

# 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

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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

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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 ( $\Delta H_{vap}$ ) 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  $\Delta H_{change}$  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<sub>2</sub>
- 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<sub>2</sub>
- 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 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  $19.283g/cm^3$  ( $136pm$ )
  - Find the density of polonium, which has sc structure and an atomic radius of  $140pm$  ( $9.20g/cm^3$ )
  - 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  $2.17\text{ g/cm}^3$  ( $l = 564\text{ pm}$ )
- 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

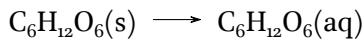
## SOLUTIONS AND COLLOIDS

**11.1 The Dissolution Process**

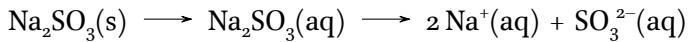
- Some vocabulary: *Solution, Solvent, Solute, and solvation*

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

- Molecular compounds dissolve to form one solute:



- Ionic compounds will dissolve into individual ions:



- 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<sub>4</sub>NO<sub>3</sub>(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



### 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  $\text{NaCH}_3\text{CO}_2$ )

- 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!)
 
$$C_{\text{gas}} = k_H P_{\text{gas}}$$
- 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*  $\Delta H_{\text{solv}}$  leads to lower solubility at higher temperatures
  - *Endothermic*  $\Delta H_{\text{solv}}$  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  $m = \frac{\text{moles}_{solute}}{kg_{solvent}}$
  - 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 produced 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
  - Raoult's law:  $P_A = \chi_A P_A^*$
  - If the solute is a liquid, we can apply Raoult'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 applied pressure can reverse this process and purify water
  - $$\pi = \frac{inRT}{V} = iMRT$$
  - 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 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**

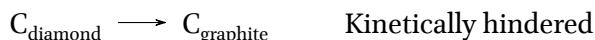
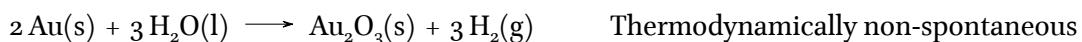
- 11.49: Molar mass from boiling point
- 11.59: Molar mass from osmotic pressure
- 11.73: Colloid particle size

## 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  $\text{H}_2\text{SO}_4$  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  $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$ ,  $rate = k [\text{A}]^m [\text{B}]^n$
  - $m$  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 on 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

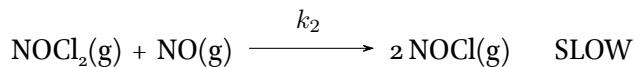
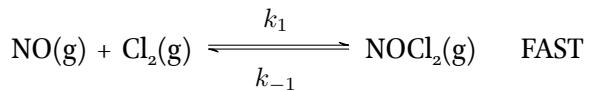
- My figure about how we often don't think about the *mechanics* of how chemical reactions proceed
- Chemical reaction *can* happen in just one step, but often proceed in two or more distinct steps
- The details of how a reaction actually proceeds is called the Reaction Mechanism
- Each step in the mechanism 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  $\text{NO}_2$  and  $\text{CO}$  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  $2 \text{NO(g)} + \text{Cl}_2(\text{g}) \longrightarrow 2 \text{NOCl(g)}$   $\text{rate} = k [\text{NO}]^2 [\text{Cl}]$
- 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:  
 $\text{rate} = k_2 [\text{NOCl}_2] [\text{NO}]$
- Substitute in our expression for  $[\text{NOCl}_2]$   
 $\text{rate} = k_2 \left( \frac{k_1}{k_{-1}} [\text{NO}] [\text{Cl}_2] \right) [\text{NO}] = \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{Cl}_2]$
- Consider the reaction:  $2 \text{NO(g)} + \text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g}) \quad \Delta H_{rxn} = -116.2 \frac{\text{kJ}}{\text{mol}}$ 
  - The observed rate law is:  $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$
  - A proposed mechanism is:  
 $\text{NO(g)} + \text{O}_2(\text{g}) \rightleftharpoons \text{NO}_3(\text{g}) \quad \text{FAST}$   
 $\text{NO(g)} + \text{NO}_3(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g}) \quad \text{SLOW}$
  - 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  $\text{HBr(aq)}$   
 $\text{H}_2\text{O}_2(\text{aq}) + 2 \text{HBr(aq)} \longrightarrow \text{Br}_2(\text{aq}) + 2 \text{H}_2\text{O(l)} \quad \text{SLOW}$   
 $\text{Br}_2(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g}) + 2 \text{HBr(aq)} \quad \text{FAST}$

