CHEM 1210 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 - 20, Online Homework - 15, Book Homework - 15, Quizzes - 10
- 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
- Submerged salt crystals grow due dynamic equilibrium
- Rubber band elasticity
- Structure of the periodic table
- Salt on ice and purifying hydrogen peroxide

CHAPTER 1

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ESSENTIAL IDEAS

1.1 Chemistry in Context

- Modern chemistry is the end result of thousands of years of humans trying to explain and control the materials around them

- Early forays into chemistry (such as alchemy) had deep mystical roots and often relied on serendipity to make good progress

- Modern chemistry is a rigorous science, relying on falsifiability and the scientific methd (Figure 1.4)

- We sometimes refer to chemistry as "The Central Science" (Figure 1.3)

- To adequately describe and understand chemical phenomena, we often talk from different perspectives

  Macroscopic Domain This is what we observe with bulk substances. Two chemicals react to produce a new chemical

  Microscopic Domain We now understand that all microscopic effects are governed by the behavior of *microscopic* actors (molecules, atoms, electrons, etc.)

  Symbolic Domain Effectively communicating chemical ideas requires new language. Chemical formulas, equations, and mechanisms are all symbolic representations

  All three domains are on display in Figure 1.5

Quiz 1.1 - Scientific Method

Homework 1.1

- 1: Thinking in terms of Chemistry

- 3: The scientific method

- 5: Domains of inquiry

1.2 Phases and Classification of Matter

- Three primary phases of matter are shown in Figure 1.5 (and 1.6)

- Plasmas are like a gas, but with electrically charged particles

- Mass vs Weight (for very fine measurements, the difference matters even on Earth due to buoyancy)

○ Figure 1.8 illustrates the *law of conservation of matter*

○ Classifying matter (Figure 1.11)

　· Pure Substances

　　∗ Elements (Anything on the *periodic table of the elements*)

　　∗ Compounds (Combinations of elements – can have very different properties from their constituent elements)

　· Mixtures

　　∗ Heterogeneous mixtures (variable composition)

　　∗ Homogeneous mixtures (i.e. solutions, continuous composition)

○ Table 1.1 shows the abundance of many elements on Earth

○ Atoms are the smallest particle of an element that has the properties of that element

　· Thought-experiment of dividing a sample in half ad-infinitum

　· Ancient atomic theories and modern Dalton atomic theory (discussed in detail later)

　· Atoms are *very* small; smaller than we could even detect until recently

○ Molecules are collections of atoms held together with chemical bonds (more nuanced definition later)

　· Many elements occur naturally as molecules, rather than atoms

　· Figure 1.14 shows many molecular elements and compounds

1.3　Physical and Chemical Properties

○ Physical Properties: Properties which can be observed without changing the chemical identity of the substance

○ Chemical Properties: Properties which can only be observed through chemical reactions (e.g. flammability, acidity, electrochemical potential, etc.)

○ Physical Changes: Any change which perserves the *chemical identity* of the substance (including phase changes)

○ Chemical Changes: Changes which alter the chemical identities of one of more substance

○ Extensive Properties: Depend on the size of hte system (double the size, double the property measurement, such as mass or volume)

○ Intensive Properties: Independent of system size (density, temperature, most chemical properties)

○ The periodic table groups elements according to their properties (Figure 1.22)

　· Metals conduct electricity and heat, are maleable and ductile

　· Non-metals are very diverse, but generally poor conductors

　· Metalloids exist at the boundary and share properties with both metals and non-metals

　· There are many other ways to group the elements, which we will learn later

Quiz 1.2 - Matter, Properties, and Change

Homework 1.2

- 17: Classifying matter

- 27: Classifying changes

1.4 Measurements

- All measurements are composed of three parts:

  - The magnitude of the measurement (the number itself)
  - The unit of measurement used (g, kg, lbs, etc.)
  - The degree of uncertainty in the measurement (this is usually implicit, and covered in the next section)

- Units are an essential part of any measuement. Develop a habit of *always* including units in your work

  - $u_{rms} = \sqrt{\dfrac{3RT}{M}}$ – example of how units can guide problem solving and "unit purgatory"
  - SI units are a collection of fundamental units from which all other units can be derived (Table 1.2)
  - Metric prefixes make it more convenient to discuss very large or very small numbers (Table 1.3)
  - Scientific notation is an even more general and robust way of representing numbers
    * The quantity is represented by a number with the decimal after the first digit
    * The magnitude is represented by a power of 10
  - Practice converting between normal numbers, metric prefixes, and scientific notation
  - For temperature, we use both K and $°C$ (But not $°F$)
    $T(K) = T(°C) + 273.15$
  - Derived units will combine the fundamental units in some way
    volume: m^3, L, ml
    velocity: m/s
    density: $kg/m^3, g/cm^3$ (Table 1.4)
    energy: $1 J \equiv kg m^2/s^2$

1.5 Measurement Uncertainty, Accuracy, and Precision

- Countable quantities are considered to be *exact* (no uncertainty)

- Measurements (and groups of measurements) always have some degree of undertainty

- Accuracy is how close a measurement is to the *true value* (usually unknown, but approximated by calibration with a well-known standard)
- Precision is how finely a measurment is made (What is the margin of error)
- Figure 1.27 and Table 1.5 illustrate the differences between precision and accuracy
- Accuracy is usually improved through calibration, and moving forward we will usually assume that measurements are as accurate as an instrument allows
- Precision is represented in the way we write the number, and can be improved with a better instrument or with repeat measurements

○ Significant figures are the way that we represent precision in a number

- The number of digits conveys the degree of precision
- Example of me saying I'm $6ft\ 2in$ tall, vs me saying I'm $6ft\ 1.6241434in$ tall
- For graduated measurements, we record one digit beyond the lowest graduation (Figure 1.26)
- For digital measurements, we record the number as it is given by the instrument
- For any given number, we should track both the *quantity* of significant figures, and the *position* of the least-significant digit
- In a written number, digits are considered significant according to the following rules:
    * All non-zeros are significant
    * All *captive* zeros (between two other significant digits) are significant
    * Trailing zeros are *always* significant
    * Leading zeros are *never* significant
    * For scientific notation, only the digits of the quantity (not the magnitude) count
    * Logarithmic quantities follow different rules which we will revisit in CHEM 1220 (chapter 14)
    * Note that for some numbers scientific notation is *required* to convey the correct precision ($3.0 \times 10^3 m$)

○ Errors propogate when multiple measurements are used in a mathematical operation

- For addition and subtraction, the least significant digit of the answer will be in the same position as the least significant digit of hte least precise input
- For multiplicationa and division, the quantity of significant digits in the answer will match the quantity of significant digits of the input with fewest significant digits
- When rounding an exact 5 (no further digits beyond the 5), round up or down to make the last digit even
- Compound problems involve multiple types of operations
    * Solve the problem in steps, applying the correct rule to each step
    * Track the significant figures (quantity and position) for each intermediate answer, but do *not* truncate or round any of these answers
    * Only round after the last step
        ○ Practice $\frac{12.3g + 34g}{12.0cm^3 + 7.7cm^3} = 2.4 g/cm^3$ (wrong answer with premature rounding)

Quiz 1.3 - Significant Figures

Homework 1.3

- 45: Scientific Notation

- 49: Counting Significant Figures

- 53: Significnat Figures and Calculations

1.6   Mathematical Treatment of Measurement Results

- Some quantities are calculated based on two or more measurements (such as velocity and density)

- These formulas can be used to relate all three quantities together (i.e. $velocity = \frac{distance}{time}$)

- The derived quantity can be interpreted as a *conversion factor* between the other two quantites

- Conversion factors and unit conversions

  - Elementary school perspective of ft to in conversions
  - Conversion factors are a ratio between two identical quantities
  - Converting units involves multiplying by 1 in the form of a conversion factor
  - Units guide the problem solving

- Dimensional Analysis is a problem-solving framework based on a series of unit conversions

  - Don't dive straight into calculations and equations
  - Identify the units you expect for the answer
  - Identify the starting point
  - Create a plan to convert units from the starting point to the answer
  - Carry out the calculations
  - Practice converting $65.0\,miles/hour$ into m/s
  - The "railroad ties" or "picket fence" method can help organize your work

- Dimensional analysis is not the only way to solve problems, but it is versatile and robust; usually my preferred choice

- Practice a more abstract problem:
  Find the $miles/gal$ if a car consumes $8036\,g$ of gasoline while driving for $40.0\,min$ at $75\,miles/hour$

Quiz 1.4 - Dimensional Analysis

Homework 1.4

- 65: Simple unit conversion

- 87: Density from volume and mass

- 89: Mass from volume

- 91: Volume from mass

CHAPTER 2
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ATOMS, MOLECULES, AND IONS

2.1 Early Ideas in Atomic Theory

○ 1807 Dalton's Atomic Theory: (1, 2 and 5 are not strictly true) (Figures 2.2-2.4)

1. Matter is composed of atoms

2. Atoms of a given element all have identical properties to each other

3. Atoms of one element differ in properties from elements of a different element

4. Chemical compounds consist of atoms of different elements combined in a specific ratio

5. Chemical reactions *rearrange* the atoms which are already there, but cannot create or destroy atoms

○ Development of Dalton's theory:

· Dalton relied on prior work by Proust who demonstrated the law of definite proportions (Table 2.1)

· This was not at all expected - my analogy with bread, or metal alloys

· Dalton further noted that ratios of these proportions followed the law of multiple proportions (Copper (I or II) Chloride example in the book)

2.2 Evolution of Atomic Theory

○ About a century later, scientists discovered that atoms are made of even smaller components

○ J. J. Thomson discovered the electron, and its charge/mass ratio (Figure 2.6)

○ Millikan's oil drop experiment found the fundamental charge (and thus mass) of an electron (Figure 2.7)

○ Figure 2.8 shows some early ideas of how the positive and negative charges were distributed in an atom

○ Ernest Rutherford discovered the atomic nucleus, consisting of very concetrated positive charge (Figures 2.9 and 2.10)

"It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

○ Different *isotopes* of atoms were discovered with techniqes that produced isotopically pure samples

○ Finally, the neutron itself was discovered in 1932, explaining what particle led to different isotopes

2.3 Atomic Structure and Symbolism

- Atoms are made up of protons, neutrons, and electrons

- Figure 2.11 shows the small scale of the atom and nucleus

- Atomic units make discussions about atoms convenient

  - The Atomic Mass Unit amu, Da, or $u = 1.6605 \times 10^{-24} g$
  - The fundamental charge $e = 1.602 \times 10^{-19} C$
  - The Angstrom Å$= 10^{-10} m$

- Table 2.2 summarizes the properties of elementary particles in atoms

- We track the composition of an atom with three numbers:

  - The atomic number is the number of protons $Z = p$
  - The mass number is the number of protons and neutrons $A = p + n$
  - The number of neutrons is therefore $n = A - Z$
  - The charge is the protons minus the electrons $q = p - e$
  - The number of electrons is $e = p - q$

