CHM 1100 General Chemistry 1

Note: You are responsible for remembering and being able to use EVERYTHING from CHM 0100. CHM 1100 is impossible to understand without the knowledge from CHM 0100. If you do not remember CHM 0100, you must review it immediately.

Chapter 3: Chemical reactions

stoichiometry

Stoichiometry is the chemistry calculation to answer the question: How much? How much of this chemical is needed to react in this reaction? How much of that chemical is produced by that reaction? How much of one chemical reacts with a certain amount of another chemical?

Stoichiometry problems are generally word problems, that never say the word "stoichiometry". That means you must interpret the ENGLISH!

When you read a stoichiometry problem, it must have three things:

1: A BALANCED CHEMICAL EQUATION. If an equation is given unbalanced, you MUST balance it before going on. If a reaction is described in English, you MUST interpret it into chemical formulae.

2: One chemical whose amount is GIVEN to you. This is what you start with. It does not need to be a reactant.

3: Another chemical whose amount is UNKNOWN, but is being asked for. This is what you need to solve for. It does not need to be a product.

If you do not have these exact three things, it is not a stoichiometry problem (or a least not a normal one)! You do not need to worry about what the reaction is used for, or why it is important in real life, because we do stoichiometry as paper-and-pencil problems.

There is a three step calculation to solve stoichiometry problems.

step 1: convert given to moles
step 2: convert given to unknown
step 3: convert unknown from moles

Notice, these are conversion calculations that use the same "dimensional analysis" fraction technique introduced back in CHM 0100. Different stoichiometry problems may skip some steps or add extra steps to these basic three steps.

If the measurements are in grams, it looks like this:

 $x \ g \ \text{given} \times \frac{mol \ \text{given}}{g \ \text{given}} \times \frac{mol \ \text{unknown}}{mol \ \text{given}} \times \frac{g \ \text{unknown}}{mol \ \text{unknown}} = y \ g \ \text{unknown}$

There are several important variations on stoichiometry: including PERCENT YIELD, LIMITING REAGENTS, SOLUTION STOICHIOMETRY, GAS STOICHIOMETRY, THERMOCHEMICAL STOICHIOMETRY and ELECTROCHEMICAL STOICHIOMETRY.

combustion analysis

In chemistry, analysis is any technique that measures compounds and their elements, so that the compound can identified.

In real science, chemicals must be identified. When you pick up a rock, there's no nice label on it telling you what is made of. Chemistry ANALYSIS are the various lab techniques used to identify unknown chemicals. One common technique is COMBUSTION ANALYSIS. The combustion part means burning the chemical in lab and measuring the masses of all the products. The analysis part is the calculations used to determine the compound's empirical formula. Since this is a lecture question, you need to imagine the lab work. In lecture, you are doing the "lab report" calculation part.

The analysis takes advantage of conservation of mass to use a 3-step stoichiometry-like calculation to determine the mass composition of the unknown compound.

The procedure is:

step 1: convert carbon dioxide and water products to moles

step 2: convert the compound moles into separate carbon and hydrogen element moles

step 3: convert the carbon and hydrogen from moles

The mass composition is then used to determine the empirical formula using the technique learned earlier.

Chapter 3: Chemical reactions Problems

Problem 1: When dinitrogen pentoxide, N_2O_5 , a white solid, is heated, it decomposes to nitrogen dioxide and oxygen.

$$2 \operatorname{N}_2\operatorname{O}_{5(g)} \xrightarrow{\Delta} 4 \operatorname{NO}_{2(g)} + \operatorname{O}_{2(g)}$$

If a sample of N_2O_5 produces 1.381 g O_2 , how many grams of NO_2 are formed?

Problem 2: Potassium superoxide, KO₂, is used in self-contained breathing apparatus used by emergency personnel as the source of oxygen. It reacts with the moisture from exhaled breaths:

$$4 \text{ KO}_{2(s)} + 2 \text{ H}_2 \text{O}_{(l)} \longrightarrow 4 \text{ KOH}_{(s)} + 3 \text{ O}_{2(g)}$$

If a self-contained breathing apparatus is charged with 750. g KO₂ and then is used to produce 188 g of oxygen, was all of the KO₂ consumed in this reaction? If the KO₂ wasn't all consumed, how much is left over?

Problem 3: Bleach is a solution of sodium hypochlorite, NaClO. It is prepared by the reaction of chlorine with sodium hydroxide.

$$2 \operatorname{NaOH}_{(aq)} + \operatorname{Cl}_{2(g)} \longrightarrow \operatorname{NaCl}_{(aq)} + \operatorname{NaClO}_{(aq)} + \operatorname{H}_2\operatorname{O}_{(l)}$$

If you have 1.56 g of NaOH in solution and 1.47 g of Cl₂ gas available to react, which is the limiting reactant? What mass of NaClO could be obtained?

Problem 4: Every year, over a billion tons of iron is used to make steel and build everything from staples to skyscrapers. However, elemental iron is almost nonexistent on Earth, and must be refined from iron ores. A common iron ore is the gray-black mineral called magnetite, Fe₃O₄. Magnetite can be smelted (heated with coke, a form of almost pure carbon made from coal) at ~1900°C to produce almost pure iron. The process' overall equation is:

$$\operatorname{Fe_3O_4}_{(s)}$$
 + 2 $\operatorname{C}_{(s)} \xrightarrow{\Delta}$ 3 $\operatorname{Fe}_{(l)}$ + 2 $\operatorname{CO_2}_{(g)}$

If smelting 57.8 tons of magnetite produces 37.3 tons of iron, what is the percent yield of iron?

Problem 5: Copper is a reddish-orange metal famous for pennies and electrical wiring. Pure elemental copper is rare in nature, and must be be refined from ores. The brownish mineral bornite (Cu₃FeS₃) is an important copper ore. When roasted (heated), the following reaction occurs:

$$2 \operatorname{Cu_3FeS_3}_{(s)} + 7 \operatorname{O_2}_{(g)} \xrightarrow{\Delta} 6 \operatorname{Cu}_{(s)} + 2 \operatorname{FeO}_{(s)} + 6 \operatorname{SO_2}_{(g)}$$

If 2.50 metric tons of Cu_3FeS_3 is reacted with excess O_2 and the process has an 86.3% yield of copper, what mass of copper is produced?

Problem 6: Isopropyl alcohol is the disinfectant chemical in rubbing alcohol. It is a compound that contains the elements carbon, hydrogen, and oxygen. If the complete combustion of a 1.802 g sample of isopropyl alcohol produces 3.959 g carbon dioxide and 2.162 g water, what is the empirical formula of isopropyl alcohol.

Problem 7: Ethyl alcohol (chemical name, ethanol) is the disinfectant chemical in hand sanitizer. It is a compound that contains the elements carbon, hydrogen, and oxygen. If the complete combustion of a 1.397 g sample of ethyl alcohol produces 2.669 g carbon dioxide and 1.639 g water, what is the empirical formula of ethyl alcohol.

Chapter 3: Chemical reactions Solutions

Solution 1: When dinitrogen pentoxide, N_2O_5 , a white solid, is heated, it decomposes to nitrogen dioxide and oxygen.

$$2 \operatorname{N}_2\operatorname{O}_{5 (s)} \xrightarrow{\Delta} 4 \operatorname{NO}_{2 (g)} + \operatorname{O}_{2 (g)}$$

If a sample of N_2O_5 produces 1.381 g O_2 , how many grams of NO_2 are formed?

given is 1.381 g O₂ with molar mass of 2 (16.00) = 32.00 g/mol unknown is NO₂ with molar mass of 14.01 + 2 (16.00) = 46.01 g/mol mole ratio is 1 mol O₂ = 4 mol NO₂

$$1.381 \ g \ O_2 \times \frac{1 \ mol \ O_2}{32.00 \ g \ O_2} \times \frac{4 \ mol \ NO_2}{1 \ mol \ O_2} \times \frac{46.01 \ g \ NO_2}{1 \ mol \ NO_2} \approx 7.942 \ g \ NO_2$$

Solution 2: Potassium superoxide, KO₂, is used in self-contained breathing apparatus used by emergency personnel as the source of oxygen. It reacts with the moisture from exhaled breaths:

$$4 \operatorname{KO}_{2(s)} + 2 \operatorname{H}_2 \operatorname{O}_{(l)} \longrightarrow 4 \operatorname{KOH}_{(s)} + 3 \operatorname{O}_{2(g)}$$

If a self-contained breathing apparatus is charged with 750. g KO_2 and then is used to produce 188 g of oxygen, was all of the KO_2 consumed in this reaction? If the KO_2 wasn't all consumed, how much is left over?

Ignoring all the extra English: given is 188 g O_2 with molar mass of 2 (16.00) = 32.00 g/ mol

unknown is KO₂ with molar mass of 39.10 + 2 (16.00) = 71.10 g/mol mole ratio is $3 \text{ mol } O_2 = 4 \text{ mol } \text{KO}_2$

$$188 \ g \ O_2 \times \frac{1 \ mol \ O_2}{32.00 \ g \ O_2} \times \frac{4 \ mol \ KO_2}{3 \ mol \ O_2} \times \frac{71.10 \ g \ KO_2}{1 \ mol \ KO_2} \approx 557 \ g \ KO_2 \text{ consumed}$$

$$750. \ g \ KO_2 \ charge - 557 \ g \ KO_2 \ consumed = 193 \ g \ KO_2 \ left \ over$$

Solution 3: Bleach is a solution of sodium hypochlorite, NaClO. It is prepared by the reaction of chlorine with sodium hydroxide.

$$2 \operatorname{NaOH}_{(aq)} + \operatorname{Cl}_{2(g)} \longrightarrow \operatorname{NaCl}_{(aq)} + \operatorname{NaClO}_{(aq)} + \operatorname{H}_2O_{(l)}$$

If you have 1.56 g of NaOH in solution and 1.47 g of Cl₂ gas available to react, which is the limiting reactant? What mass of NaClO could be obtained?

