

CHEM 1220 Lecture Notes

OpenStax Chemistry 2e

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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 O

121O REVIEW

There is a whole semester of material from 121O, and these are only the topics which are *most* important for success in 122O

- 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 121O 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 relative 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 rearrangements I've made)

$$P = Ae^{-\Delta H_{vap}/RT} \quad \ln P = -\frac{\Delta H_{vap}}{RT} + \ln A \quad \ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$
- 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 malleable 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 malleable and ductile, and conduct electricity 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 $19.283\text{g}/\text{cm}^3$ (136pm)
 - Find the density of polonium, which has sc structure and an atomic radius of 140pm ($9.20\text{g}/\text{cm}^3$)
 - 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 density of 2.17 g/cm^3 ($l = 564\text{ pm}$)
- 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

CHAPTER 11

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:

$$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$$
- Ionic compounds will dissolve into individual ions:

$$\text{Na}_2\text{SO}_3(\text{s}) \longrightarrow \text{Na}_2\text{SO}_3(\text{aq}) \longrightarrow 2 \text{Na}^+(\text{aq}) + \text{SO}_3^{2-}(\text{aq})$$
- 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 NH₄NO₃(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

$$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$$

11.3 Solubility

- 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 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 dependence 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 $\frac{m_{solute}}{m_{total}} \times 100\%$
 - *Mole fraction* is $\chi_A = \frac{n_A}{n_{total}}$
 - *Molality* is $m = \frac{moles_{solute}}{kg_{solvent}}$
 - 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: $P_A = \chi_A P_A^*$
 - If the solute is a liquid, we can apply Rault's law to the solute as well $P_{total} = \chi_A P_A^* + \chi_B P_B^*$

- 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 transition temperatures
 - Boiling point elevation is a consequence of vapor pressure lowering
 - Freezing point depression follows a similar formula
 - $\Delta T_{f/b} = iK_{f/b}m$
 - 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
 - $\pi = \frac{i n R T}{V} = i M R T$
 - 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 boundary 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

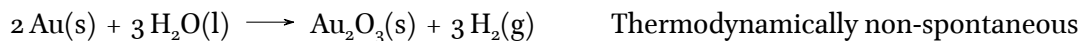
- 11.49: Molar mass from boiling point
- 11.59: Molar mass from osmotic pressure
- 11.73: Colloid particle size

CHAPTER 12

KINETICS

12.1 Chemical Reaction Rates

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



- Kinetics is the study of reaction rates (how quickly the reaction proceeds)
- The reaction rate is the rate of disappearance of reactant or production of product, normalized by the stoichiometric coefficients

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

- 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 $2 \text{H}_2\text{O}_2\text{(aq)} \longrightarrow 2 \text{H}_2\text{O(l)} + \text{O}_2\text{(g)}$ (Figures 12.2 and 12.3)

$$\text{rate} = -\frac{d[\text{H}_2\text{O}_2]}{2dt} = \frac{d[\text{H}_2\text{O}]}{2dt} = \frac{d[\text{H}_2]}{dt}$$

$$\text{rate} \approx -\frac{\Delta[\text{H}_2\text{O}_2]}{2\Delta t} = \frac{\Delta[\text{H}_2\text{O}]}{2\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t}$$