- A positively charge atom is called a cation, and a negatively charged atom is called an anion

- Chemical symbols are a shorthand way of representing everything we need about an atom

  - There is a 1 or 2 letter symbol for each element (Table 2.3 shows some make sense, some don't)
  - A is written as a left superscript
  - Z is written as a left subscript, but can be left off
  - q is written as a right superscript with the magnitude first, then the sign. q is left off if $q = 0$
  - Example: $^{13}_{6}C^{2+}$ (6 protons, 7 neutrons, 4 electrons)

- Isotopes are different versions of elements with different mass numbers

  - For the most part, different isotopes of an element behave exactly the same in chemisry
  - Isotope abundance can be found by mass spectrometry, among other methods (Figure 2.15)
  - Table 2.4 shows the natural abundances of the isotopes of several light elements
  - Atomic weight (atomic mass) is the weighted average of all the isotopes found on the Earth
    $$M = \sum_i mass_i \times \frac{\% abundance_i}{100\%}$$

2.4   Chemical Formulas

○ We can represent the actual structure and makeup of molecules at several levels of abstraction (Figures 2.16 and 2.17)

○ Molecular formulas

· Each element is listed, with the number of atoms for each element written as a subscript (H_2O)
· The order of elements follows certain patterns, with the least electronegative element often written first

○ Structural Formulas show how atoms are connected with covalent bonds represented as lines

○ Ball and Stick models show the three-dimensional geometry of a molecule

○ Space-filling models show the actual volume of space taken up by each atom in a molecule

○ Figure 2.18 illustrates the difference between subscripts within a formula, and stoichiometric coefficients in front of formulas

○ Empirical formulas show the mathematically simplified ratios of elements

· Some experimental techniques (especially early ones) could *only* give the empirical formula
· Ionic compounds are always reported with the empirical formula
· To find the empirical formula, divide all subscripts by their greatest common factor
· Some very different compounds share an empirical formula (carbohydrates CH_2O include formaldehyde, acetic acid, and sugar)
· The molecular formula can be calculated from the empirical formula's weight and the molecular weight (Chapter 3)

○ Arranging the same group of atoms in different ways produces different isomers

· Isomers share the same chemical formula, but can have very different properties
· Structural isomers differ in how the atoms are connected to each other (Figure 2.23)
· Optical isomers (or spatial isomers) are non-superimposable mirror images (Figure 2.24, glove analogy)

Quiz 2.1 - Atomic Theories

Homework 2.1

○ 7: Properties of protons and neutrons

○ 11: Atomic symbols from composition

○ 19: Composition from atomic symbols

○ 23: Atomic weight

○ 29: Molecular and empirical formulas

2.5 The Periodic Table

○ As scientists discovered and studied more and more elements, they started to notice certain natural groupings according to physical and chemical properties

○ Mendeleev arranged the atoms according to these groups and atomic weight, producing the first periodic table (Figure 2.25)

○ Mendeleev even predicted the existence of and properties of yet-undiscovered elements based on gaps in his table

○ Vocabulary around the periodic table:

   · Rows are periods or series

   · Columns are groups or families

○ Figure 2.26 is a typical periodic table, showing the metals, non-metals and metalloids (contrast with my preferred table)

○ Figure 2.27 shows many of the names we use for important groups of elements

○ The structure of the periodic table encodes rich information about the electrons in the elements, as we will learn in chapter 6

Quiz 2.2 - Periodic Table

Homework 2.2

○ 37: Classifying elements

○ 41: Using group names

2.6 Ionic and Molecular Compounds

○ An atom which gains or loses electrons (carries a charge) is called an *ion*

   · Positively charged ions are called cations, and are smaller than their neutral atom counterparts (Figure 2.28)

   · Negatively charged ions are called anions, and are larger than their neutral atom counterparts

   · We can predict which charge different elements will naturally tend to take based on their position in the periodic table (Figure 2.29)

   · Many other elements can take two or more charges, especially the transition metals

○ Some ions are composed of more than one atom and are called polyatomic ions

   · Table 2.5 gives some common polyatomic ions. Memorize the formula, name, and charge of these and their acids

- Notice some trends in the names of oxyanions (per-ate, -ate, -ite, and hypo-ite)
- We will learn about the acid names listed here (and more) in section 2.7

○ Ionic compounds are held together by ionic bonds (coulombic attractions)

- Show dot diagram of how NaCl and CaCl form from elements
- Metal + non-metal is not an adequate definition of ionic compounds (NH_4NO_3)
- Ionic compounds form an extended lattice of ions (covered more in CHEM 1220)
- Ions will combine to form neutral compounds
- Practice producing compound formulas from ions (include paranthesis for polyatomic ions where appropriate)
- Practice finding ions from formulas of compounds

○ Molecular compounds are held together by covalent bonds (shared electrons)

- Show a dot diagram of H_2, H_2O, O_2, and N_2
- Bonds between non-metals are covalent bonds
- Molecular compounds combine non-metals into discrete units called molecules
- Single, double, and triple bonds involve sharing two, four, and six electrons

2.7   Chemical Nomenclature

○ Naming ionic compounds

- Cation names are the name of the element, with the charge in roman numerals in parenthesis *if* the element could take multiple charges
- Anion names are the element name with an "-ide" ending (some element like P remove more than others)
- Polyatomic ion names are the same as you learned earlier
- For ionic compounds the name is simply cation name + anion name
- There is no indication of the quantity of atoms, that is inferred from charge neutrality
- Practice getting formulas from names and names from formulas

○ Naming hydrates

- Some ionic compounds will incorporate water into their ionic lattice
- The formulas will have a · then list the number of waters
- The names add the degree of hydration using prefixes from table 2.10 and adding "hydrate"
- The waters can be driven of with high temperature, producing the *anhydrous* form

Quiz 2.3 - Naming Ionic Compounds

Homework 2.3

- 47: Predicting bond type in compounds

- 49: Formulas from ions

- 51: Names from formulas

- 57: Names from formulas with transition metals

- 59: Formulas from names

Resuming section 2.7 Chemical Nomenclature

- Naming molecular compounds

    - There are many ways to name molecular compounds, we will focus on just two here
    - Naming binary molecular compounds
        * # + name + # + name with "-ide" ending
        * Least electronegative element (leftmost on the periodic table) goes first
        * #s come from table 2.10
        * Omit "mono-" for the first element
        * Practice going from formula to name and vice-versa (Table 2.11)
    - Naming molecular acids
        * Molecular acid names are based on the name of the anion formed when all H^+ are removed
        * -ide ions form hydro-ic acids (Table 2.12)
        * -ate ions form -ic acids
        * -ite ions form -ous acids
        * preserve the hypo- and per- prefixes
        * Table 2.13 shows some oxyacid names

Quiz 2.4 - Naming Molecular Compounds

No textbook homework to accompany this quiz due to a lack of appropriate questions!

COMPOSITION OF SUBSTANCES AND SOLUTIONS

3.1 Formula Mass and the Mole Concept

○ For chemists, the amount of a substance we care about is not grams, but the quantity of atoms

○ Analogy of hammers and feathers

○ The mole is defined as the relationship between $AMUs$ and g

$$6.022 \times 10^{23} AMU = 1g \longrightarrow 1 mol\, AMU = 1g \longrightarrow 1 AMU = 1\frac{g}{mol}$$

○ Any time we would use the AMU we could replace it with g/mol, and this is called the *molar mass*

○ Practice converting between grams and moles using atomic weight

○ For compounds, we can find the molar mass, or formula mass by adding up the atomic weights of all the atoms in the formula

○ We can count the literal number of atoms, but it is usually best to remain in units of moles

○ Practice finding formula masses for compounds, and converting between grams and moles for compounds

3.2 Determining Empirical and Molecular Formulas

○ Empirical analysis is a method to determine empirical formulas

· In our text, the masses of C, H, and O are given directly

· To get the formula, turn each mass into moles, and divide by the smallest mole number (Figure 3.11)

· Actually, this technique involves a careful combustion reaction

· The mass of C comes from the amount of CO_2 produced

· The mass of H comes from the amount of H_2O produced (remember the 2!)

· The mass of O comes from subtracting those from the original amount

· Turn the masses to moles

· Practice: $2.443g$ of unknown produce $5.368g$ of CO_2 and $2.930g$ of H_2O ($M = 60.096$, propanol)

· Practice: $3.450g$ of unknown produce $5.057g$ of CO_2 and $2.070g$ of H_2O ($M = 180.16$, hexose)

○ % Composition gives the % by mass of each element in a compound

- From masses, we can calculate the % mass composition easily
- If % mass is given, we can just assume $100.0g$ and turn the %s into g to do emipirical analysis
- From the empirical or molecular formula, we can get % mass composition: $\%_X = \dfrac{nM_X}{M_{Formula}}$

○ We can determine the molecular formula from the empirical formula if we know the molar mass

- The molecular formula will be an integer multiple of the empirical formula (could be 1)
- That formula is the ratio $n = \dfrac{M_{molar}}{M_{empirical}}$
- Find the molecular formulas of the two examples above using their molar masses

Quiz 3.1 - Molar Mass

Homework 3.1

○ 3: Calculating molar mass

○ 17: Mass from moles

○ 18: Moles from mass (sorry, no solution!)

Quiz 3.2 - Empirical Analysis

Homework 3.2

○ 33: % composition from formulas

○ 37: Empirical formulas from % composition

○ 39: Molecular formula from % composition and molar mass

3.3 Molarity

○ Molarity is the most common way of describing the *concentration* of a solute in a solution

- The unit for molarity is M, which is unfortunate because that is also used for molar masses
- Molarity is the moles of solute divided by the liters of solution $M = \dfrac{mol_{solute}}{L_{solution}}$
- Technically, the solution volume could be more or less than the solvent volume before dissolving. When we make a solution, we always describe the process as "add enough water to meet the mark"
- The molarity can now be used as a conversion between moles and volume
- Practice: Find molar concentration of solution made by dissolving $13.5g$ NaCl in $100.0ml$ of solution

- Practice: How many moles of NaCl are contained in $35.62ml$ of the solution?
- Practice: How many ml would be needed to provide $1.74 \times 10^{-3}mol$ of NaCl?

○ Solutions can be diluted or concentrated

- The number of moles of solute is the same, just the volume of solution changes (by adding or removing solvent)
- $C_1V_1 = C_2V_2$
- Practice: Find the molar concentration when $36.43ml$ of $1.5M$ HCl are diluted to $100.0ml$?
- Practice: How many ml of $0.125M$ NaNO$_3$ should be used to make $50.0ml$ of $2.4 \times 10^{-3}M$?

