CHEM 1220 Lecture Notes
OpenStax Chemistry 2e

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November 19, 2025

COURSE ADMINISTRATIVE DETAILS

- My office hours

- Intro to my research

- Introductory Quiz

- Grading details
  - Exams - 40, Final - 15, Online Homework - 15, Book Homework - 15, Quizzes - 15
  - Online homework
  - Frequent quizzes

- Importance of reading and learning on your own

- Learning resources
  - My Office Hours
  - Tutoring services - https://www.suu.edu/academicsuccess/tutoring/

- Show how to access Canvas
  - Calendar, Grades, Modules, etc.
  - Quizzes
  - Textbook

- Introduction to chemistry
  - Ruby fluorescence
  - Levomethamphetamine
  - Rubber band elasticity
  - Structure of the periodic table
  - Salt on ice and purifying hydrogen peroxide

CHAPTER 0

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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 in chemistry

  · Converting from measurements to moles and back

  · Stoichiometry and predicting amounts

  · Limiting reactants

- Enthalpy of reaction and heat equations

- Lewis structures

CHEM 1210 Review Quiz

CHAPTER 10
_____

LIQUIDS AND SOLIDS

10.1   Intermolecular Forces

○ Many physical properties of solids, liquids, and gases can be explained by the strength of attractive forces between particles (Figure 10.5)

○ Phase changes happen due to the interplay between kinetic energy and intermolecular forces (Figure 10.2)

○ Pressure can also play a role in phase changes, as discussed later

○ These *intermolecular forces* come in different varieties

  · Dispersion Forces Non-polar molecules, impacted by polarizability, molecular weight, and surface area

    * Dominant in non-polar molecules
    * Created by induced dipoles (Figure 10.6)
    * Impacted by polarizability (Table 10.1)
    * Impacted by molecular weight (hydrocarbons from methane to wax)
    * Impacted by molecule shape (Figure 10.7 compares the boiling points of pentane isomers)
  · Dipole-Dipole Forces

    * Dominant in polar molecules
    * Results from attraction between permanent dipoles (Figure 10.9)
  · Hydrogen Bonding

    * Dominant only in molecules capable of hydrogen bonding
    * Must contain a hydrogen-donor atom (H attached to N, O, or F)
    * Must contain a hydrogen-acceptor atom (lone pair of electrons attached to N, O, or F)
    * Hydrogen bonds are more than just particularly strong dipole-dipole forces. They have strong directionality according to VSEPR
    * Figures 10.10, 10.14, and other figures on the Internet show water, DNA, and proteins all organized by hydrogen bonds
    * Figures 10.11 and 10.12 illustrate how much hydrogen bonds exceed dipole-dipole forces in strength

10.2   Properties of Liquids

○ Viscosity is a fluid's resistance to flow

- We intuitively know that both water and honey flow...but at very different rates
- Viscosity is proportional to the strength of intermolecular forces (high IF = high viscosity)
- As temperature increases, kinetic energy is able to overcome intermolecular forces and viscosity decreases
- Table 10.2 gives the viscosities of some common substances (note the unusual units!)

○ Surface tension is a force which minimizes a fluid's surface area

- Cohesive vs. adhesive forces
- Bulk molecules have lower energy than surface molecules due to being *surrounded* by cohesive forces (Figure 10.16)
- Figure 10.17 illustrates a waterbug supporting itself on water surface tension
- Surface tension is often in conflict with gravity and other forces, making most liquids rounded but not perfect spheres
- Surface tension is proportional to intermolecular forces (Table 10.3)
- Surface tension can be strongly affected by addition of certain solutes, called surfactants

○ Capillary action is a force between a fluid and narrow channels or capillaries of solid materials

- Due to adhesive forces with the solid, liquids will be drawn up (or, less often, pushed down) a capillary
- Figure 10.19 shows how paper towels are made to maximize capillary action, so they soak up water-based spills
- The top of the liquid (called the meniscus) will curve differently depending on the reletive strength of cohesive and adhesive forces (Figure 10.18)
- Figure 10.20 shows capillary action in a variety of situations, including capillary repulsion
- Remember that when measuring volumes, convention is to read the *bottom* of the meniscus regardless of how it curves
- Don't worry about the formula given here

Quiz 10.1 - Intermolecular Forces and Liquid Properties

Homework 10.1

○ 10.11: Predicting trends in boiling points

○ 10.21: Identifying intermolecular forces

○ 10.25: Affect of temperature on viscosity

10.3   Phase Transitions

○ Vaporization and condensation are the transitions between liquid and gas phases

- The enthalpy of vaporization (ΔH_{vap}) is the energy required to transition from liquid to gas phase
- Enthalpy of condensation is the opposite $\Delta H_{con} = -\Delta H_{vap}$
- In a closed volume, these processes will reach a *dynamic equilibrium*
- The partial pressure of the liquid at this equilibrium state is called its *vapor pressure* (Figure 10.22)
- Higher intermolecular forces lead to lower vapor pressures
- Higher temperatures increase the vapor pressure due to increased kinetic energy (Figure 10.23)

○ Boiling points

- Figure 10.24 shows vapor pressure curves and the normal boiling points of several liquids
- Boiling points generally depend on the pressure (pressure cookers, boiling water to freezing, etc.)
- The Clausius-Clapeyron equation defines these curves (Note the rearrangments I've made)

$$P = Ae^{-\Delta H vap/RT} \qquad \ln P = -\frac{\Delta H_{vap}}{RT} + \ln A \qquad \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

○ Fusion (melting), freezing, sublimation, and deposition all have their enthalpies and transition temperatures

○ These enthalpies are state functions, such that $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$ (Figure 10.28)

○ Heating and Cooling curves

- When heat is added to a system, it will either cause a phase change, or a change in temperature
- For phase changes, $q = n\Delta H_{change}$
- For temperature changes, $q = mc\Delta T$, where c is the specific heat for that substance and phase
- Sometimes ΔH_{change} is given as a -per gram value, and sometimes c is given as a -per mole value, but usually not :(
- Figure 10.29 shows a typical heating curve (Work example 10.10 in the text)

Quiz 10.2 - Heating Curves

Homework 10.2

○ 10.31: Temperature during a phase transition

○ 10.39: Definition of normal boiling point

○ 10.51: Heating curve problem

10.4   Phase Diagrams

○ The stable phase at different temperatures and pressures is best illustrated with a phase diagram (Figures 10.30, 10.31)

○ We can tell at a glance what transitions might occur as we increase or decrease either the temperature or pressure

○ Note that at some pressures, sublimation may occur instead of fusion

○ The triple point is a unique point where liquid, solid, and gas can all exist at equilibrium (contrast with a glass of icy water on a humid day)

○ The critical point is where the distinction between liquid and solid phases disappears

○ Figure 10.34 shows the phase diagram of CO_2

○ Supercritical fluids exhibit some interesting properties, and are often great solvents (Nile Blue Youtube video)

○ Critical points vary widely depending on the intermolecular forces, and other factors (Table in text)

Quiz 10.3 - Phase Diagrams

Homework 10.3

○ 10.55: Trajectories on a phase diagram

○ 10.57: Determining state on a phase diagram

○ 10.63: Identifying phases on a blank phase diagram

10.5   The Solid State of Matter

○ Solids can be divided into *crystalline* and *amorphous* based on their structure at atomic scales

○ Figure 10.37 shows the difference generally, Figure 10.38 shows crystalline and amorphous SiO_2

○ Amorphous solids will not exhibit a sharp fusion transition temperature, but will instead grow soft and maleable over a temperature range

○ Crystalline solids are diverse but always show long-range repeating order in their structure

· Ionic solids (Figure 10.39) have high melting points, cleave along planes, and conduct electricity only in the liquid phase

· Metallic solids (Figure 10.40) have mostly high melting points, are maleable and ductile, and conduct electricty and heat well

- Covalent network solids (Figure 10.41) have very high melting points and are electrical insulators
- Molecular solids (Figure 10.42) Have low to very low melting points and are electrical insulators
- Crystalline solid properties are summarized in Table 10.4

○ Even crystalline solids do not have perfect structure. Various types of defects are illustrated in Figure 10.45

Quiz 10.4 - Classifying Solids

Homework 10.4

○ 10.69: Classify solids by formulas

○ 10.71: Classify solids by properties

10.6 Lattice Structures in Crystalline Solids

○ The structure of a crystalline solid is represented by a *unit cell*, the smallest repeatable unit of the structure

○ Sometimes this microscopic structure is evidently manifested on macroscopic scales, but sometimes it isn't

○ Unit cells are defined by lattice points that often lie at the center of certain atoms, and the cell edges often cut atoms in half, quarter, etc.

