CHEM 1210 Lecture Notes

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COURSE ADMINISTRATIVE DETAILS

○ My office hours

○ Intro to my research

○ Introductory Quiz

○ Grading details

- · Exams - 40, Final - 20, Homework - 30, 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.
- · Achieve Homework
- · Textbook

○ Algebra Review Assignment ○

○ Introduction to chemistry

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

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CHAPTER 1

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SCIENCE AND MEASUREMENT

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1.1 Classification of Matter

○ Matter is anything that has mass and occupies space

○ *Elements* are the basic building blocks of the stable matter around us

○ Atoms are the smallest, indivisible pieces of matter (demo with a copper penny)

○ Atoms bond together in chemical bonds (more on them later)

○ When 2 or more elements combine in a definite ratio, they form *compounds*

　· Definite proportions and the analogy with bread recipes

　· Chemical compounds are different from their elements (drowning in water - 89% Oxygen)

○ Pure substances vs mixtures (Figure 1.1)

○ Heterogeneous vs homogeneous mixtures (Figure 1.2)

○ "Solution" is just another name for an homogeneous mixture

1.2 Properties of Matter

○ The first categories of properties are *physical* vs *chemical*

　· Physical properties can be measured or observed without changing the *chemical identity*

　· Chemical properties can only be measured or observed by changing the *chemical identity*

　· Mass, density, color (absorption spectrum), specific heat, solubility, etc. are physical

　· Flammability, oxidization potential, acidity/basicity, corrosiveness, etc. are chemical

○ The next categories are *extensive* vs *intensive* properties

　· Extensive properties depend on the amount of a substance – mass, volume, enthalpy of combustion, heat capacity, etc.

　· Intensive properties are independent of the amount of a substance – density, temperature, reactivity, specific heat, etc.

○ Finally, we categorize *physical changes* and *chemical changes*

- Phsyical changes do not change the chemical identity of a substance, and can readily be undone - dissolving, phase changes, deformations, temperature changes, etc.

- Chemical changes cannot be undone because the chemical identity of the substance has changed - oxidation, combustion, corrosion, etc.

- Chemical changes are accompanied by either the release or absorption of energy

- Starting materials in chemical changes are called *reactants*, and the final materials are called *products*

○ Demo with air and hydrogen balloons

1.3   Matter and Energy

○ All chemical phenomena involve changes in *matter* and/or *energy*

○ Mass is the amount of substance. Contrasted with weight, mass doesn't change due to gravity

○ Energy is the capacity to do work

- Forms of energy: Heat, Chemical, Nuclear, Kinetic, Potential, Electrical, Sound, Light
- Energy can be transferred or change form, but total energy is always conserved

1.4   The Scientific Method

○ The scientific method is an orderly process for determining information about the natural world (Figure 1.8)

- Observation – Something about the natural wold inspires a question
- Hypothesis – The scientist suggests a plausible answer or explanation for the observations
- Experiment – A carefully constructed experiment will test the validity of the hypothesis
  * Results inconsistent with the hypothesis force a revision, and retesting of the new hypothesis
  * Results consistent with the hypothesis suggest the hypothesis has merit
- Results should be corroborated by other scientists in independent experiments
- A well-supported hypothesis may become a *scientific theory*

○ The scientific method is based on the principle of *falsifiability*. It proves bad hypothese false, but can never *prove* a hypothesis to be true

○ As a hypothesis survives more and more experimentation, it becomes relieable enough to be considered a *theory*. Theories can later be proven wrong, but the new explanation is almost always a marginal extension of the older theory, which better explains certain edge cases

○ Entirely revolutionary new theories, such as Einstein's general relativity, are exceptionally rare

○ Figure 1.9 illustrates the differences between scientific laws, hypotheses, and theories

○ My story about magnets on string and the importance of following the scientific method

    · Why can't we just make conclusions based on observations (as opposed to experiments)?

    · How was my bias displayed in this story?

1.5   The International System of Units

○ There are often many different units to describe the same quantity (quart, liters, cubic centimeters, etc.)

○ The International System of Units is a standardized set of units used by scientists globally

○ Base units are the fundamental units that can describe everything we measure (Table 1.3)

    · Length - m

    · Mass - kg (note that the SI unit is *not* the gram)

    · Time - s

    · Electrical Current - A

    · Temperature - K

    · Luminous Intensity - cd

    · Countable Amount - mol

○ Large or small amounts can be described using metric prefixes (Table 1.4)

    · These prefixes are mostly based on powers of 10^3

    · You must know the prefixes and their abbreviations in Table 1.4

    · Introduction to simple conversions and scientific notation

○ Derived units describe quantities that combine multiple base units together

    · Volume can be $l \times w \times h$, or generalized to any shape

    · Density is $\frac{mass}{volume}$

    · Some derived units are given a new name: $J = \frac{kgm^2}{s^2}$

○ When using the SI units, conversions tend to be easy (even for complex derived units)

○ How much energy is required to accelerate a $1.75 \; kg$ object by $0.650 \; m/s^2$ over a distance of $3.20 \; m$? ($3.64 \; J$)

1.6   Significant Digits

○ Qualitative vs quantitative descriptions

○ For quantitative descriptions, uncertainty comes in the form of *accuracy* and *precision*

　· Accuracy refers to the average of a set of measurements corresponding to the true value (within a standard deviation)

　· If inaccuracies are known, then they can be subtracted by calibration

　· Precision refers to the standard deviation of a set of measurements on the same sample

　· Figure 1.13 shows accuracy vs. precision on a dart board

　· The precision of your tool should match the magnitude of the quantity to measure

　· Estimate the position between the smallest marks on rulers, burettes, etc. (Figure 1.14)

○ Precision is communicated through *significant figures*

○ Consider measuring something $1.5\ cm$ vs $1.4973\ cm$

○ Now consider $1.5\ cm$ vs $1.5000\ cm$

○ Identifying significant figures

　· Any non-zero digits are significant

　· Leading zeros are *never* significant

　· Zeros between two significant figures are also significant

　· Trailing zeros are significant if they come *after a decimal*

　· Practice: $4010, 0.0034, 7.100, 639, 000, 6.390 \times 10^5$

○ Scientific Notation communicates precision without any ambiguity; Every digit in the coefficient is *always* significant!

○ Logs and antilogs: Digits in the characteristic are not significant but those in the mantissa are

○ Propagating sig. figs through calculations

　· Identify the # of sig figs and the position of the least significant digit for both numbers

　· $+-$: The LSD of the answer will match the position of the LSD for the less precise input

　· Practice: $120.7\ g + 34\ g = 155\ g$　|　$212\ mm - 210.95\ mm = 1\ mm$

　· $\times/$: The answer will have as many sig. figs as the input with *fewer* sig figs.