givens are 1.56 g NaOH with molar mass of 22.99 + 16.00 + 1.008 = 40.00 g/mol

and 1.47 g Cl₂ with molar mass of 2 (35.45) = 70.90 g/mol unknown is NaClO with molar mass of 22.99 + 35.45 + 16.00 = 74.44 g/mol mole ratio is 2 mol NaOH = 1 mol Cl₂ = 1 mol NaClO

step 1: convert given to moles - use molar mass; step 1A: identify limiting/excess reagents - divide by mole count

$$1.56 g \text{ NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 g \text{ NaOH}} = 0.0390 \text{ mol NaOH} \div 2 \text{ mol NaOH} = 0.0195$$
$$1.47 g \text{ Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.90 g \text{ Cl}_2} = 0.0207 \text{ mol Cl}_2 \div 1 \text{ mol Cl}_2 = 0.0207$$

Since 0.0195 is less than 0.0207, the 0.0360 mol NaOH is the limiting reagent.

step 2: convert limiting to unknown - use mole ratio; step 3: convert unknown from moles - use molar mass

$$0.0390 \ mol \ \text{NaOH} \times \frac{1 \ mol \ \text{NaClO}}{2 \ mol \ \text{NaOH}} \times \frac{74.44 \ g \ \text{NaClO}}{1 \ mol \ \text{NaClO}} \approx 1.45 \ g \ \text{NaClO produced}$$

Solution 4: Every year, over a billion tons of iron is used to make steel and build everything from staples to skyscrapers. However, elemental iron is almost nonexistent on Earth, and must be refined from iron ores. A common iron ore is the gray-black mineral called magnetite, Fe₃O₄. Magnetite can be smelted (heated with coke, a form of almost pure carbon made from coal) at ~1900°C to produce almost pure iron. The process' overall equation is:

$$\operatorname{Fe_3O_4}_{(s)}$$
 + 2 C_(s) $\xrightarrow{\Delta}$ 3 Fe_(l) + 2 CO_{2 (g)}

If smelting 57.8 tons of magnetite produces 37.3 tons of iron, what is the percent yield of iron?

Ignoring all the extra English: given is 57.8 tons Fe_3O_4 with molar mass of 3 (55.85) + 4 (16.00) = 231.6 g/mol

unknown is Fe with molar mass of 55.85 g/mol, and actual yield = 37.3 tons (since both masses are in tons, converting to grams is not necessary) mole ratio is 1 mol $Fe_3O_4 = 3$ mol Fe

57.8 tons
$$\operatorname{Fe_3O_4} \times \frac{1 \ mol \ \operatorname{Fe_3O_4}}{231.6 \ g \ \operatorname{Fe_3O_4}} \times \frac{3 \ mol \ \operatorname{Fe}}{1 \ mol \ \operatorname{Fe_3O_4}} \times \frac{55.85 \ g \ \operatorname{Fe}}{1 \ mol \ \operatorname{Fe}} \approx 41.8 \ tons \ \operatorname{Fe}$$

theoretical yield = 41.8 tons Fe

$$\% yield = \frac{actual yield}{theoretical yield} \times 100$$
$$= \frac{37.3 \ tons \ Fe}{41.8 \ tons \ Fe} \times 100$$
$$= 89.2 \% yield \ Fe$$

Solution 5: Copper is a reddish-orange metal famous for pennies and electrical wiring. Pure elemental copper is rare in nature, and must be be refined from ores. The brownish mineral bornite (Cu₃FeS₃) is an important copper ore. When roasted (heated), the following reaction occurs:

$$2 \operatorname{Cu_3FeS_3}_{(s)} + 7 \operatorname{O_2}_{(g)} \xrightarrow{\Delta} 6 \operatorname{Cu}_{(s)} + 2 \operatorname{FeO}_{(s)} + 6 \operatorname{SO_2}_{(g)}$$

If 2.50 metric tons of Cu_3FeS_3 is reacted with excess O_2 and the process has an 86.3% yield of copper, what mass of copper is produced?

Ignoring all the extra English: given is 2.50 tons Cu_3FeS_3 with molar mass of 3 (63.55) + 55.85 + 3 (32.07) = 342.7 g/mol unknown is Cu with molar mass = 63.55 g/mol and percent yield = 86.3% mole ratio is 2 mol $Cu_3FeS_3 = 6$ mol Cu

$$2.50 tons \operatorname{Cu_3FeS_3} \times \frac{1 \, mol \, \operatorname{Cu_3FeS_3}}{342.7 \, g \, \operatorname{Cu_3FeS_3}} \times \frac{6 \, mol \, \operatorname{Cu}}{2 \, mol \, \operatorname{Cu_3FeS_3}} \times \frac{63.55 \, g \, \operatorname{Cu}}{1 \, mol \, \operatorname{Cu}} \approx 1.39 \, tons \, \operatorname{Cu}$$

theoretical yield = 1.39 tons Cu

$$\% yield = \frac{actual yield}{theoretical yield} \times 100$$

$$\therefore actual yield = \% yield \times \frac{theoretical yield}{100}$$

$$= 86.3 \times \frac{1.39 \ tons \ Cu}{100}$$

$$actual yield \approx 1.20 \ tons \ Cu$$

Solution 6: Isopropyl alcohol is the disinfectant chemical in rubbing alcohol. It is a compound that contains the elements carbon, hydrogen, and oxygen. If the complete combustion of a 1.802 g sample of isopropyl alcohol produces 3.959 g carbon dioxide and 2.162 g water, what is the empirical formula of isopropyl alcohol?

givens are 3.959 g CO₂ with molar mass of 12.01 + 2(16.00) = 44.01 g/mol, 2.162 g H₂O with molar mass of 2(1.008) + 16.00 = 18.02 g/mol, and 1.802 g isopropyl alcohol sample

The combustion reaction equation must like this, although it cannot be balanced:

$$C_x H_y O_z + O_2 \longrightarrow CO_2 + H_2 O_2$$

Part 1: from combustion products to reactant mass composition:

$$3.959 g \text{ CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} \approx 1.080 \text{ g C}$$

$$2.161 g \text{ H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} \approx 0.2419 \text{ g H}$$

$$\therefore 1.802 \text{ g sample} - 1.080 \text{ g C} - 0.2419 \text{ g H} \approx 0.480 \text{ g O}$$

Part 2: from mass composition to empirical formula:

step 1: convert all elements to moles

$$1.080 \ g \ C \times \frac{1 \ mol \ C}{12.01 \ g \ C} \approx 0.08993 \ mol \ C$$
$$0.2419 \ g \ H \times \frac{1 \ mol \ H}{1.008 \ g \ H} \approx 0.2400 \ mol \ H$$
$$0.480 \ g \ O \times \frac{1 \ mol \ O}{16.00 \ g \ O} \approx 0.0300 \ mol \ O$$

step 2: divide by smallest mole count:

$$0.08993 \ mol \ C \div 0.0300 \ mol \ \approx 3 \ C$$

 $0.2400 \ mol \ H \div 0.0300 \ mol \ = 8 \ H$
 $0.0300 \ mol \ O \div 0.0300 \ mol \ = 1 \ O$

the empirical formula of isopropyl alcohol is C₃H₈O

Solution 7: Ethyl alcohol (chemical name, ethanol) is the disinfectant chemical in hand sanitizer. It is a compound that contains the elements carbon, hydrogen, and oxygen. If the complete combustion of a 1.397 g sample of ethyl alcohol produces 2.669 g carbon dioxide and 1.639 g water, what is the empirical formula of ethyl alcohol.

Part 1: from combustion to mass composition:

givens are 2.669 g CO₂ with molar mass of 12.01 + 2(16.00) = 44.01 g/mol, 1.639 g H₂O with molar mass of 2(1.008) + 16.00 = 18.02 g/mol and 1.397 g sample

The combustion reaction equation must like this, although it cannot be balanced:

$$C_x H_y O_z + O_2 \longrightarrow CO_2 + H_2 O_2$$

$$2.669 g \text{ CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} \approx 0.7284 \text{ g C}$$

$$1.639 g \text{ H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} \approx 0.1830 \text{ g H}$$

$$1.397 \text{ g sample} - 0.7284 \text{ g C} - 0.1830 \text{ g H} = 0.486 \text{ g O}$$

Part 2: from mass composition to empirical formula:

step 1: convert all elements to moles

$$0.7284 g C \times \frac{1 \ mol \ C}{12.01 \ g \ C} = 0.06065 \ mol \ C$$
$$0.1830 g H \times \frac{1 \ mol \ H}{1.008 \ g \ H} = 0.1815 \ mol \ H$$
$$0.486 g \ O \times \frac{1 \ mol \ O}{16.00 \ g \ O} = 0.0304 \ mol \ O$$

step 2: divide by smallest moles:

$$\begin{array}{rcl} 0.06065 \; mol \; \mathrm{C} \; \div \; 0.0304 \; mol \; = \; 2 \; \mathrm{C} \\ 0.1815 \; mol \; \mathrm{H} \; \div \; 0.0304 \; mol \; = \; 6 \; \mathrm{H} \\ 0.0304 \; mol \; \mathrm{O} \; \div \; 0.0304 \; mol \; = \; 1 \; \mathrm{O} \end{array}$$

the empirical formula of ethanol is C₂H₆O

Chapter 4: Aqueous solutions

In previous topics, we used pure substances. We used one chemical at a time. If we had more than one, we were relating them in chemical reactions.

A solution is a HOMOGENEOUS mixture. A SOLUTE is dissolved into a SOLVENT to make the SOLUTION.

solute + solvent = solution

If water is the solvent, the solution is called an AQUEOUS solution - abbreviated "aq." We will be using water as our solvent 99% of the time. Be careful, the solvent does not have to be water; the solvent does not even need to be a liquid.

Ionic compounds DISSOCIATE in aqueous solutions into ELECTROLYTE ions.

Some ionic compounds are SOLUBLE in water; others are INSOLUBLE in water. There are SOLUBILITY RULES.

Some soluble ionic compounds dissolve completely - they are STRONG ELECTROLYTES. However, many soluble ionic compounds dissolve incompletely - they are WEAK ELECTROLYTES. Obviously, since covalent compounds have no ions, they produce no electrolytes - if they dissolve, they produce NONELECTROLYTE solutions.

There are three major types of ionic compound aqueous solutions:

An ACID is an ionic compound that contains hydrogen ions as its positive ion (cation).

Metal oxides react with water to produce bases.

Acids generally taste SOUR.

A BASE is an ionic compound that contains the HYDROXIDE () polyatomic ion as its negative ion.

Nonmetal oxides react with water to produce acids.

Bases generally taste BITTER.

A SALT is any other ionic compound.

Most salts taste SALTY.

