Unit 5: Harnessing Chemical Change

IMPORTANT EQUATIONS:

General reaction…

$$acid + H_2O \rightleftharpoons conjugate\ base + H_3O^+$$

$$base + H_2O \rightleftharpoons conjugate\ acid + OH^-$$

Manipulation of acid equilibrium constant…

$$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{pH-pK_a}$$

Application to buffer solutions…

$$pH = pK_a + \log\frac{[A^-]_0}{[HA]_0} \text{ for } 0.1 \leq \frac{[A^-]_0}{[HA]_0} \leq 10$$

Electric potential of a cell…

$$E_{cell} = E_{right\ half-reactio} - E_{left\ half-reaction}$$

Thermodynamic applications…

$$\Delta G^o = -nFE_{cell}$$

$$E_{cell} = \frac{RT}{nF}\ln K^o$$

Nerst equation…

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q$$

EXAM: Wednesday, December 18th
5:45PM – 7:00PM @ PSYCH 105

AQUEOUS ACIDS AND BASES

Introduction to Brønsted-Lowry acid-base reactions…

Brønsted-Lowry acid	a chemical species that donates a proton (H^+) to another chemical speciees
Brønsted-Lowry base	a chemical species that accepts a proton

Introduction to Lewis acid-base reactions…

Lewis acid	a chemical species that can accept a pair of electrons
Lewis base	a chemical species that can donate a pair of electrons

General reaction…

$$acid + H_2O \rightleftharpoons conjugate\ base + H_3O^+$$

$$base + H_2O \rightleftharpoons conjugate\ acid + OH^-$$

Conjugate acid	the chemical that forms after a base accepts a proton
Conjugate base	the chemical that remains after an acid has donated a proton

Autoionization of water…

Autoionization	a substance ionizes when one molecule of the substance reacts with another molecule of some substance

➔ Autoionization constant of water: $K_w = 1.0 \cdot 10^{-14}$ @ 25℃

- Consider $H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- $K_w = [H_3O^+][OH^-]$

Amphiprotic	a molecule that can either gain a proton or lose a proton in a Brønsted-Lowry reaction
Amphoteric	a more general term for a species that may act either as an acid or a base by *any* definition

Classification of a reaction based on concentration…

Neutral	$[H_3O^+] = [OH^-]$
Acidic	$[H_3O^+] > [OH^-]$
Basic	$[H_3O^+] < [OH^-]$

Using logarithms for scaling…

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$pH = -\log[H_3O^+]$	$[H_3O^+] = 10^{-pH}$
$pOH = -\log[OH^-]$	$[OH^-] = 10^{-pOH}$
$pK_w = 14$	$pK_w = pH + pOH$

STRUCTURE-PROPERTY RELATIONSHIPS

Acid and molecular strength…

Inductive effect	induce a polarization in the distribution of electrons within the molecule

Polyprotic acids…

Monoprotic acids	acids that contain one ionizable hydrogen atoms per molecule
Monoprotic bases	bases that can accept a single proton
Diprotic acids	contain two ionizable hydrogen atoms per molecule
Triprotic acids	an acid that has three protons that undergo a stepwise dissociation

CONTROLLING MOECULAR STRUCTURE AND PROPERTIES WITH pH

Consider $K_a = \frac{[H_3O^+][A^-]}{[HA]}$…

$$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{pH-pK_a}$$

TITRATIONS AND BUFFERS

Titration curves…

➔ Titration curves show pH as a function of the volume of the titrant

Buffers…

Buffer solution	resists change in pH when small amounts of strong acid/base are added

➔ The reason the pH changes slowly around the midpoint of a weak acid-strong base titration (or weak base-strong acid)

➔ The solution at the midpoint is the buffer solution

$$pH = pK_a + \log\frac{[A^-]_0}{[HA]_0} \text{ for } 0.1 \leq \frac{[A^-]_0}{[HA]_0} \leq 10$$

Buffer capacity	amount of moles of an acid/base that can be added to a given volume of a buffer solution before the pH changes by ± 1 from the pK_a of the weak acid