　· Practice: $56.3\ miles/1.2\ h = 47\ ^{miles}/_h$　|　$1.5\ cm \times 3.62\ cm = 5.4\ cm^2$

○ Multi-step problems have two considerations:

　· Do not round intermediate answers to avoid compounding rounding errors

　· Keep track of both the # of sig. figs and the LSD for each intermediate answer

- Practice: $(0.0045 \times 20,000.0) + (2813 \times 12) = 34,000$

  $\frac{12.3g + 34g}{12.0cm^3 + 7.7cm^3} = 2.4 \, g/cm^3$ (wrong answer with premature rounding)

  $863 \times [1255 - (3.45 \times 108)] = 762,000$

1.7   Dimensional Analysis

○ Every measurement will have its associated *unit(s)*, which is just as important as the quantity itself

○ For any calculations, the units can provide a guide and a check on your process

○ Structuring your calculations around the units is a paradigm called *dimensional analysis*

- Treat units like algebraic quantities, which can cancel in calculations
- Conversions factors can be written as ratios. i.e. $1.00 \, in = 2.54 \, cm$ becomes $1 = \dfrac{2.54 \, cm}{1.00 \, in}$
- Consider both the starting and ending units, and how to convert from one to the other
- Solve the problem with the "picket fence" method
- Practice: How many m are in $1.00 \, ft$? $(0.305 \, m)$

  How many ¢ does someone make per second if their wage is $\dfrac{\$12.00}{h}$? $(0.3333 \, ¢/s)$

○ Be careful with squared or cubed units! Convert $0.05 \, m^3$ into cm^3 $(50,000 \, cm^3)$

1.8   Density

○ Density relates how much mass is in a given volume, and is responsible for buoyant forces, etc.

○ Table 1.7 gives the density of some common substances (add in $\approx 0.001 \, g/ml$ for gasses)

○ $density = \dfrac{mass}{volume}$

○ Volumes can be found by $l \times w \times h$, or by measuring the volume of displaced water

○ Practice: Find the density of a block with dimensions $1.5 \, cm \times 6.4 \, cm \times 13.2 \, cm$, and mass of $1.43 \, kg$. Can guess the material? $(11 \, g/ml - \text{Lead})$

  A gold nugget displaces $4.52 \, ml$ of water. What is its mass? $(87.2 \, g)$

1.9   Temperature Scales

○ There are three common temperature scales, Fahrenheit, Celsius, and Kelvin

○ Kelvin is based on a zero-point of absolute zero

○ Kelvin is essential to use in some formulas, but Celsius may be convenient at other times

- $T_{\circ C} = \dfrac{5}{9}\left(T_F - 32\right)$

    $T_F = \dfrac{9}{5}T_{\circ C} + 32$

    $T_K = T_{\circ C} + 273.15$

- Practice: Convert the current temperature from Fahrenheit to Celsius and Kelvin

    Find the Fahrenheit temperature of absolute zero $(-459.7^\circ F)$

CHAPTER 2

ATOMS AND THE PERIODIC TABLE

2.1   Chemical Symbols

○ Each element has a Symbol, which starts with a capital letter

○ Table 2.1 shows some common elements where the symbol doesn't match the English name

○ Compare CO and Co

○ *Chemical Formulas* use the symbols and subscripts to show how many atoms of each element are in a compound

○ Parenthesis show atom groups: How many oxygen atoms are in $Mg(ClO_3)_2$

2.2   The Laws of Chemical Combination

○ Careful experiments show reactions follow several laws

○ The Law of Conservation of Mass

○ The Law of Definite Proportions (For water, $1.00\ g$ O combines with $0.126\ g$ of H)

○ The Law of Multiple Proportions (For H_2O_2, $1.00\ g$ of O combines with $0.063\ g$ of H)
Possible ratios of N:O 1:1.14 (NO), 1:0.57 (N_2O), 1:2.29 NO_2

2.3   The History of the Atom

○ Based on these laws, Dalton formulated an atomic theory:

· Matter is made up of atoms

· Atoms of the same element are identical to each other. Atoms of different elements are different from each other

· Atoms combine to form molecules in whole-number ratios

· Different ratios of the elements give different chemical compounds

○ J.J. Thompson discovered the electron in 1897

· His cathode ray experiment showed that electrons are negatively charged

· Thompson found the $\dfrac{mass}{charge}$ ratio (Figure 2.5)

- · Millikan later found the electron mass itself (Figure 2.6)
- · Electrons were a component of atoms, but were first assumed to be distributed evenly through the atom (Figure 2.7)

○ Ernest Rutherford discovered the nucleus in 1909

- · Gold foil experimental details (firing a bullet into aluminum foil, vs. into a chainlink fence) (Figure 2.8)
- · The mass and positive charge of an atom are densely packed into the nucleus
- · Electrons exist diffusely outside of the nucleus (originally in orbits, now in clouds)
- · Atoms are mostly empty space (atom is $\approx$ 1 Å $(100,000 \ fm)$ across, and nucleous is $\approx$ 1 fm across)

○ Later, neutrons were also discovered, and are a part of the nucleus

2.4 Subatomic Particles, Isotopes, and Ions

○ The important subatomic particles are: electrons, protons, and neutrons (table 2.2)

○ For neutral atoms, $e = p$, but n could vary

○ The identity of an element depends entirely on p, so we call it the *atomic number* (Z)

○ The sum $p + n$ is the *mass number* (A)

○ Atoms of the same element with different mass numbers are *isotopes*

Practice: What is n for carbon with $A = 14$? (8) | What is n for lead with $A = 207$? (125)

○ The difference $p - e$ is the *charge* (Q). Atoms with charge $\neq 0$ are called *ions*

○ Positive charge = cation, negative charge = anion

○ Chemical symbols can show all these values like so: $^A_Z X^Q$

2.5 Atomic Masses

○ The mass of a single atom is too small to conveniently work with, so we use *atomic mass units* (AMUs)

○ The AMU is defined as $\dfrac{1}{12} M_{^{12}\text{C}}$, and is $1.00 \ g = 6.022 \times 10^{23} \ AMU$

○ The mass of a single proton or a single neutron are about $1 \ AMU$. An electron is about $\dfrac{1}{1800} \ AMU$

○ Individual isotopes have an actual, measured mass similar to their mass number

○ The masses we see on the periodic table are a weighted average, based on the isotope abundances

○ $Atomic\ Mass = \sum_{isotopes}(Fractional\ Abundance) \times (Isotope\ Mass)$

Practice: Give the atomic mass for Copper with:

	^{63}Cu	^{65}Cu
Mass (amu)	62.929601	64.927794
Abundance (%)	69.17%	30.83%

2.6 The Periodic Table

○ As the number of known elements grew, scientists began to organize them into categories

○ F_2, Cl_2, Br_2, and I_2 are highly reactive gases. Li, Na, K, and Rb are highly reactive metals

○ Arranging the elements according to reactive trends *and* size essentially gives us the periodic table

○ Dmitri Mendeleev is considered the father of the periodic table because he used his table to predict the existence and properties of undiscovered elements (Figure 2.15)

○ Gallium and Germanium were later discovered to have properties very close to what Mendeleev predicted

○ Now the periodic table is arranged by atomic number, rather than by mass

○ We have discovered all the elements up to 118, which may be the only stable elements at all

○ The periodic table is tremendously useful and information-rich in many ways which we will highlight in most chapters of the textbook

○ Structure of the periodic table:

· The periodic table is really long, but we cut out a portion to fit it on a page

· Rows are called *periods* (but I will just call them rows)

· Columns are called *groups* or *families*

· Groups are labeled by two conventions: numbered $1 - 18$, or $1A - 8A$

· Metals and non-metals are separated by the metalloids (Figure 2.19)

· Main group, transition metals, and inner-transition metals (Figure 2.18)

· Some families are named: Alkali Metals, Alkaline Earth Metals, Coinage Metals, Halogens, Noble Gases, and others you don't need to know (Figure 2.17)

