

CHEM 1220 Lecture Notes  
Chemistry: The Central Science 15e

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## COURSE ADMINISTRATIVE DETAILS

- My office hours
- Intro to my research
- Introductory Quiz
- Grading details
  - Exams - 40, Final - 15, Quizzes - 15, Homework - 15, Adaptive Assignments - 15
  - Online homework
  - Daily quizzes
- Importance of reading and learning on your own
- Learning resources
  - My Office Hours
  - TA - Sam
  - Tutoring services - <https://www.suu.edu/academicsuccess/tutoring/>
- Show how to access Canvas
  - Calendar, Grades, Modules, etc.
  - How to sign up for Online homework
    - \* Demonstrate normal vs. adaptive assignments
    - \* Textbook
- Course Overview
  - Phases and phase changes
  - Reaction rates (kinetics)
  - Equilibrium, equilibrium, equilibrium!
  - Electrochemistry (and equilibrium)
  - Nuclear Chemistry

## CHAPTER 0

## 1210 REVIEW

There is a whole semester of material from 1210, and these are only the topics which are *most* important for success in 1220

- Composition of atoms and ions (protons, neutrons and electrons)
- Chemical formulas and names
  - Formulas and molar masses
  - Polyatomic ion names
  - Naming ionic compounds
  - Naming binary molecular compounds
  - Naming acids
- Balancing molecular equations
- Solubility rules
- Fundamentals of acid/base chemistry
- Measurements vs. chemistry
  - Converting from measurements to moles and back
  - Stoichiometry and predicting amounts
  - Limiting reactants
- Enthalpy of reaction and heat equations
- Lewis structures

## CHAPTER 11

## LIQUIDS AND INTERMOLECULAR FORCES

**11.1 A Molecular Comparison of Gases, Liquids, and Solids**

- Behavior of liquids, solids, and gases can be understood from a molecular perspective
- Properties are summarized in Table 11.1
- The density of particles and how they move are illustrated in Figure 11.1
- Temperature affects mobility of particles, which in turn dictates melting and boiling points

**11.2 Intermolecular Forces**

- Chemical bonds are strong attractions between atoms or ions *within* a compound
- Intermolecular forces are weaker attractions between different molecules, or between molecules and ions
- We talk about forces between two identical molecules of a pure substance, or between solvent and solute for a solution
- Weaker forces lead to low boiling and melting points, and high vapor pressures
- Stronger forces lead to high boiling and melting points, and low vapor pressures
- There are 4 different types of intermolecular forces:
  - Dispersion forces
    - \* Even non-polar molecules exhibit weak attractions, called dispersion (or Van der Waals) forces
    - \* These forces arise from random distortions of the electric field, creating an instantaneous dipole
    - \* An instantaneous dipole can induce a matching dipole in neighbors, creating an attractive force
    - \* Figure 11.3 shows how these dipoles can form
    - \* Some atoms distort more easily, forming stronger forces. This is called *polarizability*
    - \* Larger atoms are more polarizable because the valence electrons are held less tightly
    - \* Figure 11.4 Shows the boiling points of halogens and noble gases
    - \* Larger molecules contain more atoms, giving more dispersion forces

- \* Natural gas, kerosene, and wax all are non-polar hydrocarbons – the only difference is size
- \* Shape also matters. An extended shape with more surface area will have stronger attractions
- \* Figure 11.5 shows the comparison of n-pentane and neopentane (like trampolines and a velcro wall)
- Dipole-dipole forces
  - \* Polar molecules will also be attracted to each other
  - \* Figures 11.2 and 11.6 show how polar molecules align their dipoles and experience an attractive force
  - \* Figure 11.7 compares molecules with similar molar masses but increasing dipoles
- Hydrogen bonding
  - \* Hydrogen bonds are a special type of dipole-dipole interaction that rivals true covalent bonds for strength
  - \* There are two parts to a hydrogen bond, a H donor, and a H acceptor
  - \* The donor must have a H atom bound to a highly electronegative partner (N, O, or F)
  - \* This bond is so electronegative that the electrons are mostly stripped from the H
  - \* The acceptor must have lone pairs on a highly atom (N, O, and F)
  - \* In a hydrogen bond, the lone pair from the acceptor forms a quasi-covalent bond with the exposed H
  - \* Figure 11.9 shows how hydrogen bonds work in water, HF, and ammonia
  - \* Hydrogen bonds lead hydrogens to easily hop from one water to the other
  - \* Figure 11.10 shows how the directional nature of hydrogen bonds leads to an open crystal structure in ice
  - \* Hydrogen bonds are also the forces which hold complementary strands of DNA together, and fold proteins into secondary structures (find images Online)
- Ion-dipole forces
  - \* Polar molecules (like water) have a positive side and a negative side
  - \* When an ionic compound dissolves, the ions will be exposed to the solute molecules
  - \* Figure 11.12 shows how the ions are surrounded by polar solvent molecules which orient around them in hydration shells
- Table 11.2 show the melting and boiling points for substances with different forces in play

### 11.3 Select Properties of Liquids

- The strength of intermolecular forces leads to different properties of liquids related to flow
- Viscosity is the resistance to flow
  - Substances like honey have high viscosity, and substances like acetone have low viscosity

- Higher intermolecular forces (H-bonding) lead to higher viscosity
- Temperature also affects viscosity – higher temperatures lead to lower viscosity
- Surface Tension is the tendency to liquids to minimize their surface area
  - Figure 11.16 shows how surface molecules have fewer attractive interactions, and are therefore higher in energy
  - This imbalance of forces also results in a net pull of surface molecules inward toward the bulk
  - Spheres have the lowest surface area, so liquids will curve their surfaces to approach a spherical shape
- Capillary Action is the force which pulls liquids into any narrow cavity
  - Cohesion is the attraction between like particles, adhesion is the attraction between different particles
  - Strong cohesive forces will pull a liquid into a capillary in order to create more liquid-capillary interactions
  - Capillary action is essential to life – pulling water through the xylem of plant tissues
  - Figure 11.17 shows how competing adhesion and cohesion can affect the shape of a meniscus
- Vapor pressure depends on intermolecular forces too, but gets its own section below

## 11.4 Phase Changes and Heating Curves

- Phase changes: fusion, freezing, vaporization, condensation, sublimation, deposition (Fig. 11.19)
- Each phase change has an associated change in enthalpy ( $\Delta H_{fus}$ ,  $\Delta H_{vap}$ ,  $\Delta H_{sub}$ )
- This is the energy required to overcome intermolecular interactions and change the phase
- For water,  $\Delta H_{fus} = 6.01 \frac{kJ}{mol}$  and  $\Delta H_{vap} = 40.7 \frac{kJ}{mol}$ , so  $\Delta H_{sub} = 46.7 \frac{kJ}{mol}$
- The heat required for a phase change is given by:  $q = n\Delta H$  (when  $\Delta H$  is a -per-mole value)
- Figure 11.20 shows enthalpies of phase change for a number of different substances
- As you add or remove heat through a phase change, the temperature remains constant
- Figure 11.21 shows a heating curve through two phase changes
- Find the final temperature if you add  $32.0 \text{ kJ}$  of heat to a  $10.0 \text{ g}$  sample of ice at  $-5.00^\circ\text{C}$ ? ( $186.8^\circ\text{C}$ )
- Critical temperatures and pressures represent the point at which the gas phase is so compressed it is indistinguishable from the liquid phase

- Liquefaction is only possible below the critical temperature
- At and above this critical point, a new phase is formed: supercritical fluid
- This will point will be clearly illustrated when we talk about phase diagrams below
- Table 11.5 gives critical values for a number of different substances

## 11.5 Vapor Pressure

- Every substance (liquid or solid) has a vapor pressure, meaning it will vaporize until it reaches equilibrium with the gas phase at that pressure
- Figure 11.22 illustrates how equilibrium is reached
- If equilibrium cannot be established, the entire liquid will vaporize trying to achieve it. This is how things become dry even below the boiling point
- Substances with a relatively high vapor pressure are called volatile
- Most vapor pressures are vanishingly small, making non-volatile substances
- Vapor pressure depends on intermolecular forces and temperature, just like viscosity
- Figure 11.23 shows how temperature affects the distribution of molecular kinetic energy, which in turn affects the vapor pressure
- The boiling point is where the vapor pressure is equal to atmospheric pressure
  - The boiling point at precisely 1.00 atm is called the *normal* boiling point
  - Under low pressures (like in Cedar City), the boiling points of liquids are lowered
  - Under higher pressures (like in a pressure cooker), the boiling point is raised
  - Figure 11.24 shows how vapor pressure depends on temperature for several common substances
- The Clausius Clapeyron equation relates  $\Delta H_{vap}$  to vapor pressure at different temperatures
  - There are two forms of the equation:
 
$$* \ln P_{vap} = \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T} \right) + \ln \beta$$

$$* \ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$
  - Note that the proper form of the gas constant here is  $R = 8.314 \frac{J}{mol K}$
  - Either form can be illustrated by Figure 11.26
  - Methanol has a normal boiling point of 64.60 °C and a heat of vaporization of  $35.2 \frac{kJ}{mol}$ . What is the vapor pressure of methanol at 25 °C? (0.189 atm)

- The vapor pressure for diethyl ether is  $401\text{ mmHg}$  at  $18.00^\circ\text{C}$  and  $660\text{ mmHg}$  at  $32.00^\circ\text{C}$ .  
What is  $\Delta H_{\text{vap}}$  for diethyl ether? ( $26.3\frac{\text{kJ}}{\text{mol}}$ )

## 11.6 Phase Diagrams

- The phase of a substance depends on both temperature and pressure
- A phase diagram summarizes which phase is stable under which conditions (Figure 11.27)
  - The boundaries between phases represent melting points, boiling points, and sublimation points
  - The triple point is the only combination of temperature and pressure where solid, liquid, and gas can all coexist *at equilibrium*
  - Note that a glass of ice water will not maintain all three phases forever *unless* it is precisely at the triple point
  - The critical point is shown at the end of the liquid/gas transition line
  - The solid/liquid boundary is usually very steep, but positively sloped
- Water has an unusual phase diagram because of its strong hydrogen bonds (Figure 11.28)
  - Hydrogen bonds give solid water an open structure, making it less dense than liquid water
  - This gives the solid/liquid boundary a negative slope
  - Water also has an unusually large range of conditions where the liquid phase is stable
- Carbon dioxide also has an interesting phase diagram (Figure 11.29)
  - The triple point is unusually *high* and the critical point is unusually *low*, leading to the following features:
  - The liquid phase is stable over a small range of conditions, and is absent at all temperatures below  $5.11\text{ atm}$
  - Supercritical  $\text{CO}_2$  is particularly accessible

## 11.7 Liquid Crystals

- Liquid crystals are a phase intermediate between liquid and solid which is not present in most substances
- Liquid crystals exhibit structure at the molecular scale like a solid, but still flow like a liquid
- Phase changes into and out of the liquid crystal phase are observed in heating curves as normal
- Figure 11.31 shows the liquid crystal and liquid phases of cholesteryl benzoate
- Figure 11.32 shows the molecular-scale structure of different types of liquid crystals
- Figure 11.33 illustrates the structural elements that make liquid crystal phases possible



## CHAPTER 12

## SOLIDS AND MODERN MATERIALS

**12.1 Classification and Structures of Solids**

- Solids can be classified by the types of bonds between their atoms (Fig. 12.1)
  - Metallic Solids
  - Ionic Solids
  - Covalent Network Solids
  - Molecular Solids
- Solids can be also be classified by the degree of order in their microscopic structure
  - Figure 12.2 shows how this atomic-scale order can manifest on macroscopic scales
  - Crystalline solids will have an orderly, repeating pattern across the bulk of the material
  - Crystalline solids have a distinct melting point
  - Diamonds (molecular), snowflakes (molecular), and quartz crystals (ionic) are crystalline
  - Amorphous solids are disorderly, and look like a static snapshot of a liquid phase material
  - Amorphous solids melt over a range of temperatures, becoming softer and softer until it finally melts completely
  - Glass (ionic) and chocolate (molecular) are amorphous
- Unit cells and crystal lattices describe crystalline structure
  - The unit cell is the smallest repeating volume unit of the crystalline structure
  - The particular arrangement of unit cells to create the bulk material is called a crystal lattice
  - Figures 12.3 and 12.4 illustrate 2-dimensional lattices and unit cells
  - Figure 12.6 illustrates 3-dimensional primitive lattices
  - Figure 12.7 illustrates cubic lattices
    - \* Primitive (simple) cubic
    - \* Body-centered cubic
    - \* Face-centered cubic

## 12.2 Metallic Solids

- Metallic solid properties are explained by the nature of metallic bonds
  - Atoms exist at lattice points in a "sea" of shared electrons
  - Metals are ductile, conductive, and can be readily polished to a shine
- Metals have crystalline structure (Figure 12.11)
- For any unit cell, we are interested primarily in four things:
  - Atoms per unit cell (Figure 12.12)
  - Coordination number (number of neighbors)
  - Relation of cell edge length to atomic radius
  - Density

Unit Cell	Atoms	Packing Efficiency	Coordination	Edge Length
Simple Cubic	1	52%	6	$l = 2r$
Body-Centered Cubic	2	68%	8	$l = \frac{4r}{\sqrt{3}}$
Face-Centered Cubic	4	74%	12	$l = \sqrt{8} \cdot r$

- Structures which maximize the density of atoms are called close-packed
- Figures 12.13 and 12.14 illustrate the difference between cubic and hexagonal close-packing
- Polonium has a density of  $9.196 \frac{g}{cm^3}$  and a simple cubic structure. Based on this, estimate the atomic radius of polonium (True value is  $168 \text{ pm}$ )
- Gold has an atomic radius of  $144 \text{ pm}$  and a face-centered cubic structure. Based on this, estimate the density of gold in  $\frac{g}{cm^3}$  (true value is  $19.3 \frac{g}{cm^3}$ )
- Alloys are materials which mix two or more metals
  - Substitutional alloys and interstitial alloys are illustrated in Figure 12.15
  - Heterogeneous alloys are illustrated in Figure 12.16
  - Intermetallic compounds are illustrated in Figure 12.17

## 12.3 Metallic Bonding

- Metals do not follow the normal valency rule for the number of neighbor bonds (Figure 12.18)
- Figure 12.19 illustrates the electron sea model for metallic bonds

- Molecular orbital theory can give a more robust model for metallic bonds
  - Electron sea model predicts that melting points increase across a row, but they actually peak in the middle of a row (Figure 12.20)
  - We can extend molecular orbital theory to larger and larger groups of metal atoms (Figure 12.21)
  - The discrete orbitals become so numerous that they form continuous bands for even microscopic metal samples
  - For most metals, band structure can be more complex with multiple bands originating from different atomic orbitals (Figure 12.22)
  - Partially-filled bands, and the presence of accessible empty states within those bands, give rise to the properties of metals

## 12.4 Ionic Solids

- The strength of attractive forces in ionic lattices is quantified by lattice energy
  - Ion size affects the lattice energy magnitude (Table 12.3)
  - Ion charge would also have an effect
- Ionic compounds will cleave easily along planes (Figure 12.23)
- Crystal lattices for ionic compounds must accommodate both the cations and anions
  - Figures 12.24 and 12.25 illustrate how the relative size of ions can lead to different structures
  - Figure 12.26 illustrates how the stoichiometry of an ionic compound affects the crystal structure