DO NOT, UNDER ANY CIRCUMSTANCE, TASTE ANY OF THE CHEMICALS IN THE LAB!

Since ionic compounds in aqueous solutions exist as ions, we don't always write balanced equations as the MOLECULAR EQUATIONS (from Chapter 3). Instead, we often write out the electrolytes in NET IONIC EQUATIONS.

Ionic compounds in aqueous solution undergo some important reactions. Since many compounds are insoluble, when soluble solution reactants may produce an insoluble product in a DOUBLE DISPLACEMENT (the cations and anions switch their partners). Insoluble products PRECIPITATE; they are produced as solid grains that separate from the solution. Any remaining product ions are called SPECTATOR IONS.

Acid solutions react with base solutions in a NEUTRALIZATION REACTION.

Oxidation numbers (or states) are used to keep track of electrons during a chemical reaction. The oxidation number of an ion in an ionic compound is the same as its ion charge. The oxidation number of an atom in a covalent compound, would be its charge if it were an ion.

Some rules to find the oxidation number are:

rule 1: the oxidation number of an element is zero.

rule 2: the oxidation number of a monatomic ion is its ion charge.

rule 3: the oxidation number of fluorine in compound is always -1, oxygen in compound is almost always -2, and hydrogen is +1, except for -1 in a metal hydride.

rule 4: the total oxidation number of a compound must be zero.

rule 5: the total oxidation number of a polyatomic ion must be its charge.

rule 6: the oxidation number of uncertain atoms must be determined through the context of the molecule it is part of.

redox reactions

REDOX is a contraction: it is short for "reduction" and "oxidation."

In Chemistry, REDUCTION means to gain electrons and OXIDATION means to lose electrons. In other words, a redox reaction is a two part reaction, where one side gains electrons from the other side that loses electrons. Electrons are transferred from one side to the other.

The problem: a chemical equation doesn't include electron information. You can't tell if a reaction is a redox reaction just by looking at a chemical equation (unless you've seen it before). You need to count the electrons (using oxidation numbers) of all the elements, compare the oxidation numbers of each element, reactant-versus-product, and see if any changes, to prove a reaction really is a redox reaction. Remember, since electrons have a negative charge, the change seems to work backwards (its like working with signed numbers) - an increase in oxidation number counts a loss of electrons (oxidation), a decrease in oxidation number counts a gain of electrons (reduction).

Since redox is not obvious in a normal balanced equation, redox reactions are often written as two HALF-REACTIONS that directly shows the electrons - one for the reduction half and another for the oxidation half. The reduction electron gain shows them as a reactant, an oxidation loss puts the electrons as a product.

Molarity and solution stoichiometry

A solution is not normally weighed, because it would be the total mass of the solute and solvent. Since the solute is the "important" part of a solution, we need to measure the solute alone.

The concentration of the solute in a solution is measured by Molarity. Molarity is defined:

$$Molarity = \frac{moles \ solute}{Liters \ solution}$$
$$M = \frac{mol}{L}$$

In addition to simply computing Molarity, this definition can also be used to in solution stoichiometry problems in place of molar mass in the moles conversion.

Chapter 4: Aqueous solutions Problems

Problem 1: Write the balanced equations for the dissociation reactions of the following ionic compounds in aqueous solution. If the compound is insoluble, write NR, for "No reaction," in place of the products.

a) $\operatorname{KCl}_{(s)} \longrightarrow$

b)
$$Ag_2SO_4(s) \longrightarrow$$

c)
$$Mg(NO_3)_{2(s)} \longrightarrow$$

d)
$$AgC_{2}H_{3}O_{2}(s) \longrightarrow$$

e) $NH_4NO_3(s) \longrightarrow$

f)
$$\text{Li}_3\text{PO}_{4(s)} \longrightarrow$$

g)
$$Al_2(CO_3)_{3(s)} \longrightarrow$$

h)
$$Rb_2SO_4(s) \longrightarrow$$

i)
$$\operatorname{CaBr}_{2(s)} \longrightarrow$$

j)
$$(NH_4)_2SO_4 (s) \longrightarrow$$

- k) copper(II) chloride
- 1) barium sulfate
- m) potassium chromate
- n) iron(II) sulfide

Problem 2: Write the balanced molecular and net ionic equations for the following reactants, including phase labels. If all products are soluble, write NR, for "No reaction," as the products.

- a) AlCl_{3 (aq)} + NaOH_(aq) \longrightarrow
- b) $Al(C_2H_3O_2)_{3(aq)} + NaNO_{3(aq)} \longrightarrow$
- c) $NiSO_{4(aq)} + Na_3PO_{4(aq)} \longrightarrow$
- d) $\text{Li}_2\text{CO}_{3(aq)} + \text{MgSO}_{4(aq)} \longrightarrow$
- e) $\operatorname{Na_2CO_3}_{(aq)} + \operatorname{Fe}(\operatorname{NO_3})_{3}_{(aq)} \longrightarrow$

- f) $Al(C_2H_3O_2)_{3(aq)} + NaNO_{3(aq)} \longrightarrow$
- g) iron(II) chloride and potassium sulfide
- h) ammonium chromate and chromium(III) fluoride
- i) sodium phosphate and copper(II) nitrate

Problem 3: Write the balanced equation for the neutralization of the following acids and bases, including phase labels.

- a) nitric acid and potassium hydroxide
- b) sulfurous acid and magnesium hydroxide
- c) sulfuric acid and sodium hydroxide
- d) acetic acid and calcium hydroxide
- e) phosphoric acid and magnesium hydroxide
- f) nitric acid and ammonia

Problem 4: What is the oxidation number of the underlined atom in each example:

- a) SeF₄
- b) $\underline{P}O_4^{3-}$
- c) IF
- d) $H_2 \underline{S} O_4$
- e) \underline{Co}_2O_3
- f) $Ni\underline{H}_2$
- g) Al<u>Br</u>₃
- h) $V(\underline{Cl}O_4)_5$
- i) $Na_2\underline{Cr}_2O_7$
- j) $\underline{Cl}O_2$
- k) $\underline{N}O_2^-$
- 1) $K_2 \underline{C}_2 O_4$

- m) NH_4NO_3
- n) $\underline{N}H_4NO_3$
- o) \underline{Cu}_2SO_4
- p) <u>S</u>O₃
- q) \underline{Br}_2

Problem 5: Identify the species being reduced and oxidized in the following redox reactions. Write balanced half reactions for the reduction and oxidation. (You may ignore spectator ions.)

- a) $3 \text{ Mg} + \text{Al}_2\text{O}_3 \longrightarrow 3 \text{ MgO} + 2 \text{ Al}$
- b) $Cu + 2 \text{ AgCl} \longrightarrow CuCl_2 + 2 \text{ Ag}$
- c) $Cr_2O_3 + 3 CO \longrightarrow 2 Cr + 3 CO_2$
- d) Ca + Ni(NO₃)₂ \longrightarrow Ca(NO₃)₂ + Ni

Problem 6: If 39.4 g of sodium sulfate is dissolved in water to make 796 mL of solution, what is Molarity of the solution?

Problem 7: What mass of potassium nitrate is dissolved in 398 mL of a 2.14 Molar solution?

Problem 8: Solutions of nickel sulfate, NiSO₄, and sodium phosphate, Na₃PO₄, react to give a pale yellow-green precipitate of nickel phosphate, Na₃PO₄, and a solution of sodium sulfate, Na₂SO₄

3 NiSO_{4 (aq)} + 2 Na₃PO_{4 (aq)} + \longrightarrow Ni₃(PO₄)_{2 (s)} + 3 Na₂SO_{4 (aq)}

(a) How many milliliters of 0.375 M NiSO₄ will completely react with 45.7 mL of 0.265 M Na_3PO_4 ?

(b) What mass of $Ni_3(PO_4)_2$ precipitate would form?

Problem 9: Millions of tons of hydrochloric acid are used every year for "metal pickling" - removing any rust or corrosion from metal surfaces - before final finishing. The reaction with iron(III) oxide is:

 $\operatorname{Fe_2O_3}_{(s)}$ + 6 $\operatorname{HCl}_{(aq)} \longrightarrow 2 \operatorname{FeCl}_{3(aq)}$ + 3 $\operatorname{H_2O}_{(l)}$

If a steel sheet with 5.29 g Fe_2O_3 rust is pickled with 27.5 mL of 2.45 M HCl, would all the rust be removed? (a) What concentration of $FeCl_3$ would be produced, if the final volume is 89.4 mL? (b) If the rust is the excess reagent, what mass of Fe_2O_3 would remain?

Chapter 4: Aqueous solutions Solutions

Solution 1: Write the balanced equations for the dissociation reactions of the following ionic compounds in aqueous solution. If the compound is insoluble, write NR, for "No reaction," in place of the products.

a)
$$\operatorname{KCl}_{(s)} \longrightarrow \operatorname{K}^+_{(aq)} + \operatorname{Cl}^-_{(aq)}$$

b)
$$Ag_2SO_4(s) \longrightarrow NR$$

c)
$$\operatorname{Mg(NO}_{3})_{2(s)} \longrightarrow \operatorname{Mg}_{(aq)}^{2+} + 2 \operatorname{NO}_{3(aq)}^{-}$$

d)
$$\operatorname{AgC}_{2}\operatorname{H}_{3}\operatorname{O}_{2}(s) \longrightarrow \operatorname{Ag}_{(aq)}^{+} + \operatorname{C}_{2}\operatorname{H}_{3}\operatorname{O}_{2}^{-}(aq)$$

e)
$$\operatorname{NH}_4\operatorname{NO}_3(s) \longrightarrow \operatorname{NH}_4^+(aq) + \operatorname{NO}_3^-(aq)$$

f)
$$\text{Li}_{3}\text{PO}_{4(s)} \longrightarrow 3 \text{Li}_{(aq)}^{+} + \text{PO}_{4(aq)}^{3-}$$

g)
$$Al_2(CO_3)_{3(s)} \longrightarrow NR$$

h)
$$\operatorname{Rb}_2\operatorname{SO}_{4(s)} \longrightarrow 2\operatorname{Rb}_{(aq)}^+ + \operatorname{SO}_{4(aq)}^{2-}$$

i)
$$\operatorname{CaBr}_{2(s)} \longrightarrow \operatorname{Ca}_{(aq)}^{2+} + 2 \operatorname{Br}_{(aq)}^{-}$$

j)
$$(NH_4)_2SO_4(s) \longrightarrow 2 NH_4^+(aq) + SO_4^{2-}(aq)$$

k) copper(II) chloride

$$\operatorname{CuCl}_{2(s)} \longrightarrow \operatorname{Cu}_{(aq)}^{2+} + 2 \operatorname{Cl}_{(aq)}^{-}$$

l) barium sulfate

$$BaSO_4$$
 (s) \longrightarrow NR

m) potassium chromate

$$K_2CrO_4_{(s)} \longrightarrow 2 K^+_{(aq)} + CrO^{2-}_{4_{(aq)}}$$

n) iron(II) sulfide

$$FeS_{(s)} \longrightarrow NR$$

Solution 2: Write the balanced molecular and net ionic equations for the following reactants, including phase labels. If all products are soluble, write NR, for "No reaction," as the products.