- Practice: Consider $2 \text{NH}_3\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + 3 \text{H}_2\text{(g)}$ (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 reaction doesn't practically happen at all
- Many factors affect rates, including some that can be controlled and some that cannot
- The physical 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 $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$, $\text{rate} = k [\text{A}]^m [\text{B}]^n$
 - 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: $-\frac{d[A]}{dt} = k[A]^m$
- Rearrange this to separate the infinitesimal terms and integrate: $\int \frac{d[A]}{[A]^m} = \int -k dt$
- 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: $\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt$
 - Special Half-life form: $\frac{A_t}{A_0} = \left(\frac{1}{2} \right)^{\frac{t}{t_{1/2}}}$
 - Half-life: $t_{1/2} = \frac{\ln 2}{k}$
 - Linear when plotting $\ln[A]$ vs t , with *slope* = $-k$
- Second-order
 - Linear form: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
 - Half-life: $t_{1/2} = \frac{1}{k[A]_0}$
 - Linear when plotting $\frac{1}{[A]}$ vs t , with *slope* = $+k$
- Zeroth-order
 - Linear form: $[A]_t = -kt + [A]_0$
 - Half-life: $t_{1/2} = \frac{[A]_0}{2k}$
 - 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 $\frac{1}{[A]}$ 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 $\frac{J}{mol}$, so we should use $R = 8.314 \frac{J}{mol\ K}$
 - The exponential term is called a Boltzmann factor, and gives the fraction of collisions which have enough energy
 - Figure 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
 - $\ln k = \ln (Ae^{-E_a/RT})$ becomes $\ln k = \ln A - \frac{E_a}{RT}$
 - If we plot the $\ln k$ at different temperatures against $\frac{1}{T}$, we get a linear equation
 - The slope of the line is $-\frac{E_a}{RT}$ and the intercept is $\ln A$
 - We can also create the two-point form of this equation: $\ln \left(\frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ (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: $2 \text{HI(g)} \longrightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$
 At 655 K the rate constant is $8.15 \times 10^{-8} \frac{1}{\text{M s}}$ and at 705 K the rate constant is $1.39 \times 10^{-6} \frac{1}{\text{M s}}$
 Determine the activation energy and frequency factor for this reaction $\left(218 \frac{\text{kJ}}{\text{mol}} \text{ and } 1.91 \times 10^{10} \frac{1}{\text{M s}} \right)$

Quiz 12.3 - Arrhenius Equation

Homework 12.3

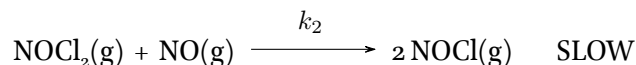
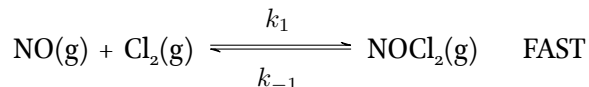
- 50: Factors in collision theory
- 58: Determining the frequency factor
- 62: Determining the activation energy

12.6 Reaction Mechanisms

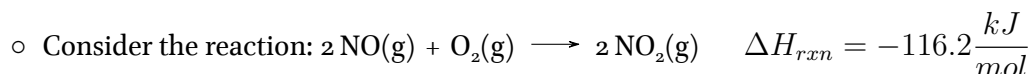
- My figure about how we often don't think about the *mechanics* of how chemical reactions proceed
- Chemical reaction *can* happen in just one step, but often proceed in two or more distinct steps
- The details of how a reaction actually proceeds is called the Reaction Mechanism
- Each step in the mechanism 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: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
 - Elementary Step 1: $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{NO}_3(\text{g})$ SLOW
 - Elementary Step 2: $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$ FAST
- The two steps add up to the total equation
- $\text{NO}_3(\text{g})$ is produced in the first step, then consumed in the second step, so it never shows up in the overall reaction
- This makes $\text{NO}_3(\text{g})$ an *intermediate*
- Intermediates are different from transition states because they are energetically stable (minimum in the reaction coordinate diagram)
- Intermediates may sometimes be observed directly in the course of the reaction, or they may be so dilute or so short-lived that they cannot be observed
- 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: $\text{AB} \longrightarrow \text{A} + \text{B}$ (cyclobutane decomposition figure)
 - * Bimolecular steps involve an encounter between two molecules: $\text{A} + \text{B} \longrightarrow \text{C}$ or $2\text{A} \longrightarrow \text{B}$ (Figure 12.17)
 - * Termolecular steps are very rare, but can occur
 - The rate law can be inferred from the stoichiometry of the step
 - * $\text{AB} \longrightarrow \text{A} + \text{B}$ gives $\text{rate} = k[\text{AB}]$
 - * $\text{A} + \text{B} \longrightarrow \text{C}$ gives $\text{rate} = k[\text{A}][\text{B}]$
 - * $2\text{A} \longrightarrow \text{B}$ gives $\text{rate} = k[\text{A}]^2$
 - 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 $\text{rate} = k[\text{NO}_2]^2$
- Any proposed mechanism must, at a minimum, add up to the total equation, and produce a rate law consistent with observations
- This is not conclusive proof of a mechanism's validity, as one could contrive infinite mechanisms within these two constraints
- Some elementary steps are reversible, and establish an equilibrium (subject of the next chapter):

