concentration of Na^+ and Cl^- in polymer solution and potential difference

Donnan Equilibrium

Neutrality

$$C_{Na^+}^{\alpha} = NC_p^{\alpha} + C_{Cl^-}^{\alpha}$$

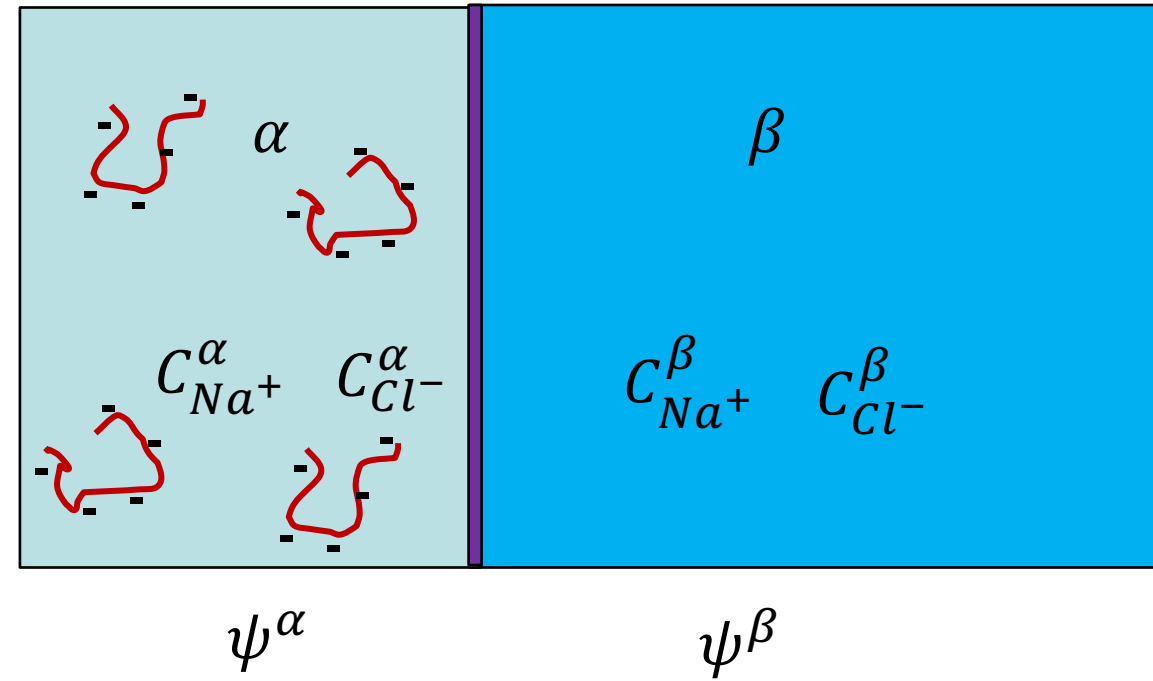
Equality of electrochemical potential
(ignore activity coefficient correction)

$$\psi^{\alpha} + RT \ln C_{Na^+}^{\alpha} = \psi^{\beta} + RT \ln C_{Na^+}^{\beta}$$

$$-\psi^{\alpha} + RT \ln C_{Cl^-}^{\alpha} = -\psi^{\beta} + RT \ln C_{Cl^-}^{\beta}$$

$$C_{Na^+}^{\alpha} C_{Cl^-}^{\alpha} = C_{Na^+}^{\beta} C_{Cl^-}^{\beta}$$

$$\psi^{\alpha} - \psi^{\beta} = -RT \ln \frac{C_{Na^+}^{\alpha}}{C_{Na^+}^{\beta}}$$



$$C_{Na^+} C_{Cl^-} = C_s^2$$

$$\Delta\psi = -RT \ln \frac{C_{Na^+}}{C_s}$$

Donnan Equilibrium

$$C_{Cl^-} = \frac{1}{2} \left(\sqrt{4C_s^2 + N^2 C_p^2} - N C_p \right) < C_s$$

$$C_{Na^+} = \frac{1}{2} \left(\sqrt{4C_s^2 + N^2 C_p^2} + N C_p \right) > C_s$$

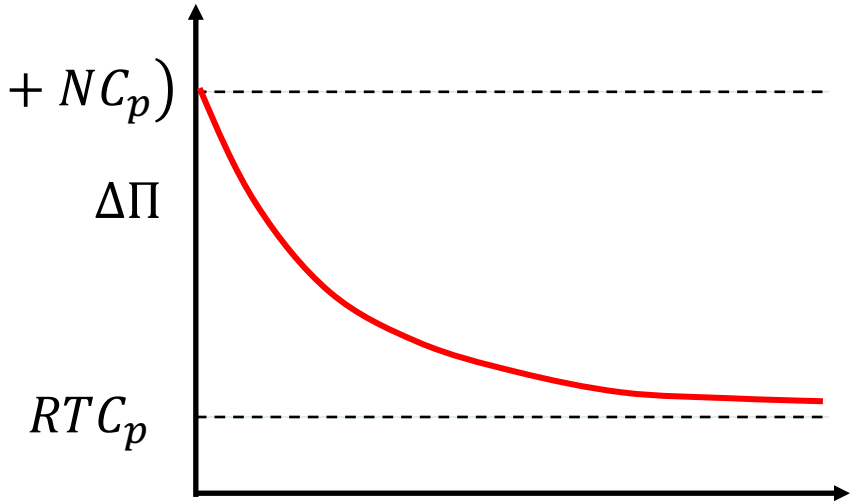
$$\Delta\psi = -RT \ln \frac{\sqrt{4C_s^2 + N^2 C_p^2} + N C_p}{2C_s} < 0$$