a) $AlCl_{3(aq)} + NaOH_{(aq)} \longrightarrow$ molecular $AlCl_{3(aq)} + 3 NaOH_{(aq)} \longrightarrow Al(OH)_{3(s)} + 3 NaCl_{(aq)}$ net ionic $Al_{(aq)}^{3+} + 3 OH_{(aq)}^{-} \longrightarrow Al(OH)_{3(s)}$

b)
$$Al(C_2H_3O_2)_{3(aq)} + NaNO_{3(aq)} \longrightarrow$$

 $Al(C_2H_3O_2)_{3(aq)} + NaNO_{3(aq)} \longrightarrow NR$

c) NiSO_{4 (aq)} + Na₃PO_{4 (aq)} \rightarrow molecular 3 NiSO_{4 (aq)} + 2 Na₃PO_{4 (aq)} \rightarrow Ni₃(PO₄)_{2 (s)} + 3 Na₂SO_{4 (aq)} net ionic 3 Ni²⁺_(aq) + 2 PO³⁺_{4 (aq)} \rightarrow Ni₃(PO₄)_{2 (s)}

d)
$$\text{Li}_2\text{CO}_{3(aq)} + \text{MgSO}_{4(aq)} \longrightarrow$$

molecular $\text{Li}_2\text{CO}_{3(aq)} + \text{MgSO}_{4(aq)} \longrightarrow \text{Li}_2\text{SO}_{4(aq)} + \text{MgCO}_{3(s)}$
net ionic $\text{CO}_{3(aq)}^{2-} + \text{Mg}_{(aq)}^{2+} \longrightarrow \text{MgCO}_{3(s)}$

e) $\operatorname{Na_2CO_3}_{(aq)} + \operatorname{Fe}(\operatorname{NO_3})_{3(aq)} \longrightarrow$ molecular $3 \operatorname{Na_2CO_3}_{(aq)} + 2 \operatorname{Fe}(\operatorname{NO_3})_{3(aq)} \longrightarrow 6 \operatorname{NaNO_3}_{(aq)} + \operatorname{Fe_2}(\operatorname{CO_3})_{3(s)}$ net ionic $3 \operatorname{CO_3^{2-}}_{3(aq)} + 2 \operatorname{Fe}_{(aq)}^{3+} \longrightarrow \operatorname{Fe_2}(\operatorname{CO_3})_{3(s)}$

f)
$$Al(C_2H_3O_2)_{3(aq)} + NaNO_{3(aq)} \longrightarrow$$

 $Al(C_2H_3O_2)_{3(aq)} + NaNO_{3(aq)} \longrightarrow NR$

g) iron(II) chloride and potassium sulfide molecular $\operatorname{FeCl}_{2(aq)} + \operatorname{K}_2S_{(aq)} \longrightarrow \operatorname{FeS}_{(s)} + 2 \operatorname{KCl}_{(aq)}$ net ionic $\operatorname{Fe}_{(aq)}^{3+} + \operatorname{S}_{(aq)}^{2-} \longrightarrow \operatorname{FeS}_{(s)}$

h) ammonium chromate and chromium(III) fluoride

molecular 3 (NH₄)₂CrO_{4 (aq)} + 2 CrF_{3 (aq)} \longrightarrow 6 NH₄F_(aq) + Cr₂(CrO₄)_{3 (s)} net ionic 3 CrO_{4 (aq)}²⁺ + 2 Cr³⁺_(aq) \longrightarrow Cr₂(CrO₄)_{3 (s)}

i) sodium phosphate and copper(II) nitrate mologular 2 Na-RO 4 Cu(NO)

molecular 2 Na₃PO_{4 (aq)} + 3 Cu(NO₃)_{2 (aq)} \longrightarrow 6 NaNO_{3 (aq)} + Cu₃(PO₄)_{2 (s)} net ionic 2 PO_{4 (aq)}³⁻ + 3 Cu²⁺_(aq) \longrightarrow Cu₃(PO₄)_{2 (s)}

Solution 3: Write the balanced equation for the neutralization of the following acids and bases, including phase labels.

a) nitric acid and potassium hydroxide
 HNO_{3 (aq)} + KOH_(aq) → KNO_{3 (aq)} + H₂O_(l)
 b) sulfurous acid and magnesium hydroxide

 $H_2SO_3{}_{(aq)} + Mg(OH)_2{}_{(aq)} \longrightarrow MgSO_3{}_{(aq)} + 2 H_2O_{(l)}$

- c) sulfuric acid and sodium hydroxide $H_2SO_4_{(aq)} + 2 NaOH_{(aq)} \longrightarrow Na_2SO_4_{(aq)} + 2 H_2O_{(l)}$
- d) acetic acid and calcium hydroxide $2 \operatorname{HC}_{2}\operatorname{H}_{3}\operatorname{O}_{2(aq)} + \operatorname{Ca}(\operatorname{OH})_{2(aq)} \longrightarrow \operatorname{Ca}(\operatorname{C}_{2}\operatorname{H}_{3}\operatorname{O}_{2})_{(aq)} + 2 \operatorname{H}_{2}\operatorname{O}_{(l)}$
- e) phosphoric acid and magnesium hydroxide $2 H_3PO_{4(aq)} + 3 Mg(OH)_{2(aq)} \longrightarrow Mg_3(PO_4)_{2(aq)} + 6 H_2O_{(l)}$
- f) nitric acid and ammonia

 $HNO_{3(aq)} + NH_{3(aq)} \longrightarrow NH_4NO_{3(aq)}$

7/8/20 version

Solution 4: What is the oxidation number of the underlined atom in each example:

a)	<u>Se</u> F ₄	+4
b)	$\underline{P}O_4^{3-}$	+5
c)	ĪĿ	+1
d)	$H_2 \underline{S} O_4$	+6
e)	\underline{Co}_2O_3	+3
f)	Ni <u>H</u> 2	-1
g)	Al <u>Br</u> ₃	-1
h)	$V(\underline{Cl}O_4)_5$	+7
i)	Na ₂ <u>Cr</u> ₂ O ₇	+6
j)	<u>Cl</u> O ₂	+4
k)	$\underline{N}O_2^-$	+3
1)	$K_2 \underline{C}_2 O_4$	+3
m)	$NH_4\underline{N}O_3$	+3
n)	$\underline{N}H_4NO_3$	-3
o)	\underline{Cu}_2SO_4	+1
p)	$\underline{S}O_3$	+6
q)	<u>Br</u> ₂	0

Solution 5: Identify the species being reduced and oxidized in the following redox reactions. Write balanced half reactions for the reduction and oxidation. (You may ignore spectator ions.)

a) $3 \text{ Mg} + \text{Al}_2\text{O}_3 \longrightarrow 3 \text{ MgO} + 2 \text{ Al}$ 0 + 3 - 2 + 2 - 2 0 $3 \text{ Mg} + \text{Al}_2\text{O}_3 \longrightarrow 3 \text{ MgO} + 2 \text{ Al}$

Mg's oxidation number increases, it loses electrons, it is oxidized (also called the reducing agent).

Al's oxidation number decreases, it gains electrons, it is reduced (also called the oxidizing agent).

red 2 Al³⁺ + 6 e⁻
$$\longrightarrow$$
 2 Al
ox 3 Mg \longrightarrow 3 Mg²⁺ + 6 e⁻

b)

$$Cu + 2 AgCl \longrightarrow CuCl_2 + 2 Ag$$

$$0 + 1 - 1 + 2 - 1 0$$

$$Cu + 2 AgCl \longrightarrow CuCl_2 + 2 Ag$$

Cu's oxidation number increases, it loses electrons, it is oxidized (also called the reducing agent).

Ag's oxidation number decreases, it gains electrons, it is reduced (also called the oxidizing agent).

red 2 Ag⁺ + 2 e⁻ \longrightarrow 2 Ag ox Cu \longrightarrow Cu²⁺ + 2 e⁻

c)
$$\operatorname{Cr}_2\operatorname{O}_3 + 3 \operatorname{CO} \longrightarrow 2 \operatorname{Cr} + 3 \operatorname{CO}_2$$

 $+3 \ ^2 + 2 \ ^2 0 + 4 \ ^2$
 $\operatorname{Cr}_2\operatorname{O}_3 + 3 \operatorname{CO} \longrightarrow 2 \operatorname{Cr} + 3 \operatorname{CO}_2$

Cr's oxidation number decreases, it gains electrons, it is reduced (also called the oxidizing agent).

C's oxidation number increases, it loses electrons, it is oxidized (also called the reducing agent).

red 2 Cr³⁺ + 6 e⁻
$$\longrightarrow$$
 2 Cr
ox 3 C²⁺ \longrightarrow 3 C⁴⁺ + 6 e⁻

d)
$$Ca + Ni(NO_3)_2 \longrightarrow Ca(NO_3)_2 + Ni$$

 $0 + 2 + 5 - 2 + 2 + 5 - 2 0$
 $Ca + Ni(NO_3)_2 \longrightarrow Ca(NO_3)_2 + Ni$

Ca's oxidation number increases, it loses electrons, it is oxidized (also called the reducing agent).