3.4   Other Units for Solution Concentration

○ There are other, less common units of concentration (including some not covered until chapter 11)

○ Mass %, or % by mass

- $\%m/m = \dfrac{m_A}{m_{total}}100\%$

○ Volume %, or % by volume

- $\%v/v = \dfrac{V_A}{V_{solution}}100\%$

○ m/V %

- $\%m/v = \dfrac{g_A}{V_{solution}}100\%$

○ ppm and ppb

- $ppm = \dfrac{m_A}{m_{total}}10^6ppm$
- $ppb = \dfrac{m_A}{m_{total}}10^9ppb$

Quiz 3.3 - Concentration

Homework 3.3

○ 49: Mass from molarity and volume

○ 53: Calculating molarity

○ 61: Dilution

○ 73: ppm

○ 77: %m/m

CHAPTER 4

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## STOICHIOMETRY OF CHEMICAL REACTIONS

4.1 Writing and Balancing Chemical Equations

- A chemical equation relates the amounts of reactants and products in a chemical reaction

- Consider the reaction: $CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$ (Figure 4.2)

- Reactants on the left, and products are on the right

- The large numbers are called *stoichiometric coefficients*

- The subscript numbers are part of the chemical identity of the reactants and products

- The stoichiometric coefficients tell the right ratio to combine reactants, and the ratio of products produced (Figure 4.3)

- Balancing chemical reactions:

  · To balance a chemical equation, we will add the proper coefficients to give the same numbers and types of atoms on both sides of the reaction arrow
  · Start with any repeated atom moieties, such as polyatomic ions, and balance them as a unit rather than counting individual atoms
  · Next balance elements that appear in only one compound on each side
  · Finally, balance any remaining elements (O is often best left to balance last)
 · If necessary, multiply all coefficients by an integer

  Practice: Balance the following chemical equation: $Fe_2O_3(s) + Al(s) \longrightarrow Al_2O_3(s) + Fe(s)$

  $\qquad Fe_2O_3(s) + 2\,Al(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s)$
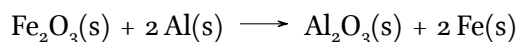
  Practice: Balance the chemical equation: $(NH_4)_3PO_4(aq) + Fe_2(CO_3)_3(aq) \longrightarrow FePO_4(s) + (NH_4)_2CO_3(aq)$

  $\qquad 2\,(NH_4)_3PO_4(aq) + Fe_2(CO_3)_3(aq) \longrightarrow 2\,FePO_4(s) + 3\,(NH_4)_2CO_3(aq)$
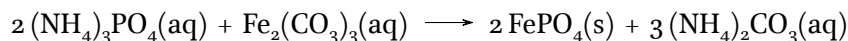
  Practice: Balance the following chemical equation: $C_3H_8(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

  $\qquad C_3H_8(l) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$
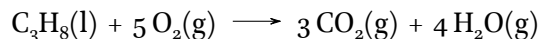
  Practice: Balance the following chemical equation: $C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

  $\qquad 2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g)$
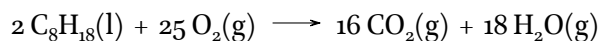
  Practice: Balance the following chemical equation: $Ag_2SO_4(aq) + NaCl(aq) \longrightarrow AgCl(s) + Na_2SO_4(aq)$

  $\qquad Ag_2SO_4(aq) + 2\,NaCl(aq) \longrightarrow 2\,AgCl(s) + Na_2SO_4(aq)$
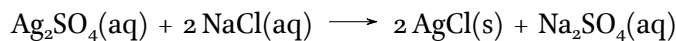
- Chemical reactions will sometimes include additional information

- · Phases (s), (l), (g), (aq)
- · Reaction conditions, such as temperature, or the presence of a catalyst (often written over the arrow)
- · Enthalpy of reaction or equilibrium constant (covered in later chapters)

○ Reactions with ionic compounds can often be written differently and simplified

- · The normal equation is called a *molecular equation* (despite involving ionic compounds)
  $$CaCl_2(aq) + 2\,AgNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2\,AgCl(s)$$
- · The *complete ionic equation* will break *soluble* ionic compounds into the separate cations and anions
- · This is a more accurate representation of soluble ionic compounds, which are not actually *together* in any chemically meaningful way
  $$Ca^{2+}(aq) + 2\,Cl^-(aq) + 2\,Ag^+(aq) + 2\,NO_3^-(aq) \longrightarrow Ca^{2+}(aq) + 2\,NO_3^-(aq) + 2\,AgCl(s)$$
- · The *net ionic equation* removes *spectator ions*, which didn't actually participate in any chemical change
- · My silly analogy about party-goers and the social interactions in a party environment
  $$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Quiz 4.1 - Balance Chemical Equations

Homework 4.1

○ 5: Balancing equations

○ 11: Net ionic equations

4.2 Classifying Chemical Reactions

○ We can categorize chemical reactions in several ways, but for this class we will focus on the types of chemical changes caused by a reaction

○ Precipitation reactions form one or more solid ionic product from all aqueous ionic reactants

- · First, predict the products by switching cations and anions
- · Next, predict the phase by using solubility rules (Table 4.1)
- · Identify and eliminate the spectator ions to get a net ionic equation
- · Some combinations of reactants will have no reaction, and some may have two solid products
- · More about precipitation reaction in CHEM 1220

Quiz 4.2 - Precipitation Reactions

Homework 4.2

- ○ 28: Predicting products of reactions with ionic compounds

Resuming Section 4.2: Classifying Chemical Reactions

- ○ Acid-Base reactions involve the transfer of a H^+ between reactants
    - · Acids will react with water to produce hydronium ion
    - · Bases will react with water to produce hydroxide ions
    - · *Strong* acids/bases react with water to completion, while *weak* acids/bases only react partially (equilibrium)
    - · Table 4.2 lists six common strong acids
    - · Alternative definition: Acids are proton donors and bases are proton acceptors
    - · A neutralization reaction produces water and a salt (ionic compound)
    - · More about acid/base reactions in CHEM 1220

- ○ Redox reactions involve the transfer of one or more electrons
    - · Consdier the reaction: $2\,Na(s) + Cl_2(g) \longrightarrow 2\,NaCl(s)$
    - · OIL RIG (or LEO says GER) to remember which is oxidation, and which is reduction
    - · Oxidizing agents and reducint agents. "Agent" describes the effect on the reaction partner
    - · Sometimes the electron transfer is not as obvious: $CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$
    - · We assign oxidation numbers to keep track of electrons
        - ∗ Elements have ox. # of 0
        - ∗ Monoatomic ions have ox. # equal to their charge
        - ∗ Within compounds, O has ox. # $= -2$, and H has ox # $= +1$
        - ∗ Oxidation #s add up to the total overall charge (this rule subsumes the first 2)
    - · Balancing redox reactions needs additional steps to account for the transferred electrons
        1. Split the reaction into half-reactions (need to find oxidation #s to do this)
        2. Balance all elements except H and O
        3. Add the electrons, based on the changes to oxidation #s
        4. Balance charge by adding H^+ in acid, or OH^- in base
        5. Balance H and O together by adding water
        6. Multiply half-reactions to balance their electrons, then add them together
        7. Make any cancellations of water, H^+, or OH^-
    - · You can balance redox reactions as a whole instead of as half-reactions if you prefer
    - · Electrochemical series and predicting if redox reactions will be spontaneous or not (Not in the book!)
    - · More about Redox reaction in ...CHEM 1220!

Quiz 4.3 - Redox Reactions

Homework 4.3

- 17: Assigning oxidation states

- 19: Classify acid/base and redox reactions

- 39: Balancing half-reactions

Electrolytes

- Electrolytes are covered in Chapter 11, but because they might appear on our final we will discuss them here too

- Electrolytes are chemical substances which yield ions when dissolved in water

  Strong Electrolytes: Produce a *stoichiometric* amount of ions. Stong acids/bases and soluble ionic compounds

  Weak Electrolytes: Produce a *sub-stoichiometric* amount of ions. Weak acids/bases

  Non-Electrolytes: Do not produce any ions. Other soluble molecular compounds

4.3   Reaction Stoichiometry

- Measured amounts should always be converted to moles in order to make comparisons to other chemical species in an equation

  · We often want to calculate the corresponding amount of different chemicals in a chemical reaction

  · Making direct comparisons will not work due to different molar masses, etc.

  · Figure 4.11 shows how to convert to moles from different measurements

  · My version of this figure ("Chemistry Land")

- Practice: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ Find other amounts for $0.75g$ of H_2

Quiz 4.4 - Stoichiometry

Homework 4.4

- 49: Stoichiometry with solid reactants

- 57: Stoichiometry with aqueous reactions

4.4   Reaction Yields

○ Often one or more reactants are provided in excess, with only one *limiting reactant*

· Pick a product, and calculate how much product would be produced for each reactant

· The lowest amount is the theoretical yield. The other amounts can be discarded

· The reactant which lead to the lowest amount is the limiting reactant

· Calculate the rest of the corresponding amounts starting from the limiting reactant

· Double-check your work using the conservation of mass

○ Practice: $2\,C_4H_{10} + 13\,O_2 \longrightarrow 8\,CO_2 + 10\,H_2O$ with $5.00g\,C_4H_{10}$ and $9.00g\,O_2$

○ Reactions rarely go perfectly, and the actual amount of product will be different from the theoretical yield

○ $\%yield = \dfrac{actual\ yield}{theoretical\ yield} \times 100\%$

○ Yields below 100% can mean that the reaction didn't go to completion, or some product was lost during a purification stage

○ Yields above 100% usually indicate that some contaminants (including perhaps excess reactant) are mixed in with the product

Quiz 4.5 - Limiting Reactants

Homework 4.5

○ 61: Limiting Reactant Problem

○ 63: Percent Yield

4.5   Quantitative Chemical Analysis

○ Quantitative analysis is the family of techniques which determine the amount of substance in a sample

○ Titrations find the concentration of an aqueous *analyte*

· React the unknown with a co-reactant of known concentration by adding titrant with a buret

· The chemical environment will change (pH, redox potential, etc.) once the reaction reaches the equivalence point

· Probes or color indicators can show when to stop the titration. This is called the end-point, and is ideally very close to the equivalence point

· $\dfrac{C_T V_T}{\nu_T} = \dfrac{C_A V_A}{\nu_A}$

- Gravimetric analysis uses a chemical reaction to change the phase of the analyte so it can be separated and weighed

  - Your % copper lab found the amount of copper by reducing it to a solid

  - Your hydrates lab found the amount of water by weighing it before and after the baking step

- Combustion analysis - We actually covered this earlier with % composition of compounds

Quiz 4.6 - Titrations

Homework 4.6

- 79: Acid/base Titration

- 81: Precipitation Titration

THERMOCHEMISTRY

5.1 Energy Basics

○ Thermochemistry is the study of heat and energy changes in chemical reactions

○ It also includes topics like entropy and spontaneity

○ Energy can come in two forms, kinetic and potential (Figure 5.3)

  · Kinetic energy is the energy of motion: $KE = \dfrac{1}{2}mv^2$

  · For chemists, the kinetic energy that matters is the movement of individual atoms, molecules, etc., manifested as temperature (Figure 5.4)

  · Heat will always flow from colder objects to warmer objects (Figure 5.6)

  · Increases in temperature almost always cause objects to increase in volume (Figure 5.5)

  · Potential energy is stored energy: Gravitaional, electrostatic, chemical, etc.