○ Unit cells of metals

- For metals, we should keep track of the quantity of atoms in a unit cell, the coordination number, and the relationship between the atomic radius and unit cell edge length
- Simple cubic (Figure 10.49) 1 atom, Coordination=6, $l = 2r$
- Body-centered cubic (Figure 10.51) 2 atoms, Coordination=8, $l = \frac{4}{\sqrt{3}}r$
- Face-centered cubic (Figure 10.52) 4 atoms, Coordination=12, $l = \sqrt{8}r$
- Figure 10.54 shows hexagonal closest packed and cubic closest packed structures
- Find the radius of a gold atom, which has fcc structure and a density of $19.283 g/cm^3$ $(136pm)$
- Find the density of polonium, which has sc structure and an atomic radius of $140pm$ $(9.20 g/cm^3)$
- Figure 10.56 shows many non-cubic structures which are common as well

○ Unit cells of ionic compounds

- Anions are generally larger than cations, so ionic lattice points are generally the centers of anions
- Cations occupy holes in the anionic lattice (Figures 10.57 and 10.58)

- Unit cells of ionic structures share names with the metallic cells but look different because of the cations
- Simple cubic (Figure 10.59)
- Face-centered cubic (rock salt structure) (Figure 10.60)
- Zinc blende (Figure 10.61)
- Find the ionic bond length for NaCl which has rock salt structure and denisty of $2.17^g/cm^3$ ($l = 564pm$)

○ Crystal structure is determined through X-ray crystallography

- X-rays reflected off a crystal surface can combine destructively or constructively to produce an interference pattern (Figure 10.63)
- The X-rays will take different pathlengths depending on the angle of the X-ray beam and the crystal lattice constant (Figure 1.64)
- An experimental setup and actual diffractogram are shown in Figures 10.65 and 10.66
- We have a powerful X-ray instrument here at SUU

Quiz 10.5 - Unit Cells

Homework 10.5

○ **10.77:** Coordination number

○ **10.81:** Density from lattice constant

○ **10.85:** Packing efficiency and density

SOLUTIONS AND COLLOIDS

11.1 The Dissolution Process

- Some vocabulary: *Solution*, *Solvent*, *Solute*, and *solvation*

- Table 11.1 shows many different types of solutions, with different phases of solvent and solute

- Molecular compounds dissolve to form one solute:

  $C_6H_{12}O_6(s) \longrightarrow C_6H_{12}O_6(aq)$

- Ionic compounds will dissolve into individual ions:

  $Na_2SO_3(s) \longrightarrow Na_2SO_3(aq) \longrightarrow 2\,Na^+(aq) + SO_3^{2-}(aq)$

- Dissolving soluble compounds is a thermodynamically *spontaneous* process

  - Spontaneity is covered in more detail in chapter 16
  - Solvation mixes solvent and solute, increasing the system *entropy* (Figure 11.3)
  - Solvation can be either *exothermic* (favors spontaneity) or *endothermic* (hampers spontaneity) depending on the strength of solvent-solvent, solute-solute, and solvent-solute intermolecular forces (Figure 11.4)
  - Demonstration, dissolving NaOH(s) and $NH_4NO_3(s)$ in water (Don't overdo the NaOH!)
  - When solvation has $\Delta H \approx 0$, the result is an *ideal solution*, whose properties best match simple laws

11.2 Electrolytes

- Electrolytes will yield ions when dissolved in water, yielding a solution which conducts electricity (Figure 11.6)

  Non-electrolytes: Do not yield ions at all when dissolved (Most molecular compounds)

  Strong electrolytes: Produce a large (stoichiometric) amount of ions when dissolved (Soluble ionic compounds and *strong* acids/bases)

  Weak electrolytes: Produce a smaller amount of ions when dissolved (*weak* acids/bases)

- Ionic electrolytes produce ions by directly *dissociating* into their cations and anions (Figure 11.7)

- Molecular electrolytes produce ions by reacting with the solvent or other molecules

  $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

11.3   Solubilty

○ Table 4.1 gave rules to predict if an ionic compound is soluble or insoluble, but in reality solubilities lie on a spectrum

○ In Chapter 15, we will explore solubility with mathematic rigor. For now, we will focus on trends and factors affecting solubility

○ Solubility is a type of reaction governed by *equilibrium*

Unsaturated solutions have not yet reached their limit of how much solute they can dissolve

Saturated solutions have met their solubility limit and are in equilibrium. You can recognize a saturated solution by the presence of undissolved solute in contact with the solution

Supersaturated solutions have exceeded their solubility limit. This situation is only *metastable* and usually contrived by quick changes in temperature or volume ("Jeremy Krug" Youtube video of supersaturated $NaCH_3CO_2$)

○ Solutions of gases in liquids

· Gas-in-liquid solvation is always exothermic and solubility depends primarily on solvent-solute interactions

· Solubility is decreases as temperature rises (Figures 11.8 and 11.9)

· Solubility also depends on the gas partial pressure, according to Henry's law. Figure 11.8 gives k_H, and Figure 11.10 illustrates how to use Henry's law to supersaturate a solution (carbonation!) $C_{gas} = k_H P_{gas}$

○ Solutions of liquids in liquids

· Miscible liquids are infinitely soluble in each other (mix in any ratio)

· Immiscible liquids have very low solubility in each other, and separate to form layers. Oil and water (Figure 11.14) are a classic example of immiscible liquids and illustrate the axiom that "like dissolves like" because their intermolecular forces are so different

· Partially miscible liquids will form two layers when mixed, but each layer contains significant amounts of the other solute liquid

○ Solutions of solids in liquids

· Figure 11.6 shows the temperature dependance of solubility for several solids

· *Exothermic* ΔH_{solv} leads to lower solubility at higher temperatures

· *Endothermic* ΔH_{solv} leads to higher solubility at higher temperatures

Quiz 11.1 - The Solvation Process

Homework 11.1

- 11.3: Energetics of solvation

- 11.9: Rule of like dissolves like

- 11.13: Classifying electrolytes

- 11.23: Henry's law

11.4   Colligative Properties

- Colligative properties of solutions depend on the *amount* of solute present, regardless of the chemical identity of the solutes

- Some colligative properties depend on less common units of concentration

  - Recall molarity from chapter 3
  - *Mass %* is $\dfrac{m_{solute}}{m_{total}} \times 100\%$
  - *Mole fraction* is $\chi_A = \dfrac{n_A}{n_{total}}$
  - *Molality* is $m = \dfrac{moles_{solute}}{kg_{solvent}}$
  - Practice interconverting between these units: $\chi_{C_6H_{12}O_6} = 0.25$ in aqueous solution
  - For electrolytes, we will also need the van't Hoff factor, $i = \#$ of particles produce on solvation

Quiz 11.2 - Concentrations

Homework 11.2

- 11.19: % by mass and solubility

- 11.31: Mole fraction

- 11.39: Molality

Back to Section 11.4 Colligative Properties

- Vapor pressure lowering

  - Figure 11.8 illustrates why solutes lower the vapor pressure of the solvent
  - Rault's law: $P_A = \chi_A P_A^\star$
  - If the solute is a liquid, we can apply Rault's law to the solute as well $P_{total} = \chi_A P_A^\star + \chi_B P_B^\star$

- This gives a different composition of the gas phase from the liquid phase, allowing for purification through distillation (Figures 11.19 and 11.20)

  ○ Changes in phase tranistion temperatures

    - Boiling point elevation is a consequence of vapor pressure lowering
    - Freezing point depression follows a similar forumula
    - $\Delta T_{f/b} = i K_{f/b} m$
    - Table 11.2 gives T_b, K_b, T_f, and K_f for several substances
    - These effects manifest on a phase diagram like in Figure 11.23

  ○ Osmotic pressure

    - Figure 11.24 shows how water will flow across a selectively permeable membrane via osmosis
    - Figure 11.25 shows how and applied pressure can reverse this process and purify water
    - $\pi = \dfrac{inRT}{V} = iMRT$
    - Figure 11.27 shows how blood salinity can impact the health of red blood cells (isotonic, hypertonic, hypotonic, hemolysis, crenation)

  ○ Measuring colligative properties can give the molar mass of an unknown, as long as we know the van't Hoff factor

Quiz 11.3 - Colligative Properties

Homework 11.3

  ○ 11.45: Freezing point depression

  ○ 11.61: Osmotic pressure

  ○ 11.65: Vapor pressures of mixtures

11.5   Colloids

  ○ Colloids occupy the blurry boundry region between homogeneous and heterogeneous mixtures (Figure 11.29)

  ○ Colloids can be identified by several properties:

    - Particle size is on a range of tens- to hundreds- of nanometers
    - Particles will not settle out on their own under the influence of gravity
    - Particles will scatter light, called the Tyndall Effect (Figure 11.30)

  ○ Table 11.4 gives some examples of colloids in various phases

  ○ Emulsifying agents can create an emulsion, or colloidal suspension of two immiscible liquids

  ○ Soaps and detergents can create colloidal suspensions of oils in water (Figure 11.33)
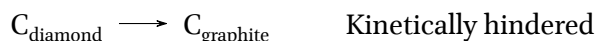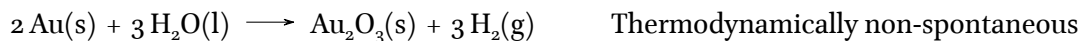
Quiz 11.4 - Molar Masses and Colloids