Ni's oxidation number decreases, it gains electrons, it is reduced (also called the oxidizing agent).

red Ni²⁺ + 2 e⁻ \longrightarrow Ni ox Ca \longrightarrow Ca²⁺ + 2 e⁻

Solution 6: If 39.4 g of sodium sulfate is dissolved in water to make 796 ml of solution, what is Molarity of the solution?

$$solute = 39.4 \text{ g Na}_2\text{SO}_4$$

+ $solvent = water$
= $solution = 796 \text{ mL}$

$$39.4 \text{ g Na}_{2}SO_{4} \times \frac{1 \text{ mol Na}_{2}SO_{4}}{142.05 \text{ g Na}_{2}SO_{4}} \approx 0.2774 \text{ mol Na}_{2}SO_{4}$$

$$M = \frac{mol}{L}$$
$$= \frac{0.2774 \ mol \ \text{Na}_2\text{SO}_4}{0.796 \ L}$$
$$\approx 0.348 \ M \ \text{Na}_2\text{SO}_4$$

Solution 7: What mass of potassium nitrate is dissolved in 398 mL of a 2.14 Molar solution?

$$solute = ? g \text{ KNO}_3$$

+ $solvent = water$
= $solution = 2.14 M, 0.398 L$

KNO₃
K =
$$39.10$$

N = 14.01
O₃ = $16.00 \times 3 = 48.00$
KNO₃ = 101.11 g/mol

$$M = \frac{mol}{L}$$

$$L \times M = mol$$

$$0.398 \ L \times \frac{2.14 \ mol \ \text{KNO}_3}{L} = mol \ \text{KNO}_3$$

$$\approx 0.8517 \ mol \ \text{KNO}_3$$

$$0.8517 mol \text{ KNO}_3 \times \frac{101.11 \text{ g KNO}_3}{1 mol \text{ KNO}_3} \approx 86.1 \text{ g KNO}_3$$

Solution 8: Solutions of nickel sulfate, NiSO₄, and sodium phosphate, Na₃PO₄, react to give a pale yellow-green precipitate of nickel phosphate, Na₃PO₄, and a solution of sodium sulfate, Na₂SO₄

$$3 \operatorname{NiSO}_{4(aq)} + 2 \operatorname{Na_3PO}_{4(aq)} + \longrightarrow \operatorname{Ni_3(PO_4)_2(s)} + 3 \operatorname{Na_2SO}_{4(aq)}$$

(a) How many milliliters of 0.375 M NiSO₄ will completely react with 45.7 mL of 0.265 M Na_3PO_4 ?

This is a solution stoichiometry problem.

part (a) given is 45.7 mL of 0.265 M Na₃PO₄ part (a) unknown is mL of 0.375 M NiSO₄ mole ratio is 3 mol NiSO₄ = 2 mol Na₃PO₄

$$45.7 \ mL \times \frac{0.265 \ mol \ \text{Na}_3\text{PO}_4}{L} \times \frac{2 \ mol \ \text{NiSO}_4}{3 \ mol \ \text{Na}_3\text{PO}_4} \times \frac{L}{0.375 \ mol \ \text{NiSO}_4} \approx 21.5 \ mL$$

It might be easier to do the three-step stoichiometry process one step at a time.

step 1: convert given to moles

$$M = \frac{mol}{L}$$

$$\therefore \quad L \times M = mol$$

$$0.0457 \ L \ \times \ 0.265 \ M \ \text{Na}_3\text{PO}_4 = mol \ \text{Na}_3\text{PO}_4$$

$$\approx 0.01211 \ mol \ \text{Na}_3\text{PO}_4$$

step 2: convert given to unknown

$$0.01211 \,mol\,\operatorname{Na_3PO_4} \times \frac{2 \,mol\,\operatorname{NiSO_4}}{3 \,mol\,\operatorname{Na_3PO_4}} \approx 0.008074 \,mol\,\operatorname{NiSO_4}$$

step 3: convert unknown from moles

$$M = \frac{mol}{L}$$

$$\therefore \quad L = \frac{mol}{M}$$

$$= \frac{0.008074 \ mol \ \text{NiSO}_4}{0.375 \ M \ \text{NiSO}_4}$$

$$\approx 0.0215 \ L$$

$$\approx 21.5 \ mL$$

(b) What mass of $Ni_3(PO_4)_2$ precipitate would form?

part (b) given is 0.0457 L of 0.265 M Na₃PO₄ part (b) unknown is grams Ni₃(PO₄)₂ with molar mass of 3 (58.69) + 2 (30.97) + 8 (16.00) = 366.0 g/mol

mole ratio is 2 mol $Na_3PO_4 = 1 mol Ni_3(PO_4)_2$

$$0.0457 L \times \frac{0.265 \,mol \,\operatorname{Na_3PO_4}}{L} \times \frac{1 \,mol \,\operatorname{Ni_3(PO_4)_2}}{2 \,mol \,\operatorname{Na_3PO_4}} \times \frac{366.0 \,g \,\operatorname{Ni_3(PO_4)_2}}{1 \,mol \,\operatorname{Ni_3(PO_4)_2}} \approx 2.22 \,g \,\operatorname{Ni_3(PO_4)_2}$$

Solution 9: Millions of tons of hydrochloric acid are used every year for "metal pickling" - removing any rust or corrosion from metal surfaces - before final finishing. The reaction with iron(III) oxide is:

$$\operatorname{Fe_2O_3}(s) + 6 \operatorname{HCl}(aq) \longrightarrow 2 \operatorname{FeCl}_3(aq) + 3 \operatorname{H_2O}(l)$$

If a steel sheet with 5.29 g Fe_2O_3 rust is pickled with 27.5 mL of 2.45 M HCl, would all the rust be removed? (a) What concentration of $FeCl_3$ would be produced, if the final

volume is 89.4 mL? (b) If the rust is the excess reagent, what mass of Fe_2O_3 would remain?

This is a solution stoichiometry problem.

givens are 5.29 g Fe₂O₃ with molar mass of $2(55.85) + 3(16.00) \approx 159.7$ g/mol, 0.0275L of 2.45 M HCl 0.0894 L FeCl₃ with molar mass of $55.85 + 3(35.45) \approx 162.2$ g/mol and mole ratio is 1 mol Fe₂O₃ = 6 mol HCl = 2 mol FeCl₃

unknowns are whether Fe_2O_3 is limiting, Molarity $FeCl_3$ produced, and Fe_2O_3 leftover (if any)

part (a)

step 1: convert both givens to moles. step 1A: identify limiting/excess reagent

5.29 g Fe₂O₃ ×
$$\frac{1 \ mol \ Fe_2O_3}{159.7 \ g \ Fe_2O_3} \approx 0.0331 \ mol \ Fe_2O_3 \quad \div 1 \ mol = 0.0331$$

$$M = \frac{mol}{L}$$

$$\therefore \quad M \times L = mol$$

2.45 M HCl × 0.0275 L = mol HCl

$$\approx 0.0674 \ mol \ \text{HCl}_4 \quad \div 6 \ mol = 0.0112$$

since 0.0112 is less than 0.0331, the 0.0674 mol HCl is the limiting reagent
and the 0.0331 mol
$$Fe_2O_3$$
 is the excess reagent.
Therefore, some of the rust will NOT be stripped.

step 2: convert limiting to unknown.

 $0.0674 \ mol \ HCl \times \frac{2 \ mol \ FeCl_3}{6 \ mol \ HCl} \approx 0.0225 \ mol \ FeCl_3$

step 3: convert unknown from moles

$$M = \frac{mol}{L}$$
$$= \frac{0.0225 mol \text{ FeCl}_3}{0.0894 L}$$
$$\approx 0.254 M \text{ FeCl}_3$$

part (b) do not repeat step 1. Take the limiting reagent identified in part (a)

step 2: convert limiting to excess. step 3: convert excess from moles

$$0.0674 \ mol \ HCl \times \frac{1 \ mol \ Fe_2O_3}{6 \ mol \ HCl} \times \frac{159.7 \ g \ Fe_2O_3}{1 \ mol \ Fe_2O_3} \approx 1.79 \ g \ Fe_2O_3 \ used up$$

$$5.29 \ g \ Fe_2O_3 \ given - 1.79 \ g \ Fe_2O_3 \ used up = 3.50 \ g \ Fe_2O_3 \ left \ over$$

Chapter 5: Thermochemistry

There are many types of energy. They include: kinetic energy, potential energy, and electrical energy. However, in Chemistry, we are concerned with heat energy.

Chemical reactions do not only involve a change of chemicals. They also have a change of energy. Some reactions absorb energy, other reactions release energy - measured as a change of heat, and usually converted to a change of enthalpy.

calorimetry

The word "calor" means heat; and "meter" means measure. Therefore, CALORIMETRY literally means "measure the heat." How? By measuring the temperature, because temperature is proportional to the heat stored in a collective object.

A calorimeter is an insulated container, usually filled with water, in which a chemical reaction is run. A thermometer in the water measures any temperature changes, which is then used to calculate the heat.

There are two versions of the calorimetry equation, depending on whether the calorimeter is measured by specific heat (s) or heat capacity (C):

$$q = -m s \Delta T$$
$$q = -C \Delta T$$

Note, the negative sign may not be necessary, if the heat is measured directly - SYSTEM vs. SURROUNDINGS. In Chemistry, the system is the chemical reaction, the surroundings is everything else.

CONSERVATION OF ENERGY says "Energy can neither be created, nor destroyed - it can only be transferred from one place to another, or transformed from one kind into another. The total energy does not change."

There are many applications of conservation of energy. One involves placing a hot object together with a cold object. Heat will transfer from the hot object to the cold object - the hot object cools down and the cold object warms up, and they will meet somewhere in the middle in an "equilibrium" temperature. Since the total energy will not change:

 $q_{system} + q_{surroundings} = 0$

thermochemical equations and stoichiometry

Since chemical reactions also involve a change of energy, the enthalpy change can be included as part of the balanced equation. This thermochemical equation can be used in stoichiometry calculations. In fact, thermochemical stoichiometry is quicker than regular stoichiometry, because energy does not need to be converted to moles - enthalpy is measured in kiloJoules per mole.

An endothermic reaction is any reaction that absorbs (gains) heat and therefore has a positive Δ H. Endothermic reactions feel cold because they absorb heat from the surroundings.

An exothermic reaction is any reaction that releases (loses) heat and therefore has a negative Δ H. Exothermic reactions feel hot because they release heat to the surroundings.

enthalpy of formation

Since Chemistry is over 250 years old, many enthalpy values have been carefully measured by experts and they have been published. It is not necessary to keep remeasuring them. You can look them up.

The basic enthalpy value is the enthalpy of formation. Formation refers to formation reactions - to produce exactly one mole of a compound from its elements.