Selecting a suitable buffer solution…

(1) The pK_a of a weak acid in the buffer should be close to the desired pH of the buffer solution
   a. This ensures similar buffer capacity for the added acid/base
   b. A buffer solution cannot have $[A^-]_0/[HA]_0$ exceed 10 or be less than 0.1

(2) Large amounts of weak acid/base would yield a buffer with a greater capacity

➔ Look for weak conjugate acid-base pairs that have $pK_{a,weak\ acid}$ near the desired pH

LEWIS ACID-BASE REACTION

Lewis acid-base reactions…

- ➔ Low E_a
- ➔ Both the forwards and revere reactions have a large rate constant

Lewis acid	chemical species that can accept a pair of electrons; electrophile
Lewis base	chemical species that can donate a pair of electrons; nucleophile

Condensation reactions…

Condensation reaction	two molecules join together to form a larger molecule and a smaller molecule side product

- ➔ H_2O or HCl

Hydrolysis	A process in which water breaks apart

- ➔ In the acid-catalyzed hydrolysis of an ester, a carboxylic acid and an alcohol are formed

ELECTROCHEMICAL CELLS

Intro to electrochemistry…

Electrochemistry	chemical reactions that deal with the transfer of electron densities
Electric current	the quantity of charge being transferred per unit of time

$$1A = 1\ C \cdot s^{-1}$$

$$q_e = 1.602 \times 10^{-19}\ C$$

Electric circuit	electric current flowing through a closed path

➔ Circuit must be closed for current to flow

Electric potential	ability of an electric field to do work on a charge

➔ A flow of charge is caused by an electrical potential difference between two points in a circuit

➔ When $1\ C$ moves through a potential $1\ V$, it gains or loses $1\ J$ of energy

$$1\ J = 1\ C \cdot 1\ V$$

Power	quantity of energy transferred per unit of time

$$1\ W = 1\ J \cdot s^{-1}$$

Redox reactions…

Half-reactions	one in which electrons are lost and one in which electrons are gained
Oxidation	the loss of electrons
Reduction	the gain of electrons
Reducing agent	species that causes reduction to occur
Oxidizing agent	species that causes oxidation to occur
Oxidation number	the charge a compound would posses if it was ionic

➔ If all electrons in each polar covalent bond were assigned to the more electronegative atom

Steps to assigning oxidation numbers…

(1) Oxidation of an atom in the elemental stage is 0

(2) Oxidation number of a monoatomic ion is equal to the ions charge

(3) The sum oxidation numbers over all atoms in a neutral compound is 0

(4) $\sum q_{atom} = q_{polyatomic\ ion}$

(5) Atoms of some elements have the same oxidation number in almost all compounds
   a. Ox# of fluorine is -1 in a compound
   b. Atoms of alkali metals gave Ox# $+1$ in nearly all compounds
   c. Atoms of alkaline earth metals have Ox# $+1$ in nearly all compounds
   d. Hydrogen has Ox# of $+1$ with nonmetals and -1 with metals

(6) Only apply the following *if* step #1-5 *don't* work
   a. Oxygen has an Ox# of -2 unless already assigned a different one

➔ When an atoms Ox# increases, an element has been oxidized

➔ When an atoms Ox# decreases, an element has been reduced

Intro to voltaic cells…

Voltaic/galvanic cells	*an electrochemical cell in which a spontaneous redox reaction produces an electric current*
Electrode	*a means for conducting electrons into/out of a solution*
Half-cell	*the container in which each half-reaction occurs*
Salt-bridge	*a solution of salt that does not mix with either the half-cell solution but allows ions to pass into/out of the half-cells*
Anode	*half-cell where oxidation occurs*
Cathode	*half-cell where reduction occurs*

Voltaic cell potential…

Cell potential	E_{cell}; measure of energy per unit of charge available from a redox reaction ($1\ V = 1\ J \cdot C^{-1}$)