- 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

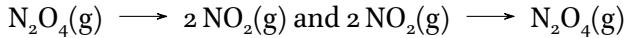
## CHAPTER 13

## FUNDAMENTAL EQUILIBRIUM CONCEPTS

**13.1 Chemical Equilibria**

- Figure 13.1 illustrates how CO<sub>2</sub> in our blood and blood pH are mediated by equilibrium reactions

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



- Such reactions will reach an equilibrium

- Equilibrium is when the forward reaction rate and the reverse reaction rate are equal
- 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:  $\text{mA} + \text{nB} \rightleftharpoons \text{xC} + \text{yD}$  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:  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$  ( $K_{C,300K} = 2.7 \times 10^8$ )
- 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  $\text{N}_2(\text{g})$  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  $[\text{CO}] = 0.0600 \text{ M}$ ,  $[\text{H}_2\text{O}] = 0.120 \text{ M}$ ,  $[\text{C}_2\text{O}] = 0.150 \text{ M}$ , 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  $K_{reverse} = K_{normal}^{(1)} - 1$
    - \* 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:  $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$   
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO(g)} \quad K = 2.0 \times 10^{-25}$   
 $2 \text{NO(g)} + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) \quad K = 6.4 \times 10^9$

### Quiz 13.2 - Working with K

#### Homework 13.2

- 19: Predict direction to reach equilibrium
- 25: Convert  $K_C$  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  $\Delta_n$ , considering only the moles of gas or aqueous substances
  - If volume increases (dilution), the reaction will shift to the side with *more* moles
  - If volume decreases (concentration), the reaction will shift to the side with *fewer* moles
  - If  $\Delta_m = 0$ , 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  $\Delta H_{rxn}$
  - We will explore this relationship mathematically later, but for now we can use a trick to determine the direction of the shift
  - Consider “heat” as a reactant for endothermic reactions, and as a product for exothermic reactions
  - Heat is not really a product or reactant (how many  $\text{g}$  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  $\text{[ ]}$  before you put them into the equilibrium expression
- Consider the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$   
 $5.00 \text{ mol H}_2$  and  $0.500 \text{ mol I}_2$  are reacted in a  $1.00 \text{ L}$  chamber and at equilibrium  $[\text{HI}] = 0.900 \text{ M}$ .  
 Find the value of  $K_C$  (324)
- Consider the reaction  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \quad K_C = 5.80$   
 Find the equilibrium conditions if initial concentrations are:  $[\text{CO}] = [\text{H}_2\text{O}] = 0.0125 \text{ M}$
- Often the equilibrium expression will lead to a quadratic equation when solving for  $x$ 
  - The quadratic formula is:  $ax^2 + bx + c = 0 \rightarrow x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
  - Consider the reaction:  $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g}) \quad K_{P,1000K} = 0.260$   
 Find the equilibrium conditions if a reaction chamber is initially charged with  $0.200 \text{ atm I}$  and  $0.00500 \text{ atm I}_2$
  - Some quadratic equations can be greatly simplified by recognizing when  $x$  is small compared to initial amounts
    - If  $x$  is small, then it can be neglected from any species with an initial amount
    - First solve the equation *assuming* that  $x$  can be neglected
    - Compare the solved value of  $x$  to the amounts it was neglected from
    - If  $x$  is less than 5% of those values then your simplification was valid
    - If not, then you must go back and solve the complete quadratic equation
  - Consider the reaction  $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq}) \quad K_C = 1.8 \times 10^{-4}$   
 Find the equilibrium conditions for a solution that begins with  $[\text{HCOOH}] = 0.250 \text{ M}$

#### Quiz 13.4 - ICE Tables

**Homework 13.4**

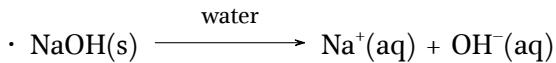
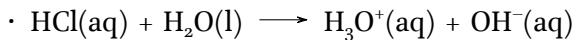
- 54: Calculate  $K$  using an ICE table
- 76: Use ICE table to calculate equilibrium amounts
- 88: Calculate pressures using an ICE table

## CHAPTER 14

## ACID-BASE EQUILIBRIA

## 14.1 Brønsted-Lowry Acids and Bases

- Arrhenius acid/base theory defines acids and bases in terms of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions



- $\text{H}^+$  vs  $\text{H}_3\text{O}^+$

- In the past, you may have used  $\text{H}^+(\text{aq})$  in your equations
- I will tend to use  $\text{H}_3\text{O}^+$  instead, but either way is acceptable
- Really,  $\text{H}^+$  is a flagrant lie. Bare protons don't exist in water.  $\text{H}_3\text{O}^+$  is also a little bit of a lie. The extra proton and the charge create clusters of many water molecules. It gets really complicated

- Arrhenius theory is unable to account for reactions that don't involve  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions directly

- Consider  $\text{HNO}_2(\text{aq}) + \text{ClO}_2^-(\text{aq}) \rightleftharpoons \text{HClO}_2(\text{aq}) + \text{NO}_2^-(\text{aq})$  – should this reaction be considered acid/base?