Enthalpies of formation are listed on tables. They can be used to find the enthalpy of any reaction by using this formula:

$$\Delta H_{rxn}^{\circ} = \sum n_p \ \Delta H_f^{\circ} (\text{products}) - \sum n_r \ \Delta H_f^{\circ} (\text{reactants})$$

Be careful: the formula uses products first, then subtracts the reactants - the opposite of the way a chemical equation is written. Note: since there is a mathematical formula, some professors consider this topic to be a Math problem, not a Chemistry problem, and therefore simple. Make sure you are comfortable with your algebra skills.

Hess' Law

"Related reactions have related enthalpies."

If there are multiple reactions that are somehow related to each other, their relationship can be used to find missing enthalpies. The problem is: What is the relationship?

I recommend a four-step procedure: Compare/Correct/Cancel/Combine

step 1: COMPARE each given equation, one at a time, to the unknown reaction. What chemical do they have, exclusively, in common.

step 2: CORRECT each given equation, one at a time, if the common chemical does not match exactly for number of moles, or is not on the side (reactant versus product) - multiply to match moles, reverse to match side.

step 3: CANCEL chemicals in the corrected equations that repeat, by checking all the reactants versus all the products, like in math equations.

step 4: COMBINE all the remaining chemicals into one final equation; all reactants together, all products together.

Chapter 5: Thermochemistry Problems

Problem 1: When 10.66 kJ of heat is added to 242 g of an unknown metal, its temperature rises from 19.5 °C to 117.6 °C. What is the specific heat of this metal?

Problem 2: When a 2.946 g sample of ethanol, C_2H_5OH , is burned with excess oxygen in a bomb calorimeter, the temperature of the calorimeter rises from 24.50°C to 33.12°C. If the heat capacity of the calorimeter and contents was 10.14 kJ/°C, what is the enthalpy of combustion per 1.00 mol of ethanol? The reaction is:

$$C_2H_5OH_{(l)} + 3 O_{2(g)} \longrightarrow 2 CO_{2(g)} + 3 H_2O_{(l)}$$

Problem 3: A 285 g sample of an unknown metal at 125.50 °C is placed into 527 g of water at 16.44 °C. When equilibrium is reached, the temperature is 27.81 °C. Since the specific heat of water is 4.184 J/g °C, what is the specific heat of the metal? Assume any heat transfer to the container is negligible.

Problem 4: Although both chemicals are highly toxic, the liquids hydrazine, N_2H_4 , and dinitrogen tetroxide, N_2O_4 are often used as rocket fuels, because of their fail-safe exothermic reaction:

$$2 N_2 H_{4(l)} + N_2 O_{4(l)} \longrightarrow 3 N_{2(g)} + 4 H_2 O_{(g)} \Delta H^{\circ} = -1049 \, kJ/mol$$

How much heat is evolved when 1 gallon $(3.01 \times 10^3 g)$ of hydrazine is completely reacted?

Problem 5: Chemical (single-use) cold packs use of a bag of ammonium nitrate crystals inside another bag of water. When the inner bag is broken, the ammonium nitrate dissolves in the water in an endothermic reaction:

$$NH_4NO_{3(s)} \longrightarrow NH_{4(aa)}^+ + NO_{3(aq)}^- \Delta H^\circ = 25.7 \ kJ/mol$$

If a cold pack can absorb 124 kJ of heat, what mass of ammonium nitrate does the pack contain?

Problem 6: The most common alternative automotive fuel is ethanol. Gasoline is normally diluted with at least 10% ethanol in the US, and many gas stations also sell 85-90% ethanol. The enthalpy of formation of ethanol is -277.9 kJ/mol. Look up the enthalpies of formation of carbon dioxide and water. What is the enthalpy of combustion of 1 mole of ethanol?

$$C_2H_5OH_{(l)} + 3 O_{2(g)} \longrightarrow 2 CO_{2(g)} + 3 H_2O_{(l)} \Delta H^{\circ} = ?$$

Problem 7: The primary component of gasoline is the 8-carbon isooctane. The thermochemical equation for the combustion of isooctane is:

$$2 C_8 H_{18(l)} + 25 O_{2(g)} \longrightarrow 16 CO_{2(g)} + 18 H_2 O_{(l)} \Delta H_{rxn}^{\circ} = -10,921.8 kJ$$

What is the enthalpy of formation of isooctane? Look up the enthalpies of formation of the other chemicals.

Problem 8: Determine ΔH° for:

$$\operatorname{CH}_{4\,(g)} \ + \ 2 \operatorname{O}_{2\,(g)} \ \longrightarrow \ \operatorname{CO}_{2\,(g)} \ + \ 2 \operatorname{H}_{2}\operatorname{O}_{(l)}$$

Use the following data:

$$C_{(s)} + 2 H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H^{\circ} = -75 \, k J/mol$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_{2}O_{(l)} \qquad \Delta H^{\circ} = -286 \, k J/mol$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^{\circ} = -394 \, k J/mol$$

Problem 9: From the following combustion data:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^{\circ} = -393.5 \, kJ/mol$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_{2}O_{(l)} \qquad \Delta H^{\circ} = -285.8 \, kJ/mol$$

$$2 C_{2}H_{6(g)} + 7 O_{2(g)} \longrightarrow 4 CO_{2(g)} + 6 H_{2}O_{(l)} \qquad \Delta H^{\circ} = -3119.6 \, kJ/mol$$
Calculate the enthalpy change for the reaction:

$$2 C_{(s)} + 3 H_{2 (g)} \longrightarrow C_2 H_{6 (g)}$$

Chapter 5: Thermochemistry Solutions

Solution 1: When 10.66 kJ of heat is added to 242 g of an unknown metal, its temperature rises from 19.5 °C to 117.6 °C. What is the specific heat of this metal?

given:
$$q = 10.66 \text{ kJ} \times \frac{1000 \text{ J}}{\text{kJ}} = 10,660 \text{ J}, m = 242 \text{ g}, T_i = 19.5^{\circ}C, T_f = 117.6^{\circ}C$$

unknown: s = ?

$$q = m \ s \ \Delta T$$

$$\therefore \ s = \frac{q}{m \ \Delta T}$$

$$= \frac{q}{m \left(T_f - T_i\right)}$$

$$= \frac{10,660 \ J}{242 \ g \left(117.6 \ ^\circ C - 19.5 \ ^\circ C\right)}$$

$$s \approx 0.449 \ J/g \cdot ^\circ C$$

Solution 2: When a 2.946 g sample of ethanol, C_2H_5OH , is burned with excess oxygen in a bomb calorimeter, the temperature of the calorimeter rises from 24.50°C to 33.12°C. If the heat capacity of the calorimeter and contents was 10.14 kJ/°C, what is the enthalpy of combustion per 1.00 mol of ethanol? The reaction is:

$$C_2H_5OH_{(l)} + 3 O_{2(g)} \longrightarrow 2 CO_{2(g)} + 3 H_2O_{(l)}$$

given: $m = 2.946 g$, $T_i = 24.50^{\circ}C$, $T_f = 33.12^{\circ}C$, $C = 10.14 kJ/{\circ}C$
unknown: $\Delta H^{\circ} = ?$

Since the calorimeter's (the surroundings') temperature is measured, not the reaction's (the system's) directly, the calorimetry equation should use a negative sign.

$$q = -C \Delta T$$

$$q = -C \left(T_f - T_i\right)$$

$$q = -10.14 \ kJ/^{\circ}C \ (33.12^{\circ}C - 24.50^{\circ}C)$$

$$q \approx -87.41 \ kJ$$

2.946 g C₂H₅OH ×
$$\frac{1 \ mol \ C_2H_5OH}{46.07 \ g \ C_2H_5OH} \approx 0.06395 \ mol \ C_2H_5OH$$

$$\Delta H = \frac{q}{mol}$$
$$\Delta H = \frac{-87.41 \ kJ}{0.06395 \ mol \ C_2H_5OH}$$
$$\Delta H \approx -1367 \ kJ/mol$$

Solution 3: A 285 g sample of an unknown metal at 125.50 °C is placed into 527 g of water at 16.44 °C. When equilibrium is reached, the temperature is 27.81 °C. Since the specific heat of water is 4.184 J/g °C, what is the specific heat of the metal? Assume any heat transfer to the container is negligible.

$$q_{metal} = m_{metal} \ s_{metal} \ \Delta T_{metal}$$
$$= (285 \ g) \ s_{metal} \ (27.81^{\circ}C - 125.50^{\circ}C)$$
$$\approx (-27,842 \ g \cdot {}^{\circ}C) \ s_{metal}$$

$$q_{water} = m_{water} \ s_{water} \ \Delta T_{water}$$

= 527 g (4.184 J/g · °C) (27.81°C - 16.44°C)
 $\approx 25,070 \ J$

$$q_{metal} + q_{water} = 0$$

$$(-27,842 \ g \cdot {}^{\circ}C) \ s_{metal} + 25,070 \ J = 0$$

$$25,070 \ J = (27,842 \ g \cdot {}^{\circ}C) \ s_{metal}$$

$$\therefore \ s_{metal} \approx 0.900 \ J/g \cdot {}^{\circ}C$$

Solution 4: Although both chemicals are highly toxic, the liquids hydrazine, N_2H_4 , and dinitrogen tetroxide, N_2O_4 are often used as rocket fuels, because of their fail-safe exothermic reaction:

$$2 N_2 H_{4(l)} + N_2 O_{4(l)} \longrightarrow 3 N_{2(g)} + 4 H_2 O_{(g)} \Delta H^\circ = -1049 \ kJ/mol$$

How much heat is evolved when 1 gallon $(3.01 \times 10^3 g)$ of hydrazine is completely reacted?

given is $3.01 \times 10^3 g \text{ N}_2\text{H}_4$, with molar mass of 2 (14.01) + 4 (1.008) = 32.05g/mol unknown is kJ of heat mole ratio is 2 mol N₂H₄ = -1049 kJ

$$3.01 \times 10^3 \text{ g } \text{N}_2\text{H}_4 \times \frac{1 \text{ mol } \text{N}_2\text{H}_4}{32.05 \text{ g } \text{N}_2\text{H}_4} \times \frac{-1049 \text{ kJ}}{2 \text{ mol } \text{N}_2\text{H}_4} \approx -4.93 \times 10^4 \text{ kJ}$$

