

## Chemical Equilibrium

CHEM 323 Physical Chemistry I

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## Thermodynamics and Equilibrium

- Observations
  - Many reactions do not give 100% yield
  - Composition of reaction mixture changes over time and then stops changing
  - Isotopic scrambling
- Have seen that Composition Change leads to Change in Chemical Potential
  - Mixtures, phase diagrams
  - Apply to chemical reactions

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## Reaction Gibbs Energy

- Definition:

$$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{p,T}$$

- Where  $\xi$  is the *extent of reaction*
- Is not a difference in  $G$ , it is a derivative
- Is not necessarily the same as the  $\Delta_r G^\circ$  that we discussed before
- Difference between  $\mu_{\text{products}}$  and  $\mu_{\text{reactants}}$  at some point in time

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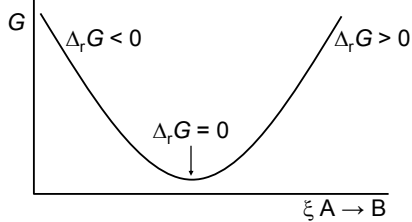
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### More on $\Delta_r G$

- For Reaction  $A \rightarrow B$  there are three Cases
  - $\mu_A > \mu_B$   $\Delta_r G < 0$  (exergonic)
  - $\mu_A < \mu_B$   $\Delta_r G > 0$  (endergonic)
  - $\mu_A = \mu_B$   $\Delta_r G = 0$  (equilibrium)




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### Equilibria of Ideal Gases

- For the Reaction  $A \rightarrow B$  of Ideal Gases

$$\Delta_r G = \Delta_r G^0 + RT \ln \left( \frac{p_B}{p_A} \right)$$

- Define Reaction Quotient,  $Q$ , for all  $p_i$

$$Q = \frac{p_B}{p_A}$$

- Special Case when  $\Delta_r G = 0$ ,  $Q = K$
- Role of Mixing in overall  $\Delta G$  for Reaction

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### Generalization

- Stoichiometric Numbers
- General Equation for any Number of Reactants and Products

$$\Delta_r G = \Delta_r G^0 + RT \ln(Q)$$

- Where

$$\Delta_r G^0 = \sum_J \nu_J \Delta_r G^0(J)$$

$$Q = \prod_J a_J^{\nu_J} \quad K = \left( \prod_J a_J^{\nu_J} \right)_{\text{equilibrium}}$$

- When  $\Delta_r G = 0$ , it follows that  $\Delta_r G^0 = -RT \ln K$

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## K in terms of Mole Fractions and Concentrations

- From Definition of Activity and Activity Coefficients we can write

$$K = K_\gamma K^*$$

- Where  $K_\gamma$  is ratio of activity coefficients in same form as  $K$
  - And  $K^*$  is equilibrium constant in terms of mole fractions or molalities
- Note on Molarities

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## Response of Equilibria to Stressors

- Le Châtelier's Principle
- Effect of Pressure
  - $K$  is independent of  $p$  (definition)
  - Reactions where number of particles change
- Effect of Temperature

- van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2} \quad \frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^0}{R}$$

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

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## Final Notes on K

- Review Solving Equilibrium Problems
  - See web page for link
- Relationships between Equilibrium Constants
  - Adding reactions
  - Multiplying stoichiometric coefficients by a constant
- Calculating  $K$  from  $\Delta_r G^0$ , Amounts present at Equilibrium, etc.

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## Thermodynamic Treatment of Reactions involving Ions

- Thermodynamic Treatment of Molecular Reactions in Solution
  - Activities from vapor pressure
  - Use activities to find  $K$  ( $\Delta_r G^\circ$ , etc.)
- When Ions involved still use Activities
  - Use Debye-Hückel (or other) to get  $\gamma_{\pm}$
  - Dependence on ionic strength (control)
  - Implications for  $K$  (and  $\Delta_r G^\circ$ , etc.)