Homework 11.4

- 11.49: Molar mass from boiling point

- 11.59: Molar mass from osmotic pressure

- 11.73: Colloid particle size

KINETICS

12.1 Chemical Reaction Rates

○ Two reactions which we can write, but do not observe:

$$2\,Au(s) + 3\,H_2O(l) \longrightarrow Au_2O_3(s) + 3\,H_2(g) \qquad \text{Thermodynamically non-spontaneous}$$

$$C_{\text{diamond}} \longrightarrow C_{\text{graphite}} \qquad \text{Kinetically hindered}$$

○ Kinetics is the study of reaction rates (how quickly the reaction proceeds)

○ The reaction rate is the rate of dissappearance of reactant or production of product, normalized by the stoichiometric coefficients

$$rate = \frac{d\,[A]}{\nu_A dt}$$

○ This is the *instantaneous* rate, and in practice can only be approximated

○ We can monitor the concentration of reactant or product over time, and calculate the average rate at different intervals

○ Consider the reaction $2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$ (Figures 12.2 and 12.3)

$$rate = -\frac{d\,[H_2O_2]}{2dt} = \frac{d\,[H_2O]}{2dt} = \frac{d\,[H_2]}{dt}$$

$$rate \approx -\frac{\Delta\,[H_2O_2]}{2\Delta t} = \frac{\Delta\,[H_2O]}{2\Delta t} = \frac{\Delta\,[H_2]}{\Delta t}$$

○ Practice: Consider $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ (Figure 12.5). Calculate the rate using each curve

12.2 Factors Affecting Reaction Rates

○ Reaction rates can vary widely from virtually instantaneous to so slow the reactiond doesn't practically happen at all

○ Many factors affecte rates, including some that can be controlled and some that cannot

○ The pysical state of the reactants

· For solids, reactions occur at the surface so fine powders react more quickly than coarse ones (Figure 12.6)

· For heterogeneous reaction, the reaction occurs at the interface

○ Temperature: All reactions increase their rate as temperature increases

- ○ Concentration of reactants

    - · Increasing reactants generally increases the rate of reaction (We won't see any exceptions in this class)

    - · Product concentration generally has no effect on reaction rates (again, no exceptions in this class)

    - · Figure 12.7 shows how degradation of statues is accelerated in areas with high H_2SO_4 concentration

- ○ The presence of a *catalyst* (more on this in section 12.7)

12.3   Rate Laws

- ○ The reaction rate can be related to reactant concentration through a *rate law*

    - · For a generic reaction aA+bB $\longrightarrow$ cC+dD, $rate = k\,[A]^m\,[B]^n$

    - · m and n are called the reaction orders, and are unrelated to the stoichiometric coefficients (equations at the end of the section)

    - · $m + n$ gives the *overall* reaction order

    - · k is called the *rate constant*, and will take different units depending on the overall reaction order (Table 12.1)

- ○ Rate laws can be determined through the *Initial Rate Method*

    - · Do several runs of the reaction with different concentrations of reactants

    - · Measure the initial rate of reaction for each run

    - · Compare runs pairwise, choosing pairs which keep one reactant concentration constant and change the other

    - · Take the ratios of the rates, equal to the ratios of the rate laws for each condition

    - · Simplify the ratio of rate laws mathematically (just show this on the whiteboard)

    - · Calculate the value of k using data from one trial (or all of them, and average the results)

    - · Practice: Work example 12.4 from the text

Quiz 12.1 - Reaction Rates

Homework 12.1

- ○ 5: Find rates from concentration data

- ○ 7: Factors affecting rate laws

- ○ 25: Initial rate method

12.4 Integrated Rate Laws

- We can set the definition of reaction rate equal to the rate law: $-\dfrac{\mathrm{d}\,[A]}{\mathrm{d}t} = k\,[A]^m$

- Rearrange this to separate the infinitesimal terms and integrate: $\int \dfrac{\mathrm{d}\,[A]}{[A]^m} = \int -k\mathrm{d}t$

- This will integrate to give different integrated rate laws depending on the reaction order

- First-order

    - Linear form: $\ln\,[A]_t = \ln\,[A]_0 - kt$

    - Two-point form: $\ln\left(\dfrac{[A]_t}{[A]_0}\right) = -kt$

    - Special Half-life form: $\dfrac{A_t}{A_0} = \left(\dfrac{1}{2}\right)^{\frac{t}{t_{1/2}}}$

    - Half-life: $t_{1/2} = \dfrac{\ln 2}{k}$

    - Linear when plotting $\ln[A]$ vs t, with $slope = -k$

- Second-order

    - Linear form: $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

    - Half-life: $t_{1/2} = \dfrac{1}{k\,[A]_0}$

    - Linear when plotting $\dfrac{1}{[A]}$ vs t, with $slope = +k$

- Zeroth-order

    - Linear form: $[A]_t = -kt + [A]_0$

    - Half-life: $t_{1/2} = \dfrac{[A]_0}{2k}$

    - Linear when plotting $[A]$ vs t, with $slope = -k$

- All the above is summarized in Table 12.2 in the text

- Determining reaction order graphically

    - Graph $[A]$, $\ln[A]$, and $\dfrac{1}{[A]}$ vs t

    - Two will be curved, while one is straight and indicates the overall reaction order

    - Making one reactant in excess will prove the reaction order of only the other reactant

    - Use my prepared spreadsheet to practice determining the rate law

Quiz 12.2 - Integrated Rate Laws

Homework 12.2

- 33: Graphically determine rate law

- 36: Half-life from rate constant

- 40: Second-order half-life

- 46: First-order decay

12.5 Collision Theory

- 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 happen in the wrong orientation to lead to reaction (Figure 12.13)

  · Some collisions don't have enough energy to overcome the activation energy barrier

- Reaction coordinate diagrams show how the energy changes over the course of a reaction

  · Figure 12.14 shows a typical reaction coordinate diagram

  · 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

- 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 $\dfrac{J}{mol}$, so we should use $R = 8.314 \dfrac{J}{mol\ K}$

  · The exponential term is called a Boltzmann factor, and gives the fraction of collisions which have enough energy

  · Figure 12.15 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

  - $\ln k = \ln\left(Ae^{-E_a/RT}\right)$ becomes $\ln k = \ln A - \dfrac{E_a}{RT}$

  - If we plot the $\ln k$ at different temperatures against $\dfrac{1}{T}$, we get a linear equation

  - The slope of the line is $-\dfrac{E_a}{RT}$ and the intercept is $\ln A$

  - We can also create the two-point form of this equation: $\ln\left(\dfrac{k_2}{k_1}\right) = -\dfrac{E_a}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ (Different from the text)

  - 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: $2\,HI(g) \longrightarrow H_2(g) + I_2(g)$

  At $655\ K$ the rate constant is $8.15 \times 10^{-8}\dfrac{1}{M\ s}$ and at $705\ K$ the rate constant is $1.39 \times 10^{-6}\dfrac{1}{M\ s}$

  Determine the activation energy and frequency factor for this reaction $\left(218\dfrac{kJ}{mol}\ \text{and}\ 1.91 \times 10^{10}\dfrac{1}{M\ s}\right)$

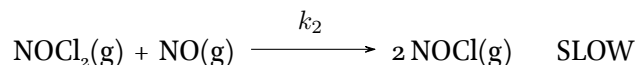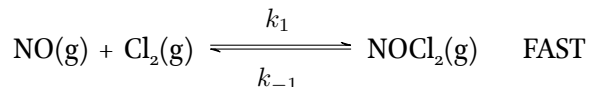**Quiz 12.3 - Arrhenius Equation**

Homework 12.3

- 50: Factors in collision theory

- 58: Determining the frequency factor

- 62: Determining the activation energy
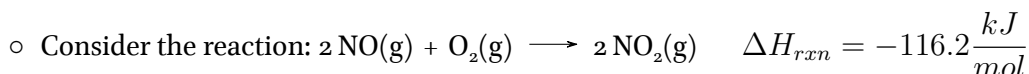
12.6   Reaction Mechanisms

- My figure about how we often don't think about the *mechanics* of how chemical reactions proceed

- 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: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Elementary Step 1: $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ SLOW

Elementary Step 2: $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ FAST

○ The two steps add up to the total equation

○ $NO_3(g)$ is produced in the first step, then consumed in the second step, so it never shows up in the overall reaction

○ This makes $NO_3(g)$ 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

○ A reaction coordinate diagram for a two-step reaction like this one will feature two peaks (Draw one on the board)

○ 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: $AB \longrightarrow A + B$ (cyclobutane decomposition figure)

      * Bimolecular steps involve an encounter between two molecules: $A + B \longrightarrow C$ or $2A \longrightarrow B$ (Figure 12.17)

      * 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 (Figure 12.18...a bit strained analogy)