  · For chemists, the potential energy that matters is the energy of chemical bonds and intermolecular forces (Figure 5.2)

○ Energy has several common units

  · The SI unit is the Joule: $1\ J = 1\ kg\dfrac{m^2}{s^2}$

  · The calorie: $1\ cal = 4.184\ J$

  · The Calorie (kcalorie): $1\ Cal = 1000\ cal = 4184\ J$

○ When we talk about changes and transfers of energy, we need to carefully define our system

  · The *system* is the part of the universe where the reaction occurs, such as a beaker or chamber with reactants

  · The *surroundings* is the rest of the universe

  · Open systems can exchange both heat and matter with the surroundings (an open beaker)

  · Closed systems can exchange heat, but not matter with the surroundings (a closed chamber)

  · Isolated systems cannot exchange either heat or matter with the surroundings (a closed, insulated flask)

○ Heat from chemical and physical changes is usually associated with temperature changes or phase changes (Figure 5.7)

  · These examples all refer to heat from the *system's* perspective

- Positive heat is observed by an "upward" phase change or a cold temperature
- Holding ice in your hand will melt the ice, and make your hand cold
- Negative heat is observed by a "downward" phase change or a hot temperature
- Burning wood in a fire feels warm because of the negative system heat

o Heat and temperature change are related by several equations (Note that we are always measuring the temperature of the *surroundings*)

- When heat is added to a system, it will either undergo a phase change, or heat up
- The specific heat gives how much heat is required to warm a given substance
- For a complete system, $q = C\Delta T$ where C is the *heat capacity*
- For a pure substance, $q = mc_S\Delta T$ where c_S is the *specific heat* of the substance and m is the mass
- Table 5.1 shows c_S for many common substances
  Practice: Find how much heat is required to raise the temperature of $15.0g$ of iron by $32°C$
  Practice: Find the temperature change when $42.5J$ of heat are added to $0.374g$ of aluminum

Quiz 5.1 - Energy

Homework 5.1

- 5: Heat capacity of samples

- 9: $q = mc_S\Delta T$

- 11: $q = mc_S\Delta T$, but solve for c_S

5.2   Calorimetry

o Whenever heat is transferred, the total energy of the universe remains constant

o For a heat transfer in an isolated system, $q_1 = -q_2$

o Consider a block of hot metal placed in a beaker of room temperature water. Heat will flow from the block into the water until the two temperature are equal to each other

o $q_1 = -q_2$ becomes $m_1c_1\left(T_f - T_{i,1}\right) = -m_2c_2\left(T_f - T_{i,2}\right)$

  Practice: A $10.0\ g$ block of iron is heated to $93.5\ °C$ and placed in $25\ ml$ of $23.0\ °C$ water. What is the final temperature? $(25.9\ °C)$

o We can also measure the heat transfer associated with a chemical reaction, called *calorimetry*

o Exothermic processes release heat into the surroundings (warm to the touch)

o Endothermic processes absorb heat from the surroundings (cool to the touch)

○ Figure 5.11 shows how a calorimeter would work for endothermic and exothermic processes

○ Figures 5.12 and 5.13 show a constant pressure (coffee-cup) calorimeter

· The reaction is carried out in aqueous solution

· q_{rxn} is the heat released or absorbed by the reaction

· The heat of reaction is exchanged with the solution: $q_{rxn} = -q_{soln} = -mc\Delta T$

· m is the solution mass, which will include the water and any solutes

· c is the solution specific heat, but this is simplified by assuming $c_{soln} = c_{water} = 4.184 \frac{J}{g\,°C}$

· $\Delta H = \dfrac{q_{rxn}}{n_{rxn}} = \dfrac{-mc\Delta T}{n_{rxn}}$ where n_{rxn} is the moles of reaction: $n_{rxn} = \left(\dfrac{n_A}{\nu_A} \right)$

· Demo – NaOH enthalpy of solvation $\left(10\ g, 100\ ml, 44.2\ \frac{kJ}{mol} \right)$

○ Figure 5.17 shows a constant volume (bomb) calorimeter

· The reaction is carried out in a chamber charged with high pressure O_2

· q_{rxn} is exchanged with the whole bomb-calorimeter apparatus

· The calorimeter is calibrated to give a *heat capacity* (C_{cal}) with units $\frac{J}{°C}$

· $q_{rxn} = -q_{cal} = -C_{cal}\Delta T$

· For constant volume, we measure U instead of H because $w = 0$

· $\Delta U = \dfrac{-C_{cal}\Delta T}{n_{rxn}}$

Quiz 5.2 - Calorimetry

Homework 5.2

○ 19: Reaching thermal equilibrium

○ 25: Coffee cup calorimetry

○ 31: Bomb calorimetry

5.3 Enthalpy

○ The sum of all types of energy in a system is the *internal energy, U*

○ Any change in the internal energy must come from heat or work: $\Delta U = q + w$

○ Work is defined as $w = f \cdot d$ or $w = -P \cdot \Delta V$

· Positive work is when the system volume decreases

· Negative work is when the system volume increases, or a force moves part of the surroundings

· This PV work is actually a bit problematic when trying to keep track of energy

- ∗ T is easy to measure with a thermometer, but both P and (especially) V are more difficult to measure
- ∗ Most of our work as chemists is done at constant pressure (open flask or in a balloon)
- ∗ Under constant pressure, we can use *Enthalpy* (H) instead of internal energy (U)
- ∗ Technically, $H = U + PV$
- ∗ While $U = q + w$, $H = q$ under constant pressure conditions (derivation in the book)
- ∗ So, we only need to worry about heat when we deal with H

○ Heat is usually associated with temperature changes or phase changes, as discussed previously

○ First Law of Thermodynamics: The energy of the universe is constant

○ Enthalpy in chemical reactions:

- · A balanced chemical reaction may also include an enthalpy of reaction ΔH
- · This tells how much heat is produced or consumed with one mole of reaction
- · ΔH can be a conversion factor between heat and amounts of reactants or products
  Practice: Consider the reaction $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$ $\Delta H = -92\frac{kJ}{mol}$
    If $2.25\ g$ of H_2 are consumed in the above reaction, how much heat is released? $(34.2\ kJ)$
      If $54.6\ kJ$ of heat are released, how many g of NH_3 will be produced? $(20.2\ g)$

Quiz 5.3 - Enthalpy

Homework 5.3

○ 41: Enthalpy of reaction from calorimetry

○ 45: Heath from enthalpy of reaction

○ 47: How much reactant from target heat output

Resume Section 5.3 – Enthalpy

○ The "Standard State" is notated by $^\circ$ and is at $1M$ concentration and $1atm$ (or $1bar$), and technically doesn't include a temperature but values are often tabulated at $25°C$

○ Standard Enthalpies of Combusion (ΔH_C°):

- · Standard enthalpy of combustion is the energy released when something reacts with oxygen
- · Table 5.2 Lists the enthalpies of combustion for many combustible substances
- · These values are not synonymous with energy density, due to molar mass and density complicating the values

○ Because enthalpy is a state function (Figure 5.20), we can calculate values of ΔH without measuring them

- Hess's Law: Any alternate path with the same starting and ending states will have the same overall ΔH

  - Drawing an energy level diagram can help to illustrate Hess's law (Figure 5.24 as an example)
  - Find ΔH for this reaction: $C_{\text{diamond}} + O_2(g) \longrightarrow CO_2(g)$ $(\Delta H = -395.4\ ^{kJ}/_{mol})$

    $C_{\text{diamond}} \longrightarrow C_{\text{graphite}}$ $\Delta H = -1.9\ ^{kJ}/_{mol}$

    $C_{\text{graphite}} + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5\ ^{kJ}/_{mol}$
  - The reverse of a reaction gives $-\Delta H$
  - Find ΔH for this reaction: $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$ $(\Delta H = -110\ ^{kJ}/_{mol})$

    $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393\ ^{kJ}/_{mol}$

    $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -283\ ^{kJ}/_{mol}$
  - Double the reaction gives double the ΔH
  - Consider trying to find ΔH for the reaction below:

    $\bigstar\ C_2H_5OH(l) + 2\ O_2(g) \longrightarrow 2\ CO(g) + 3\ H_2O(l)$ $\Delta H = ?$
  - Find an alternate path using these reactions with known ΔH:

    $\text{A}\ C_2H_5OH(l) + 3\ O_2(g) \longrightarrow 2\ CO_2(g) + 3\ H_2O(l)$ $\Delta H = -1367\ ^{kJ}/_{mol}$

    $\text{B}\ CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -283\ ^{kJ}/_{mol}$
  - The enthalpy of the first reaction can be found from the enthalpies of the other two
  - $\Delta H_\star = \Delta H_A - 2\Delta H_B = -801 \dfrac{kJ}{mol}$ (Draw the energy level diagram)

    Practice: Find the enthalpy of reaction $\bigstar$ using reactions A, B, and C

    $\bigstar\ CS_2(l) + 3\ O_2(g) \longrightarrow CO_2(g) + 2\ SO_2(g)$ $(\Delta H = -1075.0)$

    $\text{A}\ C(s) + O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5\ ^{kJ}/_{mol}$

    $\text{B}\ S(s) + O_2(g) \longrightarrow SO_2(g)$ $\Delta H = -296.8\ ^{kJ}/_{mol}$

    $\text{C}\ C(s) + 2\ S(s) \longrightarrow CS_2(l)$ $\Delta H = 87.9\ ^{kJ}/_{mol}$

Quiz 5.4 - Hess's Law

Homework 5.4

- 59: Hess's Law and enthalpy of reaction

- 63: Hess's Law and enthalpy of reaction

Resume Section 5.3 – Enthalpy

- Standard Enthalpies of Formation ΔH_f°

  - To apply Hess's law to arbitrary reactions, you would need to devise an alternate path from an encyclopedia of known reactions – this would be *very* inconvenient

· Instead of using random reactions from one state to another, it is useful to devise a *standard state* for each element

· The standard state is the most stable form of that element e.g. for O, it is $O_2(g)$, not $O_2(l)$ or $O_3(g)$

· Each compound will have a *standard formation reaction* which forms it from its elements in their standard state

For water, that's $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ (This is one time a $\frac{1}{2}$ coefficient is acceptable)

· The enthalpy for this reaction is called the compound's *Standard Enthalpy of Formation* $\left(\Delta H_f^\circ \right)$

· Elements in their standard state have $\Delta H_f^\circ = 0$

· Any reaction can be framed as a combination of standard formation reactions

   ∗ First, the reactants are broken down into their elements (the *reverse* of formation reactions)

   ∗ Then, the elements are reassembled into the products (formation reactions)

   ∗ The energy level diagram for any reaction is the same: reactants → elements → products

   ∗ This pathway doesn't need to be *practical*, it is enough to be theoretically *possible*