CHAPTER 3

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COMPOUNDS AND THE MOLE

3.1   Chemical Formulas

○ We have already discussed how *Chemical Formulas* give the # and type of atoms in a compound

○ Another word for chemical formula is *Formula Unit*, which is especially used for ionic compounds

○ Molecular compounds are compounds composed of non-metals bonded together

　· One formula unit is a *molecule*, which is a discrete particle with clear boundaries

　· Atoms in a molecular compound are held together by *covalent bonds* – more on them in chapter 10

○ Ionic compounds are compounds composed of two ions bound together

　· The simplest ionic compounds are a metal bonded to a non-metal

　· Ionic compounds form bonds in a large array called a *lattice*

　· There is no clear boundary for a single formula unit, the lattice structure just goes on in all directions

　· Different compounds will have different lattice structures

　· These atoms are held together by *ionic bonds*, which are simply the attraction between negative and positive charges

○ Metals bonded to metals for *metallic bonds*, which we will not cover in this class

○ Some elements for molecules in their natural state

　· The *diatomic* elements are: H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2

　· Some solid elements form other molecules: P_4 and S_8

　· Some elements occur in more than one natural state, or *allotrope*
　　Carbon can form coal, graphite, or diamond. Oxygen can form common O_2 or ozone (O_3). Phosphorous comes in two forms (red, and white)

3.2   Naming Binary Covalent Compounds

○ Binary molecular compounds are made up two non-metals

○ Non-metals can combine in different ratios (NO, N_2O, NO_2, N_2O_3, and more!)

○ Because of this, binary molecular compounds are named in a way that indicates how many atoms of each element are present

○ The number of atoms is indicated by Greek prefixes (Table 3.1)

○ _____ First Element Name _____ Second Element Name-"ide"

○ The element futher left on the periodic table goes first in both the formula and the name

○ "Mono-" may be left off for the *first* element (i.e. Carbon Dioxide, not Monocarbon Dioxide)

○ Binary compounds which contain H are usually called by their common names instead of using this convention (water, hydrochloric acid, and ammonia)

Practice: NO (nitrogen monoxide) N_2O (dinitrogen monoxide) NO_2 (nitrogen dioxide)

N_2O_3 (dinitrogen trioxide)

3.3   Formulas for Ionic Compounds

○ Positive ions are called *cations*, and negative ions are called *anions*

○ Ions can be a single atom (monatomic), and the magnitude of the charge can often be inferred from the element's position in the periodic table (Figure 3.7)

○ Ions can also be made from a group of atoms which carry the charge collectively (polyatomic) – Table 3.4

○ All ionic compounds are electrically neutral, so their positive and negative ions must cancel out

○ Find the LCM between the positive and negative charges to know how many of each to include

Practice: Give the formula unit for compounds made from the following pairs of ions:

Na^+ and Cl^- (NaCl) Ag^+ and S^{2-} (Ag_2S) Fe^{3+} and O^{2-} (Fe_2O_3)

○ For compounds with polyatomic ions, just be sure to include parenthesis

Practice: Give the formula unit for compounds made from the following pairs of ions:

Na^+ and CH_3COO^- ($NaCH_3COO$) Ag^+ and SO_4^{2-} (Ag_2SO_4) Ni^{2+} and PO_4^{3-} ($Ni_3(PO_4)_2$)

○ Because of this charge balance, we can calculate the cation's positive charge based on the formula

Practice: Give the positive charge of the cation in each ionic compound

VO_2 (V^{4+}) $AuCl_3$ (Au^{3+}) Al_2S_3 (Al^{3+})

3.4   Naming Ionic Compounds

○ To name an ionic compound, simply give the cation name and the anion name

○ Monoatomic cations are just the element name

○ For elements with more than one common charge, the charge is indicated in (Roman Numerals)
  Practice: Give the name of the following cations: Ba^{2+} (Barium) Cr^{2+} (Chromium(II))

○ Ammonium and hydronium are the only common polyatomic cations

○ Monoatomic anions are just the element name with an "-ide" ending

○ Polyatomic anions follow some rules, but are best just memorized

  · Oxyanions forms series' which follow the pattern shown in Table 3.3
  · Oxyanions with one or more hydrogens have "hydrogen-" "dihydrogen-" etc. added to their names
  · Table 3.4 lists common polyatomic ions (you can ignore the right column except chlorates)

  Practice: Name the following ionic compounds: Na_2SO_3 (sodium sulfite)

      NH_4NO_3 (ammonium nitrate) $Fe(HCO_3)_3$ (iron(III) hydrogen carbonate)

○ *Hydrates* are ionic compounds which naturally incorporate water into their structure

  · An integer number of water molecules are incorporated, called waters of hydration
  · If a hydrated salt is heated sufficiently, the waters will evaporate and the salt become anhydrous
  · The formula indicates the number of water molecules per formula unit with a dot $(CuSO_4 \cdot 5\,H_2O)$
  · To name the compound, give the anhydrous compound name followed by "_____ hydrate". Greek prefixes indicate the number of waters

  Practice: Give the names of the following hydrated salts

  $MgSO_4 \cdot H_2O$ (magnesium sulfate monohydrate) $MgCl_2 \cdot 6\,H_2O$ (magnesium chloride hexahydrate)

3.5   Naming Acids

○ Acids are covalent compounds which will release H ions when dissolved in water
  (this is a white lie – the actual mechanism for acids can get quite complex)

○ For example: HNO_3 will release its H in water to produce $H^+(aq)$ and $NO_3^-(aq)$

○ Not all H atoms will be released. For CH_3COOH, only the last H is ionizable

○ Often the ionizable hydrogen(s) will be written first. H_2O_2 and acetic acid are common exceptions

○ Acids with 1 ionizable hydrogen are *monoprotic.* Atoms with 2 or more are *polyprotic*

○ Binary acids are named "hydro–Element–ic acid" (hydrochloric acid, hydrofluoric acid)

○ Oxyacids are acids with H attached to an O-containing polyatomic anion

    · The acid name depends on the anion name

    · "–ate" ions become "–ic acid" (sulfate and sulfuric acid)

    · "–ite" ions become "–ous acid" (hypochlorite and hypochlorous acid)

3.6   Nomenclature Review

○ Figure 3.15 gives a comprehensive flowchart for naming chemical compounds

○ Conventions for naming organic molecules will be covered in CHEM 1220

3.7   The Mole

○ We have already gone over how $6.022 \times 10^{23} = 1\,mol$, and $1\,mol\,AMU = 1\,g$

○ We can talk about moles of anything: formula units, atoms, etc.
  Practice: How many moles of O atoms are in $2.50\,mol$ of Fe_2O_3? $(7.50\,mol)$
           How many H atoms are in $1.40\,mol$ of CH_4? $(3.37 \times 10^{24}\,atoms)$

3.8   Molar Mass

○ The *Molar Mass* gives the mass for a mole of a given substance

○ The atomic weight (on the periodic table) is the mass for a mole of atoms

○ The molecular weight or formula weight is the mass of a mole of formula units for a compound

○ I will use *Molar Mass* (M) as a general term for both

○ Many problems will involve converting between mass and moles, moles and mass

○ "Measurement Land" vs "Chemistry Land" vs "Atomic/Counting Land"
  Practice: How many O atoms are in $1.35\,g$ of CO_2? (3.69×10^{22})
           How many O atoms are in $1.35\,g$ of CO? (2.90×10^{22})
           What is the mass of $0.675\,mol$ of $C_{12}H_{22}O_{11}$? $(23.1\,g)$

3.9 Percent Composition

○ Percent composition tells what percentage of a compound (by mass) is each element

○ $\%_{Composition} = \dfrac{\nu M_{atomic}}{M_{formula}} 100\%$

Practice: Find the % composition of O in H_2O. (88.81%)

Find the % composition of O in $Fe_2(SO_3)_3$. (40.92%)

○ Percent composition can be used to find the mass of a component in a compound

○ The % composition is a conversion factor between g of the element and $100\ g$ of the compound

Practice: How many g of N are in $2.00\ g$ of NH_4NO_3?