   · Looking at the reaction of NO_2 and CO above, the first step is slower so the overall reaction rate will be $rate = k[NO2]^2$

○ 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 $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g) \quad rate = k\,[NO]^2\,[Cl]$
- This observed rate law seems consistent with a single-step *termolecular* mechanism, but termolecular reactions are exceptionally rare
- An alternative proposed mechanism is:

$$NO(g) + Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2(g) \quad \text{FAST}$$

$$NOCl_2(g) + NO(g) \overset{k_2}{\longrightarrow} 2\,NOCl(g) \quad \text{SLOW}$$

- 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 $[NOCl_2] = \dfrac{k_1}{k_{-1}}\,[NO]\,[Cl_2]$
- 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 $[NOCl_2]$
$$rate = k_2\left(\dfrac{k_1}{k_{-1}}\,[NO]\,[Cl_2]\right)[NO] = \dfrac{k_2 k_1}{k_{-1}}\,[NO]^2\,[Cl_2]$$

○ Consider the reaction: $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \quad \Delta H_{rxn} = -116.2\dfrac{kJ}{mol}$

- The observed rate law is: $rate = k\,[NO]^2\,[O_2]$
- A proposed mechanism is:
$NO(g) + O_2(g) \rightleftharpoons NO_3(g) \quad \text{FAST}$
$NO(g) + NO_3(g) \longrightarrow 2\,NO_2(g) \quad \text{SLOW}$
- 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)

12.7 Catalysis

○ Catalysts provide an alternative reaction mechanism which is faster than the uncatalyzed pathway

○ Figure 12.19 shows a typical reaction coordinate diagram for a catalyzed reaction

○ Catalysts appear in in the reaction mechanism, being first *consumed,* then *regenerated*

○ The reaction $2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$ can be catalyzed by $HBr(aq)$
$H_2O_2(aq) + 2\,HBr(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l) \quad \text{SLOW}$
$Br_2(aq) + H_2O_2(aq) \longrightarrow O_2(g) + 2\,HBr(aq) \quad \text{FAST}$

- Note that the HBr is consumed in the first step, but regenerated in the second step

- Homogeneous catalysis has the catalyst in the same phase as the reactants

- Heterogeneous catalysis has a catalyst in a different phase (Figure 12.23)

- Some ways catalysts can operate:

  - 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

- Enzymes are a special class of catalyst important for living organisms

  - Enzymes are usually large proteins, sometimes incorporating metal cofactors
  - Enzymes can be incredibly efficient by reducing the activation energy barrier to near 0
  - Figure 12.25 shows a schematic of how enzymes work

- Analyze the following reaction mechanism for additional practice:

  $C_3H_6(aq) + H^+(aq) \longrightarrow C_3H_7^+(aq)$

  $C_3H_7^+(aq) + H_2O(l) \longrightarrow C_3H_9O^+(aq)$

  $C_3H_9O^+(aq) \longrightarrow C_3H_8O(aq) + H^+(aq)$

  - Give the total overall reaction
  - Identify any catalysts and intermediates

Quiz 12.4 - Reaction Mechanisms

Homework 12.4

- 72: Rate laws of elementary steps

- 74: Validating a mechanism for a real reaction

- 78: Catalysts and mechanisms

- 80: Catalysis and reaction coordinate diagrams

FUNDAMENTAL EQUILIBRIUM CONCEPTS

13.1   Chemical Equilibria

- Figure 13.1 illustrates how CO_2 in our blood and blood pH are mediated by equilibrium reactions

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

  $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ and $2\,NO_2(g) \longrightarrow N_2O_4(g)$

- Such reactions will reach an equilibrium

  - Equilibrium is when the forward reaction rate and the reverse reaction rate are equal
  - Treating these as single-step (elementary) reactions yields: $rate_f = k_f[N_2O_4]$ and $rate_r = k_r[NO_2]^2$
  - The concentrations of reactants and products remains steady indefinitely once equilibrium is reached
  - Figure 13.2 shows how the amounts of reactant and product and the reaction rates shift over time until the rates are equalized and equilibrium is reached
  - Equilibrium is a dynamic state – reactions continue, they merely balance each other (Figure 13.3)
  - The precise concentrations at equilibrium will depend on the starting conditions

- The above two reactions can be combined into one equation: $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

- Figure 13.4 illustrates how vapor pressure is an equilibrium process ($Br_2(l) \rightleftharpoons Br_2(g)$)

13.2   Equilibrium Constants

- The current concentrations of reactants and products can be summarized with the *reaction quotient* Q

- For a generic reaction: $mA + nB \rightleftharpoons xC + yD$ the reaction quotient is:

$$Q_C = \frac{[C]^x\,[D]^y}{[A]^m\,[B]^n}$$

$$Q_P = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$

- For heterogeneous reactions, we exclude (s) and (l) species from Q and K (reasons for this are a bit complex)

- Practice with the equation: $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $(K_{C,300K} = 2.7 \times 10^8)$

- As the system approaches equilibrium, the value of Q approaches K

- K has the same mathematical form as Q, but has concentrations or pressures that are already at equilibrium

- Both K and Q are unitless, for reasons we don't cover in this class

- At a given temperature, the equilibrium conditions may be different for different starting points, but the value of K is the same

- 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

- For a given starting position, we can calculate Q to determine what direction the system needs to shift to reach equilibrium

    · If $Q < K$ then the system must shift toward products
    · If $Q > K$ then the system must shift toward reactants

- Equilibrium can be reached whether you start with reactants or start with products (Figure 13.5)

- Note that $N_2(g)$ alone or $H_2(g)$ alone cannot lead to equilibrium from the reactant side – both are needed

- 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: $K_p = \dfrac{K_c}{(RT)^2}$

Quiz 13.1 - Equilibrium Constants

Homework 13.1

- 3: Recognize when a system reaches equilibrium

- 9: Reactant-favored reactions

- 15: Reaction quotient for many reactions

Resuming Section 13.2 - Equilibrium Constants

- Using the equilibrium constant

  - · We can measure the concentrations at equilibrium and directly measure the equilibrium constant

    - * Consider the reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
    - * Find K_c if $[CO] = 0.0600\ M$, $[H_2O] = 0.120\ M$, $[C_2O] = 0.150\ M$, and $[H_2] = 0.300\ M$
    - * Figure 13.6 shows how many different reaction mixture compositions can all satisfy the equilibrium expression

  - · We can use the equilibrium constant to find an unknown concentration

    - * $CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$ $K = 1.8 \times 10^{-5}$
    - * Find $[H_3O^+]$ if $[CH_3COOH] = 0.250\ M$ and $[CH_3COO^-] = 0.350\ M$

  - · We can easily find K for doubled, reversed, or added equations (*not in your text*)

    - * For a reversed equation, reactants and products switch, so $K_{reverse} = K_{normal}^{(-1)}$
    - * For a doubled (or tripled) reaction, K should be squared (or cubed)
    - * For added reactions (multi-step) $K_{total} = K_1 K_2$

  - · Find K for the reaction: $N_2(g) + 2\,O_2(g) \rightleftharpoons 2\,NO_2(g)$
    $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $K = 2.0 \times 10^{-25}$
    $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$ $K = 6.4 \times 10^9$

Quiz 13.2 - Working with K

Homework 13.2

- 19: Predict direction to reach equilibrium

- 25: Covert K_C to K_P

- 52: Calculate K from concentrations

13.3 Shifting Equilibria: 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 $2\,H_2S(g) \rightleftharpoons 2\,H_2(g) + S_2(g)$
  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 $3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$ – How will the reaction quotient change if the volume doubles?
  - · The shift depends on Δ_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 $\Delta_m = 0$, then the reaction is unaffected by dilution and concentration

- ○ Temperature changes

  - · Unlike with the other changes, a change in T will actually change the value of K
  - · How K changes depends on ΔH_{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

Quiz 13.3 - Le Châtelier's Principle

Homework 13.3

- ○ 36: How to maximize product

- ○ 38: Temperature changes and equlibrium

- ○ 42: Predicting response to changes

13.4   Equilibrium Calculations

- ○ 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 $[]$ before you put them into the equilibrium expression

- ○ Consider the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

  $5.00\ mol$ H_2 and $0.500\ mol$ I_2 are reacted in a $1.00\ L$ chamber and at equilibrium $[HI] = 0.900\ M$. Find the value of K_C (324)

- ○ Consider the reaction $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$ $K_C = 5.80$

  Find the equilibrium conditions if initial concentrations are: $[CO] = [H_2O] = 0.0125\ M$

- ○ Often the equilibrium expression will lead to a quadratic equation when solving for x

- ○ The quadratic formula is: $ax^2 + bx + c = 0 \rightarrow x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

- ○ Consider the reaction: $I_2(g) \rightleftharpoons 2\,I(g)$ $K_{P,1000K} = 0.260$

  Find the equilibrium conditions if a reaction chamber is initially charged with $0.200\ atm$ I and $0.00500\ atm$ 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 $HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$ $K_C = 1.8 \times 10^{-4}$

  Find the equilibrium conditions for a solution that begins with $[HCOOH] = 0.250\ M$

Quiz 13.4 - ICE Tables

Homework 13.4

- 54: Calculate K using an ICE table

- 76: Use ICE table to calculate equlibrium amounts

- 88: Calculate pressures using an ICE table

ACID-BASE EQUILIBRIA

14.1 Brønsted-Lowry Acids and Bases

○ Arrhenius acid/base theory defines acids and bases in terms of H_3O^+ and OH^- ions

- $HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)$

- $NaOH(s) \xrightarrow{\text{water}} Na^+(aq) + OH^-(aq)$

○ H^+ vs H_3O^+

- In the past, you may have used $H^+(aq)$ in your equations
- I will tend to use H_3O^+ instead, but either way is acceptable
- Really, H^+ is a flagrant lie. Bare protons don't exist in water. H_3O^+ is also a little bit of a lie. The extra proton and the charge create clusters of many water molecules. It gets really complicated

○ Arrhenius theory is unable to account for reactions that don't involve H_3O^+ and OH^- ions directly

○ Consider $HNO_2(aq) + ClO_2^-(aq) \rightleftharpoons HClO_2(aq) + NO_2^-(aq)$ – should this reaction be considered acid/base?