   ∗ $\Delta H_{rxn} = \sum_{products} \nu \cdot \Delta H_f^\circ - \sum_{reactants} \nu \cdot \Delta H_f^\circ$

   ∗ This formula is general, for any reaction at all

   ∗ Instead of an encyclopedia of thousands of reactions, we only need a table of ΔH_f° values

   ∗ Appendix G includes a large number of thermodynamic values like ΔH_f°

Practice: Find ΔH_{rxn} for $P_4O_{10}(s) + 6\,H_2O(l) \longrightarrow 4\,H_3PO_4(aq)$ $\left(\Delta H_{rxn} = 454.6 \dfrac{kJ}{mol} \right)$

Find ΔH_{rxn} for $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$ $\left(\Delta H_{rxn} = -2043.9 \dfrac{kJ}{mol} \right)$

Quiz 5.5 - Enthalpies of Formation

Homework 5.5

   ○ 67: Calculate ΔH_f° from reaction enthalpies

   ○ 69: Reaction enthalpies from enthalpies of formation

CHAPTER 6

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ELECTRONIC STRUCTURE AND PERIODIC PROPERTIES OF ELEMENTS

6.1 Electromagnetic Energy

- Light is an electromagnetic wave, which can be thought of like a sound wave or a wave on a lake (Figure 6.2)

- Light has a wavelength, frequency, and speed according to the equation: $\nu\lambda = c$

- The speed of light is a constant, $2.998 \times 10^8 \, \dfrac{m}{s}$

- How far does light travel in $5.00 \, ms$? ($1.50 \, km$)

- The electromagnetic spectrum is more than just visible light (Figure 6.3)

  - Higher frequencies (shorter wavelengths) are UV light, X-rays, and gamma rays
  - Lower frequencies (longer wavelengths) are infrared light, microwaves, and radio waves
  - TV-remotes are flashy lights, and radio towers are flashlights-on-a-stick
  - There are important technical differences in how we can use these different kinds of light, but they are fundamentally the same thing (an alternating electromagnetic wave)
  - Find the wavelength of your favorite radio station (MHz is a frequency of $10^6 \, s^{-1}$)

- Light-matter interactions were central to the discovery of modern physics

- The photoelectric effect was an important matter/light interaction (Figure 6.11)

  - Sometimes light falling on a metal will eject an electron – this is the photoelectric effect
  - The kinetic energy of the ejected electron can be measured
  - The energy depended on the wavelength of light – bluer light ejected electrons at faster velocities
  - There was a threshold where electron ejection stopped, and redder light would have no effect
  - This was surprising, because light intensity had *no* effect on the photoelectron energy
  - Dim blue light would eject fast electrons, bright red light would have no effect
  - This was eventually explained by the idea that light carries energy in small discrete packets
  - These packets of energy are called *photons* and the energy they carry depends on the wavelength
  - The photoelectric effect could be described by the equation: $KE = h\nu - \phi$
  - Here, ν was a new constant, called Planck's constant, and ϕ was the metal's work function
  - The equation for the energy of light was: $E = h\nu$ where h is Planck's constant

- Light can also be *absorbed* or *emitted* by matter

    · Light is emitted by gases like Ne, Ar, or Na when high voltage passes through it

    · Light can also be absorbed by gases and other materials

    · Each substance showed a unique fingerprint of wavelengths of light emitted or absorbed (Figure 6.13)

    · He was first identified by its absorbance spectrum in sunlight

    · The unique spectra arise from the particular energy levels of a substance

    · These spectra showed how matter can only store or release energy in certain, constrained amounts (or *quanta*)

    · i.e. in addition to the energy of light, the energy of matter was *quantized* as well

- Ultraviolet Catastrophe (Figures 6.10 and 6.9)

- Wave/Particle duality (not in the textbook)

    · These experiments show that light behaves like both a *wave* (interference) and a *particle* (quantization)

    · It is wrong to say light is either of those things – rather, it is a new thing with similarities to both (rhinosceros vs dragon + unicorn)

    · On very small scales, matter behaves like both a wave and a particle as well!

    · Electrons, in particular, are strongly wave-like, with a characteristic wavelength

    · The IBM quantum corral image dramatically showed the real physicality of electron waves

    · This wave-like nature of electrons is important for understanding modern models of atomic structure

- All of these phenomena can be explained in terms of standing waves (Figures 6.7 and 6.8)

6.2   The Bohr Model

- The Rydberg Equation: (Figure 6.14)

    · School teacher Rydberg recognized a pattern in the wavelengths of light in the H spectrum

    · $\dfrac{1}{\lambda} = 1.097 \times 10^7 m^{-1} \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$

    · His equation can be re-written in terms of energy

    · $E = 2.179 \times 10^{-18} \, J \left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right)$

- The Bohr model of the atom: (Figure 6.15)

    · There was no real explanation for *why* the absorption and emission spectra of different elements showed different discreet energies

- Niels Bohr proposed that electrons orbit around the nucleus only at fixed distances
- Absorption is when an electron shifts to a higher orbit, using a photon's energy
- Emission is when an electron shifts to a lower orbit, releasing energy as a photon
- The lowest energy state is the *ground state*, all others are *excited states*
- The discrete orbits represent states where the circumference of the orbit is equal to a number of wavelengths for the electron (Figure 6.17)
- $E_n = -2.179 \times 10^{-18} \ J \left(\dfrac{1}{n^2} \right)$

Practice: What is the wavelength of the $2 \leftarrow 4$ transition in the H spectrum? $(486.1 \ nm)$

Quiz 6.1 - Light and the Bohr Model

Homework 6.1

- 3: Frequency to wavelength
- 5: Wavelength to energy
- 23: Energy of a Bohr state
- 27: Energy of a Bohr transition

6.3 Development of Quantum Theory

- Quantum mechanics continued to develop
- Heissenberg Uncertainty Principle: We cannot simultaneously measure the position and velocity of an electron (or any other quantum mechanical particle)
- This means that we generally speak of where an electron is *most probable* to be found, rather than where it *actually is*
- The Schrödinger wave equation describes matter starting from a wave-like perspective
    - DeBroglie began from the equation for the momentum of light: $p = \frac{h}{\lambda}$
    - Light has no mass, but replacing p with mv give us: $mv = \frac{h}{\lambda}$ and rearranging gives: $\lambda = \frac{h}{mv}$
    - This equation describes how anything with momentum has a characteristic wavelength
    - Figure 6.18 illustrates one way electrons behave like waves
    - Schrödinger went even further, adapting Maxwell's wave equations for matter with momentum (required some postulates)
    - The Schrödinger equation gives mathematical functions which describe the electron probability distribution
    - Each solution is called an *orbital*, like the orbits of the Bohr model but 3-dimensional

- ○ Orbitals are organized into *shells* and *subshells*

    - · Subshells are groups of orbitals with similar shapes and the same energy
    - · Subshells are named s, p, d, and f
    - · An s subshell has only one orbital (2 es), p has 3 (6 es), d has 5 (10 es), and f has 7 (14 es)
    - · Subshells are grouped into shells, which are indicated by numbers (1, 2, 3, etc.)
    - · These numbers are the numbers in the Rydberg equation, and are the principle energy levels
    - · The first shell only has an s subshell, and each shell beyond that adds one type

    Practice: How many electrons can be placed in a p subshell? (6)

    How many electron can be placed in the 3rd shell? (18)

    Which of the following subshells does *not* exist? $2s$, $3f$, $3p$, $5d$ ($3f$)

- ○ Subshells each have orbitals with different *shapes* (Figure 6.21)

    - · Because of the Heissenberg uncertainty principle, we describe region where an electron is likely to be found
    - · These regions have shapes based on the mathematical functions which form them
    - · s orbitals are spherical, p orbitals are dumbells, d orbitals are clover-leafed

- ○ Quantum Numbers

    - · Remember that orbitals are actually mathematical functions
    - · Certain parts of those functions depend on integer numbers (like n in the Rydberg equation)
    - · These integer numbers are called *quantum numbers*
    - · Quantum numbers can be thought as an "address" for each electron (Street, Buildling, Unit, Name)
        - ∗ n – Principal quantum number (1, 2, ...) gives orbital shell, energy, and size
        - ∗ l – Angular momentum quantum number ($0, 1, ..., n-1$) gives orbital subshell and shape
        - ∗ l is why not all shells have all orbital types
        - ∗ m_l – Magnetic quantum number ($-l, ..., l$) gives orbital within a subshell (different spatial orientations)
        - ∗ m_l is why subshells have different numbers of orbitals
        - ∗ m_s – Spin quantum number $\left(\pm\frac{1}{2}\right)$ gives "spin" of the electron (up- or down- arrow, Figure 6.23)
    - · Each electron in an atom/ion must have a *unique* set of quantum numbers – Pauli Exclusion Principle
    - · You should be able to point to the right electron given a set of quantum numbers, or give the 4 quantum numbers for an indicated electron in an energy level diagram

        Practice: Give numbers or indicate electrons on an energy level diagram

Quiz 6.2 - Orbitals and Quantum Numbers

Homework 6.2

- 33: Properties associated with quantum numbers

- 35: Identifying the subshell from quantum numbers

- 41: Orbital shapes and other properties

6.4   Electronic Structure of Atoms (Electron Configurations)

- Electronic energy level diagrams

    - The orbitals within each subshell are precisely equal in energy (degenerate)
    - The subshells themselves differ in energy (their order will be explained shortly)
    - Draw the subshells with one line for each orbital
    - Each orbital can hold two electrons, drawn as up- and down-arrows
    - Find the total number of electrons for the element or ion
    - Aufbau Principle – Fill up the orbitals with electrons from the bottom-up
    - Hund's Rule – Fill a subshell with one electron in each orbital before pairing them up (like roommates in an apartment)
    - This is the ground-state configuration of the element

- We can use the periodic table as a cheat-sheet to the order of the subshells and electron configurations (Figure 6.27)

    - The P. T. is actually quite long – Lanthanides and Actinides have been cut and pasted
    - Each region of the P. T. represents a different subshell
    - The rows represent different shells
    - The number of elements in each block is the number of electrons each shell can hold
    - The d-block and f-block trail the row number by 1 and 2 ($d(-1)$ and $f(-2)$)
    - The order of the subshells is found by simply following the elements and noting in which block they reside

- The arrangements of the electrons can be written as an electron configuration

- Write the subshells, with their number of electrons as a superscript

    Practice: Write the electronic configurations for O, Zr, and Bi

- Especially for large elements like Pb, these configurations are very unwieldy

- We can shorten them by referencing the configuration of the *preceding* noble gas

- The electrons which make up this noble gas configuration are buried inside the atom, and called *core* electrons

○ For Bi, we get $[\text{Xe}]\, 6s^2 4f^{14} 5d^{10} 6p^3$

○ The outermost electrons (The ones we write) are called *valence* electrons, and are the ones involved in bonding and ion formation