$(M = 80.0434\ ^g/_{mol}, \%_N = 34.9978\%, \text{ and } 0.700\ g)$

3.10 Empirical Formulas

○ Some analytical techniques can only give % composition, not the true molecular formula

○ The *empirical formula* is the most mathematically reduced form of a chemical formula

○ Many molecular formulas may share the same empirical formula (i.e. CH_2O, $C_2H_4O_2$ and $C_6H_{12}O_6$)

○ Finding empirical formulas requires converting masses to moles

· Sometimes you will be given masses (See combustion analysis below)

· If you only have % composition, assume a mass of $100\ g$ and the %s become g

· Convert the masses to moles using atomic weights

· Reduce the moles of each atom to a ratio of whole numbers

· Table 3.6 shows the decimal ending for common fractional equivalents

Practice: Give the empirical formula for a $20\ g$ sample with $1.34\ g$ H, $8.00\ g$ C and $10.7\ g$ O.

(CH_2O)

Practice: Give the empirical formula for a compound which is 69.94% Fe and 30.06% O by mass.

(Fe_2O_3)

3.11 Molecular Formulas

○ The molecular formula gives the actual number of atoms of each type in a single molecule

○ The molecular formula will be some integer multiple (possibly 1) of the empirical formula

○ The compound's molar mass will be the same multiple of the empirical formula's molar mass

3.12   Combustion Analysis

○ Combustion analysis is a laboratory technique for finding the empirical formula of combustible compounds

○ It involves combusting a carefully weighed mass of compound in excess oxygen, and measuring the amount of water and carbon dioxide produced

○ The C in the carbon dioxide and the H in the water came exclusively from the unknown compound

○ Any unaccounted-for mass is assumed to be oxygen

○ Process for solving combustion analysis:

- Calculate moles of C atoms from CO_2 mass
- Calculate moles of H atoms from H_2O mass
- Calculate mass of C and H atoms
- subtract C and H masses from sample mass – This is the O mass
- Calculate moles of O from the O mass
- Reduce all mole ratios to whole numbers (perhaps relying on Table 3.6)
- This is the empirical formula

Practice: $4.24\ g$ of an unknown are combusted to yield $6.21\ g$ of CO_2 and $2.54\ g$ of H_2O

(Empirical Formula is CH_2O)

Practice: $2.50\ g$ of an unknown are combusted to yield $5.79\ g$ of CO_2 and $1.18\ g$ of H_2O

(Empirical Formula is $C_8H_8O_3$)

Practice: The molar masses for the two compounds above are: $120.10\ g/mol$ and $152.15\ g/mol$
What are the molecular formulas?

(The formulas are: $C_4H_8O_4$ and $C_8H_8O_3$)

CHEMICAL REACTIONS AND AQUEOUS SOLUTIONS

4.1 Chemical Equations

○ Chemical equations show how *reactants* (on the left) are converted into *products* (on the right)

○ When properly balanced, an equation also shows the proportions of reactants and products

○ Equations also can show the *phase* of each chemical and any reaction conditions

○ Aqueous solutions are when a substance is dissolved in water

○ Balancing chemical equations:

  · 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 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

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

  $(Fe_2O_3(s) + 2\,Al(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s))$
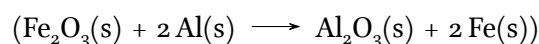
Practice: Balance the following chemical equation: $C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

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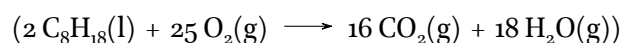
Practice: Balance the following chemical equation: $Ag_2SO_4(aq) + NaCl(aq) \longrightarrow AgCl(s) + Na_2SO_4(aq)$

  $(Ag_2SO_4(aq) + 2\,NaCl(aq) \longrightarrow 2\,AgCl(s) + Na_2SO_4(aq))$

4.2 Types of Chemical Reactions

○ Reactions can be grouped into broad categories

○ Synthesis or Combination reactions:

  · Two or more reactants combine to form a single product

  · $2\,Na(s) + Cl_2g \longrightarrow 2\,NaCl(s)$

○ Decomposition reactions:

  · One reactant decomposes into two or more products

- $2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)$

○ Single and Double Replacement reactions:

- One (or two) element or polyatomic ion is replaced by another in the product
- $Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$
- $2\,KI(aq) + Pb(NO_3)2(aq) \longrightarrow PbI_2(s) + 2\,KNO_3(aq)$

○ Acid/Base reactions (A type of replacement reaction):

- One or more H^+ are exchanged
- $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

○ Precipitation reactions (A type of replacement reaction):

- Aqueous reactants produce one or more solid products (called precipitates)

○ Combustion reactions:

- A substance is reacted with O_2 to produce CO_2 and H_2O
- $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$

○ Redox reactions (synthesis, decomposition, single replacement, and combustion reactions)

- We will see later how redox reactions involve the exchange of electrons

○ Not all reactions we can write down will actually proceed in nature

○ Reactions actually happen because of driving forces which make products more thermodynamically stable than the reactants

- Precipitation reactions have stable solid products with strong ionic bonds
- Acid/Base reactions have stronger bonds to H after the neutralization
- Redox reactions transfer electrons to make more stable electronic configurations

4.3 Compounds in Aqueous Solution

○ When ionic compounds dissolve in water, they dissociate into their cations and anions

○ Figure 4.14 shows how ions are hydrated by the water molecules when they dissolve

○ Solutions of ionic compounds and acids/bases are called electrolytes because they conduct electricity

- Strong electrolytes will dissociate completely and produce a lot of ions
- Weak electrolytes dissociate only partially, and produce few ions
- Soluble ionic compounds and strong acids/bases (Table 4.3) are strong electrolytes
- Weak acids/bases are weak electrolytes

○ Solutions of other molecular compounds are non-electrolytes – They don't dissociate in water

4.4 Precipitation Reactions

○ Not every ionic compound will actually dissolve in water. For example, most rocks and crystals are ionic compounds which don't readily dissolve in water

○ *Soluble* compounds will dissolve in water, *insoluble* compounds will not

○ Solubility guidelines help predict if a compound is soluble or not

  · Ammonium and Group I cations *always* form soluble compounds
  · Nitrate, chlorate, perchlorate, and acetate *always* form soluble compounds
  · Chlorides, bromides, and iodides are soluble *except* with Ag^+, Pb^{2+}, and Hg_2^{2+}
  · Sulfates are soluble *except* with Pb^{2+}, Hg_2^{2+}, and "heavy" group II ions
  · Carbonate, sulfite, phosphate, and chromate generally form *insoluble* compounds
  · S^{2-} and OH^- form *insoluble* compounds, except with group I, ammonium, and "heavy" group II ions
  · Ag^+, Pb^{2+}, and Hg_2^{2+} generally form *insoluble* compounds
  · Table 4.5 gives a comprehensive list, but you will be fine just memorizing the points above