○ Brønsted-Lowry theory defines acids as proton *donors* and bases as proton *acceptors*

○ HNO_2 is the acid, and ClO_2 is the base

○ Conjugate pairs

- We can also consider the reverse reaction, where $HClO_2$ is the acid and NO_2^- is the base
- We call these linked species *conjugate pairs*
- HNO_2 is the conjugate acid to NO_2^-, while NO_2^- is the conjugate base to 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 $H_2SO_3 \rightleftharpoons HSO_3^- \rightleftharpoons SO_3^{2-}$
- Or the series $H_3PO_4 \rightleftharpoons H_2PO_4^- \rightleftharpoons HPO_4^{2-} \rightleftharpoons PO_4^{3-}$
- H_2SO_3 is a diprotic acid, and SO_3^{2-} is a dibasic base because they can exchange 2 protons
- H_3PO_4 is a triprotic acid, and PO_4^{3-} is a tribasic base because they can exchange 3 protons
- The intermediates, HSO_3^-, $H_2PO_4^-$ and 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

14.2   pH and pOH

○ Autoionization of Water

· Water is also amphoteric: $H_3O^+ \rightleftharpoons H_2O \rightleftharpoons OH^-$

· Because of this, water will undergo autoionization: $2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $K_w = 1.00 \times 10^{-14}$

· For pure water, this leads to concentrations of $\left[H_3O^+\right] = [OH^-] = 1.00 \times 10^{-7}$

· 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 $(NH_3(aq) + HNO_2(aq) \longrightarrow NH_4^+(aq) + NO_2^-aq)$, water is actually mediating the proton exchange behind the scenes

· Because of this, acidity and basicity are defined by the balance between $\left[H_3O^+\right]$ and $[OH^-]$ (Table 14.1)

* $\left[H_3O^+\right] > [OH^-]$ is an acid
* $\left[H_3O^+\right] < [OH^-]$ is a base
* $\left[H_3O^+\right] = [OH^-]$ is neutral

· We can always find $\left[H_3O^+\right]$ or $[OH^-]$ from the other, based on $K_w = \left[H_3O^+\right]\left[OH^-\right]$

○ Acidity of a solution is summarized by the quantity $pH = -\log\left[H_3O^+\right]$

○ Neutral solutions have $pH = 7$, acidic solutions have $pH < 7$, and basic solutions have $pH > 7$

○ 0 and 14 are actually not boundaries at all, and you *can* have solutions with $pH < 0$ or $pH > 14$

○ We can find the $\left[H_3O^+\right]$ by $\left[H_3O^+\right] = 10^{-pH}$

○ Table 14.2 shows both the pH and $\left[H_3O^+\right]$ 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 14.5 shows how a universal indicator pH paper works

· We can also measure an electrochemical response using a pH probe (Figure 14.4)

· How these pH probes work is a bit complicated, but they can measure $\left[H_3O^+\right]$ across a wide range

Quiz 14.1 - pH **and** pOH **Calculations**

Homework 14.1

    ○ 19: pH and pOH of strong acid/base solutions

    ○ 21: $[\text{H}^+]$ and $[\text{OH}^-]$ from pH

    ○ 25: $[\text{H}^+]$ from $[\text{OH}^-]$

14.3   Relative Strengths of Acids and Bases

    ○ 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

        · Figure 14.6 lists some strong 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

    ○ Figure 14.8 shows the K_a and K_b values for a number of different acids and bases, with more in the appendices

    ○ 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: $K_a = \dfrac{[\text{A}^-]\left[\text{H}_3\text{O}^+\right]}{[\text{HA}]}$

        · Weak bases always follow the same format: $K_b = \dfrac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$

        · 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: $K = \dfrac{K_a K_b}{K_w}$

○ 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 (Figure 14.11)
  * Electronegative groups nearby pull electrons away from the H bond and make it weaker (Figure 14.12)
- 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

Quiz 14.2 - Acid/Base Reactions

Homework 14.2

○ 11: Definition of Amphiprotic

○ 27: Conjugates of weak and strong species

○ 37: Comparing strength based on K_b and K_a values

○ 58: K_a from K_b for a conjugate pair

14.4 Hydrolysis 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:

- 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 CaF_2

○ Some metal cations are acidic in a surprising way

- The metal cation will complex one or more water molecules
- The bound water molecules have weaker O-H bond strengths, so one H^+ is donated
- Figure 14.13 shows this process for Al^{3+}
- The text lists the pK_a for several metal cations
- This type of acid is sometimes called a *Lewis* acid

14.5 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 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, $[H_2C_6H_6O_6]$, $[HC_6H_6O_6^-]$, and $[C_6H_6O_6^{2-}]$ for a $0.500\ F$ solution of Ascorbic acid

- First, solve the ICE table for the first deprotonation
- Then, use the $[H_3O^+]$ and $[HC_6H_6O_6^-]$ as starting values for the second deprotonation
- Because the $[H_3O^+]$ will not change much, we don't have to revisit the first equilibrium

Quiz 14.3 - Weak Acid/Base Reactions

Homework 14.3

○ 60: ICE tables for weak acids and bases

○ 64: ICE tables for a diprotic base

14.6 Buffers

○ 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: $HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$

* Adding $NaNO_2$ will affect this equilibrium because it adds nitrite ion to solution

* Le Châtelier's principle will shift the reaction left, reducing the effect HNO_2 has on pH

* Any equilibrium reaction involving ions can be affected by addition of other salts containing those emails – 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 14.14 shows how pH changes after adding $1ml$ of $0.01M$ HCl in a buffered and unbuffered solution starting at $pH = 8.00$

* The buffer can only absorb a certain amount of acid or base, called the buffer capacity, which will be covered later

* Figure 14.15 shows how concentrations of the buffering species change when acid or base are added

○ The Henderson-Hasselbach Equation

· For a buffer solution, we can solve an ICE table with initial amounts of both HA and A$^-$

· In this case, the equilibrium expression simplifies to: $\left[H_3O^+\right] = K_a \dfrac{[HA]}{[A^-]}$

· We can calculate the pH from here to be: $pH = pK_a - \log \dfrac{[HA]}{[A^-]}$

· 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 ± 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 $\left[HPO_4^{2-}\right] \approx 0.200\ M$, find the $\left[H_2PO_4^-\right]$ 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?

Quiz 14.4 - Buffer Solutions

Homework 14.4

○ 78: Mechanism of acid/base buffers

○ 80: $\left[H_3O^+\right]$ of a buffer solution

○ 82: $[OH^-]$ of a buffer solution

○ 86: pH of a buffer solution

○ 88: Preparing a buffer solution

14.7   Acid-Base Titrations

○ 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

○ Titrations can use either a pH probe or a color indicator to determine the end-point (find figures from the Internet)

○ Figure 14.18(a) shows a titration curve for a strong acid with a strong base

    · Point A will be the pH of the analyte solution, $pH = -\log\left[H_3O^+\right] = -\log\left[HA\right]$

    · 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

○ At the equivalence point, moles of titrant added is equal to moles of analyte

○ This relation can be summarized as $M_a V_a^\circ = M_t V_{eq}$

Quiz 14.5 - Strong Acid-Base Titrations

No Associated Homework

Resume Section 14.7 - Acid-Base Titrations

- ○ 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 14.18(b))
        - ∗ The starting point A must be solved using a 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
        - ∗ These curves can be very different for different acids, even at the same concentration
        - ∗ Note the strong inflection in curves for very weak acids
    - · The equivalence point is recognized as the point with steepest pH change
    - · Multiprotic acids or bases will pass through more than one equivalence point (Draw titration curve)
- ○ 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$_2$O(l) $\rightleftharpoons$ A−(aq) + H$_3$O$^+$(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 14.20 shows how the end point and equivalence point are situated in a titration curve
        - ∗ Figure 14.19 shows the appropriate ranges for some common indicators