○ A few transition metals have anomalous configurations (memorize only Cr and Cu)

○ The Lanthanum and Actinium boundary also shows some anomalies (don't memorize them)

○ Figure 6.29 gives the valence configuration of every element's ground state

○ Technically, filled d and f subshells count as *core*, and only the outermost s and p electrons will always count as *valence*

○ This means that only the main group elements have a reliable pattern in their number of valence electrons

○ The number of valence electrons is the same as the "A" column names

○ We can write the configurations of ions as well

· For most, simply add or remove electrons according to the normal pattern

· Transition metals will lose the outermost s electrons before they lose any d electrons (This is why so many transition metals have a stable $2+$ ion)

· Ions and atoms with identical configurations are called *isoelectronic* to each other

Practice: List several stable ions which are isoelectronic with Ar

Quiz 6.3 - Electronic Configurations

Homework 6.3

○ 49: Complete electron configurations

○ 53: Energy level diagram of valence electrons

○ 55: Identify an atom from its configuration

○ 57: Identify an ion from its configuration

○ 63: Electron configuration of an ion

○ 79: Isoelectronic configurations

6.5   Periodic Variations in Element Properties

○ The sizes of atoms and ions is controlled by the attractive and repulsive forces between electrons and protons

- Electron and protons attract each other, shrinking the atomic size
- Electrons repel each other, increasing the atomic size

○ Effective nuclear charge (Z_{eff}) attempts to summarize these interactions

- The actual nuclear charge (Z) is just the number of protons (quite high for larger elements)
- Core electrons will counteract much of the actual nuclear charge (called *shielding*)
- $Z_{eff} = Z - S$ S stands for "Shielding"
- S can be closely approximated by the number of core electrons
  Practice: Find Z_{eff} for Mg, S, and Br (2, 6, and 7)
- Slater's rules gives a more sophisticated and accurate value for S
- 1 for deep core electrons, 0.85 for $V - 1$ electrons, and 0.35 for all but one V electron
- Note that Slater's rules are not in your textbook
  Practice: Find Z_{eff} for the same elements using Slater's rules (2.85, 5.45, and 7.6)

○ Atomic radius increases down a column because you are adding and entire new shell for each row

○ Atomic radius decreases across a row because of the increasing Z_{eff}

○ This makes He the smallest element, and Fr the largest (Figure 6.30 and 6.31)

○ Anions are much larger and cations are much smaller than their neutral counterparts (Figure 6.32)

○ Ionization energy (IE) is the energy required to remove an electron

- For example, it is the energy for this process: Li $\longrightarrow$ Li$^+$ + e$^-$
- The two factors which control IE are radius, and Z_{eff}
- It is easier to remove electrons (smaller IE) from larger atoms
- It is easier to remove electrons (smaller IE) from atoms with lower Z_{eff}
- Opposite to radius, He has the highest IE, and Fr has the lowest IE
- There are breaks in this trend at the beginning and middle of the p block (Figure 6.33 and 6.34)

○ Second- and third- ionization energy is the energy to remove a second and third electron (Table 6.3)

- Each successive electron is harder to remove
- After the valence electrons are gone, removing a core electron is *much* harder to remove

○ Electron affinity (EA) is the energy released when an electron is added

- Electron affinity is usually exothermic, so these values are mostly negative
- The *magnitude* of EA follows the same trend as IE
- There are lots of breaks in the trend (Figure 6.35 is a mess), so don't worry too much about EA

Quiz 6.4 - Periodic Trends

Homework 6.4

- 67: Atomic radius trend

- 71: Ionization energy trend

- 75: Ranking atomic radii

- 77: Ranking ionic radii

- 85: Second ionization energy

CHAPTER 7

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CHEMICAL BONDING AND MOLECULAR GEOMETRY

7.1 Ionic Bonding

○ Metal and nonmetal elemental atoms will react to form an ionic compound (Figure 7.2)

○ The number of electrons gained/lost will result in noble gas configurations for both elements

○ The cation and anion are now attracted to each other, and bind together in a lattice structure

○ A *formula unit* is the smallest unit which builds the extended lattice (Figure 7.3)

○ Ions will combine in the correct ratio to balance the charge

　· Find the least common multiple of the positive and negative charges
　· Some high school classes teach a shortcut that doesn't always work: (TiO_2)

○ Electronic configuration of many ions will be isoelectronic with a noble gas

7.2 Covalent Bonding

○ In both ionic and covalent compounds, bonds will form to complete the atoms' *octets* (*duets* in the case of H)

○ Instead of transferring electrons to form ions, covalent compounds will share electrons

○ The electrons in a covalent bond will count toward the octets of both bonding partners

○ Drawing dot structures, we can see how many bonds an atom might need to form to fill its octet

○ We'll usually represent two shared electrons in a bond by a dash – this is the beginning of Lewis structures

○ Electron pairs not involved in a bond are called *lone pairs*

○ Single, Double and Triple bonds share 2, 4, and 6 electrons, respectively

○ Double and triple bonds are shorter and stronger than single bonds

　Practice: Draw dot diagrams and Lewis diagrams for the diatomics F_2, O_2, and N_2
　　　　　　Identify the bonds by their type, as well as any lone pairs

○ Figure 7.4 shows the energetics of covalent bonds

○ Bond polarity

- Figure 7.5 shows electrons being shared unequally between bonding partners
- The electrons will favor the element with greater electronegativity (Figure 7.6)
- The uneven distribution of charge is called a *dipole* and the bond is called *polar*
- Polar covalent bonds exist along a continuum from purely covalent to purely ionic (Figure 7.8)
- Greater electronegativity differences give greater ionic character to the bond
- Similar (or identical) electronegativities create non-polar bonds
- The dipole moment is $\mu = qr$, and can be measured
- Real dipole moments can be compared to the value for a complete transfer of electrons to give $\% \ ionic \ character$
- $\% \ ionic \ character = \dfrac{\mu_{measured}}{\mu_{ionic}} \times 100\%$

7.3   Lewis Symbols and Structures

- For more complex molecules, dot diagrams are not robust enough to predict the proper structure

- Follow these 8 steps:

  - Find the total number of valence electrons, considering any overall charge
  - Write the peripheral atoms around the central atom
    * Central atom will be the least electronegative (except H)
    * This is often the first atom written in a formula (except H)
    * H will never be the central atom because it can only form 1 bond
  - Connect each peripheral atom to the central atom with single bonds
  - Place the remaining valence electrons around the peripheral atoms until their octets are complete
  - If any electrons remain, place them on the central atom
  - Convert peripheral lone pairs into double or triple bonds according to these two rules
    * Make multiple bonds until the central atom has a complete octet
    * Make multiple bonds in a way that minimizes *formal charges* (more on this later)
  - Verify that the octet and duet rule are followed for all atoms in the structure
  - If there is a charge, enclose the structure in square brackets and write the charge

  Practice: CH_4, H_2O, NH_3, HCN, CH_2O, NO_3^-, CO_3^{2-}, and NH_4^+

Quiz 7.1 - Lewis Structures

Homework 7.1

- 15: Comparing electronegativities

- 21: Comparing bond polarities

- 29: Drawing Lewis structures

- 31: More challenging Lewis structures

7.4 Formal Charges and Resonance

- Resonance and Formal Charge

  - Often times we will have an arbitrary choice about which peripheral atom to form a double bond with

  - Consider CO_3^{2-}, you could form the double bond with any of the three oxygens

  - In these instances, the molecules will exhibit a phenomenon called *resonance*

    * Resonance is when electrons in a double (or triple) bond are shared between two or more bonding locations

    * CO_3^{2-} forms a bond with *all three* oxygen atoms

    * It is not nearly as strong as a normal double bond, because the electrons are spread between three bonding centers

    * This is called *delocalization*, and sometimes the trio of bonding locations are collectively called a delocalized bond

    * The bond lengths are all the same, somewhere between a single and double bond length

  - We represent resonance two ways: First, resonance structures

    * Draw a different structure for each bonding location

    * Enclose each structure in square brackets (even for neutral structures)

    * Draw double-headed arrows between the structures

  - The other method is hybrid structures

    * Draw a single structure, with dotted lines for each bonding location

    * These structures are closer to an accurate picture of reality

    * Counting electrons in these structures is impossible (bonds and lone-pairs)

    Practice: Draw the resonance structures and hybrid structure for NO_3^- and O_3

  - Formal charge compares how many electrons an atom has within an molecule to its number of valence electrons

    * First draw a Lewis structure

    * Count the electrons around an atom, dividing the bonding electrons between bonding partners

    * Subtract this number from the number of valence atoms

- Formal charge can be used to determine which structures are best when there are options
  - ∗ Minimize the total formal charge
  - ∗ Favor structures with negative formal charges on the more electronegative atoms
  - Practice: Find the best structures for OCN and N_2O

Quiz 7.2 - Formal Charges and Resonance

Homework 7.2

- 45: Resonance in Lewis Structures (Note that some figures are omitting the lone pair and multiple-bond electrons)

- 51: Determining formal charges

- 55: Formal charges in resonance structures

- 57: Using formal charge to determine the best structure

Resume Section 7.4

- Exceptions to the Octet Rule

  - A few elements will have *fewer* than 8 electrons
    - ∗ Be has only 2 electrons, so it can form only 2 bonds
    - ∗ B has only 3 electrons, so it can form only 3 bonds
  - Radicals are compounds with an unpaired electron
    - ∗ Radicals tend to be very reactive
    - ∗ Many radicals contain N (NO and NO_2)
  - Some elements can have *more* than 8 electrons
    - ∗ Only elements in the 3rd row or below can exceed the octet rule
    - ∗ This is because the extra electrons go into the d subshell
    - ∗ This can occur in order to minimize formal charges
      Practice: Find proper Lewis structures for SO_4^{2-}, PO_4^{3-}, ClO_3^-, and ClO_4^-
    - ∗ It can also occur because there are simply too many outer atoms
      Practice: Find proper Lewis structures for SF_6, ClF_5, and PCl_5

Quiz 7.3 - Violations of the Octet Rule

Homework 7.3

- 58: Sulfur dioxide, how formal charge motivates violations to the octet rule

- 63: Sulfuric acid structure

7.5   Strengths of Ionic and Covalent Bonds

○ Covanet Bond Enthalpy

   · Bond enthalpy is the energy required to break a bond
   · Really, not every $C-H$ bond is the same. The surrounding atoms affect bond enthalpy
   · We can take the average enthalpy of a given bond type over many molecules (Table 7.2)
   · This gives us a new way to calculate reaction enthalpies

      * Draw a Lewis structure for each reactant and product
      * identify the numbers and types of bonds
      * Consider first breaking all the bonds of the reactants to produce individual atoms
      * Then form new bonds between the atoms to make products
      * $\Delta H_{rxn} = \sum\limits_{Bonds\ Broken} n \cdot \Delta H_{Bond} - \sum\limits_{Bonds\ Formed} n \cdot \Delta H_{Bond}$
      * This will give an *approximate* reaction enthalpy