## 12.5 Molecular and Covalent Network Solids

- Molecular Solids are composed of molecular units held together by intermolecular forces
- Melting points and boiling points are generally determined by the strength of intermolecular forces
- Figure 12.27 provides an interesting counter-example: Toluene is unable to pack efficiently in the solid phase, and has an anomalously low melting point
- Covalent network solids are composed of atoms connected by covalent bonds across the bulk of the substance (Figure 12.28)
- Covalent network solids can be very hard and have very high melting points due to the strength of these bonds
- Covalent network solids can also be viewed from a molecular orbitals model, much like metals

- Unlike for metals, the bands in covalent network solids are not always partially filled
- Bands are often either completely full (valence band) or completely empty (conduction band), with a sizeable gap between them
- Semiconductor band structure is illustrated in Figure 12.29
- Semiconductor properties are explained by this model
- Semiconductor band structure can be modulated by adding impurities (dopants) in small quantities
- n-type semiconductors are doped with an atom which has extra electrons (such as P in Si)
- p-type semiconductors are doped with an atom which has fewer electrons (such as Al in Si)
- Figure 12.20 shows how dopants change band structure of silicon
- Just a few ppm of dopant atoms can increase the conductivity of a semiconductor by a factor of millions
- Diodes, transistors, and other electronic components take advantage of combining differently doped semiconductors to carefully control the flow of electrons under different conditions (we will not go over these in detail in this class)

## 12.6 Polymers

- Polymers are large molecules made up of many smaller repeating units, called *monomers*
- Plastics are polymers
  - Thermoplastics may be reshaped by heating them up
  - Thermosetting plastics can only have their shape set once
  - Elastomers are polymer plastics which exhibit elasticity
- Table 12.5 shows many of the abbreviations used for common plastics
- Addition polymers are formed by breaking a double-bond to form links to neighboring monomers (Figure 12.33)
- Condensation polymers are formed by removing H and OH atoms from the monomers to form a new bond and release water (Figure 12.34)
- Table 12.6 lists many of the most common polymers in modern industry
- Factors in polymer formation can have a large impact on the final polymer properties
  - Crystallinity (or degree of order) (Figure 12.38)
  - Cross-linking (such as vulcanization) (Figure 12.39)

## 12.7 Nanomaterials

- Sometimes the properties of a chemical substance change depending on the physical dimensions of the sample
- Quantum dots nanoparticles
  - The electronic band model for metals and semiconductors is only valid if the sample size is large enough
  - As particles get smaller, the band gap will generally increase, changing the absorption and emission spectra of the particles
  - Figure 12.41 shows a  $\text{Cd}_3\text{P}_2$  quantum dot series
  - Figure 12.42 shows photoluminescence for a CdSe quantum dot series
- Metals dispersed in glass have different spectral properties (stained glass)
- Very small metal particles are also very reactive, relative to their bulk samples
- Figure 12.44 illustrates a microporous zeolyte material
- Carbon can form a range of different nanomaterials with interesting properties
  - Fullerenes are spheres and prolate molecules made of enclosed carbon mesh (Figure 12.45)
  - Graphene is a flat sheet of carbon atoms (Figure 12.47)
  - Nanotubes are tubular structures, like graphene rolled up in a sheet (Figure 12.46)
  - All of these systems exhibit delocalized electrons and metallic/semiconductor properties
  - They are also mechanically very stable and rigid structures

## CHAPTER 13

## SOLUTIONS

# Old Notes from older text begin here

## 13.1 The Solution Process

- A *solution* is any homogeneous mixture (not just things dissolved in water)
- The *solvent* is the majority component of the mixture
- The *solutes* are all other components of the mixture
- Table 13.1 shows diverse types of solutions in everyday life
- Solvation is the process of dissolving a solute in a solvent
  - The rule “Like dissolves like” refers to intermolecular forces
  - Figure 13.2 shows how ionic compounds are dissolved in water
  - To dissolve, solute-solute and solvent-solvent interactions are replaced by solvent-solute interactions
  - Figure 13.3 shows the energetics involved, which can be exothermic or endothermic
  - When water is the solvent,  $\Delta H_{sol}$  is sometimes called the *hydration energy*

## 13.2 Saturated, Unsaturated, and Supersaturated Solutions

- Most solutes will only dissolve to a certain limit, and no more
- This limit is called the *solubility*, and it depends on the solute, solvent, and temperature
- The units of solubility are usually in units of  $\frac{g_{solute}}{g_{solvent}}$
- Higher temperatures will increase the solubility (sometimes by a lot) of most solids, but decrease the solubility of gases
- Gases decrease in solubility at higher temperature because molecules with more kinetic energy are more likely to escape into the gas phase
- Figure 13.4 shows the temperature dependence of solubility for several compounds
- A solute can be purified through *recrystallization*

- Dissolve the solute and any impurities in a minimum of hot solvent
- Cool the solvent, reducing the solubility and crashing out the solute
- Any impurities which are *more* soluble will remain in solution and can be washed away
- *Supersaturated* solutions have more solute than the solubility should allow
  - Heat up a solution to dissolve solute while the solubility is high
  - Carefully cool the solution down, and some solutes will not crash out
  - The supersaturated solution is unstable - a seed crystal or even a shock can nucleate recrystallization
  - Supersaturated sodium acetate demo
- The solubility of a gas is also dependent on the partial pressure of the gas
- $[gas] = kP$  is called Henry's Law
- $\text{CO}_2$  has a Henry's Law constant  $k = 0.034 \frac{M}{atm}$ . Cans of soda have a pressure of about 2.5 atm. What is the molar concentration of  $\text{CO}_2$  in a can of soda?
- Liquids which can mix together in any ratios are called *miscible*
- Liquids which are mostly insoluble together are called *immiscible*

### 13.3 Concentration Units

- Molarity is only one convenient unit of concentration
- For these units we need to be careful to distinguish between solvent, solute, and solution
- $\% \text{ by Mass} = \frac{\text{Solute Mass}}{\text{Solution Mass}} * 100\%$
- $\text{Molality} = \frac{\text{Moles of Solute}}{\text{kg of Solvent}}$
- Mole Fraction:  $\chi_A = \frac{\text{Moles of A}}{\text{Total Moles}}$
- Table 13.2 summarizes each of these concentration units
- Give the concentration in these three units for a solution with 12.5 g of  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  in 100.0 ml of water

### 13.4 Colligative Properties of Nonelectrolytes

- Colligative properties depend on the concentration of solute particles, but do not depend on the identity of those particles
- Vapor-pressure lowering, freezing-point depression, boiling-point elevation, and osmotic pressure are colligative properties
- Vapor-pressure lowering
  - Figure 13.10 shows how solute molecules block solvent access to the surface
  - This will reduce the vapor pressure
  - Raoult's law:  $P_A = \chi_A P_A^\circ$
  - $P_A^\circ$  is the vapor pressure of pure solvent
  - A solution which follows Raoult's law is called an *ideal solution* and has A-B interactions similar in strength to A-A and B-B interactions
  - Solutions with strong A-B interactions will exhibit lower vapor pressures, and solutions with weak A-B interactions will exhibit higher vapor pressures compared to an ideal solution
  - For a mixture of two volatile components,  $P_{total} = \chi_A P_A^\circ + \chi_B P_B^\circ$
- Vapor composition
  - The composition of the vapor phase will not be equal to the composition of the solution phase
  - $\frac{n_A}{n_B} = \frac{P_A}{P_B}$
  - $\chi_{A,gas} = \frac{P_A}{P_{total}}$
- Freezing-point depression and boiling-point elevation
  - Figure 13.12 shows how a solute can disrupt freezing and depress the freezing point
  - For freezing point depression,  $T_{f,solution} = T_{f,solvent} - K_f m$
  - $m$  is molality and  $K_f$  is the freezing point depression constant for the solvent
  - For boiling point elevation,  $T_{b,solution} = T_{b,solvent} + K_b m$
  - $m$  is molality and  $K_b$  is the boiling point elevation constant for the solvent
  - $K_b$  and  $K_f$  are independent of the solute
  - Table 13.3 gives some values for freezing point depression and boiling point elevation
  - Find the freezing point for a solution which contains 300 g of Naphthalene in 500.0 g of cyclohexane
- Osmotic pressure



- A semipermeable membrane will allow water to pass through it, but not any dissolved solutes
- Water will flow across such a membrane to equalize the molality on either side (draw diagram)
- This flow is powered by osmotic pressure
- $\Pi = \frac{nRT}{V} = MRT$  where  $M$  is the molar concentration
- IV solutions must be *isotonic* to avoid hemolysis or crenation of blood cells
- Calculate  $\Pi$  for a solution which contains 75 g of  $C_{12}H_{22}O_{11}$  in 200.0 g of water

### 13.5 Colligative Properties of Electrolytes

- When electrolytes dissolve, they produce more than a molar amount of ions in solution
- We account for this with a van't Hoff factor:  $i = \frac{n_{particles}}{n_{solute}}$
- In principle,  $i$  can become very complicated because dissolved ions form clusters, but we will assume that electrolytes dissociate completely
- For NaCl,  $i = 2$       for  $CaCl_2$ ,  $i = 3$       for  $HNO_3$ ,  $i = 2$
- Each different particle counts toward the total osmotic pressure
- For electrolytes,  $\Pi = iMRT$

## CHAPTER 14

## CHEMICAL KINETICS

**14.1 Rates of Reactions**

- One of the most important ideas in chemistry is not what a reaction produces, but how quickly it is produced
- The study of reaction rates is called *chemical kinetics*
- Kinetics are controlled by 5 factors:
  - Particle size of solid reactants (surface area)
  - Concentration of dissolved and gas reactants
  - Temperature
  - The nature of the reaction (activation energy, sterics, etc.)
  - The presence of a *catalyst*
- Reaction rates are expressed mathematically
  - $rate = \frac{\Delta [A]}{\nu_A \Delta t}$
  - $\frac{\Delta [A]}{\Delta t}$  is the change in concentration over time
  - $\nu$  is the stoichiometric coefficient in the balanced chemical reaction
  - $\nu$  is positive for products, and negative for reactants, so the rate is always positive
- Figures 14.1 through 14.4 show concentration curves for many different types of reactions
- We can sometimes directly measure the concentrations of reactants and products
  - Some chemical species can be monitored by an electrochemical potential (voltage)
  - Others absorb light and can be monitored by spectroscopy
  - Beer's law relates how much light is absorbed:  $A = \alpha l c$

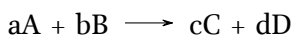
**14.2 Reaction Rates and Concentration: Rate Laws**

- There are two ways to measure reaction rates
  - If your data has low time resolution, the *average* rate is given by  $\frac{\Delta [A]}{\nu_A \Delta t}$

- With high enough time resolution, the average rate essentially becomes an *instantaneous* rate (calculus!)
  - These two methods are really the same, taking the slope of a tangent line
- Use the table below to calculate the reaction rate at different times for the reaction  $A \longrightarrow 2 B$

Time (s)	0	5	10	15
$[B] (M)$	0	0.0160	0.0295	0.0503

- The reaction rate changes with reactant according to the *rate law*
- For reaction  $aA + bB \longrightarrow cC + dD$ , the rate law will be  $rate = k [A]^m [B]^n$
  - Only reactants are included in the rate law
  - $m$  and  $n$  are the reaction order with respect to each reactant, and have nothing to do with stoichiometry
  - Reaction rates can be *zero order*, *first order*, and *second order* w.r.t. each reactant
  - The overall reaction order is the sum of  $m$  and  $n$
  - Consider the effect of doubling the concentration of a reactant that is zero, first, and second order
  - These ideas extend to reactions with more or fewer reactants than shown here
- The rate law is related to the rate by:  $\frac{\Delta [A]}{\nu_A \Delta t} = k [A]^m [B]^n$
- The initial rate method for determining reaction order:
- Run a reaction under several different careful conditions (double  $[A]$  or  $[B]$ )
  - Measure the initial rate (rate at the very beginning of the reaction)
  - Check the numbers against expectations for doubling a zero, first, and second order reactant
  - There is a mathematically rigorous way to deal with this, but doubling the reactant concentrations makes it very simple
- After finding the reaction orders, you can take any data point and back-calculate the value of  $k$
- Note that the units of  $k$  depend on the overall reaction order as shown in Table 14.4
- Use the data below to find the complete rate law (including the value of  $k$ ) for the reaction:



Trial	$[A] (M)$	$[B] (M)$	Initial rate ( $M/s$ )
1	0.0250	0.0250	$2.04 \times 10^{-3}$
2	0.0500	0.0250	$8.16 \times 10^{-3}$
3	0.0500	0.0500	$1.63 \times 10^{-2}$

### 14.3 Integrated Rate Laws and Half-lives

- We can take the relation of concentration to the rate law, and rearrange it collect like terms on the same side
- $-\frac{\Delta [A]}{\Delta t} = k [A]^m$  becomes  $-\frac{\Delta [A]}{[A]^m} = k \Delta t$
- If we change our  $\Delta$ s to  $ds$ , then we can integrate to get a function of  $[A]$  over time
- Perhaps the most important part of this function is the *half-life*
  - The half-life is the time it takes for half of a reactant to be consumed (Figure 14.11)
  - Sometimes the half-life changes over the course of the reaction
  - Sometimes the half-life is totally independent of concentration and is constant across time
- First-order kinetics:
  - $\int -\frac{d[A]}{[A]} = \int k dt$  integrates to:  $\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt$
  - We can rearrange this into a linear format:  $\ln [A]_t = -kt + \ln [A]_0$
  - The line slope is  $-k$
  - The half-life is given by:  $t_{1/2} = \frac{\ln 2}{k}$
- Second-order kinetics:
  - $\int -\frac{d[A]}{[A]^2} = \int k dt$  integrates to:  $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
  - The line slope is  $+k$
  - The half-life is given by:  $t_{1/2} = \frac{1}{k [A]_0}$
- Zeroth-order kinetics:
  - $\int -d[A] = \int k dt$  integrates to:  $[A]_t = -kt + [A]_0$
  - The line slope is  $-k$
  - The half-life is given by:  $t_{1/2} = \frac{[A]_0}{2k}$
- Table 14.5 summarizes the integrated rate laws and half-lives
- Determining reaction order graphically:
  - The linear forms of the integrated rate laws are all different
  - Graph  $[A]$ ,  $\ln [A]$ , and  $\frac{1}{[A]}$  vs  $t$

- Two will be curved, but one will be straight, indicating the overall reaction order
- Making one reactant in excess will probe the reaction order of only the other reactant
- Figure from Example 14.10a shows how to graph real concentration data to determine the reaction order
- Use my prepared Excell spreadsheet to look at real data