Quiz 14.6 - Weak Acid-Base Titrations

Homework 14.6

- ○ 92: Choosing an appropriate color indicator

- ○ 94: pH at different points of a weak acid titration

EQUILIBRIA OF OTHER REACTION CLASSES

15.1   Precipitation and Dissolution

- ○ Solubility Products

    - · Most insoluble salts are really just *sparingly* soluble (Figure 15.2)
    - · This means that the solvation of the solid salt is a reactant-favored equilibrium
    - · For PbI_2, the equation is: $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$ $K_{sp} = 9.8 \times 10^{-9}$
    - · The equilibrium expression here would be: $K_{sp} = [Pb^{2+}]\,[I^-]^2$
    - · K_{sp} determines the ion concentrations, but is not mathematically equivalent to the solubility (Appendix J)
    - · 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 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 $1.35 \times 10^{-3}\ M$
        - ＊ The same equation can be used in reverse to find K_{sp} from the molar solubility

    - · Find the molar solubility for $Sr_3(PO_4)_2$
    - · Find K_{sp} for AgI, which has a molar solubility of $9.0 \times 10^{-9}\ M$

- ○ The Common Ion effect

    - · 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
    - · NaCl has a $K_{sp} = 37.66$. Find how many grams of NaCl can dissolve in $100.0\ ml$ of a $12\ M$ 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 OH^- and drive the reaction toward products

* Even very low K_{sp} salts will dissolve if the $[OH^-]$ is held low by the pH

○ Solubility and precipitation

· 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

Quiz 15.1 - Molar Solubility

Homework 15.1

○ 7: Weak base anions and solubility

○ 9: K_{sp} for ionic compounds

○ 11: K_{sp} from $g/100ml$ solubility

○ 13: Molar solubility from K_{sp}

○ 15: Common ion effect

○ 31: Predicting precipitation from concentrations and K_{sp}

15.2 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 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 BF_3 with NH_3

○ Many metal cations can act as a Lewis acid by forming coordinate bonds with water molecules

$Al^{3+}(aq) + 6 H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq)$

○ Carbonic acid makes gas due to Lewis acid action: $H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O(l)$

○ Lewis acids and *formation reaction* equilibria

· 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

· Appendix K gives formation constants for several common complex ions – note that they tend to be large numbers

· Find the equilibrium concentrations for a $Co(NH_3)_6^{2+}$ formation reaction

  ∗ Suppose you start with $[Co^{2+}] = 0.0200\ M$ and $[NH_3] = 0.100\ M$

  ∗ 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
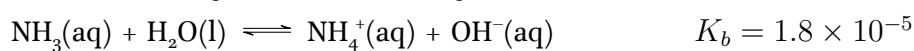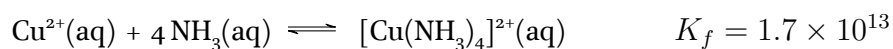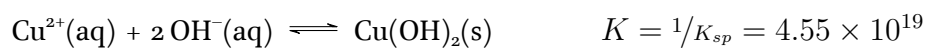
Quiz 15.2 - Lewis Acids

Homework 15.2

- 76: Lewis acid/base reactions

15.3 Coupled Equilibria

- This section is actually just a repeat of how the equilibrium constants of chained reactions are combined, as we covered in section 13.2

- If we have time, we could talk about the copper system from the Le Châtelier's Principle lab

$$Cu^{2+}(aq) + 2\,OH^-(aq) \rightleftharpoons Cu(OH)_2(s) \qquad K = {}^1\!/\!_{K_{sp}} = 4.55 \times 10^{19}$$

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \qquad K_f = 1.7 \times 10^{13}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

Quiz 15.3 - Formation Reactions

Homework 15.3

- 64: Formation equilibrium

- 74: Formation reactions used to increase solubility

CHAPTER 16

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THERMODYNAMICS

16.1 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, ΔH_{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)

- $\text{C}_{\text{Diamond}} \longrightarrow \text{C}_{\text{Graphite}}$ – Diamonds do convert to graphite. . . but over *very* long timescales (like, > the age of the universe)

- 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, and the reverse will actually be spontaneous

○ Spontaneous processes in nature tend to "spread out" both matter and energy

- Figure 16.4 shows a gas expansion
- Figure 16.5 shows heat transfer

○ First Law of Thermodynamics

- The total energy of the universe is constant
- This leads to our understanding of enthalpy, ΔH
- Any chemical potential energy lost or gained by the chemical reaction must be given to or taken from the surroundings

16.2 Entropy

○ Reversibility is also an important idea in thermodynamics

- This is a more nuanced condition that simple a process which *can* be run in reverse
- A process is *thermodynamically* reversible if it is at equilibrium at every step of the process

- This includes thermal equilibrium of all parts and the surroundings
- In practice, reversible processes must be slow to allow everying to remain at equilibrium

○ A colloquial defintion of entropy is: *disorder*

○ The original definition of entropy is: $\mathrm{d}S = \dfrac{\mathrm{d}q_{rev}}{T}$

○ This definition was based on studies of the efficiency of heat engines

○ The Boltzmann definition of entropy is: $S = k_B \ln W$

- k_B, the Boltzmann constant, is actually $\dfrac{R}{N_A} = 1.38 \times 10^{-23} \dfrac{J}{K}$
- W is the number of microstates for the current macrostate, or microscopic configurations of the system with the same observable state variables
- Figure 16.8 shows how expansion of a gas increases the value of W
- Figure 16.9 shows how spreading out thermal energy increases the value of W
- My spheres_demo program showing how systems tend toward macrostates with greatest W
- For a simple system of distinguishable particles, $W = (\# \ of \ states)^{\# \ of \ particles}$
- Practice: Find W for passwords and dice rolls

○ We can use these principles to examine when $\Delta S > 0$ for simple processes

- An upward phase change (s $\longrightarrow$ l, l $\longrightarrow$ g) (Figure 16.10)
- Mixing (including solvation of a solid into aqueous solution)
- Increasing the temperature (Figure 16.11)
- Increasing the number of particles (positive Δn)
- Increasing the volume of an aqueous or gaseous system

Quiz 16.1 - Entropy

Homework 16.1

○ 3: Spontaneity in common processes

○ 11: Boltzmann entropy and a toy model system

○ 15: Comparing entropies of similar molecules

○ 17: Predicting entropy changes for processes

16.3   The Second and Third Laws of Thermodynamics

○ The second Law of Thermodynamics

· Spontaneous processes always result in an increase in the entropy of the universe (though not necessarily the system)

· $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$

· $\Delta S_{surr} = \dfrac{-q_{sys}}{T_{surr}} = \dfrac{-\Delta H_{sys}}{T_{surr}}$ for constant pressure processes

· Note that the formula in the text uses a poor definition of q as the "heat transferred," then define the system as the hotter object. In the end, $q_{sys} = -q$ and $q_{surr} = +q$ by their definition

· This law gives us a new definition for spontanaety *without* using Gibbs energy (discussed later)

* Spontaneous: $\Delta S_{universe} > 0$
* Non-spontaneous: $\Delta S_{universe} < 0$
* Equilibrium: $\Delta S_{universe} = 0$
* Find $\Delta S_{universe}$, ΔS_{sys}, and ΔS_{surr} for combustion of 1 mol of methane at room temperature
* Find $\Delta S_{universe}$, ΔS_{sys}, and ΔS_{surr} for condensing 1.00 g of water vapor ($\Delta H_{vap} = 2257 \dfrac{J}{g}$)

○ The 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 $\ln W = 0$
· From there, we can find the entropy at different temperatures through calorimetry (Figure 16.11)

○ Substances at 298 K have a standard molar enthalpy $S°$ based off of this 0 standard

○ Table 16.2 and Appendix G give the standard molar enthalpies for several common substances

○ For a reaction, we can find $\Delta S_{rxn}°$ just like ΔH_{rxn}

○ $\Delta S_{rxn}° = \displaystyle\sum_{i,products} \nu_i S_i° - \sum_{j,reactants} \nu_j S_j°$

16.4   Free Energy

○ 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: $\Delta G° = \Delta H° - T\Delta S°$, which is under standard conditions
· Standard conditions means 1 M for solutes and 1 bar (≈ 1 atm) for gases
· G is called *Gibbs free energy*, and is a measure of spontanaety (CHEM 3610 for technical definition of G)