   · Table 7.3 gives average values for bond lengths as well

   Practice: Using Table 7.2, estimate the reaction enthalpy for the combustion of methane $\left(-810\, \dfrac{kJ}{mol} \right)$

Quiz 7.4 - Bond Enthalpies

Homework 7.4

○ 65: ΔH_{rxn} based on bond enthalpies

○ 67: Determining the more stable isomer

Resume section 7.5

○ Lattice Energy

   · Consider the reaction: $K(s) + \frac{1}{2} Cl_2(g) \longrightarrow KCl(s)$ $\Delta H_f^{\circ} = -437\, \dfrac{kJ}{mol}$
   · The energy of formation is more than just the IE of the metal and EA of the non-metal
   · The Born-Haber Cycle is an alternate route for formation reactions of ionic compounds:

      * The steps of the Born-Haber cycle are shown in Figure 7.13
      * Sublimating the metal, breaking the diatomic bond, IE, EA, and lattice energy
      * The lattice energy is directly related to the attractive force between the ions

   · Lattice energy is controlled by two factors:

      * Ions with larger charges have higher lattice energies
      * Smaller ions have higher lattice energies

Quiz 7.5 - Ionic Bonds

Homework 7.5

- 77: Identifying smallest lattice energy

- 79: Effect of charge on lattice energy

- 81: Comparing lattice energies

7.6   Molecular Structure and Polarity

- VSEPR Theory and Geometry

  - The three-dimensional shape of a molecule is important to its properties
  - *Isomers* are molecules with the same chemical formula, but a different 3-dimensional arrangement of its atoms
  - Isomers might have quite different properties despite their identical composition
  - Valence Shell Electron Pair Repulsion (VSEPR) model: (Figure 7.16)
    * VSEPR is based on the idea that electron pairs will arrange themselves to be as far apart from each other as possible.
    * This model gives accurate geometries for covalent molecules
    * First, draw a good Lewis structure
    * *Electron Domains* are the regions around the central atom where electrons group – A single bond, a double bond, a triple bond, and a lone pair are all electron domains
    * The number of electron domains will give the *electron geometry* – This electron geometry is the template on which molecular geometry is based
    * Demo: Balloons naturally adopt the electron geometries
    * Next, count how many domains are bonding vs lone pairs
    * The number of bonds within the electron geometry determines the molecular geometry (Figure 7.18)
    * Figure 7.19 sums it all up nicely – Just memorize this table
    * Trigonal Bipyramidal electron geometry
      - The 2 axial and 3 equatorial positions are different (Figure 7.20)
      - Lone pairs will occupy the equatorial positions first
      - Linear molecules are symmetrical (this will matter later)
    * Octahedral electron geometry
      - All the positions are equivalent
      - The second lone pair will be opposite the first one
      - Square planar molecules are symmetrical (this will matter later)
  - For larger molecules, you can apply VSEPR to each bonding center (consider CH_3CO_2H)

- ○ Molecular Polarity

    - · We already discussed electronegativity and its role in making polar *bonds*
    - · For molecules with many polar bonds, those dipoles might cancel each other out or work together to make a polar molecule
    - · The *molecular dipole* is the vector sum of all the bond dipoles (Figure 7.27)
    - · Factors that make non-polar molecules:
        - ✳ No polar bonds like diatomic elements and O_3
        - ✳ Symmetry in the polar bonds (no lone pairs, or linear and square planar molecules)
    - · Factors that make polar-molecules:
        - ✳ Lone pairs which break symmetry
        - ✳ Bonds with different atoms (CH_2Cl_2)

Quiz 7.6 - Molecular Geometry and Polarity

Homework 7.6

- ○ 87: Electron geometry vs. molecular geometry

- ○ 89: Non-polar molecules which contain polar bonds

- ○ 93: Finding electron and molecular geometries

- ○ 97: Identifying molecular dipoles

CHAPTER 8

ADVANCED THEORIES OF COVALENT BONDING

8.1   Valence Bond Theory

○ Figure 8.1 shows the paramagnetic behavior of Oxygen, which cannot be explained by previous bonding theories

○ Why should sharing electrons lead to a bond?

○ Figure 8.2 shows how the energy changes with internuclear distance in H_2

○ When the orbitals from both bonding partner overlap, these forces are optimized to form a bond

○ Figure 8.4 shows a σ bond, where the overlap region is directly between the two bonding atoms

○ Figure 8.5 shows a π bond, where the overlap regions are above and below the bond axis

○ Every bond contains a σ bond, and multiple bonds add one or two π bonds

8.2   Hybrid Atomic Orbitals

○ Orbital overlap cannot explain the actual geometries we see in molecules. No atomic orbitals have a tetrahedral or trigonal planar geometry, for example

○ Figure 8.6 shows a model of water with $90°$ bond angles (derpy water) predicted by atomic orbital overlap

○ Hybridization is the linear combination (mixing) of atomic orbitals

   · Remember that orbitals are simply mathematical functions
   · Consider the functions $f_1(x) = x^2$, $f_2(x) = x^3$, and $g(x) = f_1(x) + f_2(x)$
   · Atomic orbitals can similarly be combined to form new orbitals, called *hybrid* orbitals
   · Show my hybridization figures
   · The number of hybrid orbitals is equal to the number of atomic orbitals mixed together
   · We name the orbitals and the type of hybridization by the atomic orbitals used (sp, sp^2, and sp^3)
   · These hybridization types correspond to the electron geometries (Figure 8.7)

○ Different hybridization types

   sp: Linear geometry. Figures 8.8 and 8.9

sp^2: Trigonal planar geometry. Figures 8.10-14

sp^3: Tetrahedral geometry. Figures 8.15-17

sp^3d: Trigonal bipyramidal geometry. Figures 8.18-19

sp^3d^2: Octahedral geometry. Figure 8.20

○ Hybridization geometries are summarized in Figure 8.21

Quiz 8.1 - Hybridization

Homework 8.1

○ 9: Motivating hybridization

○ 11: Limits on sp^3d hybridization

○ 13: Relating hybridization to geometry

○ 15: Hybridization from Lewis Structures

8.3   Multiple Bonds

○ Hybrid orbitals are used for 2 purposes: forming σ bonds, and housing lone pairs

○ σ bonds have electron density aligned along the bond axis

○ Single bonds are σ bonds, and multiple bonds each contain a σ bond

○ For sp and sp^2 hybridized atoms, unhybridized p orbitals remain

○ These unhybridized p orbitals are used to form π bonds

○ π bonds have electron density along either side of the bond axis

○ Double bonds

· Double bonds contain 1 π bond

· Figure 8.22 shows the energy levels of the orbitals in a double bond

· Figure 8.23 shows the orbitals of an ethene molecule

○ Triple bonds

· Triple bonds contain 2 π bonds

· Figure 8.24 shows the atomic and hybrid orbitals of an sp atom

· Figure 8.25 shows the orbitals of an acetylene molecule (ethyne)

○ Multiple p orbitals overlap in molecules which exhibit resonance (like benzene and nitrate) (Figure 8.26)

- Use BLMB Figures 9.23-9.28

- Valence bond theory and secondary structure

  - Molecules can twist around their bonds without changing bond lengths or angles
  - These rotations create different *conformations* (show with molecular models)
  - The differences between σ and π bonds has significance to how molecules can move
  - σ bonds have the same overlap no matter how you rotate them, so rotation does not break the bond
  - This makes rotating around σ bonds energetically free and easy
  - π bonds, however, would break if you twist them by $90°$ because they lose their overlap
  - π bonds are constrained, and cannot rotate without a substantial energy input

Quiz 8.2 - Valence Bond Theory

Homework 8.2

- 23: Composition of a triple bond

- 25: Hybridization and multiple bonds

- 29: Hybridization and electron delocalization

8.4 Molecular Orbital Theory

- In hybrid orbital theory, we combined atomic orbitals from the same atom to create new hybrid orbitals

- These hybrid orbitals had new shapes, which could explain bonding geometries

- We can apply the same trick to molecules - combine atomic orbitals from *different* atoms across a molecule to create new orbitals

- These new orbitals span the whole molecule, and are called *molecular orbitals*

- Molecular orbitals are the closest approximations to the true Schrödinger equation solutions

- Molecular orbitals can combine in two ways (Figures 8.28-29):
  - Adding orbitals together creates constructive interference between the orbitals
  - Orbitals which combine constructively increase the electron density between the atoms
  - This leads to stronger bonds, so these MOs are called *bonding* orbitals
  - Subtracting orbitals creates destructive interference between the orbitals
  - Orbitals which combine destructively decrease the electron density between the atoms
  - This leads to weaker bonds, so these MOs are called *antibonding* orbitals (and get a * label)

- Both of the orbitals formed from s orbitals have electron density along the bond axis, so they are called the σ_{ns} and σ_{ns}^* orbitals

○ p orbitals can combine as well

- Head-on combination creates two more σ orbitals (Figure 8.30)
- Sideways combination creates orbitals with density along either side of the bond axis, so they are π_{2p} and π_{2p}^* MOs (Figure 8.31)
- Because there are two pairs of p orbitals that can combine this way, there are two degenerate π_{2p} and two degenerate π_{2p}^* orbitals
- The ordering of the π_{2p} and σ_{2p} orbitals is different for different elements (Figure 8.37)

○ Molecular orbital diagrams

- When we draw molecular orbital diagrams, it is helpful to show the atomic orbitals which gave rise to the MOs
- Draw the atomic energy level diagram for each atom on either side of the MO energy levels
- Draw dotted lines showing how the atomic orbitals combine to produce new MOs
- Fill the MO energy levels from the bottom-up as usual (Figure 8.34)
- HOMO and LUMO orbitals are the most important for most chemical properties

○ We can tell the *bond order* (single, double, or triple bond) of a diatomic from its MO diagram

- Electron pairs which occupy a bonding orbital increase the bond order by 1
- Electron pairs which occupy a non-bonding orbital decrease the bond order by 1
- Molecules with a bond order of 0 (Ne_2) don't form a bond at all, and so don't occur naturally

○ Figure 8.37 shows the configurations for all period 2 homonuclear diatomics (note the different orbital ordering)

○ Figure 8.38 illustrates the change in orbital order due to s-p mixing (More mixing for Li-N)

○ Figure 8.40 shows a complete molecular orbital energy level diagram for O_2

○ Magnetic properties are also indicated by the MO diagram

- *All* materials are either attracted to or repelled by a magnetic field
- *Diamagnetic* materials are repelled by a magnetic field, while *paramagnetic* materials are attracted by a magnetic field. Ferromagnetism (regular old magnetism) is like a cooperative paramagnetic effect in some metals
- Diamagnetism comes from having all electrons paired. C_2, N_2, and F_2 are diamagnetic
- Paramagnetism comes from at least one unpaired electron. B_2 and O_2 are paramagnetic

○ Molecules that exhibit resonance will have π bonding MOs which span all of the bonding locations