Effects of Donnan Equilibrium on Osmotic Pressure

$$\Delta\Pi = RT [(C_p + C_{cl^-} + C_{Na^+}) - 2C_s]$$

$$RT(C_p + NC_p)$$

$$\Delta\Pi = RT \left(C_p + \sqrt{4C_s^2 + N^2C_p^2} - 2C_s \right)$$



Limiting behavior

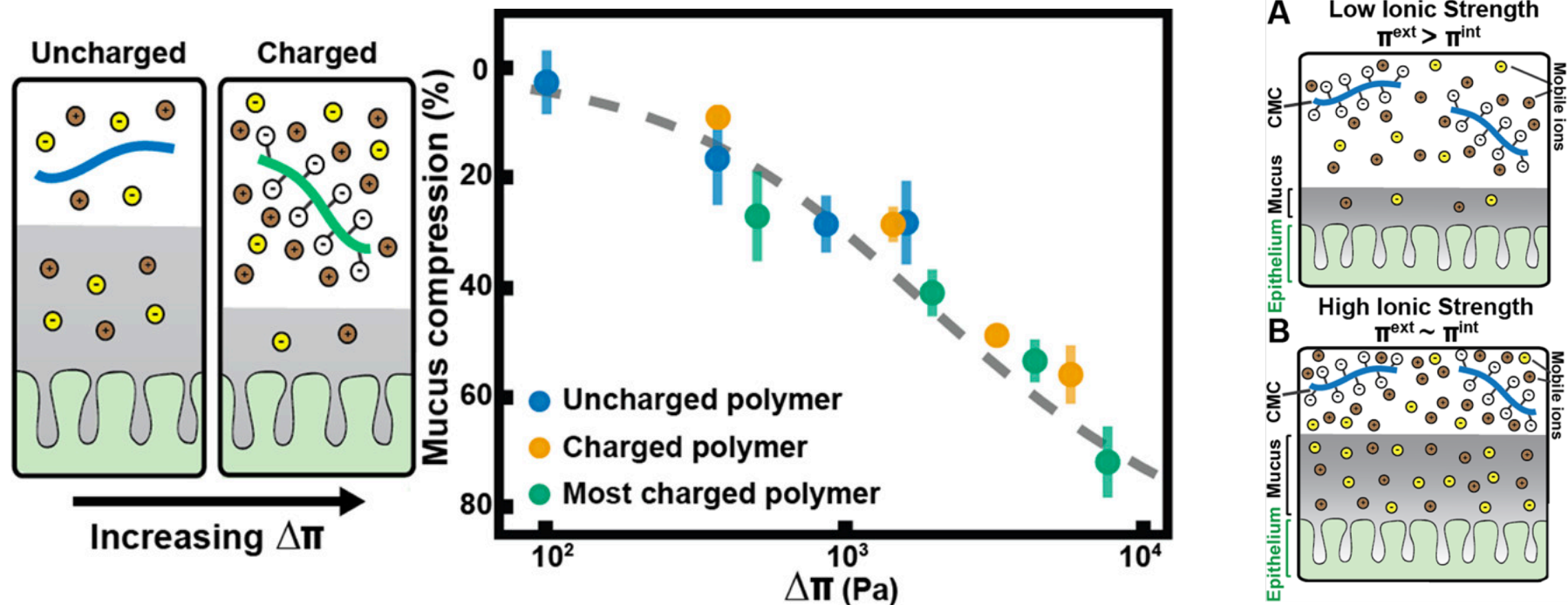
low salt: $\Delta\Pi = RT \left(C_p + NC_p + \frac{2C_s^2}{NC_p} - 2C_s \right) \rightarrow RT(C_p + NC_p)$

high salt: $\Delta\Pi = RT \left(C_p + \frac{N^2C_p^2}{C_s} \right) \rightarrow RTC_p$

↑
counterions

└ effective 2nd virial; decreases with C_s

Application of Donnan Equilibrium



Food Polyelectrolytes Compress the Colonic Mucus Hydrogel by a Donnan Mechanism

Asher Preska Steinberg,[†] Zhen-Gang Wang,[†] and Rustem F. Ismagilov^{*,†,‡}

Biomacromolecules 2019, 20, 2675–2683

Tips for Taking Exam

- Relax, stay calm!
 - One step at a time; make sure each step makes sense
 - No need to derive if you are not asked to
 - If problem statement has multiple interpretations, take the **simplest yet nontrivial** one
 - Use schematics and words to explain
 - Label graphs: axis, origin, points of interest, etc.
 - Check to see your results make sense
- a) Has **right sign**
 - b) Has **right trend**
 - c) Has **right units**