* $\Delta G < 0$ for spontaneous processes, and $\Delta G > 0$ for non-spontaneous processes
    * Systems at equlibrium will have $\Delta G = 0$
- Find ΔG for the reaction: $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$ $\Delta H_{rxn} = -483.6\,\dfrac{kJ}{mol}$ $\Delta S_{rxn} = -89.0\,\dfrac{J}{mol\,K}$
    * At $T = 298\ K$
    * At $T = 5500\ K$ (Assume ΔH_{rxn} and ΔS_{rxn} are independent of temperature)
    * Note that ΔS should be converted to $^{kJ}/_{mol}$ in these problems
- Appendix G also has ΔG_f° values, so you don't have to calculate ΔH_{rxn}° and ΔS_{rxn}° 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 ΔS_{rxn}
- The ΔG_{rxn} for dissolving a substance is called the free energy of solution
- G is called "Free energy" becuase it is the maximum amount of non-expansion work that a process can do
- For coupled reactions, we can calculate ΔG_{rxn} using Hess's law just like ΔH_{rxn}

○ 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 quadrant diagram for $\pm \Delta H_{rxn}$ and $\pm \Delta S_{rxn}$ (Figure 16.12)

		ΔH_{rxn}	
		$+$	$-$
ΔS_{rxn}	$+$	Spontaneous @ High T	Always Spontaneous
	$-$	Never Spontaneous	Spontaneous @ Low T

- We can find the threshold temperature by solving the Gibbs energy equation for $\Delta G_{rxn} = 0 \to 0 = \Delta H_{rxn} - T\Delta S_{rxn}$
- This simplifies to: $T_{threshold} = \dfrac{\Delta H_{rxn}}{\Delta S_{rxn}}$
- Figure 16.13 shows how ΔG_{rxn} changes with temperature for different types of reactions

Quiz 16.2 - Gibbs Energy and Temperature

Homework 16.2

○ 29: Calculating standard entropies of reaction

- 31: Determine spontanaeity from enthalpy and entropy

- 33: Calculating standard Gibbs energies of reaction

- 35: Gibbs energy and Hess's law

- 37: Gibbs energy and temperature

Resuming Section 16.4

- 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: $\Delta G = \Delta G° + RT \ln Q$
    * Q is the reaction quotient
    * R is the gas constant, $R = 8.314 \dfrac{J}{mol\ K}$
    * 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: $\Delta G° = -RT \ln K$ and therefore $K = e^{\left(-\dfrac{\Delta G°}{RT}\right)}$
  · Figure 16.14 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 $\Delta G°_{soln}$ for NaCl

Quiz 16.3 - Gibbs Energy and Equilibrium

Homework 16.3

- 39: Calculating G from K

- 41: Calculating K from G

- 62: Calculating G under non-standard conditions

CHAPTER 17
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ELECTROCHEMISTRY

17.1 Review of Redox Chemistry

- 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: $2\,Al(s) + 3\,Cl_2(g) \longrightarrow 2\,AlCl_3(s)$
    - Aluminum is oxidized in the half-reaction: $Al \longrightarrow Al^{3+} + 3\,e^-$
    - Chlorine is reduced int he half-reaction: $Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$
    - 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 $3\,Cl_2$

- 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: $2\,Cu^+(aq) \longrightarrow Cu(s) + Cu^{2+}(aq)$
    - One Cu^+ ion is reduced and one is oxidized, making Cu^+ both the oxidizing and the reducing agent

- Balancing Redox reactions (Slightly different than in your book)

    - Some redox reactions are particularly difficult to balance
        * First, some reactants or products are often left out (H_2O, OH^-, and H_3O^+)
        * Second, there is a hidden constraint that the electrons lost in one half-reaction must match the number of electrons gained in the 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 to balancing redox reactions:
        1. Split the reaction into half-reactions (need to find oxidation #s to do this)
        2. Balance all elements except H and O
        3. Add the electrons, based on the changes to oxidation #s
        4. Balance charge by adding H^+ in acid, or OH^- in base

5. Balance H and O together by adding water
6. Multiply half-reactions to balance their electrons, then add them together
7. Make any cancellations of water, H^+, or OH^-

- Practice balancing $S_2O_3^{2-}(aq) + Cl_2(g) \longrightarrow SO_4^{2-}(aq) + Cl^-(aq)$
- Practice balancing $Cr_2O_7^{2-}(aq) + Sn^{2+}(aq) \longrightarrow Cr^{3+}(aq) + SnO_2(s)$

Quiz 17.1 - Balancing Redox Reactions

Homework 17.1

- 1: Identifying redox half-reactions

- 3: Simple balancing redox reaction problems

- 6: Balancing more complex reactions (no answers for this one. Sorry!)

17.2 Galvanic Cells

- Redox reactions can occur in solution with electrons directly transferring between partners (Figure 17.2)

- 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.)
  - $Zn(s)$ 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 17.3 shows a simple voltaic cell made from the reaction of $Ag^+(aq)$ with $Cu(s)$

- 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 Cu electrode is where oxidation occurs, and is called the anode
  - Sometimes the whole left half the cell is called the anode
  - The Ag 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
  - · Figure 17.4 shows a cell with an *inert* electrode

○ 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 $Zn(s)/Cu^{2+}(aq)$ cell would be: $Zn(s)|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu(s)$

○ Write the cell notation for a voltaic cell made from a reaction of Ag^+ ions with $Cu(s)$ under standard conditions

○ Draw a diagram of the $Cu(s)/Ag^+$ cell

  - · Identify the cathode and anode
  - · Show the flow of electrons and ions, assuming the salt-bridge contains KNO_3

17.3   Electrode and Cell Potentials

○ In voltaic cells, each half-cell has its own electrochemical potential

○ This potential is measured relative to a standard hydrogen electrode (Figures 17.5 and 17.6)

○ Table 17.1 shows the reduction potentials of many common half-reactions relative to the SHE

- Note that these are potentials under standard conditions ($1.00\ M$ and $1.00\ atm$)

- 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 $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

- 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 Zn(s)|Zn²⁺(1 M)||Cu²⁺(1 M)|Cu(s) cell ($1.10\ V$)

- Interpreting cell potentials:

    · Positive voltages indicate a spontaneous reaction (under standard conditions)

    · Negative voltages indicate a non-spontaneous reaction (under standard conditions)

    · Table 17.1 is also called an electrochemical series, with the most reactive reducing agents on the reactant side of the top half-reactions and the most reactive oxidizing agents on the product side of the bottom half-reactions

    · A reaction will be spontaneous if the cathode half-reaction is above the anode half-reaction on this table

17.4 Potential, Fee Energy, and Equilibrium

- Positive E_{cell} and negative ΔG both mean that a reaction is spontaneous under the current conditions

- E and ΔG are actually related by: $\Delta G = -nFE$

- Here, F is the Faraday constant, which gives the charge of a mole of electrons: $F = 96,485\ \dfrac{C}{mol}$

- 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} found above for the Zn(s)/Cu²⁺ cell ($1.10\ V$), find ΔG° $\left(-212\ \dfrac{kJ}{mol}\right)$

- Now, because $\Delta G^\circ = -RT\ln K$, we can now also relate E° and K: $\quad E^\circ = \dfrac{RT}{nF}\ln K$

- Figure 17.7 summarizes the relationships between ΔG°, E°, and K

- Using the E°_{cell} found above for the Zn(s)/Cu²⁺ cell ($1.10\ V$), find K $\quad (1.62 \times 10^{37})$

- The Nernst equation gives the voltage under non-standard conditions:

- Most of the time, we want to construct electrochemical cells under non-standard conditions
- The relationships between E and ΔG give us the foothold to find voltages of non-standard cells
- $\Delta G = \Delta G^\circ + RT \ln Q \rightarrow -nFE = -nFE^\circ + RT \ln Q \rightarrow E = E^\circ - \dfrac{RT}{nF} \ln Q$
- 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)/Cu²⁺ cell with $[\text{Zn}^{2+}] = 0.00500\ M$ and $[\text{Cu}^{2+}] = 3.00\ M$ $(1.18\ V)$
- 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 $[\text{Cu}^{2+}]$ in each cell
    * The balanced equation is: Cu(s) + Cu²⁺(aq, cathode) $\rightleftharpoons$ Cu(s) + Cu²⁺(aq, anode)
    * For such a cell, $Q = \dfrac{[\text{Cu}^{2+}]_{anode}}{[\text{Cu}^{2+}]_{cathode}}$ and $E^\circ = 0$
- Find E for a Cu concentration cell with $[\text{Cu}^{2+}]_{anode} = 0.00200\ M$ and $[\text{Cu}^{2+}]_{cathode} = 5.50\ M$ $(0.102\ V)$

17.5   Batteries and Fuel Cells

○ Dry Cells (common batteries – Figure 17.9)

- 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

○ Alkaline batteries (Improvement on dry cells – Figure 17.10)

- These have better energy density than dry cells, but will leak KOH

○ Rechargable NiCd batteries (Figure 17.11)

○ Lithium Ion Polymer (LiPo) Cells (Figure 17.12)

- 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, Li⁺ ions are forced into the positively chaged anode polymer matrix
- As it dischages, the 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

○ A common electrochemical cell is the lead storage battery used in cars, boats, etc. (Figure 17.13)