- Consider the reaction $2 \text{NO(g)} + \text{Cl}_2\text{(g)} \longrightarrow 2 \text{NOCl(g)}$ $rate = k [\text{NO}]^2 [\text{Cl}_2]$
- This observed rate law seems consistent with a single-step *termolecular* mechanism, but termolecular reactions are exceptionally rare
- An alternative proposed mechanism is:



- The first step will reach an equilibrium, where the forward rate will equal the reverse rate
 $k_1 [\text{NO}] [\text{Cl}_2] = k_{-1} [\text{NOCl}_2]$
- Rearrange this to give the equilibrium concentration of the intermediate $[\text{NOCl}_2] = \frac{k_1}{k_{-1}} [\text{NO}] [\text{Cl}_2]$
- The reaction rate is ultimately determined by the formation of product in the second step:
 $rate = k_2 [\text{NOCl}_2] [\text{NO}]$
- Substitute in our expression for $[\text{NOCl}_2]$
 $rate = k_2 \left(\frac{k_1}{k_{-1}} [\text{NO}] [\text{Cl}_2] \right) [\text{NO}] = \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{Cl}_2]$



- The observed rate law is: $rate = k [\text{NO}]^2 [\text{O}_2]$
- A proposed mechanism is:
 $\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons \text{NO}_3\text{(g)} \quad \text{FAST}$
 $\text{NO(g)} + \text{NO}_3\text{(g)} \longrightarrow 2 \text{NO}_2\text{(g)} \quad \text{SLOW}$
- Is the reaction mechanism consistent with the observed rate law?
- What is the value of k in terms of the elementary step rate constants?
- Draw a basically accurate reaction coordinate diagram for this reaction

- Reaction mechanisms can become complex and interesting for certain reactions (harpoon mechanism and collisional activation)

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 the reaction mechanism, being first *consumed*, then *regenerated*
- The reaction $2 \text{H}_2\text{O}_2\text{(aq)} \longrightarrow 2 \text{H}_2\text{O(l)} + \text{O}_2\text{(g)}$ can be catalyzed by HBr(aq)
 $\text{H}_2\text{O}_2\text{(aq)} + 2 \text{HBr(aq)} \longrightarrow \text{Br}_2\text{(aq)} + 2 \text{H}_2\text{O(l)} \quad \text{SLOW}$
 $\text{Br}_2\text{(aq)} + \text{H}_2\text{O}_2\text{(aq)} \longrightarrow \text{O}_2\text{(g)} + 2 \text{HBr(aq)} \quad \text{FAST}$

- 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:

$$\text{C}_3\text{H}_6(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{C}_3\text{H}_7^+(\text{aq})$$

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

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

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

CHAPTER 13

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

$$\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g}) \text{ and } 2 \text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$$
- 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: $rate_f = k_f[\text{N}_2\text{O}_4]$ and $rate_r = k_r[\text{NO}_2]^2$
 - 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: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
- Figure 13.4 illustrates how vapor pressure is an equilibrium process ($\text{Br}_2(\text{l}) \rightleftharpoons \text{Br}_2(\text{g})$)

13.2 Equilibrium Constants

- The current concentrations of reactants and products can be summarized with the *reaction quotient* Q
- For a generic reaction: $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$ the reaction quotient is:

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

$$Q_P = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$
- For heterogeneous reactions, we exclude (s) and (l) species from Q and K (reasons for this are a bit complex)

- Practice with the equation: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ ($K_{C,300\text{K}} = 2.7 \times 10^8$)
- 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 $\text{N}_2(\text{g})$ alone or $\text{H}_2(\text{g})$ 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: $K_p = \frac{K_c}{(RT)^2}$