➔ $E_{cell} > 0 \Longrightarrow$ how much more a spontaneous reaction in a voltaic cell can do per unit of charge moving through the circuit

$$E_{cell} = E_{right\ half-reaction} - E_{left\ half-reaction}$$

or when $c = 1\ M$…

$$E^o_{cell} = E^o_{right\ half-reaction} - E^o_{left\ half-reaction}$$

Cell notation…

Active electrode	participates in redox reaction
Inert electrode	does *not* participate in the redox reaction but must be present to complete the electrical circuit

CONTROLLING CHEMICAL POTENTIAL

Standard half-cell potential…

- ➔ Cell potential is caused by a difference in electrical potential between half-cells

$$E^o_{cell} = E^o_{right\ half-reaction} - E^o_{left\ half-reactio}$$

Implications of standard half-cell potentials…

- ➔ The oxidizing agent on the reactant side of the reduction half-reaction equation
- ➔ Strongest oxidizing agents (most easily reduced) have the largest *positive* E^o_{cell}
- ➔ The reducing agent is on the product side of a reduction half-reaction equation
- ➔ Strongest reducing agents (most easily oxidized) have the most negative E^o_{cell} values
- ➔ A redox reaction is product-favored when a stronger oxidizing agent reacts with a stronger reducing agent
- ➔ Half-cell reactions are reversible

Thermodynamic applications…

Faraday's constant	F; the amount of charge per one mole of electrons; $F = 96{,}485\ C \cdot mol^{-1} = 96{,}485\ J \cdot mol^{-1} \cdot V^{-1}$

$$W_{elec} = Q_{transfered} E_{cell}$$

$$Q_{transfered} = nF \Rightarrow W_{elec} = nFE_{cell}$$

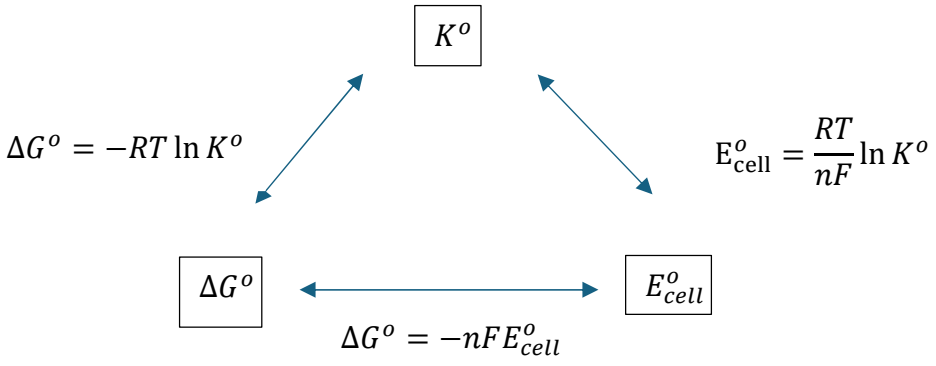
$$\Delta G^o = -W_{elec} \Rightarrow \Delta G^o = -nFE_{cell}$$

$$E_{cell} = \frac{RT}{nF} \ln K^o$$

Nerst equation…

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q$$

Equation summary…



Concentration cells…

Concentration cell	*a type of voltage cell where the electrodes are all the same materials but the half cells have different concentrations of soluble space*

ELECTROLYSIS & BUFFERS

Electrolysis and an initial application…

Electrolysis	a process that supplies electrical energy causing a nonspontaneous redox reaction to occur
Electroplating	forms a thin coating of metal on top of a conducting surface

$$I = \frac{Q}{t}$$

$$Q = nF = It$$

Batteries and fuel cells…

Battery	an electrochemical cell or series of cells that produce an electric current
Primary batteries	single-use batteries that cannot be recharged
Dry cell	zinc-carbon battery

➔ Zinc serves as both the container and anode

➔ Cathode is a carbon rode surrounded by a past of MnO_2, NH_4Cl, $ZnCl_2$, and a small amount of water

Secondary batteries	batteries that are rechargeable; the reaction that powers the battery can be reversed so that the original reactants can be regenerated
Lead-acid battery	a type of secondary battery used to start gas-powered automobiles
Lithium-ion battery	a type of secondary battery used to power mobile devices; produces high currents
Fuel cells	produces electricity as long as fuel is present