- Anode: Pb(s) + SO₄²⁻(aq) $\longrightarrow$ PbSO₄(s) + 2 e⁻

- Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$
- 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 H_2SO_4 solution
- The concentrated H_2SO_4 solution ensures that concentrations don't change much as the cell discharges, keeping the voltage relatively constant

- Fuel Cells (Figure 17.4)

  - A fuel cell is any cell where the reactants are replenished as the reaction proceeds
  - In practice, fuel cells usually use combustion reactions like $2\,H_2 + O_2 \longrightarrow 2\,H_2O$
  - This reaction is technically a redox reaction and can be separated into half-reactions like we see in ordinary cells
  - Anode: $H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-$
  - Cathode: $O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
  - As H^+ ions migrate from anode to cathode across the electrolyte, electrons flow the same way through the external circuit to maintain charge balance
  - H_2 fuel cells have a much higher theoretical limit of efficiency than H_2 combustion engines

17.6 Corrosion

- Corrosion (rusting) is the unintended oxidation of metal
- Figure 17.6 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 17.17)

  - A vital metal is placed in contact with a more reactive metal – the sacrifical anode
  - When corrosion occurs, the sacrifical anode is oxidized first, leaving the vital metal intact
  - Galvanized steel has been coated with a layer of Zn to offer cathodic protection

17.7 Electrolysis

- Figure 17.18 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 $\left(1\ A = 1\ \dfrac{C}{s}\right)$
- Recall that F relates C to mol: $1\ mol\ e^- = 96,485\ C$
- Find the mass of Al(s) produced if an electrolytic cell runs at $0.575\ A$ for $40\ min$
- $40\ min \rightarrow 2400\ s \rightarrow 1380\ C \rightarrow 0.0143\ mol\ e^- \rightarrow 0.00477\ mol$ Al $\rightarrow 0.129\ g$ Al
- A LiPo cell-phone battery has a full charge of $3000\ mAh$. How many g of Li$^+$ ions does the battery contain (assume complete migration of the ions) $(0.78\ g)$

○ Applications of Electrolysis

- Figure 17.19 shows the electrolysis of water
- Figure 17.20 shows a simple electroplating process
- Electroplating is used to make galvanized materials, white gold jewelry, and more
- Electrolytic refining of copper

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NUCLEAR CHEMISTRY

21.1   Nuclear Structure and 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 β decay

  · Nuclides below the belt will likely decay through α 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

21.2   Nuclear Equations

21.3   Radioactive Decay

○ 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, elbeit 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 ($^4_2$He nuclide)
- · Balance the α decay of $^{238}_{92}$U: $^{238}_{92}$U $\longrightarrow$ $^{234}_{90}$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 β decay of $^{210}_{81}$Tl: $^{210}_{81}$Tl $\longrightarrow$ $^{210}_{82}$Pb + $^0_{-1}\beta$

○ $^{234}_{90}$Th decays into $^{234}_{91}$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 $^{119}_{50}$Sn: $^{119}_{50}$Sn $\longrightarrow$ $^{119}_{50}$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 $^{18}_9$F: $^{18}_9$F $\longrightarrow$ $^{18}_8$O + $^0_{+1}\beta$

○ Electron Capture:

- · Electron capture consumes an electron to convert a proton into a neutron

- Balance the electron capture decay of $^{11}_{6}C$: $\quad ^{11}_{6}C + ^{0}_{-1}e \longrightarrow ^{11}_{5}B$

○ $^{40}_{19}K$ decays into $^{40}_{18}Ar$ 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 $^{238}_{92}U$

○ Measuring radioactivity:

- Activity is defined as disintegrations per unit time
- The becquerel is the SI unit: $1\ Bq = 1\ \dfrac{d}{s}$
- The curie is a much more useful unit: $1\ Ci = 3.7 \times 10^{10}\ Bq$
- A Geiger counter is a common instrument for measuring radioactivity
- Radioisotopes can be used as *tracers* in medical imaging, and in determining reaction mechanisms

○ Half-lives

- Decay activity depend only the number of radioactive nuclides present $A = kN$
- This is just a form of 1st-order kinetics: $rate = k\,[\mathrm{A}]$
- 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: $\ln\left(\dfrac{N_0}{N}\right) = \left(\dfrac{\ln 2}{T_{1/2}}\right)t$
- A $10.0\ g$ sample of ^{131}I $(t_{1/2} = 8\ d)$ is left out for 2 weeks. How many g remain? $(10\ g \cdot e^{-1.213} = 2.97\ g)$
- Rearrange the above eqution to get: $t = ln\left(\dfrac{N_0}{N}\right)\left(\dfrac{t_{1/2}}{\ln 2}\right)$
- ^{90}Sr has $t_{1/2} = 28.8\ y$. How long does it take for a ^{90}Sr sample to decay to $\dfrac{1}{3}$ of its initial amount? $(45.6\ y)$

○ 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}U and ^{206}Pb, or ^{40}K and ^{40}Ar can give dates on the order of billions of years

- ^{238}U has $t_{1/2} = 4.47 \times 10^9\ y$ and ^{40}K has $t_{1/2} = 1.250 \times 10^9\ y$
- Calculate the age of a rock which contains $5.5\ g$ of ^{206}Pb and $29.6\ g$ of ^{238}U $(1.3 \times 10^8\ y)$
- Carbon dating:
    * ^{14}C has $t_{1/2} = 5730\ y$
    * ^{14}C is also useful because it is naturally generated in the upper atmosphere, at rates that keep the ^{14}C abundance in the atmosphere constant
    * ^{14}C is then incorporated into living tissues of plants and animals at that same abundance
    * Once an organism dies, its ^{14}C decays and we can use it to predict the date of death
    * The ^{14}C decay product (^{14}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 $15.3\ \dfrac{d}{min\ g}$, and an ancient wooden tool exhibits an activity of $14.4\ \dfrac{d}{min\ g}$. How old is the wooden tool? $(501\ y)$

21.4   Transmutation and Nuclear Energy

- 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 α particle)
    - Figure 20.9 shows the most common nuclear fission reaction:
      $^{235}_{92}$U + $^{1}_{0}$n $\longrightarrow$ $^{141}_{56}$Ba + $^{92}_{36}$Kr + 3 $^{1}_{0}$n
    - This reaction requires a neutron to initiate, and that neutron must have low kinetic energy
    - Becaues 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}U or ^{239}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}U or ^{239}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:
  $$^{235}_{92}U + \, ^{1}_{0}n \longrightarrow \, ^{137}_{52}Te + \, ? + 2 \, ^{1}_{0}n \qquad \left(^{97}_{40}Zr \right)$$

○ Nuclear Fusion

- Some reactions will combine nuclides to create bigger ones
- These reactions are called *fusion* reactions
- Fusion reactions power the sun itself
  - $^{1}_{1}H + \, ^{1}_{1}H \longrightarrow \, ^{2}_{1}H + \, ^{0}_{+1}\beta$
  - $^{1}_{1}H + \, ^{2}_{1}H \longrightarrow \, ^{3}_{2}He + \, ^{0}_{0}\gamma$
  - $^{3}_{2}He + \, ^{3}_{2}He \longrightarrow \, ^{4}_{2}He + 2 \, ^{1}_{1}H$
  - $^{2}_{1}H$ is called deuterium, and its nucleus is called a deuteron
  - $^{3}_{1}H$ 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

○ Energetics of nuclear reactions and nuclear binding energy

- 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: $^{238}_{92}U \longrightarrow \, ^{234}_{90}Th + \, ^{4}_{2}He$

Isotope	Mass (u) or $\left(\dfrac{g}{mol} \right)$
$^{238}_{92}U$	238.00033
$^{234}_{90}Th$	233.99423
$^{4}_{2}He$	4.00151

  - Adding up the products gives a mass $0.00459 \, \dfrac{g}{mol}$ less than the mass of $^{238}_{92}U$
  - This change is mass can be used to find the energy released: $\Delta E = \delta mc^2$ (convert to kg)

* So, the reaction released $4.125 \times 10^{11} \; \dfrac{J}{mol}$, or $4.125 \times 10^8 \; \dfrac{kJ}{mol}$
        * Note that this is 100,000 times more energy than any chemical reactions
        * This is an α-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
  · We can see a similar mass/energy relationship in any nucleus
  · Consider a helium nucleus:

Particle	Mass (u) or $\left(\dfrac{g}{mol}\right)$
proton ^1_1p	1.00728
neutron ^1_0n	1.00866
^4_2He	4.00151

        * The mass of ^4_2He is less than the sum of its parts by $0.03037 \; \dfrac{g}{mol}$!
        * 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

21.5   Uses of Radioisotopes

21.6   Biological Effects of Radiation

ERRATA

- Just general typographical inconsistency. Some chemical formulas are in normal font with subscripts and superscripts, while some chemical formulas are written in TeX and rendered with MathJax (probably). It would be a great improvement to make formulas consistently in TeX.

- The solution to problem 15.78 a) shows PH_3 as a cation in the Lewis structure, when it should be neutral