○ Precipitation reactions:

  · When two soluble ionic compounds react, there is the possibility of a precipitate forming
  · First, identify the products when cations and anions switch partners
  · Then determine if any of the products will be insoluble – these are the precipitates
  · If no precipitate forms, then no reaction really took place at all

○ Demos: $Mg(NO_3)_2$ with NaOH, and $Ca(NO_3)_2$ with Na_2CO_3

○ Net ionic equations:

  · Ionic equations acknowledge that soluble ionic compounds do not exist with anions and cations paired together. Rather, the anions are solvated and the cations are solvated separately by themselves
  · To form an ionic equation, write the cations and anions separately for all aqueous (soluble) ionic compounds
  · Insoluble compounds are still written with ions paired together because they actually are
  · Some ions appear solvated on both sides of the equation – they are called "spectators"
  · These spectators don't actually do anything at all – they are as irrelevant to the reaction as the solvent, other trace solutes (N_2 and O_2), etc.
  · To form a *net* ionic equation, simply eliminate the spectators

 Practice: Write the net ionic equations for the two demonstrations above

$$Mg^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Mg(OH)_2(s)$$
$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$
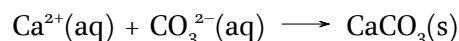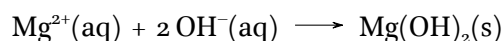
4.5   Acid-Base Reactions

○ Recognize acid/base reactions by the exchange of a H^+ ion

○ When acids react with OH^- (strong bases), water will be produced

○ When acids react with weak bases, the H^+ switches over to the base

○ Balance acid/base reactions just like any other reaction

○ For ionic and net ionic equations, only *strong* acids should be written as dissociated ions

4.6   Oxidation States and Redox Reactions

○ Oxidation states (or numbers) keep track of how many electrons reside on an atom (like a charge)

○ To determine the oxidation states in a compound, follow these rules:

· A neutral elements (not a part of a compound) has an oxidation number of 0

· Monoatomic ions have oxidation numbers equal to their charge

· The sum of oxidation numbers in any formula is equal to the total charge

· Oxygen tends to have an oxidation number of -2 in compounds

· Hydrogen tends to have an oxidation number of $+1$ in compounds

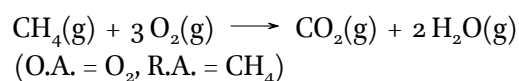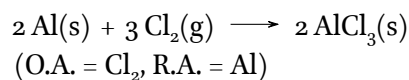· All other elements can be determined from the rules above

Practice: Identify the oxidation states for all elements in the following compounds
NH_3, N_2O, NO_3^-
(N=-3, H=+1), (N=+1, O=-2), (N=+5, O=-2)
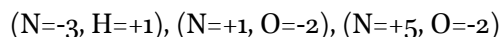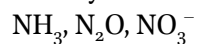
○ Oxidation is the process of *losing* electrons. The oxidation number increases

○ Reduction is the process of *gaining* electrons. The oxidation number decreases

○ Two mnemonic devices to keep them straight:

· OIL RIG (oxidation is losing, reduction is gaining)

· *Chemical* reduction involves a *mathematical* reduction of the oxidation number

○ To identify redox reactions involve the exchange of electrons

· To identify a redox reaction, first find the oxidation state of all reactants and products

· If the oxidation state of any elements changes, then this is a redox reaction

· The element whose oxidation number decreases is *reduced*

· The element whose oxidation number increases is *oxidized*

- · Any electrons lost by the oxidized element have gone to the reduced element – they are connected both chemically and mathematically by the electrons
- · The compound which contains the reduced element has oxidized its reaction partner. Therefore, it is the "oxidizing agent"
- · The compound which contains the oxidized element has reduced its reaction partner. Therefore, it is the "reducing agent"

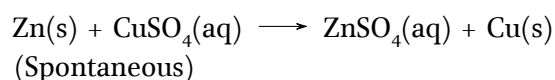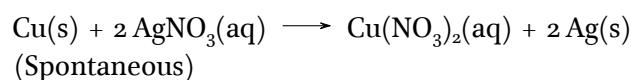Practice: Identify the reducing agent and the oxidizing agent in each chemical reaction

$$2\,Al(s) + 3\,Cl_2(g) \longrightarrow 2\,AlCl_3(s)$$
$$(O.A. = Cl_2,\ R.A. = Al)$$

$$CH_4(g) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$
$$(O.A. = O_2,\ R.A. = CH_4)$$

- ○ Balancing redox reactions can be quite complicated. You will learn how in CHEM-1220

4.7   Predicting the Products of Redox Reactions

- ○ Synthesis and decomposition reactions are very often redox reactions

  - · Sythesis of ionic compounds from elements, and decomposition of ionic compounds to elements
  - · The oxidation states of metals in compounds will match the charges they can take as ions

- ○ Single-replacement reactions are also very often redox reactions

  - · Often, the replaced elements involve an element and an ion swapping places
  - · One element goes from neutral to positively charged – it is oxidized – it is a reducing agent
  - · The other element goes from positively charged to neutral – it is reduced – it is an oxidizing agent
  - · Some elements are easier to oxidize, and some ions are easier to reduce
  - · These processes are linked – an element which is easy to oxidize has an ion which is difficult to reduce
  - · Table 4.7 shows an activity series for common elements in these reactions
  - · A reaction will proceed spontaneously if the reducing agent is higher in the table than the oxidizing agent

- ○ Demos: Copper wire in silver solution and Zn piece in copper solution

Practice: Predict whether each demonstrated reaction will proceed spontaneously

$$Cu(s) + 2\,AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$$
$$(Spontaneous)$$

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$
$$(Spontaneous)$$

CHAPTER 5

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STOICHIOMETRY

5.1 Mole Calculations for Chemical Reactions

○ *Stoichiometry* refers to the ratios between substances in chemical reactions

○ These ratios are expressed in the coefficients of a balanced chemical equation

○ Use the coefficients to create a conversion factor between substances

○ My problem-solving diagram ("Measurement Land" vs "Chemistry Land")
  Practice: Consider the reaction $2\,P\ +\ 3\,Cl_2\ \longrightarrow\ 2\,PCl_3$

  How many moles of Cl_2 are needed to react with $0.250\,mol$ of P? $(0.375\,mol)$

  How many moles of PCl_3 would be produced? $(0.250\,mol)$

5.2 Mass Calculations for Chemical Reactions

○ We will usually be concerned about finding *masses* rather than moles

○ You cannot compare masses directly, but rather have to go through the molar stoichiometry

○ Problems are structured as: $mass_A \rightarrow mol_A \rightarrow mol_B \rightarrow mass_B$
  Practice: Consider the reaction $3\,O_2\ +\ 2\,KCl\ \longrightarrow\ 2\,KClO_3$

  How many g of O_2 are needed to react with $0.850\,g$ of KCl? $(0.547g)$

  How many g of $KClO_3$ would be produced? $(1.40g)$

○ Note that the total mass on the reactant side should equal the total mass on the product side

5.3 Problems Involving Limiting Quantities

○ Reactants are often not mixed in the perfect, proper ratio

○ One reactant will be consumed and run out first, it is called the *limiting reactant*

○ The reaction stops once the limiting reactant runs out, so the limiting reactant controls how much product is produced

○ There are many ways to solve limiting reactant problems. I suggest the following:

  · Looking ahead, choose a product which you are interested in

- For each reactant, calculate the amount of product it could produce
- Compare the product amounts – the smallest value is the only value you keep
- Throw out all other values, they are just wishful thinking and will never really happen
- The reactant which gave the smallest amount of product is the limiting reactant
- Start with the limiting reactant for all future calculations

○ Sometimes you need to find the amount of excess reactant(s) which remains

- Starting from the limiting reactant, find the amount of excess reactant required
- Subtract that mass from the initial value – this is the amount left over

○ Here, the total mass at the end will match the total mass at the beginning

Practice: Consider the reaction $2\,CH_3OH(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(g)$

If $16.0\ g$ of O_2 react with $48.1\ g$ of CH_3OH, which is the limiting reactant?   (O_2)

How many g of each substance will be present after the reaction completes?
($0\ g\ O_2$, $37.4\ g\ CH_3OH$, $14.7\ g\ CO_2$, and $12.0\ g\ H_2O$)

Practice: Consider the reaction $3\,Fe(s) + 4\,H_2O(l) \longrightarrow Fe_3O_4(s) + 4\,H_2(g)$

If $5.00\ g$ of Fe react with $5.00\ g$ of H_2O, which is the limiting reactant?   (Fe)

How many g of each substance will be present after the reaction completes?
($0\ g$ Fe, $2.85\ g\ H_2O$, $6.91\ g\ Fe_3O_4$, and $0.241\ g\ H_2$)

5.4   Theoretical Yield and Percent Yield

○ The amount of product you calculate above is the *theoretical yield*

○ In the lab, your *actual yield* may be more, or less due to errors and random factors

○ We can calculate the % yield based on these two values

$$Percent\ Yield = \left(\frac{Actual\ Yield}{Theoretical\ Yield} \right) \cdot 100\%$$

Practice: If you run the first reaction above and recover $10.7\ g$ of H_2O, what is the % yield?
(89.2%)

If you run the second reaction above and recover $7.05\ g$ of Fe_3O_4, what is the % yield?
(102%)

5.5   Definition and Uses of Molarity

○ The *solvent* is the substance doing the dissolving, the *solute* is the substance being dissolved, and the *solution* is the homogeneous mixture after dissolving

○ Concentrated solutions have a lot of solute, dilute concentrations have little solute

○ The most common unit of concentration is *Molarity*: $M = \dfrac{Moles\ of\ Solute}{L\ of\ Solution}$ or $\left(M = \dfrac{n}{V}\right)$

○ Molarity is sometimes notated with square brackets (i.e. $\left[H_2SO_4\right]$)

○ This can be rearranged to give: $Moles_{Solute} = Molarity \cdot L_{Solution}$ or $(n = M \cdot V)$

○ For small volumes (ml), we can use millimoles $(mmol)$ for convenience

Practice: What is the molar concentration when $2.50\ g$ of *NaCl* are dissolved to make $0.100\ L$ of solution? $(0.428\ M)$

Practice: What mas of $C_{12}H_{22}O_{11}$ should be dissolved to make $0.500\ L$ of a $0.125\ M$ solution? $(21.4\ g)$

○ Dilution is when water is added to a solution to make it less concentrated

○ Because only solvent is added, the moles of solute is the same at the end as at the beginning

○ This gives a simple equation for dilution: $M_1V_1 = M_2V_2$

Practice: What is the final concentration when $25.0\ ml$ of $0.832\ M$ are diluted to $150.0\ ml$? $(0.139\ M)$

Practice: How much $0.650\ M$ solution should be used to make $250.0\ ml$ of a $0.100\ M$ solution? $(38.5\ ml)$

○ We can now add to the "Measurement Land" and "Chemistry Land" diagram

· Moles can be calculated from $n = MV$

· ml of the co-reactant can be found instead of g

· For finding concentrations of the product, consider the *additive* volumes of the reactants

Practice: Consider the following reaction: $2\ HCl(aq) + Na_2CO_3(s) \longrightarrow 2\ NaCl(aq) + H_2CO_3(aq)$

How many ml of $0.250\ M$ should be used to react with $0.125\ g$ of Na_2CO_3? $(9.43\ ml)$

5.6   Molarities of Ions

○ When ionic compounds dissolve, the ions dissociate

○ The concentration of the *compound* may be different from the concentration of a given ion

○ Multiply the formula concentration by the number of ions in the formula

Practice: Consider dissolving $1.45\ g$ of $MgCl_2$ to make $125\ ml$ of solution

What is the concentration of $MgCl_2$?
$(1.22\ M)$

What is the concentration of Mg^{2+} and Cl^- ions?
$(1.22\ M$ and $2.44\ M)$

5.7   Calculations Involving Other Quantities

○ Volume is one way to express an amount of a substance

○ We have so far dealt with volumes of solutions, where $n = MV$

○ For a pure substance, the volume must be dealt with very differently

· Volume must first be converted to mass through density: $m = d \cdot v$

· Then mass is converted to moles through the molar mass

Practice: Sodium metal has a density of $0.97 ^{g}/cm^3$, and reacts with water according to the
following reaction: $2\,\text{Na(s)} + 2\,\text{H}_2\text{O(l)} \longrightarrow 2\,\text{NaOH(aq)} + \text{H}_2\text{(g)}$
If $0.750\,cm^3$ of Na react with $200.0\,ml$ of water, what is the final $[\text{NaOH}]$? $(0.158\,M)$

○ The subscripts in a chemical formula can also relate the number of atoms of a particular element

Practice: In the reaction above, how many H *atoms* are released as gas? $(1.91 \times 10^{22}\,\text{H}\,atoms)$

5.8   Calculations with Net Ionic Equations

○ Stoichiometric calculations with net ionic equations are just like with regular equations

○ To calculate moles of ions from g of solid salt, you must know the full salt formula

○ Subscripts indicate when multiple ions come from a single formula unit

Practice: How many g of $\text{Ca}_3(\text{PO}_4)_2$ are needed to make $0.250\,L$ with $[\text{Ca}^{2+}] = 0.100\,M$? $(2.58\,g)$

5.9   Titration

○ *Titration* is a technique to determine the concentration of a solution

○ The unknown is reacted with a solution with precisely known concentration (a *standard solution*)

○ A precisely measured volume of one reactant is placed in an erlenmeyer flask (for easy mixing)

○ The other reactant (the titrant) is slowly added using a buret, to measure the volume added

○ The *equivalence point* is the exact point when the unknown is completely consumed by the reaction

○ The *end point* is when you actually stop the titration

· End point is usually identified by a color-changing indicator

· For acid/base reactions, the indicator changes color with pH

· Redox reactions also have appropriate color indicators

· The indicator is chosen so that the end point is as close as possible to the equivalence point

○ The stoichiometric coefficients (ν) are included in the titration equation: $\dfrac{M_A V_A}{\nu_A} = \dfrac{M_B V_B}{\nu_B}$

Practice: Find $[\text{NaOH}]$ when $25.00\ ml$ of NaOH are titrated with $37.8\ ml$ of $0.100\ M$ HCl
($0.151\ M$)

Practice: Find $\left[\text{HNO}_3\right]$ when $50.00\ ml$ of HNO_3 are titrated with $21.3\ ml$ of $0.150\ M$ Ca(OH)_2
($0.128\ M$)

THERMOCHEMISTRY

6.1   Energy and Energy Units

○ 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

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

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

○ 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): $1\ Cal = 1000\ cal = 4184\ J$

6.2   Energy, Heat, and Work

○ 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 (an closed, insulated flask)

○ Work and heat are the ways energy can enter or leave the system

○ We always talk from the perspective of the system, even though we are a part of the surroundings

○ 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

○ Heat is usually associated with temperature changes or phase changes

- 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

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

○ Internal energy is the sum of all kinetic and potential energy in a system

- Over a process, the sum of work and heat is the change in internal energy
- $\Delta U = q + w$

Practice: A fire piston is a device for starting fires by rapidly plunging an airtight piston with a combustible material on its end.