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

- $\text{HNO}_2$  is the acid, and  $\text{ClO}_2^-$  is the base

- Conjugate pairs

- We can also consider the reverse reaction, where  $\text{HClO}_2$  is the acid and  $\text{NO}_2^-$  is the base
- We call these linked species *conjugate pairs*
- $\text{HNO}_2$  is the conjugate acid to  $\text{NO}_2^-$ , while  $\text{NO}_2^-$  is the conjugate base to  $\text{HNO}_2$
- The strengths of a conjugate pair are inverse to each other – A stronger acid has a weaker conjugate base and vice-versa

- Some acids are *multiprotic* and some bases are *multibasic*

- Consider the series  $\text{H}_2\text{SO}_3 \rightleftharpoons \text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-}$
- Or the series  $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-}$
- $\text{H}_2\text{SO}_3$  is a diprotic acid, and  $\text{SO}_3^{2-}$  is a dibasic base because they can exchange 2 protons
- $\text{H}_3\text{PO}_4$  is a triprotic acid, and  $\text{PO}_4^{3-}$  is a tribasic base because they can exchange 3 protons
- The intermediates,  $\text{HSO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  can act as either an acid or a base
- These types of ions are called *amphoteric* or *amphiprotic*
- Whether they act as an acid or a base depends on the context – what is their reaction partner

## 14.2 pH and pOH

- Autoionization of Water

- Water is also amphoteric:  $\text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{O} \rightleftharpoons \text{OH}^-$
- Because of this, water will undergo autoionization:  $2 \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_w = 1.00 \times 10^{-14}$
- For pure water, this leads to concentrations of  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7}$
- This water ionization equilibrium is the great arbiter of acid/base chemistry. It defines what is an acid, what is a base, and what are their various strengths
- Even for reactions which don't explicitly contain water ( $\text{NH}_3(\text{aq}) + \text{HNO}_2(\text{aq}) \longrightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq})$ ), water is actually mediating the proton exchange behind the scenes
- Because of this, acidity and basicity are defined by the balance between  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  (Table 14.1)
  - \*  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  is an acid
  - \*  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$  is a base
  - \*  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  is neutral
- We can always find  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  from the other, based on  $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$

- Acidity of a solution is summarized by the quantity  $pH = -\log [\text{H}_3\text{O}^+]$
- 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  $[\text{H}_3\text{O}^+]$  by  $[\text{H}_3\text{O}^+] = 10^{-pH}$
- Table 14.2 shows both the  $pH$  and  $[\text{H}_3\text{O}^+]$  for several common substances
- We can make similar calculations for  $[\text{OH}^-]$  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  $[\text{H}_3\text{O}^+]$  across a wide range

## Quiz 14.1 - pH and pOH Calculations

### Homework 14.1

- 19:  $pH$  and  $pOH$  of strong acid/base solutions
- 21:  $[H^+]$  and  $[OH^-]$  from  $pH$
- 25:  $[H^+]$  from  $[OH^-]$

### 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:  $K_a = \frac{[A^-][H_3O^+]}{[HA]}$
  - Weak bases always follow the same format:  $K_b = \frac{[HB^+][OH^-]}{[B]}$
  - We will often be able to use the simplification that the change is much less than the initial amounts
- Find the  $pH$  for a  $0.250\text{ F}$  solution of nitrous acid ( $K_a = 4.0 \times 10^{-4}$ )
- Find the  $pH$  for a  $0.325\text{ F}$  solution of pyridine ( $K_b = 1.7 \times 10^{-9}$ )
- A few useful relations that are not in your textbook:
  - For conjugate acid/base pairs:  $K_a K_b = K_w$

- For the reaction between an acid and a base:  $K = \frac{K_a K_b}{K_w}$
- 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:
  - $\text{NH}_4^+$  and others based off of it are weak acids
  - Some metal cations can act as acids – we will cover this more in the Lewis Acids section
- The anions are usually where the activity lies:

- Many anions are neutral, such as the conjugates to strong acids
- Some anions are amphoteric, and their effect depends on their  $K_a$  and  $K_b$  values
- If  $K_a > K_b$ , then the anion will be acidic, and if  $K_a < K_b$ , then the ion will be basic
- Some anions are simply weak bases
- You can then find the  $pH$  based on the acid/base activity of the individual ions
- Find the  $pH$  of a  $0.125\text{ M}$  solution of  $\text{CaF}_2$
- 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  $\text{H}^+$  is donated
  - Figure 14.13 shows this process for  $\text{Al}^{3+}$
  - 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,  $[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]$ ,  $[\text{HC}_6\text{H}_6\text{O}_6^-]$ , and  $[\text{C}_6\text{H}_6\text{O}_6^{2-}]$  for a  $0.500\text{ F}$  solution of Ascorbic acid
  - First, solve the ICE table for the first deprotonation
  - Then, use the  $[\text{H}_3\text{O}^+]$  and  $[\text{HC}_6\text{H}_6\text{O}_6^-]$  as starting values for the second deprotonation
  - Because the  $[\text{H}_3\text{O}^+]$  will not change much, we don't have to revisit the first equilibrium

### 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

## Lewis Acids: Not in the text

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

$$\text{Al}^{3+}(\text{aq}) + 6 \text{H}_2\text{O(l)} \longrightarrow \text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq})$$
- Carbonic acid makes gas due to Lewis acid action:  $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$

### Quiz 14.4 - Lewis Acids

#### No Associated Homework

## 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:  $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
    - \* Adding  $\text{NaNO}_2$  will affect this equilibrium because it adds nitrite ion to solution
    - \* Le Châtelier's principle will shift the reaction left, reducing the effect  $\text{HNO}_2$  has on  $pH$
    - \* Any equilibrium reaction involving ions can be affected by addition of other salts containing those ions – This is the common ion effect
  - Buffer solutions contain amounts of both members of a weak conjugate acid/base pair
    - \* Adding strong acid or strong base to the buffer will react with the weak base/acid rather than with water, resulting in a suppressed change in  $pH$

- \* Figure 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:  $[H_3O^+] = K_a \frac{[HA]}{[A^-]}$
  - We can calculate the  $pH$  from here to be:  $pH = pK_a - \log \frac{[HA]}{[A^-]}$
  - 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  $\pm 1$  of  $pK_a$ , the buffer capacity is exceeded and the buffer will stop working
    - \* Higher concentrations of HA and  $A^-$  can absorb more acid or base before its capacity is exceeded
  - $H_2S$  has  $K_a = 9.1 \times 10^{-8}$ . Find the  $pH$  of a solution if 2.7 g of  $H_2S$  and 1.5 g of NaHS are dissolved in 0.50 L of water
  - $H_2PO_4^-$  has  $pK_a = 6.8$  and is responsible for regulating the  $pH$  of blood at  $pH = 7.4$ .
    - \* If  $[HPO_4^{2-}] \approx 0.200 M$ , find the  $[H_2PO_4^-]$  to maintain proper blood  $pH$
    - \* How many g of HCl could be added to 5.0 L of blood before the buffer capacity is exceeded?
    - \* How many g of NaOH could be added to 5.0 L of blood before the buffer capacity is exceeded?

### Quiz 14.5 - Buffer Solutions

#### Homework 14.5

- 78: Mechanism of acid/base buffers
- 80:  $[H_3O^+]$  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
- Figures 17.3 and 17.4 show typical titration setups, with different methods of determining the exact point where the analyte is consumed (called the *equivalence point*)
- Figure 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,  $pH = -\log [H_3O^+] = -\log [HA]$
  - In region B the base is reacting with the acid and causing the  $pH$  to rise
  - Solve the  $pH$  using a BCA table
  - At point C, the equivalence point, the base has precisely neutralized the acid, and  $pH = 7.00$  exactly
  - In region D, the  $pH$  changes as excess base is added
- 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 14.6 - 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
    - \*  $\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{A}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
    - \* HA is one color, and  $\text{A}^-$  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  $\text{A}^-$  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  $\text{A}^-$  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 14.7 - Weak Acid-Base Titrations

#### Homework 14.7

- 92: Choosing an appropriate color indicator
- 94:  $pH$  at different points of a weak acid titration

CHAPTER 15

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EQUILIBRIA OF OTHER REACTION CLASSES

**15.1 Precipitation and Dissolution**

**15.2 Lewis Acids and Bases**

**15.3 Coupled Equilibria**

CHAPTER 16

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THERMODYNAMICS

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**16.2 Entropy**

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CHAPTER 17

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CHAPTER 21

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NUCLEAR CHEMISTRY

**21.1 Nuclear Structure and Stability**

**21.2 Nuclear Equations**

**21.3 Radioactive Decay**

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**21.5 Uses of Radioisotopes**

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