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: $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
 - * Find K_c if $[\text{CO}] = 0.0600\text{ M}$, $[\text{H}_2\text{O}] = 0.120\text{ M}$, $[\text{CO}_2] = 0.150\text{ M}$, and $[\text{H}_2] = 0.300\text{ M}$
 - * 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
 - * $\text{CH}_3\text{CO}_2\text{H(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{CH}_3\text{CO}_2^-\text{(aq)} \quad K = 1.8 \times 10^{-5}$
 - * Find $[\text{H}_3\text{O}^+]$ if $[\text{CH}_3\text{COOH}] = 0.250\text{ M}$ and $[\text{CH}_3\text{COO}^-] = 0.350\text{ M}$
 - We can easily find K for doubled, reversed, or added equations (*not in your text*)
 - * For a reversed equation, reactants and products switch, so $K_{\text{reverse}} = K_{\text{normal}}^{-1}$
 - * For a doubled (or tripled) reaction, K should be squared (or cubed)
 - * For added reactions (multi-step) $K_{\text{total}} = K_1 K_2$
 - Find K for the reaction: $\text{N}_2\text{(g)} + 2\text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$

$$\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)} \quad K = 2.0 \times 10^{-25}$$

$$2\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)} \quad K = 6.4 \times 10^9$$

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 $2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$
How would the reaction shift if each species is added or removed in turn?
- Changing volume
 - If the reaction volume changes, all the concentrations or pressures will change together
 - The effect this has depends on the stoichiometry of the reaction
 - Consider the reaction $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ – How will the reaction quotient change if the volume doubles?
 - The shift depends on 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 $\Delta_n = 0$, 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 equilibrium
- 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 M before you put them into the equilibrium expression
- Consider the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 5.00 mol H_2 and 0.500 mol I_2 are reacted in a 1.00 L chamber and at equilibrium $[\text{HI}] = 0.900\text{ M}$.
 Find the value of K_C (324)
- Consider the reaction $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \quad K_C = 5.80$
 Find the equilibrium conditions if initial concentrations are: $[\text{CO}] = [\text{H}_2\text{O}] = 0.0125\text{ M}$
- Often the equilibrium expression will lead to a quadratic equation when solving for x
- The quadratic formula is: $ax^2 + bx + c = 0 \rightarrow x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
- Consider the reaction: $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g}) \quad K_{P,1000\text{K}} = 0.260$
 Find the equilibrium conditions if a reaction chamber is initially charged with 0.200 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 $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq}) \quad K_C = 1.8 \times 10^{-4}$
 Find the equilibrium conditions for a solution that begins with $[\text{HCOOH}] = 0.250\text{ M}$

Quiz 13.4 - ICE Tables

Homework 13.4

- 54: Calculate K using an ICE table
- 76: Use ICE table to calculate equilibrium amounts
- 88: Calculate pressures using an ICE table

CHAPTER 14

ACID-BASE EQUILIBRIA

- 14.1 Brønsted-Lowry Acids and Bases
- 14.2 pH and pOH
- 14.3 Relative Strengths of Acids and Bases
- 14.4 Hydrolysis of Salts
- 14.5 Polyprotic Acids
- 14.6 Buffers
- 14.7 Acid-Base Titrations

CHAPTER 15

EQUILIBRIA OF OTHER REACTION CLASSES

15.1 Precipitation and Dissolution

15.2 Lewis Acids and Bases

15.3 Coupled Equilibria

CHAPTER 16

THERMODYNAMICS

16.1 Spontaneity

16.2 Entropy

16.3 The Second and Third Laws of Thermodynamics

16.4 Free Energy

CHAPTER 17

ELECTROCHEMISTRY

- 17.1 Review of Redox Chemistry**
- 17.2 Galvanic Cells**
- 17.3 Electrode and Cell Potentials**
- 17.4 Potential, Free Energy, and Equilibrium**
- 17.5 Batteries and Fuel Cells**
- 17.6 Corrosion**
- 17.7 Electrolysis**

CHAPTER 21

NUCLEAR CHEMISTRY

- 21.1 Nuclear Structure and Stability**
- 21.2 Nuclear Equations**
- 21.3 Radioactive Decay**
- 21.4 Transmutation and Nuclear Energy**
- 21.5 Uses of Radioisotopes**
- 21.6 Biological Effects of Radiation**

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