Solution 5: Chemical (single-use) cold packs use of a bag of ammonium nitrate crystals inside another bag of water. When the inner bag is broken, the ammonium nitrate dissolves in the water in an endothermic reaction:

$$NH_4NO_{3(s)} \longrightarrow NH_{4(aq)}^+ + NO_{3(aq)}^- \Delta H^\circ = 25.7 \ kJ/mol$$

If a cold pack can absorb 124 kJ of heat, what mass of ammonium nitrate does the pack contain?

given is 124 kJ of heat,

unknown is *g* NH₄NO₃, with molar mass of 2 (14.01) + 4 (1.008) + 3(16.00) = 80.05/mol mole ratio is 1 mol NH₄NO₃ = 25.7 kJ

$$124 \ kJ \times \frac{1 \ mol \ \text{NH}_4\text{NO}_3}{25.7 \ kJ} \times \frac{80.05 \ g \ \text{NH}_4\text{NO}_3}{1 \ mol \ \text{NH}_4\text{NO}_3} \approx 386 \ g \ \text{NH}_4\text{NO}_3$$

Solution 6: The most common alternative automotive fuel is ethanol. Gasoline is normally diluted with at least 10% ethanol in the US, and many gas stations also sell 85-90% ethanol. The enthalpy of formation of ethanol is -277.9 kJ/mol. Look up the enthalpies of formation of carbon dioxide and water. What is the enthalpy of combustion of 1 mole of ethanol?

$$C_2H_5OH_{(l)} + 3 O_{2(g)} \longrightarrow 2 CO_{2(g)} + 3 H_2O_{(l)} \Delta H^\circ = ?$$

given:
$$\Delta H_{f}^{\circ} \left[C_{2}H_{5}OH_{(l)} \right] = -277.6 \ kJ/mol, \ \Delta H_{f}^{\circ} \left[O_{2 \ (g)} \right] = 0 \ kJ/mol$$

 $\Delta H_{f}^{\circ} \left[CO_{2 \ (g)} \right] = -393.5 \ kJ/mol, \ \Delta H_{f}^{\circ} \left[H_{2}O_{(l)} \right] = -285.8 \ kJ/mol$
unknown: $\Delta H_{rxn}^{\circ} = ?$

$$\Delta H_{rxn}^{\circ} = \sum n_p \ \Delta H_f^{\circ} (\text{products}) - \sum n_r \ \Delta H_f^{\circ} (\text{reactants})$$

$$\Delta H_{rxn}^{\circ} = (2 \ \text{CO}_{2(g)} + 3 \ \text{H}_2\text{O}_{(l)}) - (\text{C}_2\text{H}_5\text{OH}_{(l)} + 3 \ \text{O}_{2(g)})$$

$$= \left(2 \left(-393.5 \ kJ/mol\right) + 3 \left(-285.8 \ kJ/mol\right)\right)$$

$$- \left(-277.6 \ kJ/mol + 3 \left(0 \ kJ/mol\right)\right)$$

$$\Delta H_{rxn}^{\circ} = -1366.8 \ kJ/mol$$

Solution 7: The primary component of gasoline is the 8-carbon isooctane. The thermochemical equation for the combustion of isooctane is:

 $2 C_8 H_{18(l)} + 25 O_{2(g)} \longrightarrow 16 CO_{2(g)} + 18 H_2 O_{(l)} \Delta H_{rxn}^{\circ} = -10,921.8 kJ$

What is the enthalpy of formation of isooctane? Look up the enthalpies of formation of the other chemicals.

given:
$$\Delta H_{rxn}^{\circ} = -10,921.8 \ kJ/mol, \ \Delta H_{f}^{\circ} \left[O_{2(g)}\right] = 0 \ kJ/mol$$

 $\Delta H_{f}^{\circ} \left[CO_{2(g)}\right] = -393.5 \ kJ/mol, \ \Delta H_{f}^{\circ} \left[H_{2}O_{(l)}\right] = -285.8 \ kJ/mol$
unknown: $\Delta H_{f}^{\circ} \left[C_{8}H_{18(l)}\right] = ?$

$$\Delta H_{rxn}^{\circ} = \sum n_p \ \Delta H_f^{\circ} \ (\text{products}) - \sum n_r \ \Delta H_f^{\circ} \ (\text{reactants})$$

$$\Delta H_{rxn}^{\circ} = \left(16 \ \text{CO}_{2(g)} + 18 \ \text{H}_2\text{O}_{(l)}\right) - \left(2 \ \text{C}_8\text{H}_{18(l)} + 25 \ \text{O}_{2(g)}\right)$$

$$-10,921.8 \ kJ/mol = \left(16 \ (-393.5 \ kJ/mol\right) + 18 \ (-285.8 \ kJ/mol\right)\right)$$

$$-\left(2x + 25 \ (0 \ kJfmol\right)$$

$$-10,921.8 \ kJ/mol = -11,440.4 \ kJ/mol - 2x$$

$$\therefore x = \frac{-11,440.4 \ kJ/mol - (-10,921.8 \ kJ/mol)}{2}$$

$$\Delta H_f^{\circ} \left[\text{C}_8\text{H}_{18(l)}\right] = x = -259.3 \ kJ/mol$$

Solution 8: Determine ΔH° for:

$$\operatorname{CH}_{4\,(g)} \ + \ 2 \operatorname{O}_{2\,(g)} \ \longrightarrow \ \operatorname{CO}_{2\,(g)} \ + \ 2 \operatorname{H}_2\operatorname{O}_{(l)}$$

Use the following data:

$$C_{(s)} + 2 H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H^{\circ} = -75 \ kJ/mol$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_{2}O_{(l)} \qquad \Delta H^{\circ} = -286 \ kJ/mol$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^{\circ} = -394 \ kJ/mol$$

step 1: when comparing given reaction 1 with the unknown reaction, they have $CH_{4(g)}$ in common. However, it is a product in the given, but needs to be a reactant to match the unknown.

step 2: therefore, reaction 1 needs to be corrected by being reversed - including the enthalpy - to match the unknown:

$$CH_{4(g)} \longrightarrow 2 H_{2(g)} + C_{(s)} \Delta H^{\circ} = +75 \ kJ/mol$$

repeat step 1: when comparing given reaction 2 with the unknown reaction, they have $H_2O_{(l)}$ exclusively in common. (Ignore the oxygen, because it also appears in reaction 3.) However, there are 1 mol in the given, but needs to be 2 mol to match the unknown.

repeat step 2: therefore, reaction 2 needs to be multiplied by 2 - including the enthalpy - to match the unknown:

$$2 \operatorname{H}_{2(g)} + \operatorname{O}_{2(g)} \longrightarrow 2 \operatorname{H}_{2}\operatorname{O}_{(l)} \Delta H^{\circ} = -572 \ kJ/mol$$

Notice, the original balanced equation has a fraction coefficient. This is the only chapter in CHM 1100 where fraction coefficients are OK.

repeat step 1: when comparing given reaction 3 to the unknown reaction, they have $CO_{2(g)}$ exclusively in common. (Ignore the oxygen, because it also appears in reaction 2.) They are both 1 mol products.

repeat step 2: since the $CO_{2(g)}$ matches exactly, no correction is required. Just copy it:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H^{\circ} = -394 \ kJ/mol$$
step 3: looking at all three corrected equations together, there are 1 mol $C_{(s)}$ and 2 mol $H_{2(g)}$ on both the reactant and the product sides, and can be cancelled:

$$CH_{4(g)} \longrightarrow 2 H_{2(g)} + \zeta_{(s)} \qquad \Delta H^{\circ} = +75 \ kJ/mol$$

$$2 H_{2(g)} + O_{2(g)} \longrightarrow 2 H_{2}O_{(l)} \qquad \Delta H^{\circ} = -572 \ kJ/mol$$

$$\zeta_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^{\circ} = -394 \ kJ/mol$$

step 4: looking at what's left, the remaining 1 mol $CH_{4(g)}$ and 2 mol $O_{2(g)}$ reactants and 1 mol $CO_{2(g)}$ and 2 mol $H_2O_{(l)}$ products are added into one combined equation:

$$CH_{4(g)} + 2 O_{2(g)} \longrightarrow CO_{2(g)} + 2 H_2O_{(l)}$$

The check is to make sure this combined equation exactly matches the original unknown equation. If you have the correct total equation, you will get the correct total enthalpy by combining (adding) the corrected enthalpies:

$$\Delta H^{\circ} = +75 \ kJ/mol + (-572 \ kJ/mol) + (-394 \ kJ/mol)$$
$$\Delta H^{\circ} = -891 \ kJ/mol$$

Solution 9: From the following combustion data:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^{\circ} = -393.5 \ kJ/mol$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_{2}O_{(l)} \qquad \Delta H^{\circ} = -285.8 \ kJ/mol$$

$$2 C_{2}H_{6(g)} + 7 O_{2(g)} \longrightarrow 4 CO_{2(g)} + 6 H_{2}O_{(l)} \qquad \Delta H^{\circ} = -3119.6 \ kJ/mol$$

Calculate the enthalpy change for the reaction:

$$2 C_{(s)} + 3 H_{2(g)} \longrightarrow C_2 H_{6(g)}$$

step 1: in comparing given reaction 1 with the unknown reaction, they have $C_{(s)}$ exclusively in common. (Ignore the oxygen, because it also appears in the other reactions.) However, there are 1 mol in the given, but needs to be 2 mol to match the unknown.

step 2: therefore, reaction 1 needs to be multiplied by 2 - including the enthalpy - to match the unknown:

$$2 C_{(s)} + 2 O_{2(g)} \longrightarrow 2 CO_{2(g)} \quad \Delta H^{\circ} = -787.0 \ kJ/mol$$

repeat step 1: in comparing given reaction 2 with the unknown reaction, they have $H_{2(g)}$ exclusively in common. (Ignore the oxygen, because it also appears in the other reactions.) However, there are 1 mol in the given, but needs to be 3 mol to match the unknown.

repeat step 2: therefore, reaction 2 needs to be multiplied by 3 - including the enthalpy - to match the unknown:

$$3 H_{2(g)} + \frac{3}{2} O_{2(g)} \longrightarrow 3 H_2 O_{(l)} \Delta H^{\circ} = -857.4 \, kJ/mol$$

repeat step 1: in comparing given reaction 3 with the unknown reaction, they have $C_2H_{6(g)}$ exclusively in common. (Ignore the oxygen, because it also appears in the other reactions.) However, it is 2 mol reactant in the given, but needs to be 1 mol product.