## 14.4 Reaction Rates and Temperature: Activation Energy

- Reaction coordinate diagrams show how the energy changes over the course of a reaction
  - Figure 14.14 and 14.15 show typical reaction coordinate diagrams
  - For simple reactions the x-axis can represent actual measurements, like bond lengths
  - Generally, the x-axis just represents progress in the reaction from reactants to products
  - The diagram shows if the reaction is exothermic or endothermic
  - The highest energy point is called the *transition state*
  - At the transition state, reactant bonds are nearly broken but product bonds have barely started to form
  - The activation energy is the energy required to reach the transition state
- Collision theory explains reaction rates in terms of molecular collisions
  - Reactions only occur when reactant molecules encounter each other in collisions, but not all collisions will lead to a reaction
  - Some collisions don't have enough energy to overcome the activation energy barrier
  - Some collisions happen in the wrong orientation to lead to reaction (Figure 14.16)
  - These considerations are summarized by the Arrhenius Equation:  $k = Ae^{-E_a/RT}$
  - $k$  is the rate constant from the rate law
  - $A$  is the frequency factor, and it includes both the rate of collisions, and the fraction of those collisions which lead to reaction
  - $A$  is dependent only weakly temperature, so we'll assume that it is constant
  - $E_a$  is the activation energy in  $\frac{J}{mol}$ , so we should use  $R = 8.314 \frac{J}{mol K}$
  - The exponential term is called a Boltzmann factor, and gives the fraction of collisions which have enough energy
  - Figure 14.17 shows how temperature affects the kinetic energy of collisions
- We can use the Arrhenius Equation to measure the activation energy
  - Take the natural log of both sides of the Arrhenius equation

- $\ln k = \ln (Ae^{-E_a/RT})$  becomes  $\ln k = \ln A - \frac{E_a}{RT}$
- If we plot the  $\ln k$  at different temperatures against  $\frac{1}{T}$ , we get a linear equation
- The slope of the line is  $-\frac{E_a}{RT}$  and the intercept is  $\ln A$
- We can also create the two-point form of this equation:  $\ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$
- Measure the reaction rate and get the rate constant at two or more temperatures
- Put the values into the two-point equation to get  $E_a$
- The decomposition of HI proceeds as follows:  $2 \text{HI(g)} \longrightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$   
 At 655 K the rate constant is  $8.15 \times 10^{-8} \frac{1}{\text{M s}}$  and at 705 K the rate constant is  $1.39 \times 10^{-6} \frac{1}{\text{M s}}$   
 Determine the activation energy and frequency factor for this reaction  $\left( 218 \frac{\text{kJ}}{\text{mol}} \text{ and } 1.91 \times 10^{10} \frac{1}{\text{M s}} \right)$

## 14.5 Reaction Mechanisms

- Chemical reaction *can* happen in just one step, but often proceed in two or more distinct steps
- The details of how a reaction actually proceeds is called the Reaction Mechanism
- Each step in the mechanism cannot be broken down or simplified further, and is called an *elementary step*
- Elementary steps involve either the spontaneous decomposition of a single molecule, or an encounter between two molecules
- Consider the following reaction:  $\text{NO}_2\text{(g)} + \text{CO(g)} \longrightarrow \text{NO(g)} + \text{CO}_2\text{(g)}$   
 Elementary Step 1:  $\text{NO}_2\text{(g)} + \text{NO}_2\text{(g)} \longrightarrow \text{NO(g)} + \text{NO}_3\text{(g)}$  SLOW  
 Elementary Step 2:  $\text{NO}_3\text{(g)} + \text{CO(g)} \longrightarrow \text{NO}_2\text{(g)} + \text{CO}_2\text{(g)}$  FAST
- The two steps add up to the total equation
- $\text{NO}_3\text{(g)}$  is produced in the first step, then consumed in the second step, so it never shows up in the overall reaction
- This makes  $\text{NO}_3\text{(g)}$  an *intermediate*
- Intermediates are different from transition states because they are energetically stable (minimum in the reaction coordinate diagram)
- Intermediates may sometimes be observed directly in the course of the reaction, or they may be so dilute or so short-lived that they cannot be observed
- Figure 14.19 shows the reaction coordinate diagram for a two-step reaction like this one

- Elementary steps each have their own reaction rates:
  - The rate law for an elementary step depends on the *molecularity* of the step
    - \* Unimolecular steps have only one reactant:  $AB \longrightarrow A + B$
    - \* Bimolecular steps involve an encounter between two molecules:  $A + B \longrightarrow C$  or  $2A \longrightarrow B$
    - \* Termolecular steps are very rare, but can occur
  - The rate law can be inferred from the stoichiometry of the step
    - \*  $AB \longrightarrow A + B$  gives  $rate = k [AB]$
    - \*  $A + B \longrightarrow C$  gives  $rate = k [A] [B]$
    - \*  $2A \longrightarrow B$  gives  $rate = k [A]^2$
  - While each step has its own rate, the overall reaction can only proceed at the rate of the *slowest* step
  - The slowest step is therefore called the *rate-limiting* step of the reaction
  - Looking at the reaction of  $NO_2$  and CO above, the first step is slower so the overall reaction rate will be  $rate = k [NO_2]^2$
- Any proposed mechanism must, at a minimum, add up to the total equation, and produce a rate law consistent with observations
- This is not conclusive proof of a mechanism's validity, as one could contrive infinite mechanisms within these two constraints
- Some elementary steps are reversible, and establish an equilibrium (subject of the next chapter):
  - Consider the reaction  $2 NO(g) + Cl_2(g) \longrightarrow 2 NOCl(g)$   $rate = k [NO]^2 [Cl]$
  - This observed rate law seems consistent with a single-step *termolecular* mechanism, but termolecular reactions are exceptionally rare
  - An alternative proposed mechanism is:
 
$$NO(g) + Cl_2(g) \xrightleftharpoons[k_{-1}]{k_1} NOCl_2(g) \quad \text{FAST}$$

$$NOCl_2(g) + NO(g) \xrightarrow{k_2} 2 NOCl(g) \quad \text{SLOW}$$
  - The first step will reach an equilibrium, where the forward rate will equal the reverse rate  $k_1 [NO] [Cl_2] = k_{-1} [NOCl_2]$
  - Rearrange this to give the equilibrium concentration of the intermediate  $[NOCl_2] = \frac{k_1}{k_{-1}} [NO] [Cl_2]$
  - The reaction rate is ultimately determined by the formation of product in the second step:  $rate = k_2 [NOCl_2] [NO]$
  - Substitute in our expression for  $[NOCl_2]$ 

$$rate = k_2 \left( \frac{k_1}{k_{-1}} [NO] [Cl_2] \right) [NO] = \frac{k_2 k_1}{k_{-1}} [NO]^2 [Cl_2]$$

- Consider the reaction:  $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g}) \quad \Delta H_{\text{rxn}} = -116.2 \frac{\text{kJ}}{\text{mol}}$ 
  - The observed rate law is:  $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$
  - A proposed mechanism is:
 
$$\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{NO}_3(\text{g}) \quad \text{FAST}$$

$$\text{NO}(\text{g}) + \text{NO}_3(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g}) \quad \text{SLOW}$$
  - Is the reaction mechanism consistent with the observed rate law?
  - What is the value of  $k$  in terms of the elementary step rate constants?
  - Draw a basically accurate reaction coordinate diagram for this reaction
- Reaction mechanisms can become complex and interesting for certain reactions (harpoon mechanism and collisional activation)

## 14.6 Catalysis

- Catalysts provide an alternative reaction mechanism which is faster than the uncatalyzed pathway
- Figure 14.21 shows a typical reaction coordinate diagram for a catalyzed reaction
- Catalysts appear in the reaction mechanism, being first *consumed*, then *regenerated*
- The reaction  $2 \text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$  can be catalyzed by  $\text{HBr}(\text{aq})$ 

$$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{HBr}(\text{aq}) \longrightarrow \text{Br}_2(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \quad \text{SLOW}$$

$$\text{Br}_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g}) + 2 \text{HBr}(\text{aq}) \quad \text{FAST}$$
- Note that the  $\text{HBr}$  is consumed in the first step, but regenerated in the second step
- Catalysts can be *homogeneous* ( $\text{HBr}$  above) or *heterogeneous* (catalytic converters)
- (not in the book) Catalysts can operate in several ways:
  - Heterogeneous catalysts confine reactants to a surface, increasing the encounter frequency
  - Enzymes hold the reactants in precise configurations, improving the steric component of the frequency factor and stabilizing the activated complex
  - Homogeneous catalysts produce new compounds which shift electron density and weaken bonds which must be broken for the reaction to proceed
- Analyze the following reaction mechanism:
 
$$\text{C}_3\text{H}_6(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{C}_3\text{H}_7^+(\text{aq})$$

$$\text{C}_3\text{H}_7^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{C}_3\text{H}_9\text{O}^+(\text{aq})$$

$$\text{C}_3\text{H}_9\text{O}^+(\text{aq}) \longrightarrow \text{C}_3\text{H}_8\text{O}(\text{aq}) + \text{H}^+(\text{aq})$$
  - Give the total overall reaction
  - Identify any catalysts and intermediates

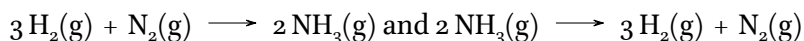


## CHAPTER 15

## CHEMICAL EQUILIBRIUM

## 15.1 Introduction to Equilibrium

- Some reactions can go in both the forward and reverse directions



- Such reactions will reach an equilibrium
  - Equilibrium is when the forward reaction rate and the reverse reaction rate are equal
  - The concentrations of reactants and products remains steady indefinitely once equilibrium is reached
  - Figure 15.2 shows how the amounts of reactant and product shift over time until equilibrium is reached
  - Equilibrium is a dynamic state – reactions continue, they merely balance each other
  - The precise concentrations at equilibrium will depend on the starting conditions
- The above two reactions can be combined into one equation:  $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
- Equilibrium can be reached whether you start with reactants or start with products (Figure 15.1)
- Note that  $\text{N}_2(\text{g})$  alone or  $\text{H}_2(\text{g})$  alone cannot lead to equilibrium from the reactant side – both are needed

## 15.2 Equilibrium Constants

- Consider the equilibrium reaction:  $2 \text{I}(\text{g}) \rightleftharpoons \text{I}_2(\text{g})$ 
  - Since the forward and reverse reaction rates are equal, set them equal to each other
  - Assume the reaction is single-step (elementary)
  - $k_1 [\text{I}]^2 = k_{-1} [\text{I}_2]$
  - We can rearrange this to:  $\frac{k_1}{k_{-1}} = \frac{[\text{I}_2]}{[\text{I}]^2}$
  - The ratio  $\frac{k_1}{k_{-1}}$  is called the equilibrium constant, and given the symbol  $K$
  - Now we can give the equilibrium expression without reference to rate constants:  $K = \frac{[\text{I}_2]}{[\text{I}]^2}$
  - Because  $[\text{I}]$  is squared, the ratio of  $[\text{I}]$  to  $[\text{I}_2]$  will depend on initial conditions (Figure 15.3)

- Equilibrium expressions can be generalized:  $aA + bB \rightleftharpoons cC + dD$   $K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
- Products over reactants, raised to the power of their stoichiometric coefficients
- Solids and pure liquids will be *absent* from the equilibrium expression – only include solvated and gaseous species
- $K$  is actually unitless, for reasons we don't go into in this class
- Give the equilibrium expression for the formation of ammonia above:  $K = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3}$
- Although the particular concentrations of reactants and products will depend on starting conditions, the equilibrium expression will be the same (at constant  $T$ )
- The magnitude of  $K$  can tell about general conditions at equilibrium
  - If  $K \gg 1$  then equilibrium will favor products
  - If  $K \ll 1$  then equilibrium will favor reactants
- Equilibrium expressions can be given in terms of pressures, instead of molar concentrations
  - We have technically been using  $K_c$  up until now, which works for (aq) and (g) species
  - If we use pressures instead, we instead use  $K_p$ , which only works for gases
  - We can show that  $K_p = K_c (RT)^{\Delta n}$  by substituting in  $P = MRT$
  - Give the relationship between  $K_p$  and  $K_c$  for the formation of ammonia:  $K_p = \frac{K_c}{(RT)^2}$

### 15.3 Using Equilibrium Expressions

- We can measure the concentrations at equilibrium and directly measure the equilibrium constant
  - Consider the reaction:  $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
  - Find  $K_c$  if  $[\text{CO}] = 0.0600\text{ M}$ ,  $[\text{H}_2\text{O}] = 0.120\text{ M}$ ,  $[\text{CO}_2] = 0.150\text{ M}$ , and  $[\text{H}_2] = 0.300\text{ M}$
- We can use the equilibrium constant to find an unknown concentration
  - $\text{CH}_3\text{CO}_2\text{H(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{CH}_3\text{CO}_2^-\text{(aq)}$   $K = 1.8 \times 10^{-5}$
  - Find  $[\text{H}_3\text{O}^+]$  if  $[\text{CH}_3\text{COOH}] = 0.250\text{ M}$  and  $[\text{CH}_3\text{COO}^-] = 0.350\text{ M}$
- We can easily find  $K$  for doubled, reversed, or added equations
  - For a reversed equation, reactants and products switch, so  $K_{\text{reverse}} = K_{\text{normal}}^{-1}$
  - For a doubled (or tripled) reaction,  $K$  should be squared (or cubed)
  - For added reactions (multi-step)  $K_{\text{total}} = K_1 K_2$

- Find  $K$  for the reaction:  $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$   
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \quad K = 2.0 \times 10^{-25}$   
 $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) \quad K = 6.4 \times 10^9$

## 15.4 The Reaction Quotient

- The equilibrium expression is really only true once equilibrium has been reached
- On short time scales, a reaction can be far from equilibrium
- The reaction quotient,  $Q$  has the same formula of  $K$  but is calculated away from equilibrium
- Comparing  $Q$  to  $K$  can tell which direction the reaction must shift to reach equilibrium
  - If  $Q < K$  then the reaction must produce more product, shifting right
  - If  $Q > K$  then the reaction has too much product and must shift left
  - If  $Q = K$  then the reaction has reached equilibrium

## 15.5 Calculations Using ICE Tables

- If we know the equilibrium constant, we can find equilibrium concentrations based on the initial conditions
- We do this using an ICE table:
  - I – Initial conditions (often one or more species will have an initial concentration of 0)
  - C – Change. Express the change in terms of  $x$  and be sure to consider stoichiometry
  - E – Equilibrium conditions. These values (I + C) should be put in the equilibrium expression
  - Once you have the equilibrium expression you can calculate the change amount ( $x$ )
  - You can do this technique with pressures or molar concentrations, depending on the form of  $K$
  - If you do your change calculations in pure moles, be sure to change them into  $P$  or  $M$  before you put them into the equilibrium expression
- Consider the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$   
 $5.00 \text{ mol H}_2$  and  $0.500 \text{ mol I}_2$  are reacted in a  $1.00 \text{ L}$  chamber and at equilibrium  $[\text{HI}] = 0.900 \text{ M}$ .  
 Find the value of  $K_C$  (324)
- Consider the reaction  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \quad K_C = 5.80$   
 Find the equilibrium conditions if initial concentrations are:  $[\text{CO}] = [\text{H}_2\text{O}] = 0.0125 \text{ M}$
- Often the equilibrium expression will lead to a quadratic equation when solving for  $x$

- The quadratic formula is:  $ax^2 + bx + c = 0 \rightarrow x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
- Consider the reaction:  $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g}) \quad K_{P,1000\text{K}} = 0.260$   
Find the equilibrium conditions if a reaction chamber is initially charged with  $0.200 \text{ atm I}$  and  $0.00500 \text{ atm I}_2$
- Some quadratic equations can be greatly simplified by recognizing when  $x$  is small compared to initial amounts
  - If  $x$  is small, then it can be neglected from any species with an initial amount
  - First solve the equation *assuming* that  $x$  can be neglected
  - Compare the solved value of  $x$  to the amounts it was neglected from
  - If  $x$  is less than 5% of those values then your simplification was valid
  - If not, then you must go back and solve the complete quadratic equation
- Consider the reaction  $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq}) \quad K_C = 1.8 \times 10^{-4}$   
Find the equilibrium conditions for a solution that begins with  $[\text{HCOOH}] = 0.250 \text{ M}$

## 15.6 Le Châtelier's Principle

- When changes are made to a system at equilibrium, it will shift in response to that change to maintain equilibrium
- This is called Le Châtelier's Principle
- We can calculate  $Q$  after the change and compare it to  $K$
- In practice, though, a few simple rules are sufficient without any calculations
- Adding or removing a reactant or product
  - If a reactant or product is added or removed, the system will respond to counteract the change
  - A U-pipe with water is a good analogy for this shift
  - Consider the reaction  $2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$   
How would the reaction shift if each species is added or removed in turn?
- Changing volume
  - If the reaction volume changes, all the concentrations or pressures will change together
  - The effect this has depends on the stoichiometry of the reaction
  - Consider the reaction  $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$  – How will the reaction quotient change if the volume doubles?