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## Redox Reactions

- Formal Transfer of Electrons from one Chemical Species to another
  - One-electron processes (radicals)
  - Two-electron processes (atom transfer)
  - Connection with Lewis acids and bases
- All Redox Reactions have two Parts
  - Half reactions
- Oxidation Numbers
- Balancing Redox Reactions

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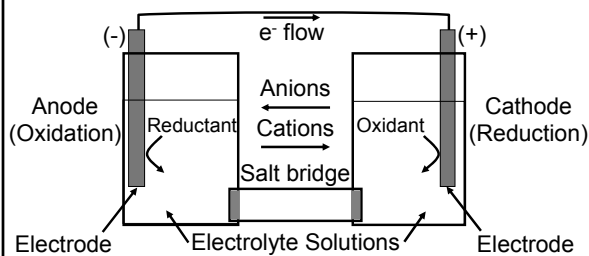
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## Electrochemical Cells

- Galvanic (shown below), Electrolytic, Concentration
  - Chemical potential



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## Electrochemical Cells

- Types of Electrodes
  - Pure metal in contact with its cation ( $\text{Ag}/\text{Ag}^+$ )
  - Metal and an insoluble salt ( $\text{Ag}/\text{AgCl}$ )
  - Inert metal ( $\text{Au}$ ,  $\text{Pt}$ ) or other solid ( $\text{C}$ )
  - Gas electrodes ( $\text{H}_2$  electrode)
  - Membrane electrodes (pH electrode)
- Electrolytes
  - Typically chosen based on solubility
  - Commonly salts of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PF}_6^-$

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## Galvanic Cell Line Notation

- Shorthand Notation for Cells
    - | indicates phase boundary
    - || indicates interface ( $E_{\text{junction}} = 0$ )
    - : denotes a liquid junction ( $E_{\text{junction}} = ?$ )
    - “Electrode, species” indicates species in each half cell
    - Oxidation on left, reduction on right
- $\text{Zn (s)} + 2 \text{HCl (aq)} \longrightarrow \text{ZnCl}_2 \text{ (aq)} + \text{H}_2 \text{ (g)}$
- $\text{Zn (s)} | \text{ZnCl}_2 \text{ (aq)} || \text{HCl (aq)} | \text{H}_2 \text{ (g)}, \text{Pt (s)}$

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## Electromotive Force (EMF)

- Potential Difference between Electrodes
  - Drives electron flow (galvanic) or opposes flow (electrolytic)
- Define a *Standard Cell Potential*,  $E^0_{\text{cell}}$ 
  - EMF at standard conditions, unit activity
  - Junction potentials
- Define *Standard Hydrogen Electrode* (S. H. E.) with  $E^0 = 0.000 \text{ V}$ 
  - Standard conditions, unit activity for  $\text{H}^+$   
 $2 \text{H}^+ \text{ (aq)} + 2 \text{e}^- \rightleftharpoons \text{H}_2 \text{ (g)}$

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## Standard Reduction Potentials

- Define  $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$ 
  - Can tabulate of  $E^0$  for half reactions
  - By convention written as reductions
- Properties
  - Multiplying half-reaction by a constant
  - Reversing reaction and sign of  $E^0$
  - Spontaneous direction and sign of  $E^0_{\text{cell}}$

- Relationship of  $E$  to  $\Delta_r G$

$$-v \cdot F E = \Delta_r G$$

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## Nernst Equation

- Describes Cell Potential under non-standard Conditions

$$E = E^0 - \frac{RT}{vF} \ln Q$$

- At Equilibrium  $Q = K$  and  $E = 0$ , which gives

$$\ln K = \frac{vFE^0}{RT}$$

- What does  $E = 0$  mean?
- Implications

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## Measuring $E^0$ , Activities and Thermodynamic Quantities

- Standard Cell Potential
  - Harned cell
  - Secondary reference electrodes
- Activities
  - First measure cell's  $E^0$
  - Measure  $E$  and use Nernst equation
- Thermodynamic Quantities

$$\frac{dE^0}{dT} = \frac{\Delta_r S^0}{vF} \quad \Delta_r H^0 = -vF \left( E^0 - T \frac{dE^0}{dT} \right)$$

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