If you push the plunger with a force of $750\ N$ over a distance of $10\ cm$, what is w for the fire piston? ($75\ J$)

If the fire piston is not perfectly insulated, and loses $5\ J$ of heat to the surroundings, what is ΔU for the system? ($70\ J$)

6.3 Energy as a State Function

○ Some quantities are *Path Functions*, while others are *State Functions*

○ To understand a state function, first consider a path function

- Path functions depend on the path taken
- If I push a chair to one side of the room, then pull it back, it will be in the exact same state as it started, but the total w done on the system is not 0
- Work is a path function, and depends on the path (I might increase the work by taking a different path)

○ State functions do not depend on the path, but only on the state

- If I lift a chair up, then place it on the ground again, its final elevation will be the same, regardless of the path it took
- Temperature, elevation, and many thermodynamic quantities are state functions
- State functions are useful because you only need to know the current state to know the function's value

○ While q and w are path functions, U is a state function

- ○ Consider two very different ways to produce ethanol gas:
    - · $C_2H_6O(s, -115\,°C) \longrightarrow C_2H_6O(g, 79\,°C)$
    - · $2\,C(s) + 3\,H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow C_2H_6O(g, 79\,°C)$
    - · Because the final states are identical, the final Us are identical
    - · Any other process (maybe with many steps) will have the same final U as long as it has the same final state

6.4   Energy and Enthalpy

- ○ All chemical reactions involve at least *some* exchange of heat, but many involve work as well
- ○ When gasses are produced or consumed, the pressure and volume will change, doing some work
- ○ This work is measured by $w = -P\Delta V$, where $1\,Latm = 101.325\,J$
- ○ 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)
    - · While $U = q + w$, $H = q$ under constant pressure conditions
    - · So, we only need to worry about heat when we deal with H
- ○ Processes with $-H$ are called *exothermic*
- ○ Examples of exothermic processes are downward phase changes, combustion reactions, etc.
- ○ Processes with $+H\ (+q)$ are called *endothermic*
- ○ Examples of endothermic processes are upward phase changes, ice-pack chemical reactions, etc.
- ○ Demo – An endothermic reaction: $8.5\,g$ NH_4SCN with $16.0\,g$ $Ba(OH)_2 \cdot 8\,H_2O$

6.5   Specific Heat

- ○ 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
- ○ $q = mc\Delta T$ where m is the mass, c is the specific heat, and ΔT is the temperature change
- ○ Table 6.3 includes specific heats for a number of common substances

    Practice: How much heat is required to heat $12.5\,g$ of water by $5.75\,°C$? ($30.1\,J$)

    If a $5.23\,g$ block of Al at $22.0\,°C$ is given $75.0\,J$ of heat, what will its final T be? ($38.1\,°C$)

6.6 Calorimetry: Measuring Energy Changes

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

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

○ 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

○ $q_1 = -q_2$ becomes $m_1 c_1 (T_f - T_{i,1}) = -m_2 c_2 (T_f - T_{i,2})$

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? $(25.9\,°C)$

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

○ Constant-pressure (coffee-cup) calorimetry

· 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 $\left(10\,g,\,100\,ml,\,44.2\,\frac{kJ}{mol}\right)$

○ Constant-volume (bomb) calorimetry

· 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 $w = 0$

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

6.7 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 $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)\ \Delta H = -92\frac{kJ}{mol}$

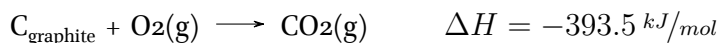If $2.25\,g$ of H_2 are consumed in the above reaction, how much heat is released? $(34.2\,kJ)$

If $54.6\,kJ$ of heat are released, how many g of NH_3 will be produced? $(20.2\,g)$

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

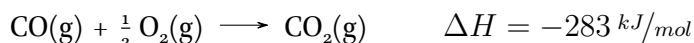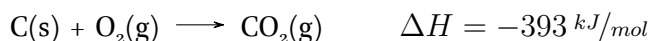○ Hess's Law: Any alternate path with the same starting and ending states will have the same overall ΔH

○ Drawing an energy level diagram can help to illustrate Hess's law

○ Find ΔH for this reaction: $C_{diamond} + O2(g) \longrightarrow CO2(g)$ $(\Delta H = -395.4\ kJ/mol)$

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

$C_{graphite} + O2(g) \longrightarrow CO2(g)$ $\Delta H = -393.5\ kJ/mol$

○ The reverse of a reaction gives $-\Delta H$

○ Find ΔH for this reaction: $C(s) + \frac{1}{2}O2(g) \longrightarrow CO(g)$ $(\Delta H = -110\ kJ/mol)$

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

$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -283\ kJ/mol$

○ Double the reaction gives double the ΔH

○ Consider trying to find ΔH for the reaction below:

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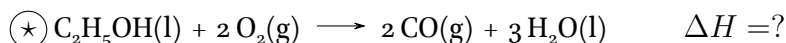
○ Find an alternate path using these reactions with known ΔH:

(A) $C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$ $\Delta H = -1367\ kJ/mol$

(B) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -283\ kJ/mol$
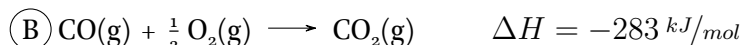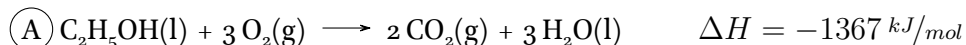
○ The enthalpy of the first reaction can be found from the enthalpies of the other two

○ $\Delta H_{\star} = \Delta H_A - 2\Delta H_B = -801\dfrac{kJ}{mol}$ (Draw the energy level diagram)

Practice: Find the enthalpy of reaction (★) using reactions (A), (B), and (C)

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

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

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

(C) $C(s) + 2\,S(s) \longrightarrow CS_2(l)$ $\Delta H = 87.9\ kJ/mol$
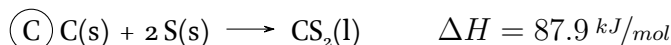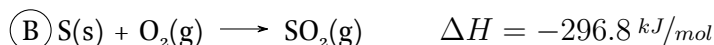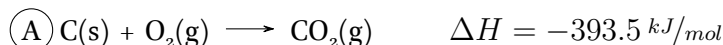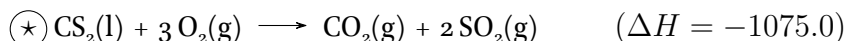
6.8 Standard Enthalpies of Formation

○ 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*
· $\Delta H_{rxn} = \sum\limits_{products} \nu \cdot \Delta H_f^\circ - \sum\limits_{reactants} \nu \cdot \Delta H_f^\circ$
· 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
· Table 6.4 gives a few values, but appendix A2 is much more comprehensive