- The shift depends on  $\Delta_n$ , considering only the moles of gas or aqueous substances
- If volume increases (dilution), the reaction will shift to the side with *more* moles
- If volume decreases (concentration), the reaction will shift to the side with *fewer* moles
- If  $\Delta_n = 0$ , then the reaction is unaffected by dilution and concentration
- Figure 15.6 illustrates this principle
- Temperature changes
  - Unlike with the other changes, a change in  $T$  will actually change the value of  $K$
  - How  $K$  changes depends on  $\Delta H_{rxn}$
  - We will explore this relationship mathematically later, but for now we can use a trick to determine the direction of the shift
  - Consider “heat” as a reactant for endothermic reactions, and as a product for exothermic reactions
  - Heat is not really a product or reactant (how many  $g$  of heat are produced)
  - Lowering  $T$  removes heat and the reaction will respond just like removing any other reactant or product
  - Raising  $T$  adds heat and will have the same effect as adding any other reactant or product
- Equilibrium is often not the most important factor in industrial settings. The Haber process is run at high temperatures to increase the reaction rate even though it pushes equilibrium toward reactants
- Addition of a catalyst has *no* effect on the equilibrium position

## CHAPTER 16

## ACID-BASE THEORY

## 16.1 Ionization Reactions of Acids and Bases

- Arrhenius acid/base theory defines acids and bases in terms of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions
  - $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
  - $\text{NaOH}(\text{s}) \xrightarrow{\text{water}} \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- Acids and bases can be *strong* or *weak*
  - Strong acids and bases are those which dissociate completely (or, at least, nearly so)
  - Weak acids and bases establish an equilibrium which is usually highly reactant-favored
  - Figures 16.1 and 16.2 show the extent of ionization for strong and weak acids and bases
- $\text{H}^+$  vs  $\text{H}_3\text{O}^+$ 
  - In the past, you may have used  $\text{H}^+(\text{aq})$  in your equations
  - I will tend to use  $\text{H}_3\text{O}^+$  instead, but either way is acceptable
  - Really,  $\text{H}^+$  is a flagrant lie. Bare protons don't exist in water.  $\text{H}_3\text{O}^+$  is also a little bit of a lie. The extra proton and the charge create clusters of many water molecules. It gets really complicated

## 16.2 Brønsted-Lowry Theory

- Arrhenius theory is unable to account for reactions that don't involve  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions directly
- Consider  $\text{HNO}_2(\text{aq}) + \text{ClO}_2^-(\text{aq}) \rightleftharpoons \text{HClO}_2(\text{aq}) + \text{NO}_2^-(\text{aq})$  – should this reaction be considered acid/base?
- Brønsted-Lowry theory defines acids as proton *donors* and bases as proton *acceptors*
- $\text{HNO}_2$  is the acid, and  $\text{ClO}_2^-$  is the base
- Conjugate pairs
  - We can also consider the reverse reaction, where  $\text{HClO}_2$  is the acid and  $\text{NO}_2^-$  is the base
  - We call these linked species *conjugate pairs*
  - $\text{HNO}_2$  is the conjugate acid to  $\text{NO}_2^-$ , while  $\text{NO}_2^-$  is the conjugate base to  $\text{HNO}_2$

- The strengths of a conjugate pair are inverse to each other – A stronger acid has a weaker conjugate base and vice-versa
- Some acids are *multiprotic* and some bases are *multibasic*
  - Consider the series  $\text{H}_2\text{SO}_3 \rightleftharpoons \text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-}$
  - Or the series  $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-}$
  - $\text{H}_2\text{SO}_3$  is a diprotic acid, and  $\text{SO}_3^{2-}$  is a dibasic base because they can exchange 2 protons
  - $\text{H}_3\text{PO}_4$  is a triprotic acid, and  $\text{PO}_4^{3-}$  is a tribasic base because they can exchange 3 protons
  - The intermediates,  $\text{HSO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  can act as either an acid or a base
  - These types of ions are called *amphoteric* or *amphiprotic*
  - Whether they act as an acid or a base depends on the context – what is their reaction partner

### 16.3 Autoionization of Water

- Water is also amphoteric:  $\text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{O} \rightleftharpoons \text{OH}^-$
- Because of this, water will undergo autoionization:  $2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_w = 1.00 \times 10^{-14}$
- For pure water, this leads to concentrations of  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7}$
- This water ionization equilibrium is the great arbiter of acid/base chemistry. It defines what is an acid, what is a base, and what are their various strengths
- Even for reactions which don't explicitly contain water ( $\text{NH}_3(\text{aq}) + \text{HNO}_2(\text{aq}) \longrightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq})$ ), water is actually mediating the proton exchange behind the scenes
- Because of this, acidity and basicity are defined by the balance between  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ 
  - $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  is an acid
  - $[\text{H}_3\text{O}^+] < [\text{OH}^-]$  is a base
  - $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  is neutral
- We can always find  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  from the other, based on  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

### 16.4 pH Calculations

- Acidity of a solution is summarized by the quantity  $\text{pH} = -\log [\text{H}_3\text{O}^+]$
- Neutral solutions have  $\text{pH} = 7$ , acidic solutions have  $\text{pH} < 7$ , and basic solutions have  $\text{pH} > 7$
- 0 and 14 are actually not boundaries at all, and you *can* have solutions with  $\text{pH} < 0$
- We can find the  $[\text{H}_3\text{O}^+]$  by  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

- Table 16.1 shows both the  $pH$  and  $[H_3O^+]$  for several common substances
- We can make similar calculations for  $[OH^-]$  and  $pOH$
- This gives us the interesting relationship that  $pH + pOH = 14$  – draw the conversion rectangle
- We can measure  $pH$  in several ways:
  - Color indicators are chemicals which change color based on  $pH$  conditions
  - We will see that these indicators are themselves weak acids/base conjugate pairs
  - Indicators can be dissolved in the solution or applied onto paper strips
  - By mixing several indicators, we can get a different value at each  $pH$ , making a “universal indicator”
  - Figure 16.5 shows how a universal indicator  $pH$  paper works
  - We can also measure an electrochemical response using a  $pH$  probe
  - How these  $pH$  probes work is a bit complicated, but they can measure  $[H_3O^+]$  across a wide range

## 16.5 Weak Acids and Bases

- Weak acids and weak bases will react with water to reach an equilibrium
- Because equilibrium concentrations are different from initial concentrations, pedantic people (like me!) will sometimes use *formal* concentration,  $F$ , instead of molar concentration
- The equilibrium constant for their hydrolysis reactions are given the name  $K_a$  for acids, and  $K_b$  for bases
- Table 16.2 shows the  $K_a$  and  $K_b$  values for a number of different acids and bases
- It is also sometimes useful to find the  $pK_a = -\log K_a$  or the  $pK_b = -\log K_b$
- We can use these equilibrium constants with an ICE table to find the  $pH$  of a solution under different circumstances
  - Weak acids always follow the same format:  $K_a = \frac{[A^-][H_3O^+]}{[HA]}$
  - Weak bases always follow the same format:  $K_b = \frac{[HB^+][OH^-]}{[B]}$
  - We will often be able to use the simplification that the change is much less than the initial amounts
- Find the  $pH$  for a 0.250  $F$  solution of nitrous acid ( $K_a = 4.0 \times 10^{-4}$ )
- Find the  $pH$  for a 0.325  $F$  solution of pyridine ( $K_b = 1.7 \times 10^{-9}$ )



- A few useful relations that are not in your textbook:
  - For conjugate acid/base pairs:  $K_a K_b = K_w$
  - For the reaction between an acid and a base:  $K = \frac{K_a K_b}{K_w}$

## 16.6 Polyprotic Acids

- For polyprotic acids and bases, each step has its own  $K_a$  or  $K_b$  values
- Each successive proton loss will have significantly lower acid strength
- Table 16.3 shows  $K_a$  values for several polyprotic acids
- Amphoteric species can establish multiple simultaneous and interdependent equilibria, but we will only look at the simple problems
- Find pH,  $[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]$ ,  $[\text{HC}_6\text{H}_6\text{O}_6^-]$ , and  $[\text{C}_6\text{H}_6\text{O}_6^{2-}]$  for a 0.500 *F* solution of Ascorbic acid
  - First, solve the ICE table for the first deprotonation
  - Then, use the  $[\text{H}_3\text{O}^+]$  and  $[\text{HC}_6\text{H}_6\text{O}_6^-]$  as starting values for the second deprotonation
  - Because the  $[\text{H}_3\text{O}^+]$  will not change much, we don't have to revisit the first equilibrium

## 16.7 Acid-Base Properties of Salts

- Some salts have no effect on *pH* when dissolved on water, while others do
- To determine the acid/base strength of a salt, look at the individual ions which dissociate in the water
- Cations are usually neutral with two exceptions:
  - $\text{NH}_4^+$  and others based off of it are weak acids
  - Some metal cations can act as acids – we will cover this more in the Lewis Acids section
- The anions are usually where the activity lies:
  - Many anions are neutral, such as the conjugates to strong acids
  - Some anions are amphoteric, and their effect depends on their  $K_a$  and  $K_b$  values
  - If  $K_a > K_b$ , then the anion will be acidic, and if  $K_a < K_b$ , then the ion will be basic
  - Some anions are simply weak bases
- You can then find the *pH* based on the acid/base activity of the individual ions
- Find the *pH* of a 0.125 *M* solution of  $\text{CaF}_2$

## 16.8 Relating Acid Strength to Structure

- Acid strength ultimately comes from the strength of the H bond and the stability of the product ions
- Bond strength:
  - Weaker H bonds lead to stronger acids
  - Longer bonds tend to be weaker, hence the strength of HI is greater than the strength of HF (Table 16.6)
  - Electronegative groups nearby pull electrons away from the H bond and make it weaker (Table 16.7)
- Ion stability:
  - Even strong H bonds can be acidic if the anion after deprotonation is particularly stable
  - Consider the structure of acetic acid and acetate
    - \* Acetic acid does not exhibit resonance, but acetate ion does
    - \* By losing a hydrogen, the acetate ion can stabilize with resonance
    - \* This makes acetic acid stronger than we might have assumed based only on the O–H bond strength

## 16.9 Lewis Acids and Bases

- Coordinate bonds are bonds where both shared electrons come from a single bonding partner, rather than one electron from each
- Brønsted bases can accept a  $\text{H}^+$  because they have a lone pair of electrons which can form a coordinate covalent bond
- We could define bases in terms of donating electrons instead of accepting protons, and this is the Lewis definition
  - A Lewis base is an electron pair donor
  - A Lewis acid is an electron pair acceptor – the proton itself for Brønsted acids
  - The molecule formed by the coordinate bond (Brønsted conjugate acid) is called a Lewis adduct
- The Lewis definition expands acid/base reactions to reactions which don't involve the exchange of a proton at all
- Consider the reaction of  $\text{BF}_3$  with  $\text{NH}_3$
- Many metal cations can act as a Lewis acid by forming coordinate bonds with water molecules
 
$$\text{Al}^{3+}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq})$$
- Carbonic acid makes gas due to Lewis acid action:  $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

## CHAPTER 17

## AQUEOUS EQUILIBRIA

## 17.1 Introduction to Buffer Solutions

- Buffer solutions resist a change in  $pH$  when acid or base is added to them
- Buffer solutions are everywhere in nature – blood, soil, ocean water, etc.
- The common-ion effect is critical to how buffer solutions work
  - Consider the equilibrium reaction:  $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
  - Adding  $\text{NaNO}_2$  will affect this equilibrium because it adds nitrite ion to solution
  - Le Châtelier's principle will shift the reaction left, reducing the effect  $\text{HNO}_2$  has on  $pH$
  - Any equilibrium reaction involving ions can be affected by addition of other salts containing those ions – This is the common ion effect
- Buffer solutions contain amounts of both members of a weak conjugate acid/base pair
  - Adding strong acid or strong base to the buffer will react with the weak base/acid rather than with water, resulting in a suppressed change in  $pH$
  - Figure 17.1 shows how  $[\text{HA}]$  and  $[\text{A}^-]$  change in this case
  - The buffer can only absorb a certain amount of acid or base, called the buffer capacity, which will be covered later

## 17.2 The Henderson-Hasselbach Equation

- For a buffer solution, we can solve an ICE table with initial amounts of both HA and  $\text{A}^-$
- In this case, the equilibrium expression simplifies to:  $[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$
- We can calculate the  $pH$  from here to be:  $pH = pK_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$
- This is the Henderson-Hasselbach equation
- Buffer capacity describes the range of  $pH$  values where a buffer works
  - The buffer performs best (smallest  $pH$  changes) when  $pH = pK_a$
  - $pH$  changes become more pronounced as more acid or base is added

- Once the  $pH$  strays beyond  $\pm 1$  of  $K_a$ , the buffer capacity is exceeded and the buffer will stop working
- Higher concentrations of HA and  $A^-$  can absorb more acid or base before its capacity is exceeded
- $H_2S$  has  $K_a = 9.1 \times 10^{-8}$ . Find the  $pH$  of a solution if 2.7 g of  $H_2S$  and 1.5 g of NaHS are dissolved in 0.50 L of water
- $H_2PO_4^-$  has  $pK_a = 6.8$  and is responsible for regulating the  $pH$  of blood at  $pH = 7.4$ .
  - If  $[HPO_4^{2-}] \approx 0.200\text{ M}$ , find the  $[H_2PO_4^-]$  to maintain proper blood  $pH$
  - How many g of HCl could be added to 5.0 L of blood before the buffer capacity is exceeded?
  - How many g of NaOH could be added to 5.0 L of blood before the buffer capacity is exceeded?