○ Some molecules without traditional resonance will still show delocalization (1,3-butadiene)

○ Show some MOs in Avogadro on my laptop

Quiz 8.3 - Molecular Orbital Theory

Homework 8.3

- 41: Bond order of diatomic molecules

- 43: HOMO and ionization energy

- 47: Bond order of diatomic ions

- 49: MO diagrams and magnetic properties

GASES

9.1 Gas Pressure

○ Figure 7.1 shows the different phases from a molecular perspective

○ The force a gas exerts is called pressure

○ Pressure can be measured in many ways, including with a barometer (Figure 7.2)

○ Atmospheric pressure depends on elevation, temperature, and humidity

○ $1\ atm$ is just a standard for pressure under certain conditions

○ There are two other common units for pressure: $1\ atm = 760\ torr = 760\ mmHg$

○ And two less common units for pressure: $1\ atm = 101.325\ kPa = 1.01325\ bar$

○ Standard Temperature and Pressure (STP) is $0°C$ and *either* $1\ atm\ or\ 1\ bar$, so until this dual usage is resolved it is unfortunately not a useful reference

9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

○ Boyle's Law

· In the 17th and 18th century, scientists were studying how gases responded to temperature and pressure

· Boyle studied how volume changed with pressure at constant temperature (Figure 7.4)

· Higher pressures lead to proportionately lower volumes

· $V \propto \dfrac{1}{P} \qquad PV = k \qquad P_1V_1 = P_2V_2$

○ Charles's Law

· Charles studied how volume changed with temperature at constant pressure (Figure 7.10)

· Higher temperatures led to proportionately higher volumes

· Figure 7.9 shows how the V/T curve can be extrapolated back to absolute 0 – Indeed, this method gave rise to the notion of absolute 0

· Consider doubling the temperature at $1\ K$ and at $1\ °C$. In the Kelvin scale, "double the temperature" has real, physical meaning (doubling the thermal energy)

· We *must* use the Kelvin temperature scale in these types of problems

- $V \propto T$ $\dfrac{V}{T} = k$ $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

  o The Combined Gas Law

    - Boyle's law and Charles's law can be combined to compare states with different temperatures, volumes, and pressures

    - $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$

      Practice: A balloon with $V = 1.25\ L$ at $P = 0.850\ atm$ and $T = 284\ k$ is released into the atmosphere where $P = 0.430\ atm$ and $T = 243\ K$. What is the new volume? $(2.11\ L)$

  o Avogadro's Law

    - For the previous laws, the proportionality constants k were always different for different gases

    - Once we established molar masses, scientists could investigate the relationship between n (# of moles) and P, V, and T

    - Avogadro's law states that V is proportional to n at constant T and P

  o Ideal Gas Law

    - Avogadro's law was the final piece to get a universal gas constant. k became R

    - $\dfrac{PV}{nT} = R$ is usually rearranged as $PV = nRT$

    - $R = 0.08206\ \dfrac{L\ atm}{mol\ K}$, but there are also other useful units (see Wikipedia page for R)

    - This is called the *ideal gas law*. An *ideal gas* is one that follows this law perfectly

    - Real gases will deviate from this law a little, but it is reliable at normal temperatures and pressures

      Practice: Standard temperature and pressure are defined as $0.00\ °C$ and $1.00\ atm$
      Find the volume of $1.00\ mol$ of an ideal gas at STP $(22.4\ L)$

Quiz 9.1 - Gas Laws

Homework 9.1

  o 5: Units of pressure

  o 15: Measuring pressure with an open-end manometer

  o 25: Using PV=nRT

  o 27: Gas laws

  o 33: PV=nRT and grams

  o 45: Combined gas law

9.3   Stoichiometry of Gaseous Substances, Mixtures, and Reactions

○ Dalton's Law of Partial Pressures

· In a mixture of gases, each component will exhibit a pressure the same as if the others weren't there

· The total pressure is the sum of all these *partial pressures*

· This means that we can find the total pressure of a mixture of gasses by counting the total moles of all gases present

· We can find the pressure of one component from the total pressure and the relative composition

· $P_A = \chi_A P_{total}$

Practice: O_2 accounts for about 21% of the molecules in our atmosphere. Find the partial pressure of O_2 based on today's barometric pressure

○ Molar Mass and Density in Gas Law Calculations

· We can modify the ideal gas law to relate the molar mass of a gas to its density

· $PV = nRT \rightarrow \dfrac{n}{V} = \dfrac{P}{RT} \rightarrow \dfrac{nM}{V} = \dfrac{PM}{RT} \rightarrow d\left(\dfrac{g}{L}\right) = \dfrac{PM}{RT}$

· Note that this is a density in $\dfrac{g}{L}$. Gases are very diffuse and have very low densities

Practice: There are two ways we commonly create buoyancy in the atmosphere: He, and hot air. Calculate the density of regular air (assume pure N_2) and He at STP, and the density of regular air at $325\,°C$ ($0.625\,g/L$, $0.179\,g/L$, and $0.285\,g/L$)

Practice: An unknown gas is found to have density of $0.575\,\dfrac{g}{L}$ at $22.4\,°C$ and $0.87\,atm$. Give a reasonable guess for the chemical identity of the unknown gas (CH_4)

○ Gases in Chemical Reactions

· We can also use the ideal gas law to predict volumes or pressures of a product in a chemical reaction

Practice: $0.25\,g$ of Na are reacted with acid according to the following equation:
$2\,Na(s) + 2\,H^+(aq) \longrightarrow 2\,Na^+(aq) + H_2(g)$
If $T = 295\,K$ and $P = 0.875\,atm$, what volume will the $H_2(g)$ product occupy? ($0.150\,L$)

Practice: Consider the reaction: $2\,Hg_2O(s) \longrightarrow 4\,Hg(l) + O_2(g)$
$2.50\,g$ of Hg_2O are placed in a sealed $0.500\,L$ chamber at $0.82\,atm$ and decomposed through heat. Once thermal equilibrium is reached at $T = 297.5\,K$, what will be the final pressure inside the chamber? ($0.97\,atm$)

Quiz 9.2 - Calculations with Gases

Homework 9.2

- 49: Density of a gas sample

- 53: Molar mass from gas properties

- 57: Partial pressures

- 63: Partial pressure for a gas collected over water

- 65: Gas laws and reaction stoichiometry

9.4 Effusion and Diffusion of Gases

- The equation for the 5$^{\text{th}}$ postulate is: $KE_{avg} = \dfrac{3}{2}k_B T$

- KE_{avg} is the average kinetic energy, and k_B is the *Boltzmann* constant

- We don't really need to use the Boltzmann constant because $N_A k_B = R$, and it is useful to talk about molar amounts anyway

- So, we get $KE_{avg} = \dfrac{3}{2}RT$ You should actually use $R = 8.314\ \dfrac{J}{mol\ K}$

- We also know that $KE = \dfrac{1}{2}Mv^2$ (note that this is also a molar amount), so we can write: $\dfrac{1}{2}Mv^2 = \dfrac{3}{2}RT$

- This can be solved to give the rms average velocity for a gas particle: $v_{rms} = \sqrt{\dfrac{3RT}{M}}$

- Note the "unit purgatory" issue here – you must use $J \equiv \dfrac{kg\ m^2}{s^2}$, and express M in kg

- *rms velocity* is the square-root of the average of the squared velocities

- v_{rms} is used rather than mean velocity because the temperature is proportional to v^2, rather than v itself

- Figures 10.13 and 10.14 from BLMB show different velocity distributions for different gases and conditions

  Practice: Find v_{rms} for N$_2$, SF$_6$, and He at $-20.00\ °C$ and $150.0\ °C$

           $-20\ °C(474.8\ ^m/_s, 207.9\ ^m/_s, 1256\ ^m/_s)$ $150\ °C(613.8\ ^m/_s, 269.4\ ^m/_s, 1624\ ^m/_s)$

- Diffusion is the spread of a gas from areas of high concentration to areas of low concentration

  · Diffusion happens much more slowly than v_{rms} because the molecules collide so frequently

  · Gas molecules take a random walk, deflected in a new direction with each collision

- The *mean free path* is only about $70\ nm$ for STP
- Higher pressures decrease the mean free path and slow down diffusion
- In a vacuum, the diffusion rate approaches v_{rms}

○ Effusion is the slow leak of a gas through a hole

○ These two processes both depend on v_{rms}

○ Graham's law compares the effusion/diffusion rates of two gases: $\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$

Practice: Effusion can be observed by reinforcing a balloon with tape, then poking a hole through the tape

Compare the effusion rate for a He and N_2 balloon $\left(r_{\text{He}} = 2.65 r_{N_2}\right)$

9.5   The Kinetic-Molecular Theory

○ The kinetic molecular theory of gases is a model which can be used to derive the ideal gas law from first principles

○ There are five postulates which define the theory:

1. Gases are composed of small particles that are in constant, random motion (Video 7.20)
2. The volume that is taken up by the molecules themselves is vanishingly small compared to the total volume of the gas
3. Forces between the particles are negligible
4. Molecular collisions are perfectly elastic
5. The average kinetic energy of the gas molecules is directly proportional to the temperature

○ These postulates are grounded in mathematical equations which can be analyzed through statistical dynamics to apply to large ensembles of particles and give observable state properties

- Pressure results from the billions of collisions between gas particles and the chamber walls
- Adding more gas particles will increase the frequency of collisions, raising the pressure
- The average kinetic energy depends only on temperature, not chemical identity of the gas. This explains Dalton's law of partial pressures

9.6   Non-Ideal Gas Behavior

○ The ideal gas law is *technically* only valid for an ideal gas with no attractive/repulsive forces

○ Real gas particles *are* attracted to each other, albeit weakly

○ These attractions are particularly important at high pressures and temperatures

○ For one mole of an ideal gas, $\dfrac{PV}{RT} = 1$ at all temperatures and pressures

○ Figure 7.26 shows how $\dfrac{PV}{RT}$ varies with pressure and temperature

○ Figures 10.19 and 10.20 from BLMB show the compression factor for different gases and conditions

○ The van der Waals equation is an improvement on the ideal gas law, which works better for real gases

· $$\left[P + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT \quad \text{–or–} \quad P = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

· The a term accounts for attractions between gas particles and reduces the pressure of real gases

· The b term accounts for the finite volume of gas particles and increases the pressure of real gases

· Table 7.4 gives van der Waals a and b terms for many common gases

Practice: Use both the ideal gas law and the van der Waals equation to find the pressure for:
1.00 mol of CCl_4 at 250 K in 10.0 L and 1.00 L

(2.0515 atm, 1.881 atm, 20.515 atm, and 37.79 atm)

Quiz 9.3 - Gas Kinetics

Homework 9.3

○ 81: Comparing rates of effusion

○ 93: Molar mass and speed distribution

○ 99: Charts and non-ideal gas behavior

○ 101: Conditions which deviate from ideality

○ 103: Molecular volume of real gases

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

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