Practice: Find ΔH_{rxn} for $P_4O_{10}(s) + 6 H_2O(l) \longrightarrow 4 H_3PO_4(aq)$ $\left(\Delta H_{rxn} = -1042.6 \frac{kJ}{mol}\right)$

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

CHAPTER 7

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GASES

7.1 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: $1\ atm = 101.325\ kPa = 1.01325\ bar$

7.2 Boyle's Law

- In the 17$^{\text{th}}$ and 18$^{\text{th}}$ 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

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

7.3 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 $1\ ^{\circ}C$. 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

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

7.4   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? $(2.11\ L)$

7.5   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

7.6   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 $0.00\ {}^\circ C$ and $1.00\ atm$
Find the volume of $1.00\ mol$ of an ideal gas at STP $(22.4\ L)$

7.7   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

7.8 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)

7.9 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? ($0.97\ atm$)

7.10 Kinetic Molecular Theory of Gases

○ 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

7.11   Movement of Gas Particles

○ The equation for the þ5 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 $KE = \dfrac{1}{2} M v^2$ (note that this is also a molar amount), so we can write: $\dfrac{1}{2} M v^2 = \dfrac{3}{2} RT$

○ 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 $\left(r_{He} = 2.65 r_{N_2}\right)$

7.12   Behavior of Real Gases

- ○ 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
    - · $\left[P + a\left(\dfrac{n}{V}\right)^2\right](V - nb) = nRT$ –or– $P = \dfrac{nRT}{V - nb} - a\left(\dfrac{n}{V}\right)^2$
    - · 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 $37.79 \ atm)$

THE QUANTUM MODEL OF THE ATOM

8.1 A Brief Exploration of Light

- Light is an electromagnetic wave, which can be thought of like a wave on a lake (Figure 8.2)

- 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 8.4)

  - 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

  - 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 8.5)

· 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

○ 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

8.2   The Bohr Model of the Atom

○ The Rydberg Equation:

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

· 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:

· 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

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

8.3 Electron Shells, Subshells, and Orbitals

- 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

  - 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 3$^{\text{rd}}$ shell? (18)

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

- Subshells each have orbitals with different *shapes* (Figure 8.14)

  - 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

8.4 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

8.5 Electron Configurations

○ We can use the periodic table as a cheat-sheet to the order of the subshells and electron configurations

   · 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)

○ 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

8.6 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
- 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)

○ 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

CHAPTER 9

PERIODICITY AND IONIC BONDING

9.1 Valence Electrons

○ 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

9.2 Atomic and Ionic Sizes

○ 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 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 V all but one V electron

· Note that this is different than what the textbook gives
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 9.3)

○ Anions are much larger and cations are much smaller than their neutral counterparts (Figure 9.4)

9.3 Ionization Energy and Electron Affinity

○ 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 9.6)

○ Second- and third- ionization energy is the energy to remove a second and third electron

· 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 9.9 is a mess), so don't worry too much about EA

9.4 Ionic Bonding

○ Metal and nonmetal elemental atoms will react to form an ionic compound

○ 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 9.11)

9.5 Lattice Energy

○ Consider the reaction: $K(s) + \frac{1}{2} Cl_2(g) \longrightarrow KCl(s) \quad \Delta H_f^\circ = -437 \, \frac{kJ}{mol}$

○ 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 9.13

· 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 (Table 9.2)

· Smaller ions have higher lattice energies (Figure 9.14)

CHAPTER 10

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COVALENT BONDING

10.1 Formation of Covalent Bonds

○ 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

10.2 Lewis 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^+

10.3   Resonance and Formal Charges

○ 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

○ Electrons are not actually shared equally between bonding partners

    · *Electronegativity* is the measure of how strongly an atom pulls on shared electrons

    · Electronegativity increases across a row and up a column (Figure 10.7)

    · Less electronegative atoms will be central atoms (except H)

- o 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

- o 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

10.4 Exceptions to the Octet Rule

- o 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

- o Radicals are compounds with an unpaired electron

    - · Radicals tend to be very reactive
    - · Many radicals contain N (NO and NO_2)

- o 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

10.5 Polar Bonds and the Bonding Continuum

- o Figure 10.14 shows electrons being shared equally and unequally between bonding partners

- o The electrons will favor the element with greater electronegativity

- o The uneven distribution of charge is called a *dipole* and the bond is called *polar*

- o Polar covalent bonds exist along a continuum from purely covalent to purely ionic

○ 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 $\% \: ionic \: character$

○ $\% \: ionic \: character = \dfrac{\mu_{measured}}{\mu_{ionic}} \times 100\%$

10.6 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 10.3)

○ 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

· $\Delta H_{rxn} = \sum\limits_{Bonds \: Broken} \Delta n \cdot H_{Bond} - \sum\limits_{Bonds \: Formed} n \cdot \Delta H_{Bond}$

· This will give an *approximate* reaction enthalpy

○ Table 10.4 gives average values for bond lengths as well

Practice: Using Table 10.3, estimate the reaction enthalpy for the combustion of methane $\left(-810 \: \dfrac{kJ}{mol} \right)$

CHAPTER 11

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MOLECULAR SHAPE AND BONDING THEORIES

11.1 VSEPR and Molecular 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:

  · 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

  · Table 11.1 sums it all up nicely – Just memorize this table

  · Trigonal Bipyramidal electron geometry

    * The 2 axial and 3 equatorial positions are different
    * 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)

11.2 Polar and Non-polar Molecules

○ 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

○ 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)

11.3 Valence Bond Theory: Hybrid Orbitals and Bonding

○ Covalent bonding basics:

   · Why should sharing electrons lead to a bond?
   · Draw the attractive and repulsive forces in H_2
   · When the orbitals from both bonding partner overlap, these forces are optimized to form a bond
   · Figure 11.17 shows how the energy changes with internuclear distance in H_2

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

○ 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

○ Hybrid orbitals and bonding

- 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 (Figures 11.24 and 11.26)
- These unhybridized p orbitals are used to form π bonds
- π bonds have electron density along either side of the bond axis
- Double bonds contain one π bond, and triple bonds contain 2 π bonds
- A double bond is like a hot dog in a bun – a triple bond is like a hot-dog with 2 buns
- Use BLMB Figures 9.23-9.28
- Multiple p orbitals overlap in molecules which exhibit resonance (like benzene and nitrate)

11.4   Using Valence Bond Theory

○ 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 (Figure 11.3)

○ π bonds are constrained, and cannot rotate without a substantial energy input

11.5   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 (Figure 11.32):

- 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

○ 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

○ p orbitals can combine as well

- Head-on combination creates two more σ orbitals (Figure 11.35)
- Sideways combination creates orbitals with density along either side of the bond axis, so they are π_{2p} and π_{2p}^* MOs
- 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 11.37)

○ Figure 11.38 shows the configurations for all period 2 homonuclear diatomics (note the different orbital ordering)

○ 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

○ 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

ERRATA

○ In Section 4.7, the decomposition of mercury(II) oxide should be: $2\,HgO(s) \longrightarrow 2\,Hg(l) + O_2(g)$

○ The formation of water given in Section 6.8 should produce only 1 mole of water as a product

○ Slater's Rules in section 9.2 should treat deep core and V-1 electrons differently

○ Lattice energy is often referenced as positive values, instead of the negative values used here. This convention makes explaining the Born-Haber cycle a little easier because you only need to reverse one value $\left(\Delta H_f^\circ\right)$