### 17.3 Titrations of Strong Acids and Strong Bases

- A titration is the gold standard technique for determining the concentration of a solute
- The unknown substance is called the *analyte*
- A solution of suitable reaction partner, called the *titrant* is slowly added until the analyte is completely consumed
- Acid/base, redox, and precipitation reactions can all be titrated, though the first two are by far more common
- Figures 17.3 and 17.4 show typical titration setups, with different methods of determining the exact point where the analyte is consumed (called the *equivalence point*)
- Figure 17.5 shows a titration curve for a strong acid with a strong base
  - Point A will be the pH of the analyte solution,  $pH = -\log [H_3O^+] = -\log [HA]$
  - In region B the base is reacting with the acid and causing the  $pH$  to rise
  - Solve the  $pH$  using a BCA table
  - At point C, the equivalence point, the base has precisely neutralized the acid, and  $pH = 7.00$  exactly
  - In region D, the  $pH$  changes as excess base is added
- Figure 17.6 shows a titration curve for a strong base with a strong acid
- At the equivalence point, moles of titrant added is equal to moles of analyte
- This relation can be summarized as  $M_a V_a^\circ = M_t V_{eq}$

## 17.4 Titrations of Weak Acids and Weak Bases

- Titrating a weak acid or base follows a similar process as titrating a strong acid or base
- The buffering property of weak acids and bases does change the details of the titration curve (Figure 17.8)
  - The starting point A must be solved using an ICE table after the concentration is known
  - Region B is called the buffer region, and will be centered around  $K_a$
  - Solve for the  $pH$  using the Henderson-Hasselbach equation
  - $pH = pK_a$  at precisely half of the equivalence volume
  - Point C, the equivalence point, will have a pH determined by the strength of the conjugate base (Solve using an ICE table)
  - In region D, the  $pH$  is governed by the excess base added as in strong acid/base titrations
  - Figure 17.9 shows how these curves can be very different for different acids, even at the same concentration
  - Note the strong inflection in curves for very weak acids
- Figure 17.11 shows an analogous titration of weak base with strong acid
- The equivalence point is recognized as the point with steepest  $pH$  change
- Multiprotic acids or bases will pass through more than one equivalence point (Figure 17.12)

## 17.5 Indicators in Acid-Base Titrations

- Color indicators are often used in titrations instead of  $pH$  probes
- Color indicators are themselves weak acid/base conjugate pairs
  - $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$
  - HA is one color, and  $A^-$  is another
  - The indicator is in such low concentration, that the  $pH$  is governed by the titrant and analyte rather than by the indicator
  - The ratio of HA and  $A^-$  responds to the  $pH$  according to the H-H equation
  - Over the buffer range ( $pK_a \pm 1$ ) the indicator goes from primarily HA to primarily  $A^-$  and the solution color changes
- A color indicator should be carefully chosen to match the titration it will be used for
  - The expected equivalence point  $pH$  should lie within the buffer range for the indicator
  - The point of color change, when you actually stop the titration, is called the *end point* and should be close to the true equivalence point
  - Figure 17.13 shows how the end point and equivalence point are situated in a titration curve
  - Table 17.1 shows the appropriate ranges for some common indicators

## 17.6 Solubility Product Constant, $K_{sp}$

- Most insoluble salts are really just *sparingly* soluble
- This means that the solvation of the solid salt is a reactant-favored equilibrium
- For  $\text{PbI}_2$ , the equation is:  $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq}) \quad K_{sp} = 9.8 \times 10^{-9}$
- The equilibrium expression here would be:  $K_{sp} = [\text{Pb}^{2+}] [\text{I}^{-}]^2$
- $K_{sp}$  determines the ion concentrations, but is not mathematically equivalent to the solubility
- Solubility is usually defined as the moles of the salt which will dissolve in 1.00 L of solution
  - We solve the molar solubility with an ICE table just like with other equilibria
  - Be careful about the stoichiometry
  - $x$  will represent the molar solubility
  - For  $\text{PbI}_2$ , this would be:  $9.8 \times 10^{-9} = x (2x)^2 = 4x^3$ , which solves to:  $x = 1.35 \times 10^{-3}$
  - The molar solubility is  $1.35 \times 10^{-3} \text{ M}$
  - The same equation can be used in reverse to find  $K_{sp}$  from the molar solubility
- Find the molar solubility for  $\text{Sr}_3(\text{PO}_4)_2$
- Find  $K_{sp}$  for  $\text{AgI}$ , which has a molar solubility of  $9.0 \times 10^{-9} \text{ M}$

## 17.7 The Common-Ion Effect and the Effect of pH on Solubility

- If either cations or anions from the compound are already present in solution, solubility will be suppressed
- This is apparent when we put them in as initial concentrations on the ICE table
- Solubility in a salt solution will not be the same as solubility in pure water
- Even very soluble salts will become insoluble with the common ion effect
- $\text{NaCl}$  has a  $K_{sp} = 37.66$ . Find how many grams of  $\text{NaCl}$  can dissolve in 100.0 mL of a 12 M  $\text{HCl}$  solution
- Many hydroxide salts are insoluble in pure water but soluble in acidic solutions
  - This can be explained because even insoluble salts have some small amount of ions in solution
  - Acidic solutions will react with the tiny amount of  $\text{OH}^{-}$  and drive the reaction toward products
  - Even very low  $K_{sp}$  salts will dissolve if the  $[\text{OH}^{-}]$  is held low by the  $\text{pH}$

## 17.8 Precipitation: $Q$ vs $K_{sp}$

- Unlike other equilibrium reactions, solvation reactions are often stuck in non-equilibrium states
- Consider first a fairly soluble salt when very little salt is added to solution:
  - If all of the salt dissolves, it has likely not reached equilibrium
  - There are simply not enough ions to reach  $K_{sp}$ , and  $Q < K$
  - Such a solution is called *unsaturated*
  - NaCl has a  $K_{sp} = 37.66$ . Calculate  $Q$  if 2.00 g of NaCl are dissolved in 100.0 ml of water
- A solution which has achieved equilibrium is called *saturated*
  - You can tell a solution is saturated when some solid salt remains behind
  - The salt will not lose mass because the ion concentration has already reached its maximum amount
  - This equilibrium is a dynamic state (ions are dissolved and deposited at the same rate)
  - Show my 3-year salt solution with larger crystals due to dynamic equilibrium
- Sometimes a solution can have  $Q > K$ 
  - This type of solution is called *supersaturated*
  - A supersaturated solution can be made taking advantage of the temperature dependence of solubility
  - A lot of salt is dissolved in hot water, which is then carefully cooled to make a supersaturated solution
  - This solution is metastable, and will form precipitate once a seed crystal is introduced
  - Demonstrate supersaturated sodium acetate solution
- Figure 17.17 shows these three situations

## 17.9 Qualitative Analysis

- You don't need to memorize this process at all - just know the general solubility rules and general principle
- We can take advantage of the solubility properties of ions to identify a solution with unknown ions
- Figure 17.18 shows one pathway for separating metal cations in a solution
- Other schema can be used as well

### 17.10 Complex Ion Equilibria, $K_f$

- Transition metals will often act as Lewis acids and form coordinate covalent bonds with other species in solution
- The Lewis adduct is called a complex ion, and the Lewis bases are called *ligands*
- These complex ions will be formed by an equilibrium reaction whose equilibrium constant is called a formation constant  $K_f$
- Table 17.3 gives formation constants for several common complex ions – note that they tend to be large numbers
- Find the equilibrium concentrations for a  $\text{Co}(\text{NH}_3)_6^{2+}$  formation reaction
  - Suppose you start with  $[\text{Co}^{2+}] = 0.0200\text{ M}$  and  $[\text{NH}_3] = 0.100\text{ M}$
  - Trying to find the concentrations with a normal ICE table will lead to problems because  $x$  is so large
  - The equilibrium condition will be reached from different starting conditions as long as they are consistent
  - First, assume that the complex ion is formed completely in a limiting reactant problem
  - Then, do an ICE table where  $x$  represents the dissociation of the complex ion



## CHAPTER 18

## CHEMICAL THERMODYNAMICS

## 18.1 Entropy and Spontaneity

- Thermodynamics is the study of how heat and work are involved in chemical reactions
- For us, thermodynamics primarily concerns the *spontaneity* of a process
  - We can write a well-balanced reaction and talk about its products,  $\Delta H_{rxn}$ , etc, but some reactions simply will *not* happen
  - $2 \text{Au(s)} + 3 \text{H}_2\text{O(l)} \longrightarrow \text{Au}_2\text{O}_3\text{(s)} + 3 \text{H}_2\text{(g)}$  – Gold doesn't corrode in water (Gold coins in old shipwrecks still shine)
  - Reactions that happen under the current conditions are called *spontaneous*, while those that don't are called *non-spontaneous*
  - Some spontaneous reactions are slow – perhaps they take millions of years – but they will eventually happen
  - Non-spontaneous reactions will *never* happen, unless conditions change
- First Law of Thermodynamics
  - The total energy of the universe is constant
  - This leads to our understanding of enthalpy,  $\Delta H$
  - Any chemical potential energy lost or gained by the chemical reaction must be given to or taken from the surroundings
- Second Law of Thermodynamics
  - Spontaneous processes always result in an increase in the entropy of the universe (though not necessarily the system)
  - *Entropy* ( $S$ ) was originally defined as an abstract thermodynamic potential,  $\int \frac{dq}{T}$
  - Today, we usually talk about entropy as a measure of disorder or randomness in a system
  - Higher  $S$  systems have more potential configurations – are more disordered
  - The following processes have positive  $\Delta S$ 
    - \* An upward phase change ( $s \longrightarrow l, l \longrightarrow g$ )
    - \* Mixing (including solvation of a solid into aqueous solution)
    - \* Increasing the temperature
    - \* Increasing the number of particles (positive  $\Delta n$ )

\* Increasing the volume of an aqueous or gaseous system

- The Boltzmann definition of entropy is:  $S = k_B \ln W$ 
  - $k_B$ , the Boltzmann constant, is actually  $\frac{R}{N_A} = 1.38 \times 10^{-23} \frac{J}{K}$
  - $W$  is the number of microstates for the current macrostate, or microscopic configurations of the system with the same observable state variables
  - Figure 18.2 shows how expansion increases the value of  $W$
  - Figure 18.3 explores the value of  $W$  in an idealized system
  - My spheres\_demo program showing how systems tend toward macrostates with greatest  $W$

## 18.2 Entropy Changes – Both Chemical and Physical

- Third Law of Thermodynamics
  - The third law defines 0 entropy as the entropy of a perfectly ordered crystal at absolute 0
  - For such a crystal,  $W = 1$ , so  $\ln W = 0$
- Substances at 298 K have a standard molar enthalpy  $S^\circ$  based off of this 0 standard
- Table 18.1 gives the standard molar enthalpies for several common substances
- For a reaction, we can find  $\Delta S_{rxn}^\circ$  just like  $\Delta H_{rxn}$
- $$\Delta S_{rxn}^\circ = \sum_{i, products} \nu_i S_i^\circ - \sum_{j, reactants} \nu_j S_j^\circ$$

## 18.3 Entropy and Temperature

- While we do see reactions with  $\Delta S_{rxn}^\circ < 0$ , the second law requires that  $\Delta S_{universe} > 0$
- $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$
- We can calculate the entropy change of the surroundings based on the heat released by the system
- For isothermal processes,  $\Delta S_{surr} = \frac{-q_{sys}}{T}$ , and at constant pressure this is:  $\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$
- Find  $\Delta S_{universe}$ ,  $\Delta S_{sys}$ , and  $\Delta S_{surr}$  for combustion of 1 mol of methane at room temperature
- Find  $\Delta S_{universe}$ ,  $\Delta S_{sys}$ , and  $\Delta S_{surr}$  for condensing 1.00 g of water vapor ( $\Delta H_{vap} = 2257 \frac{J}{g}$ )

## 18.4 Gibbs Free Energy

- A new equation can be derived from the second law:  $\Delta G = \Delta H - T\Delta S$
- We will often use the form:  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , which is under standard conditions
- Standard conditions means 1 M for solutes and 1 bar ( $\approx 1 \text{ atm}$ ) for gases
- $G$  is called *Gibbs free energy*, and is a measure of spontaneity
- $\Delta G < 0$  for spontaneous processes, and  $\Delta G > 0$  for non-spontaneous processes
- Systems at equilibrium will have  $\Delta G = 0$
- Find  $\Delta G$  for the reaction:  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{H}_2\text{O}(\text{g})$   $\Delta H_{rxn} = -483.6 \frac{\text{kJ}}{\text{mol}}$   $\Delta S_{rxn} = -89.0 \frac{\text{J}}{\text{mol K}}$ 
  - At  $T = 298 \text{ K}$
  - At  $T = 5500 \text{ K}$  (Assume  $\Delta H_{rxn}$  and  $\Delta S_{rxn}$  are independent of temperature)
- Appendix A.2 also has  $\Delta G_f^\circ$  values, so you don't have to calculate  $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$  values independently – These values *only* work at 298 K
- Endothermic reactions must have a sufficiently large  $T\Delta S_{rxn}$  to make  $\Delta G_{rxn} < 0$
- Solvation reactions are prominent examples - dissolving a regular, ordered crystal lattice has a very large  $\Delta S_{rxn}$
- The  $\Delta G_{rxn}$  for dissolving a substance is called the free energy of solution

## 18.5 Free-Energy Changes and Temperature

- Looking at  $\Delta G = \Delta H - T\Delta S$ , we can see that temperature plays a role in the spontaneity of a process
- Draw my quadrant diagram for  $\pm\Delta H_{rxn}$  and  $\pm\Delta S_{rxn}$

		$\Delta H_{rxn}$	
		+	–
$\Delta S_{rxn}$	+	Spontaneous @ High $T$	Always Spontaneous
	–	Never Spontaneous	Spontaneous @ Low $T$

- We can find the threshold temperature by solving the Gibbs energy equation for  $\Delta G_{rxn} = 0 \rightarrow 0 = \Delta H_{rxn} - T\Delta S_{rxn}$
- This simplifies to:  $T_{threshold} = \frac{\Delta H_{rxn}}{\Delta S_{rxn}}$

## 18.6 Gibbs Free Energy and Equilibrium

- We will often have to deal with reactions that are not at the standard state
- We can relate any conditions to standard conditions through:  $\Delta G = \Delta G^\circ + RT \ln Q$ 
  - $Q$  is the reaction quotient
  - $R$  is the gas constant,  $R = 8.314 \frac{J}{mol\ K}$
  - $T$  must be in Kelvin
  - $\ln$  is the base- $e$  natural logarithm
- When a system is at equilibrium,  $\Delta G = 0$  and  $Q = K$
- This transforms the above equation into:  $\Delta G^\circ = -RT \ln K$  and therefore  $K = e^{\left(-\frac{\Delta G^\circ}{RT}\right)}$
- Figure 18.9 shows how  $G$  varies with reaction progress for various reactions
- Find the equilibrium constant for the combustion of hydrogen gas at 298  $K$  and 5500  $K$
- Solvation of NaCl at 298  $K$  has  $K_{sp} = 37.66$  Calculate  $\Delta G_{soln}^\circ$  for NaCl

## CHAPTER 19

## ELECTROCHEMISTRY

## 19.1 Redox Reactions

- Electrochemistry studies the links between chemistry and electricity
- Electricity is the flow of charge (usually electrons), and only redox reactions can facilitate that flow
- Redox reactions can be split into half-reactions, addressing reduction and oxidation separately
  - Consider the reaction:  $2 \text{Al}(\text{s}) + 3 \text{Cl}_2(\text{g}) \longrightarrow 2 \text{AlCl}_3(\text{s})$
  - Aluminum is oxidized in the half-reaction:  $\text{Al} \longrightarrow \text{Al}^{3+} + 3 \text{e}^-$
  - Chlorine is reduced in the half-reaction:  $\text{Cl}_2 + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-$
  - The electrons gained by chlorine come from the aluminum
  - To combine these half-reactions, the total number of electrons must match
  - So, we combine 2 Al with 3  $\text{Cl}_2$
- We will revisit half-reactions (and see why they are useful) later
- Sometimes a single reactant can be both oxidized and reduced
  - Such reactions are called *disproportionation* reactions
  - Consider the reaction:  $2 \text{Cu}^+(\text{aq}) \longrightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$
  - One  $\text{Cu}^+$  ion is reduced and one is oxidized, making  $\text{Cu}^+$  both the oxidizing and the reducing agent

## 19.2 Balancing Redox Reactions

- Some redox reactions are particularly difficult to balance
  - First, some reactants or products are often left out ( $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , and  $\text{H}_3\text{O}^+$ )
  - Second, there is a hidden constraint that the electrons lost in one half-reaction must match the number of electrons gained in the other
  - A related fact is that redox reactions must balance total *charge*, and not just the numbers and types of atoms
- There are seven steps for balancing redox reactions in acidic conditions:

1. Balance any elements other than H and O as usual
  2. Assign oxidation numbers to all elements in the equation
  3. Identify the elements which are reduced and oxidized
  4. Modify the coefficients, if necessary, to balance the electron exchange
  5. Balance any missing O atoms by adding water molecules
  6. Balance any missing H atoms by adding  $\text{H}^+$  ions
  7. Verify that all atoms and the overall charges are balanced
- Balancing  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{Cl}_2(\text{g}) \longrightarrow \text{SO}_4^{2-}(\text{aq}) + \text{Cl}^-(\text{aq})$ :
    1.  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 2\text{Cl}^-(\text{aq})$
    2.  $\text{S}:+2 \quad \text{O}:-2 \quad \text{Cl}:0 \longrightarrow \text{S}:+6 \quad \text{O}:-2 \quad \text{Cl}:-1$
    3.  $\text{S}:+2 \rightarrow +6$  (lost  $4\text{e}^-$ ) and  $\text{Cl}:0 \rightarrow -1$  (gained  $1\text{e}^-$ )
    4.  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 4\text{Cl}_2(\text{g}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 8\text{Cl}^-(\text{aq})$
    5.  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 4\text{Cl}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 8\text{Cl}^-(\text{aq})$
    6.  $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 4\text{Cl}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 8\text{Cl}^-(\text{aq}) + 10\text{H}^+(\text{aq})$
  - Practice balancing  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \longrightarrow \text{Cr}^{3+}(\text{aq}) + \text{SnO}_2(\text{s})$   
 $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq}) + 14\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{SnO}_2(\text{s}) + 7\text{H}_2\text{O}(\text{l})$
  - To balance in basic conditions, add four steps:
    1. For each  $\text{H}^+(\text{aq})$  ion in the equation, add one  $\text{OH}^-$  ion to *both* sides
    2. Combine  $\text{H}^+$  and  $\text{OH}^-$  ions on the same side to form  $\text{H}_2\text{O}$
    3. Cancel out any  $\text{H}_2\text{O}$  that appears on both sides
    4. Verify that all atoms and total charges are balanced
  - Balance the previous two equations in base instead of in acid:
    - $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 4\text{Cl}_2(\text{g}) + 10\text{OH}^-(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + 8\text{Cl}^-(\text{aq}) + 5\text{H}_2\text{O}(\text{l})$
    - $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{Sn}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{SnO}_2(\text{s}) + 2\text{OH}^-(\text{aq})$

### 19.3 Redox Titrations

- Redox reactions can be used to titrate unknowns with redox reactivity
- The endpoint can be detected in three ways:
  - The titrant itself may be colored (purple  $\text{MnO}_4^-$  is an oxidizing agent that turns to colorless  $\text{Mn}^{2+}$  ions in redox reactions)
  - A secondary redox reaction acting as a color indicator (starch and  $\text{I}_3^-$  like in your lab)

- An electrochemical probe (just like a  $pH$  probe)
- Redox reactions will often have complex stoichiometry which must be taken into account when solving a titration problem
- A 15.00  $ml$  solution of methanol ( $CH_3COH$ ) required 7.35  $ml$  of 0.0887  $M$   $NaCr_2O_7^{2-}$  according to the reaction:  $3 CH_3OH(aq) + 2 Cr_2O_7^{2-}(aq) + 16 H^+(aq) \longrightarrow 3 CH_2O_2(aq) + 4 Cr^{3+}(aq) + 11 H_2O(l)$  (0.0652  $M$ )

## 19.4 Voltaic Cells

- Redox reactions can occur in solution with electrons directly transferring between partners
- If we physically separate the reactants, we can force the electrons to travel through a wire to complete the reaction – We can even force them to do work on their way!
- This is how electrochemical cells work
  - Voltaic (or galvanic) cells use spontaneous chemical reactions to produce a voltage and electron flow (batteries)
  - Electrolytic cells use an external voltage source to force electron flow and drive a non-spontaneous reaction (recharging spent batteries, electroplating, etc.)
  - The activity series given in Table 4.7 shows which metal/ion pairs will react spontaneously
  - $Zn(s)$  with  $Cu^{2+}(aq)$ , for example, will react spontaneously and thus can make a voltaic cell
  - $Ag(s)$  with  $Cu^{2+}(aq)$ , however, is non-spontaneous and will make an electrolytic cell
- Figure 19.4 shows a simple voltaic cell made from the reaction of  $Zn(s)$  with  $Cu^{2+}(aq)$
- The solid metal bars are called *electrodes*
  - If a solid reactant is not a part of the chemical reaction, one or both of the electrodes can be made of any conductive but chemically inert material, such as graphite or platinum
  - The  $Zn$  electrode is where oxidation occurs, and is called the anode
  - Sometimes the whole left half the cell is called the anode
  - The  $Cu$  electrode is where reduction occurs, and is called the cathode
  - Again, sometimes that whole half of the cell is called the cathode
  - *Anode* and *oxidation* both start with vowels, while *cathode* and *reduction* both start with consonants
  - The cathode is labeled “+”, and has a “t” in the middle of it which looks a bit like a “+”
  - Use whatever method you need to always know which is anode and which is cathode
- To complete the electrical circuit, a *salt bridge* is also required
  - As electrons flow, charges would quickly build up and stop the reaction

- The salt bridge prevents this buildup by providing ions to counteract the build-up of charge
- Anions from the bridge flow into the anode to balance out the new metal cations formed
- Cations from the bridge flow into the cathode to replace the lost cations
- Electricity flows through the salt bridge, completing the circuit – it is electricity in the form of moving ions, rather than moving electrons
- Reactions in electrochemical cells are often split up into two parts
  - Each half of the cell is called a “half-cell”
  - Each half-cell has its own electrochemical potential (voltage)
  - The total cell potential depends on the two half-cells it is constructed from
  - Half-cells are modular – you can swap out one to get a different voltage
- Cell notation is a simple map of the physical construction of a cell
  - Cell notation is much simpler and more useful than complete, balanced chemical reactions
  - Start with the anode, and work toward the cathode writing all the chemical species present
  - Single vertical lines indicate phase boundaries, while double vertical lines indicate a salt bridge
  - Our  $\text{Zn(s)}/\text{Cu}^{2+}(\text{aq})$  cell would be:  $\text{Zn(s)}|\text{Zn}^{2+}(1\text{ M})||\text{Cu}^{2+}(1\text{ M})|\text{Cu(s)}$
- Write the cell notation for a voltaic cell made from a reaction of  $\text{Ag}^+$  ions with  $\text{Cu(s)}$  under standard conditions
- Draw a diagram of the  $\text{Cu(s)}/\text{Ag}^+$  cell
  - Identify the cathode and anode
  - Show the flow of electrons and ions, assuming the salt-bridge contains  $\text{KNO}_3$

## 19.5 Cell Potential

- In voltaic cells, each half-cell has its own electrochemical potential
- This potential is measured relative to a standard hydrogen electrode (Figure 19.5)
- Table 19.2 shows the reduction potentials of many common half-reactions relative to the SHE
- Note that these are potentials under standard conditions ( $1.00\text{ M}$  and  $1.00\text{ atm}$ )
- These are also only reduction reactions - it is easiest to tabulate only reduction potentials
- To find the potential (voltage) of a complete voltaic cell, use  $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$
- We don't need to balance the reaction or consider the number of electrons exchanged
- Note that these are both *reduction* potentials, though oxidation occurs at the anode – That's why we *subtract* the anode's potential
- Find the standard cell potential for the  $\text{Zn(s)}|\text{Zn}^{2+}(1\text{ M})||\text{Cu}^{2+}(1\text{ M})|\text{Cu(s)}$  cell ( $1.10\text{ V}$ )



## 19.6 Free Energy and Cell Potential

- Positive  $E_{cell}$  and negative  $\Delta G$  both mean that a reaction is spontaneous under the current conditions
- $E$  and  $\Delta G$  are actually related by:  $\Delta G = -nFE$
- Here,  $F$  is the Faraday constant, which gives the charge of a mole of electrons:  $F = 96,485 \frac{C}{mol}$
- $n$  is the number of electrons which are transferred in the properly balanced chemical equation
- Note that the units for  $nFE$ ,  $CV$  are actually equal to a  $J$  (i.e.  $1 CV = 1 J$ ) so a  $J$  to  $kJ$  conversion is necessary
- This equation is often expressed under standard conditions as:  $\Delta G^\circ = -nFE^\circ$
- Using the  $E_{cell}^\circ$  found above for the  $Zn(s)/Cu^{2+}$  cell ( $1.10 V$ ), find  $\Delta G^\circ$   $\left(-212 \frac{kJ}{mol}\right)$
- Now, because  $\Delta G^\circ = -RT \ln K$ , we can now also relate  $E^\circ$  and  $K$ :  $E^\circ = \frac{RT}{nF} \ln K$
- Figure 19.8 summarizes the relationships between  $\Delta G^\circ$ ,  $E^\circ$ , and  $K$
- Using the  $E_{cell}^\circ$  found above for the  $Zn(s)/Cu^{2+}$  cell ( $1.10 V$ ), find  $K$   $(1.62 \times 10^{37})$

## 19.7 The Nernst Equation and Concentration Cells

- Most of the time, we want to construct electrochemical cells under non-standard conditions
- The relationships between  $E$  and  $\Delta G$  give us the foothold to find voltages of non-standard cells
- $\Delta G = \Delta G^\circ + RT \ln Q \rightarrow -nFE = -nFE^\circ + RT \ln Q \rightarrow E = E^\circ - \frac{RT}{nF} \ln Q$
- This is called the Nernst equation
- The Nernst equation can be applied to a half-cell or to a whole cell
- Calculate  $E$  for a  $Zn(s)/Cu^{2+}$  cell with  $[Zn^{2+}] = 0.00500 M$  and  $[Cu^{2+}] = 3.00 M$   $(1.18 V)$
- Concentration cells are made from two half-cells of the same type
  - The Nernst equation shows how different concentrations lead to different potentials
  - A concentration cell made from two Cu half-cells would have different  $[Cu^{2+}]$  in each cell
  - The balanced equation is:  $Cu(s) + Cu^{2+}(aq, cathode) \rightleftharpoons Cu(s) + Cu^{2+}(aq, anode)$
  - For such a cell,  $Q = \frac{[Cu^{2+}]_{anode}}{[Cu^{2+}]_{cathode}}$  and  $E^\circ = 0$
- Find  $E$  for a Cu concentration cell with  $[Cu^{2+}]_{anode} = 0.00200 M$  and  $[Cu^{2+}]_{cathode} = 5.50 M$   $(0.102 V)$

## 19.8 Voltaic Cell Applications

- A common electrolytic cell is the lead storage battery used in cars, boats, etc. (Figure 19.10)
  - Anode:  $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
  - Cathode:  $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$
  - Note that all redox active species in this cell are solid
  - This eliminates the need for a salt bridge – both electrodes can share the same solution
  - For higher voltage multiple pares of electrodes can share the same  $\text{H}_2\text{SO}_4$  solution
  - The concentrated  $\text{H}_2\text{SO}_4$  solution ensures that concentrations don't change much as the cell discharges, keeping the voltage relatively constant
- Dry Cells (common batteries – Figure 19.11)
  - Dry cells use mobile ions in a gel or paste rather than an aqueous solution
  - The salt bridge is usually a thin sheet of porous paper soaked in an electrolyte gel
  - The first dry cells used acidic paste, while later “alkaline” cells used basic paste
- Lithium Ion Polymer (LiPo) Cells
  - In LiPo cells, no metal is actually oxidized or reduced in the common way
  - The cathode and anode are open network polymers with permanent charges
  - In a charged LiPo cell,  $\text{Li}^+$  ions are forced into the positively charged anode polymer matrix
  - As it discharges, the  $\text{Li}^+$  ions migrate and intercalate themselves into the negatively charged cathode
  - This flow of charge induces a complementary flow of electrons from the anode to the cathode through the external circuit
- Fuel Cells (Figure 19.13)
  - A fuel cell is any cell where the reactants are replenished as the reaction proceeds
  - In practice, fuel cells usually use combustion reactions like  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
  - This reaction is technically a redox reaction and can be separated into half-reactions like we see in ordinary cells
  - Anode:  $\text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
  - Cathode:  $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O(l)}$
  - As  $\text{H}^+$  ions migrate from anode to cathode across the electrolyte, electrons flow the same way through the external circuit to maintain charge balance
  - $\text{H}_2$  fuel cells have a much higher theoretical limit of efficiency than  $\text{H}_2$  combustion engines
- Corrosion (rusting) is the unintended oxidation of metal

- Figure 19.14 shows how water can mediate corrosion
- Acidic conditions and dissolved salts can exacerbate the problem of corrosion
- Cathodic protection is a way of preventing corrosion (Figure 19.15)
  - \* A vital metal is placed in contact with a more reactive metal – the sacrificial anode
  - \* When corrosion occurs, the sacrificial anode is oxidized first, leaving the vital metal intact
  - \* Galvanized steel has been coated with a layer of Zn to offer cathodic protection

## 19.9 Electrolytic Cells and Applications of Electrolysis

- Figure 19.16 illustrates how electrolytic cells work like the voltaic cells in reverse
- We can reduce even very reactive metals (like Na and K) using electrolysis
- Aluminum was more expensive than gold until electrolysis was discovered because chemically reducing aluminum was impossible at the time
- Electrolysis Calculations
  - We can measure the flow of electrons using amperes  $\left(1\text{ A} = 1\frac{\text{C}}{\text{s}}\right)$
  - Recall that  $F$  relates  $C$  to  $\text{mol}$ :  $1\text{ mol } e^- = 96,485\text{ C}$
  - Find the mass of Al(s) produced if an electrolytic cell runs at  $0.575\text{ A}$  for  $40\text{ min}$
  - $40\text{ min} \rightarrow 2400\text{ s} \rightarrow 1380\text{ C} \rightarrow 0.0143\text{ mol } e^- \rightarrow 0.00477\text{ mol Al} \rightarrow 0.129\text{ g Al}$
  - A LiPo cell-phone battery has a full charge of  $3000\text{ mAh}$ . How many  $\text{g}$  of  $\text{Li}^+$  ions does the battery contain (assume complete migration of the ions) ( $0.78\text{ g}$ )
- Applications of Electrolysis
  - Figure 19.18 shows a simple electroplating process
  - Electroplating is used to make galvanized materials, white gold jewelry, and more
  - Figure 19.19 shows electrolytic refining of copper

## CHAPTER 20

## NUCLEAR CHEMISTRY

## 20.1 Natural Radioactivity

- Until now, we have talked exclusively about *chemical reactions*
- Table 20.1 shows how *nuclear reactions* differ from chemical ones
- Nuclei are sequestered from the outside world inside their hermitage with electron walls – environmental and chemical conditions don't seem to affect nuclear reactions in any way
- Nuclear chemistry realizes the alchemist's dream of nuclear transmutation, albeit within strict limits
- "Isotope" and "nuclide" are near-synonyms. Technically, isotope is the whole atom while nuclide omits the electrons
- Radioactive decay:
  - Isotopes which spontaneously undergo nuclear decay are called radioactive
  - Nuclear radiation is the energy and matter cast off in a nuclear reaction
  - Table 20.2 lists the different types of nuclear radiation
  - Each type of radiation has a symbol, like an atomic symbol, which is useful for balancing nuclear reactions
  - The reactant is called a parent nuclide, and the product is called a daughter nuclide
  - Balance the reactions by balancing the mass # and charge #
- Alpha decay:
  - Alpha decay ejects an alpha particle ( ${}^4_2\text{He}$  nuclide)
  - Balance the  $\alpha$  decay of  ${}^{238}_{92}\text{U}$ : 
$${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^4_2\alpha$$
- Beta decay:
  - Beta decay converts a neutron into a proton and an electron, and ejects the electron
  - Beta decay does *not* imply that a neutron is simply a proton plus an electron – talk to the physicists because I've never quite understood the standard model
  - Balance the  $\beta$  decay of  ${}^{210}_{81}\text{Tl}$ : 
$${}^{210}_{81}\text{Tl} \longrightarrow {}^{210}_{82}\text{Pb} + {}^0_{-1}\beta$$
- ${}^{234}_{90}\text{Th}$  decays into  ${}^{234}_{91}\text{Pa}$ . What decay process is involved? (beta decay)
- Gamma decay:

- A gamma ray is simply a very high energy photon
- Most nuclear reactions will release a gamma ray, but some reactions release nothing else
- Balance the gamma decay of  $^{119}_{50}\text{Sn}$ :  $^{119}_{50}\text{Sn} \longrightarrow ^{119}_{50}\text{Sn} + ^0_0\gamma$
- Positron Emission:
  - Positron emission converts a proton into a neutron and emits a positron
  - A positron is the anti-matter equivalent of an electron
  - Balance the positron emission decay of  $^{18}_9\text{F}$ :  $^{18}_9\text{F} \longrightarrow ^{18}_8\text{O} + ^0_{+1}\beta$
- Electron Capture:
  - Electron capture consumes an electron to convert a proton into a neutron
  - Balance the electron capture decay of  $^{11}_6\text{C}$ :  $^{11}_6\text{C} + ^0_{-1}\text{e} \longrightarrow ^{11}_5\text{B}$
- $^{40}_{19}\text{K}$  decays into  $^{40}_{18}\text{Ar}$  and a radiation particle. What decay process is involved? (positron emission)
- Radioactive Series:
  - Some nuclear reaction products are themselves also radioactive
  - A whole chain of nuclear reactions can take place, until a stable product is reached
  - Figure 20.3 shows the radioactive series for  $^{238}_{92}\text{U}$
- Measuring radioactivity:
  - Activity is defined as disintegrations per unit time
  - The becquerel is the SI unit:  $1\text{ Bq} = 1 \frac{d}{s}$
  - The curie is a much more useful unit:  $1\text{ Ci} = 3.7 \times 10^{10}\text{ Bq}$
  - A Geiger counter is a common instrument for measuring radioactivity
  - Radioisotopes can be used as *tracers* in medical imaging, and in determining reaction mechanisms

## 20.2 Nuclear Stability

- Why are some nuclei stable, while others are radioactive?
- The *strong* nuclear force holds protons and neutrons together in a nucleus despite the repulsions between protons
- Too many neutrons, though, can also destabilize the nucleus
- Table 20.3 shows how pairing neutrons and protons seems to lend stability
- Magic numbers:

- Ions tend to be stable when they have certain #s of electrons (2, 10, 18, 36, etc.)
  - Similarly, nuclides are stable with certain numbers of neutrons or protons
  - These numbers are called “magic numbers” (terrible name), and suggest energy level structures for nuclides like electronic energy levels for ions
- Belt of Stability
    - Figure 20.5 shows the belt of stability
    - Lead is the largest element with a stable isotope – all elements beyond lead show radioactivity for all their isotopes
    - Nuclides above the belt will likely decay through  $\beta$  decay
    - Nuclides below the belt will likely decay through  $\alpha$  decay
    - We can estimate if an isotope is above or below the belt by comparing its mass number to the atomic weight found on the periodic table (weights are based on stable isotopes)
    - Some models predict that there is an “island of stability” much further out – promising whole new stable elements to be discovered in particle accelerators

### 20.3 Half-Life

- Decay activity depend only the number of radioactive nuclides present  $A = kN$
- This is just a form of 1st-order kinetics:  $rate = k[A]$
- So, the half-life does not depend on the amount of the sample (Figure 20.6)
- Table 20.4 shows the half-life for some common radioactive isotopes
- One form of 1st-order integrated rate law:  $\ln \left( \frac{N_0}{N} \right) = \left( \frac{\ln 2}{T_{1/2}} \right) t$
- A 10.0 g sample of  $^{131}\text{I}$  ( $t_{1/2} = 8\text{ d}$ ) is left out for 2 weeks. How many g remain?  
( $10\text{ g} \cdot e^{-1.213} = 2.97\text{ g}$ )
- Rearrange the above equation to get:  $t = \ln \left( \frac{N_0}{N} \right) \left( \frac{t_{1/2}}{\ln 2} \right)$
- $^{90}\text{Sr}$  has  $t_{1/2} = 28.8\text{ y}$ . How long does it take for a  $^{90}\text{Sr}$  sample to decay to  $\frac{1}{3}$  of its initial amount?  
(45.6 y)

### 20.4 Radiometric Dating

- Because of the reliability of radioactive decay, we can use decay rates to accurately measure time

- We can measuring the ratio of parent and daughter nucleides in an old sample to determine how long ago that sample contained pure parent nucleide
- This process is called radiometric dating
- Comparing  $^{238}\text{U}$  and  $^{206}\text{Pb}$ , or  $^{40}\text{K}$  and  $^{40}\text{Ar}$  can give dates on the order of billions of years
- $^{238}\text{U}$  has  $t_{1/2} = 4.47 \times 10^9 \text{ y}$  and  $^{40}\text{K}$  has  $t_{1/2} = 1.250 \times 10^9 \text{ y}$
- Calculate the age of a rock which contains 5.5 g of  $^{206}\text{Pb}$  and 29.6 g of  $^{238}\text{U}$  ( $1.3 \times 10^8 \text{ y}$ )
- Carbon dating:
  - $^{14}\text{C}$  has  $t_{1/2} = 5730 \text{ y}$
  - $^{14}\text{C}$  is also useful because it is naturally generated in the upper atmosphere, at rates that keep the  $^{14}\text{C}$  abundance in the atmosphere constant
  - $^{14}\text{C}$  is then incorporated into living tissues of plants and animals at that same abundance
  - Once an organism dies, its  $^{14}\text{C}$  decays and we can use it to predict the date of death
  - The  $^{14}\text{C}$  decay product ( $^{14}\text{N}$ ) is ubiquitous, so we cannot use the parent/daughter ratio – instead we compare the sample activity to the activity of current living tissues
  - Living biomatter has an activity of  $15.3 \frac{d}{\text{min g}}$ , and an ancient wooden tool exhibits an activity of  $14.4 \frac{d}{\text{min g}}$ . How old is the wooden tool? (501 y)

## 20.5 Fission and Fusion

- In addition to natural decay processes, entirely different nuclear reactions can be induced and controlled to produce energy
- These reactions often involve isotopes produced in other nuclear reactions or in particle accelerators
- The first of these reactions involved bombarding stable nuclei with alpha particles, but it was later discovered that neutrons can induce reactions as well
- Nuclear Fission
  - Fission is when a large nuclide breaks apart into two smaller daughter nuclides (not simply an  $\alpha$  particle)
  - Figure 20.9 shows the most common nuclear fission reaction:
 
$$^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3 {}^1_0\text{n}$$
  - This reaction requires a neutron to initiate, and that neutron must have low kinetic energy
  - Because these constraints, this reaction doesn't occur naturally except under very ideal conditions

- Each fission produces three new neutrons which *can* trigger three new fission reactions
- This type of reaction can rapidly grow out of control, and is called a *chain reaction*
- The reaction of  $^{235}\text{U}$  or  $^{239}\text{Pu}$  is allowed to escalate exponentially in nuclear weapons, resulting in an enormous amount of energy released in a very short time
- Detonation is triggered by bringing two sub-critical masses of  $^{235}\text{U}$  or  $^{239}\text{Pu}$  together to make a critical mass
- For nuclear power generation, the reaction is carefully controlled to run at a steady rate
- Figure 20.11 shows a simple diagram of a nuclear power plant
- Water around the fuel rods moderates the kinetic energy of the neutrons and absorbs energy to be converted to electricity in a standard steam generator
- Carbon or zirconium control rods will absorb neutrons, removing them from the reaction and slowing the reaction down
- A “nuclear melt-down” is when the fuel rods literally melt, which circumvents the ability of the control rods to stop a chain reaction
- Fusion reactions can have different products. Finish balancing the following reaction:  

$$^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{137}_{52}\text{Te} + ? + 2 {}^1_0\text{n} \quad \left( {}^{97}_{40}\text{Zr} \right)$$

#### ○ Nuclear Fusion

- Some reactions will combine nuclides to create bigger ones
- These reactions are called *fusion* reactions
- Fusion reactions power the sun itself
  - \*  ${}^1_1\text{H} + {}^1_1\text{H} \longrightarrow {}^2_1\text{H} + {}^0_{+1}\beta$
  - \*  ${}^1_1\text{H} + {}^2_1\text{H} \longrightarrow {}^3_2\text{He} + {}^0_0\gamma$
  - \*  ${}^3_2\text{He} + {}^3_2\text{He} \longrightarrow {}^4_2\text{He} + 2 {}^1_1\text{H}$
  - \*  ${}^2_1\text{H}$  is called deuterium, and its nucleus is called a deuteron
  - \*  ${}^3_1\text{H}$  is called tritium, and its nucleus is called a triton
  - \* Different elements are generated depending on the age and size of the star, with the largest elements only being generated in cataclysmic supernova events
- These reactions require very high temperatures and pressures
- Nuclear fusion power plants are only in early research stages
- Nuclear fusion weapons, called thermonuclear weapons or “H-bombs”, require a fission bomb to first generate the energy to drive the fusion reaction

## 20.6 Energetics of Nuclear Reactions

- In exothermic chemical reactions, the energy given off comes from the formation of stable chemical bonds
- In nuclear reactions, the energy given off comes from the formation of stable nuclei



- The energy lost is so great, it manifests as a lost mass according to  $E = mc^2$
- Consider the reaction:  ${}_{92}^{238}\text{U} \longrightarrow {}_{90}^{234}\text{Th} + {}_2^4\text{He}$

Isotope	Mass ( $u$ ) or $\left(\frac{g}{mol}\right)$
${}_{92}^{238}\text{U}$	238.00033
${}_{90}^{234}\text{Th}$	233.99423
${}_2^4\text{He}$	4.00151

- Adding up the products gives a mass  $0.00459 \frac{g}{mol}$  less than the mass of  ${}_{92}^{238}\text{U}$
- This change in mass can be used to find the energy released:  $\Delta E = \delta mc^2$  (convert to  $kg$ )
- So, the reaction released  $4.125 \times 10^{11} \frac{J}{mol}$ , or  $4.125 \times 10^8 \frac{kJ}{mol}$
- Note that this is 100,000 times more energy than any chemical reactions
- This is an  $\alpha$ -decay reaction, fission and fusion reactions are still more energetic!
- Nuclear reactions are often described as converting mass into energy – this is a bit misleading – rather, energy has its own mass, and enough energy is lost that we can observe it when we measure mass

## 20.7 Nuclear Binding Energy

- We can see a similar mass/energy relationship in any nucleus
- Consider a helium nucleus:

Particle	Mass ( $u$ ) or $\left(\frac{g}{mol}\right)$
proton ${}_1^1\text{p}$	1.00728
neutron ${}_0^1\text{n}$	1.00866
${}_2^4\text{He}$	4.00151

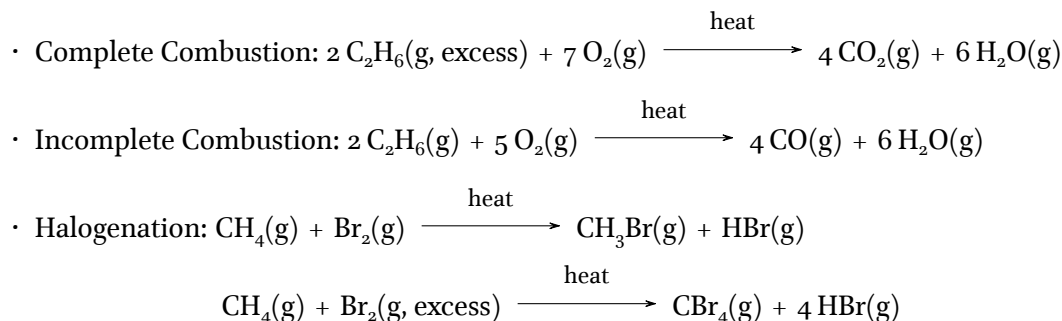
- The mass of  ${}_2^4\text{He}$  is less than the sum of its parts by  $0.03037 \frac{g}{mol}$ !
- This discrepancy is called the mass defect
- The mass defect is due to binding energy holding all nucleons together in a stable nucleus
- The binding energy per nucleon increases sharply through the small elements until it reaches a maximum at Fe, and begins to slowly drop
- This means that it is energetically favorable to combine small elements up until Fe, and it is energetically favorable to break down large elements down until Fe

## CHAPTER 21

## ORGANIC CHEMISTRY

**21.1 Introduction to Hydrocarbons**

- Organic chemistry is the study of compounds which contain carbon
- Carbon's small size, tendency to form 4 bonds, and ability to bond into long chains makes it possible to form many complex organic compounds
- The simplest organic molecules are hydrocarbons, composed of only hydrogen and carbon
- Because structural information is relevant to organic molecules, a chemical formula is usually not sufficient
- Table 21.1 shows different ways to represent organic molecules
- Alkanes, or saturated hydrocarbons, have only single bonds and a chemical formula of  $C_nH_{2n+2}$
- Alkane carbons are  $sp^3$ -hybridized, with tetrahedral geometry and  $109.5^\circ$  bond angles
- Alkanes are named according to their own rules
  1. The name is based on the longest continuous chain of carbons
    - These names use uncommon prefixes given in Table 21.1
    - These are the parent names, which we will add to in the other rules
  2. Branches are named according to their length as shows in Table 21.3
  3. The position of a branch is counted from the end, such that the first branch point has the lowest possible number
  4. For multiple substituents, use the prefixes di-, tri-, tetra-, etc.
  5. An apparent branch on the first or final carbon is not actually a branch, but a continuation of the main longest chain
  6. Numbers *may* be omitted when the branch position is unambiguous, but I recommend including them anyway
  7. Different substituents are listed in alphabetical order (excluding prefixes)
  8. Halogen substituents are called fluoro-, chloro-, bromo-, and iodo-
- Practice naming 4-ethyl-2-methylhexane
- Draw 2,2-dichloro-4,5-methylhexane
- All alkanes undergo similar reactions regardless of their length:



## 21.2 Unsaturated Hydrocarbons

- Alkenes are hydrocarbons with one or more C-C double bond
- Alkenes will have fewer Hs than alkanes, so they are called *unsaturated*
- Alkene carbons are  $sp^2$ -hybridized, with trigonal planar geometry and  $120^\circ$  bond angles
- Alkenes are named like alkanes, ending in -ene
- The double-bond position is numbered according to the carbon closest to the start of the chain
- Alkenes can undergo addition reactions across their double-bond:
  - $\text{CH}_2=\text{CH}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow \text{CH}_2\text{Br}-\text{CH}_2\text{Br}(\text{g})$
  - $\text{CH}_2=\text{CH}_2(\text{g}) + \text{HBr}(\text{g}) \longrightarrow \text{CH}_3-\text{CH}_2\text{Br}(\text{g})$
  - $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow{\text{Acid Catalyst}} \text{CH}_3-\text{CH}_2\text{OH}(\text{g})$
  - $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{Nickel Catalyst}} \text{CH}_3-\text{CH}_3(\text{g})$
- Alkynes are hydrocarbons with one or more C-C triple bond
- Alkynes are even further unsaturated
- Alkyne carbons are  $sp$ -hybridized, with linear geometry and  $180^\circ$  bond angles
- Alkynes are named just like alkenes, but ending in -yne
- Alkynes can undergo double addition reactions across their triple-bond:
  - $\text{CH}\equiv\text{CH}(\text{g}) + 2 \text{Br}_2(\text{g}) \longrightarrow \text{CHBr}_2-\text{CHBr}_2(\text{g})$
  - $\text{CH}\equiv\text{CH}(\text{g}) + 2 \text{H}_2(\text{g}) \xrightarrow{\text{Catalyst}} \text{CH}_3-\text{CH}_3(\text{g})$
- Aromatic hydrocarbons contain multiple delocalized double bonds
- Alternating single and double bonds allows the electrons to be shared across  $\pi$  bonds

- Benzene and its derivatives are examples of aromatic hydrocarbons
- Aromatic double-bonds do not undergo addition reactions like in alkenes, but can be halogenated like alkanes
- Figure 21.9 shows two different ways to name substituted benzenes

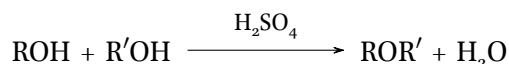
### 21.3 Introduction to Isomerism

- Atoms can be arranged in different ways to make different molecules with the same chemical formula
- These are called *isomers*, and they have different chemical and physical properties
- Structural isomers have different bonds between different atoms
  - Butane and 2-methylpropane are structural isomers
  - The larger a chemical formula is, the more structural isomers it will have
  - Figure 21.12 shows how butane can rotate around its bond to make different conformers, but they are still the same isomer
- *Cis/trans* isomers are arranged differently around a double bond
  - Figure 21.13 shows why  $\pi$  bonds cannot rotate
  - This creates the possibility of *cis/trans* isomers
  - Figure 21.14 shows *cis/trans* isomers of 2-butene
  - *cis*- isomers put the substituents on the same side of the double bond
  - *trans*- isomers put the substituents on opposite sides of the double bond
  - *Cis/trans* isomers can't exist if either side of the double bond has two identical groups
- Optical isomers are not superimposable on their mirror image
  - Molecules which have optical isomers are called *chiral*
  - Figure 21.15 shows an analogy between optical isomers and right/left handed-ness
  - A left and a right glove have the same parts in the same places (thumb next to the pointer, etc.), but they only fit on the correct hand
  - Molecules are chiral if there is one tetrahedral center with four unique groups
  - $\text{CHClBrF}$  is chiral, and there are two non-superimposable versions of it
  - 3-chloro-3-methylhexane is also chiral, with the 3rd carbon acting as a chiral center
  - Macrostructures can also be chiral, like protein helixes
  - Levomethamphetamine is a decongestant, and rectomethamphetamine is a controlled drug

## 21.4 Organic Halides, Alcohols, Ethers, and Amines

- Organic molecules will often contain *heteroatoms* – atoms other than C and H
- Heteroatoms make up *functional groups* – moieties of atoms which control the reactive properties of atoms
- Organic molecules can be viewed as modular, like Legos, with different functional groups attaching at different points and performing different functions
- Alkyl groups are often notated as R (R', R'', etc. for different alkyl groups)
- Organic halides, or alkyl halides were already covered in the alkanes section
- Alcohols contain an OH functional group

- Alcohols are named with an -ol ending to the parent name
- The alcohol is numbered according to the carbon which is bonded to the OH group
- Alcohols can react with reactive metals like Na and K in the same way that water does
- Alcohols can react with each other to produce ethers in dehydration reactions



- Ethers contain two alkyl groups linked through an O
  - Ethers are named by the longer alkyl chain, with the other alkyl chain making a substituent with an -oxy ending (methoxyethane)
  - An older convention is to just name the two alkyl groups and end with ether (ethyl methyl ether)
  - Ethers are structural isomers of alcohols with the general formula of  $\text{C}_n\text{H}_{2n+2}\text{O}$
- Amines contain a nitrogen bound to one or more alkyl groups
  - Amines are named by listing the alkyl groups and ending with amine
  - Figure 21.18 shows primary, secondary, and tertiary amines

## 21.5 Aldehydes, Ketones, Carboxylic Acids, Esters, and Amides

- Aldehydes and ketones both contain a carbonyl group ( $\text{C}=\text{O}$ )
  - Aldehydes have the  $\text{C}=\text{O}$  on a terminal carbon, while ketones have it in the body of the chain
  - Aldehydes are named with an -al ending on the parent name
  - Ketones end in -one, with a number indicating the carbonyl position

- Aldehydes and ketones result from the oxidation of alcohols (see Figure 21.19)
- Carboxylic acids contain the  $\text{CO}_2\text{H}$  group on a terminal carbon
  - A carboxylic acid looks like an aldehyde and an alcohol together, but its reactive properties are *very* different from either of those
  - The OH group on a carboxylic acid is acidic
  - Carboxylic acids are named with an -oic acid ending
  - Carboxylic acids are formed by further oxidizing aldehydes
- Esters contain the  $\text{RCOOR}'$  functional group
  - Esters are formed by combining a carboxylic acid with an alcohol in a condensation reaction
 
$$\text{RCOOH} + \text{R}'\text{OH} \longrightarrow \text{RCOOR}' + \text{H}_2\text{O}$$
  - Esters are named by the carboxylic acid name with an -oate ending, and the alcohol's parent alkyl name (methylpropanoate)
  - Esters will often have pleasant aromas (think banana laffy-taffys)
  - Esters linkages can also be used to form polymers, covered in the next section
- Amides are like esters, but with an amine in place of the alcohol ( $\text{RCONR}'\text{R}''$ )
  - Amides are also formed by condensation reactions
 
$$\text{RCOOH} + \text{NHR}'\text{R}'' \longrightarrow \text{RCONR}'\text{R}'' + \text{H}_2\text{O}$$
  - Amides are named like esters, but with the -amide ending (methylethylpropanamide)
  - Amide bonds can also be used to form polymers, like proteins made from amino acids
- Table 21.7 summarizes how to recognize and name these classes of organic compounds

## 21.6 Polymers

- Polymers are very large molecules made from repeating smaller units over and over again
- The smaller building blocks are called monomers
- Figure 21.21 shows formation of a condensation polymer
  - By using dicarboxylic acids and dialcohols, ester formation can continue in both directions
  - Polymers formed this way are called polyesters
- Figure 21.22 shows formation of an addition polymer
  - Alkene monomers are reacted to form one enormous alkane polymer
  - We won't cover the reaction mechanism in this class, but the electrons in the  $\pi$  bonds are used to form new covalent bonds between monomers

- Polymers have very different properties than their monomers, but the monomers *do* affect the polymer properties
- The discovery of polymer chemistry started a second mini industrial revolution based on plastics

## CHAPTER 22

## COORDINATION CHEMISTRY

**22.1 Review of Using Oxidation States in Naming Compounds**

- For metal cations which can take more than one charge (transition metals and a few main group metals), the charge must be indicated in the compound name with a Roman numeral
- For example,  $\text{Cu}_2\text{SO}_4$  is copper(I)sulfate and  $\text{CuSO}_4$  is copper(II)sulfate

**22.2 The Properties of Transition Metals**

- Chemical properties of transition metals depend on the electronic configuration in the d-subshell
- Table 22.1 gives the configurations for three rows of transition metals – note exceptions like Cr, Cu, Pd, etc.
- Ions of transition metals will usually lose *s* electrons before *d* electrons
- Table 22.2 shows the possible oxidation states for one row of transition metals
- Periodic trends in the transition metals follow general trends, but the changes are smaller than expected
- Figure 22.2 shows atomic radius in the transition metals – note the lanthanoid contraction
- Figure 22.3 shows ionization energies – Note a few deviations from the trend like Ag and Cr
- Figure 22.4 shows electronegativities – There are quite a few exceptions here because electronegativity depends complexly on the other properties

**22.3 Introduction to Coordination Compounds**

- Complexes are composed of a metal cation (Lewis acid), and one or more ligands (Lewis bases)
  - The resulting Lewis adduct is called a coordination compound or a complex ion depending on whether it has an overall charge
  - The primary coordination sphere consists of ligands covalently bonded to the cation
  - The coordination # is the number of ligand atoms bonded to the cation (not necessarily the same as the # of ligands)
  - Other ions or molecules can bind to the complex through intermolecular forces – called the secondary coordination sphere



- Figure 22.5 shows the coordination spheres of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- Bonds in coordination complexes are coordinate covalent bonds (dative bonds)
  - The atoms which donate the electron pair are called *donor atoms*
  - Figure 22.6 shows how ligands donate electron pairs to form dative bonds
  - Some ligands can bond through more than one atom – called polydentate ligands
  - Complexes with polydentate ligands are particularly stable, known as the chelate effect
  - Table 22.3 shows a list of common ligands and how they form bonds
  - Figure 22.7 shows hexadentate EDTA bonding with a cation – EDTA is sometimes used to neutralize toxic metals
- Coordination compounds bond in similar geometries to those predicted in VSEPR theory (Table 22.4)

## 22.4 Nomenclature of Coordination Compounds

- The overall charge of a coordination compound or complex ion is the sum cation and ligand charges
- Naming coordination compounds is complex and not important enough to warrant attention during our unplanned distance learning
- You'll learn this nomenclature again in inorganic chemistry

## 22.5 Isomerism in Coordination Compounds

- Coordination compounds can exhibit both structural and stereo isomerism
- Structural isomers are further divided coordination and linkage isomers
  - Coordination isomers switch ligands between the primary and secondary coordination spheres
  - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$  are coordination isomers (The textbook has a small error here)
  - Linkage isomers connect ligands through different donor atoms
  - Thiocyanate can form bonds either through the S or the N
  - Thiocyanate ligands will be written SCN or NCS depending on the linkage
  - $[\text{Pd}(\text{NH}_3)_2\text{Cl}(\text{SCN})]$  and  $[\text{Pd}(\text{NH}_3)_2\text{Cl}(\text{NCS})]$  are linkage isomers
- Stereoisomers are also divided into cis/trans and optical isomers
  - Cis/trans in this case is different than what we've seen before – there are no double bonds here

- Figure 22.10 shows cisplatin and transplatin coordination compounds
- Figure 22.11 shows how some bidentate ligands can make the complex chiral, leading to optical isomerism

## 22.6 Crystal Field Theory

- The donated electrons from coordination bonds will affect the energies of the  $d$ -orbitals in the cation because of their mutual repulsion
- Crystal field theory predicts electronic, magnetic, and spectroscopic properties of coordination compounds based on these interactions
- Figure 22.12 shows how ligands and  $d$ -orbitals are oriented in an octahedral complex
  - The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals point directly to a ligand, raising their energies
  - The  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals point between ligands, minimizing the repulsion from ligand electrons
  - Figure 22.13 shows how the energies for all  $d$  orbitals split when a complex forms
  - The energy splitting is on the order of the energy cost for pairing electrons in the same orbital
  - Electrons will fill the orbitals differently depending on how wide the splitting is (Figure 22.14)
    - \* For small splittings, electrons will spread out, making a high-spin complex
    - \* For large splittings, electrons will pair up, making a low-spin complex
  - Figure 22.15 shows all possible electron configurations for octahedral complexes
- Figure 22.16 shows how ligands and  $d$ -orbitals are oriented in a tetrahedral complex
  - The  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals point mostly away from the ligands, minimizing the repulsion from ligand electrons
  - The  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals point more toward the ligands, raising their energies
  - Figure 22.17 shows the splitting of  $d$  orbitals when a complex forms
  - High-spin and low-spin complexes exist for tetrahedral geometries as well
- Figure 22.18 shows how ligands and  $d$ -orbitals are oriented in a square planar complex
  - The splitting in this case is more complicated, as shown in Figure 22.19

## 22.7 The Spectrochemical Series, Color, and Magnetism

- Different ligands will lead to different magnitude crystal field splittings
- Ligands which cause large splittings and form low-spin complexes are called strong-field ligands

- Ligands which cause small splittings and form high-spin complexes are called weak-field ligands
- The range of ligands from weak-field to strong-field is called the spectrochemical series
- $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{N}_3^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{Cr}_2\text{O}_4^{2-} < \text{py} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- = \text{CO}$
- The magnitude of the crystal field splitting determines the color of a complex
  - Most electronic transitions are in the ultraviolet, but all  $d - d$  transitions are relatively low in energy
  - When the energy of transition falls in the visible light range, the compound will be colored
  - The absorbed wavelength can be found by  $\Delta E = \frac{hc}{\lambda}$
  - The observed color of the complex will be complementary to the color absorbed (See Figure 22.20)
- The magnitude of the crystal field splitting also determines magnetic properties
  - Recall that compounds with all paired electrons are diamagnetic, and compounds with at least one unpaired electron is paramagnetic
  - Whether electrons pair or not depends on whether the complex is high-spin or low-spin
  - Consider  $\text{ZnCl}_4$ , and octahedral complex
    - \* The  $\text{Zn}^{4+}$  ion has 6  $d$  electrons
    - \* If  $\text{ZnCl}_4$  is low-spin, all electrons will be paired. If it is high-spin, 4 electrons will be unpaired (This compound is actually high-spin and paramagnetic)