repeat step 2: therefore, reaction 2 needs to be reversed and divided by 2 - including the enthalpy - to match the unknown:

$$3 H_2O_{(l)} + 2 CO_{2(g)} \longrightarrow \frac{7}{2} O_{2(g)} + C_2H_{6(g)} \Delta H^\circ = +1559.8 \, kJ/mol$$

step 3: looking at all three corrected equations, there are 3 mol $H_2O_{(l)}$, 2 mol $C_{(s)}$ and 3 ¹/₂ mol $O_{2(g)}$ are on both the reactant and the product sides, and can be cancelled:

$$2 C_{(s)} + 2 O_{2(g)} \longrightarrow 2 CO_{2(g)} \qquad \Delta H^{\circ} = -787.0 \ kJ/mol$$

$$3 H_{2(g)} + \frac{3}{2} O_{2(g)} \longrightarrow 3 H_{2}O_{(l)} \qquad \Delta H^{\circ} = -857.4 \ kJ/mol$$

$$3 H_{2}O_{(l)} + 2 CO_{2(g)} \longrightarrow \frac{7}{2} O_{2(g)} + C_{2}H_{6(g)} \qquad \Delta H^{\circ} = +1559.8 \ kJ/mol$$

step 4: only the 2 mol $C_{(s)}$, 3 mol $H_{2(g)}$ and 1 mol $C_2H_{6(g)}$ are left, to be combined into one equation:

$$2 C_{(s)} + 3 H_{2(g)} \longrightarrow C_2 H_{6(g)}$$

Finish by combining (adding) the corrected enthalpies:

$$\Delta H^{\circ} = -787.0 \ kJ/mol + (-857.4 \ kJ/mol) + (+1559.8 \ kJ/mol)$$

$$\Delta H^{\circ} = -84.6 \ kJ/mol$$

Chapter 10: Gases

There are three physical PHASEs of matter: SOLIDs, LIQUIDs and GASes.

• A solid has a definite volume and a definite shape.

• A liquid has a definite volume, but no definite shape. A liquid will flow to take the shape of the bottom of its container.

• A gas has neither a definite volume nor shape. A gas will expand to take the volume and shape of its container.

Since gases have no definite shape or volume, the mass in grams of a gas gives incomplete information about the amount of a gas. In place of the mass, gases are measured by:

pressure (P), measured in atmospheres

volume (V), measured in Liters

and temperature (T), measured in Kelvins (do not use Celsius, like in all other CHM 1100 topics)

Remember your unit conversions:

1 atm = 760 mm Hg = 760 torr. (In British units, you will see psi [pounds per square inch], where 1 atm = 14.7 psi.) 1 L = 1000 mL. $K = {}^{\circ}C + 273$.

the Gas Laws

Since these three measurements refer to one gas at a time, they must be related to each other. If you know some values, the gas laws allow to you to calculate other values:

Boyle's Law - pressure and volume are inversely proportional

$$P_1 V_1 = P_2 V_2$$

Charles' Law - volume and temperature are directly proportional

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Avogadro's Law - moles and volume are directly proportional

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

Ideal Gas Law - the gas pressure, volume and temperature is enough information to determine gas moles

$$P V = n R T$$

where the gas constant $R \approx 0.0821 L \cdot atm/mol \cdot K$

Dalton's Law (for gas mixtures)

part 1: the total pressure is the sum of the partial pressures

$$P_{total} = P_A + P_B + P_C + \dots$$

part 2: the mole fraction is proportional to pressure fraction

$$\chi_A = \frac{n_A}{n_{total}} = \frac{P_A}{P_{total}}, \quad \chi_B = \frac{n_B}{n_{total}} = \frac{P_B}{P_{total}}, \quad \chi_C = \frac{n_C}{n_{total}} = \frac{P_C}{P_{total}}, \quad \dots$$

Graham's Law (of effusion and diffusion)

$$\frac{rate_1}{rate_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

gas density

$$d = \frac{m}{V} = \frac{\mathcal{M}P}{RT}$$

The Ideal Gas Law is the most important of the gas laws, because (1) the other gas laws can be derived from it and (2) it is used in gas stoichiometry calculations, since it has moles.

The Kinetic Molecular Theory of Gases is an explanation of what a gas is, atom-byatom, molecule-by-molecule, and predicts gas behavior under various conditions. How

do the atoms/molecules of a gas behave: gas atoms/molecules have approximately zero size (compared to the whole); have negligible forces with each other; are always in random motion and collide elastically with surroundings to produce pressure; their velocity/kinetic energy is proportional to Kelvin temperature

These postulates are the starting point for a huge amount of theoretical work - that we don't worry about, because it's mostly Physics.

We do use a gas law for root-mean-squared velocity, which is the average speed of gas atoms/molecules depending on temperature.

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

Be careful: this formula comes from Physics, so the molar mass must be in kilograms per mole, and the gas constant, $R = 8.314 \ J/mol \cdot K$.

Notice: since the temperature is in the numerator of the fraction, higher temperature goes with faster speed, and vice versa. Notice also: since the molar mass is in the denominator of the fraction, heavier molar mass goes with slower speed, and vice versa.

Please understand that an ideal gas is an approximation. Real gases have real atomic size and their atoms and molecules can interact. Therefore, using these gas laws will give only an approximate answer. For example, the van der Vaal's Equation gives the real "correct" answer, compared to the Ideal Gas Law.

Real gases behave most nearly ideally only at high temperatures and low pressures

Chapter 10: Gases Problems

Problem 1: A weather balloon is inflated with helium gas to a volume of 158 L at sea level at 30 °C and 770 torr. The balloon rises into the stratosphere, where it is -30 °C and 180 torr. What will be the ballon's volume?

Problem 2: Formic acid can be decomposed with sulfuric acid to produce carbon monoxide gas. If the carbon monoxide is collected over water, at a total pressure of 765 mm Hg, in a 720 mL flask at 22 °C, what mass of CO is collected? The vapor pressure of water at 22 °C is 20. torr.

Problem 3: When 0.564 g of a liquid compound is vaporized, it fills a volume of 356 mL, at 90°C and 753 mmHg. What is the molar mass of the compound?

Problem 4: The carbon dioxide exhaled by astronauts is absorbed from the spacecraft air by lithium hydroxide:

$$2 \operatorname{LiOH}_{(s)} + \operatorname{CO}_{2(g)} \longrightarrow \operatorname{Li}_2 \operatorname{CO}_{3(s)} + \operatorname{H}_2 \operatorname{O}_{(l)}$$

A person exhales about 5.8×10^2 L of carbon dioxide (at STP) every day. What mass of lithium hydroxide is required to absorb this carbon dioxide for each astronaut per day?

Problem 5: A high explosive is any chemical that undergoes an extremely rapid, exothermic reaction with lots of gas products to produce the blast front. Nitroglycerin is the explosive in dynamite. Its reaction is:

$$4 C_{3}H_{5}(ONO_{2})_{3 (l)} \longrightarrow 6 N_{2 (g)} + 12 CO_{2 (g)} + 10 H_{2}O_{(g)} + O_{2 (g)}$$

What is the total volume of gases produced at 400 °C and 2 atm, by the explosion of 200. g of nitroglycerin?

Problem 6: Propane is the gas burned by gas barbecues. The thermochemical equation for the combustion of methane is:

$$C_{3}H_{8(g)} + 5 O_{2(g)} \longrightarrow 3 CO_{2(g)} + 4 H_{2}O_{(l)} \Delta H^{\circ} = -2219.0 \ kJ/mol$$

If a 5.0 L propane tank at 30.0 °C and under 2.50×10^4 mm Hg pressure is completely burned, how much heat would be produced?

Chapter 10: Gases Solutions

Solution 1: A weather balloon is inflated with helium gas to a volume of 1.58×10^3 L at sea level at 30 °C and 770. torr. The balloon rises into the stratosphere, where it is -30 °C and 180. torr. What will be the ballon's volume?

given is
$$V_1 = 1.58 \times 10^3 \text{ L}$$
, $T_1 = 30 \,^{\circ}\text{C} + 273 = 303 \text{ K}$,
 $P_1 = 770. \ torr \times \frac{1 \ atm}{760 \ torr} \approx 1.013 \ atm$,
 $T_2 = -30 \,^{\circ}\text{C} + 273 = 243 \text{ K}$, $P_2 = 180. \ torr \times \frac{1 \ atm}{760 \ torr} \approx 0.233 \ atm$

unknown is $V_2 = ?$

Since pressure, volume and temperature are all changing, use the Combined Gas Law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \quad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$= \frac{1.013 \ atm (1.58 \times 10^3 \ L) (243 \ K)}{303 \ K (0.233 \ atm)}$$

$$V_2 \approx 5.51 \times 10^3 \ L$$

Solution 2: Formic acid can be decomposed with sulfuric acid to produce carbon monoxide gas. If the carbon monoxide is collected over water, at a total pressure of 765 mm Hg, in a 720 mL flask at 22 °C, what mass of CO is collected? The vapor pressure of water at 22 °C is 20. torr.

This is multi-part problem. Gas collection over water results in a gas mixture - Dalton's Law. Finding mass requires knowing moles - Ideal Gas Law.

part 1:

given is $P_{total} = 765 torr$, $P_{H_2O} = 22 torr$ unknown is $P_{CO} = ?$

$$P_{total} = P_{CO} + P_{H_2O}$$

$$\therefore \quad P_{CO} = P_{total} - P_{H_2O}$$

$$= 765 \ torr - 20 \ torr$$

$$P_{CO} = 745 \ torr$$

part 2:

given is $P = 745 torr \times \frac{1 atm}{760 torr} \approx 0.9803 atm$ V = 0.720 L, T = 22 °C + 273 = 295 Kmolar mass of CO = 28.01 g/mol

unknown is $n_{CO} = ?$, $m_{CO} = ?$

$$PV = n R T$$

$$\therefore \quad n = \frac{PV}{RT}$$

$$n_{CO} = \frac{0.9803 \ atm (0.720 \ L)}{0.0821 \ L \cdot atm/mol \cdot K \ (295 \ K)}$$

$$n_{CO} \approx 0.0291 \ mol \ CO$$

$$0.0291 \ mol \ \text{CO} \times \frac{28.01 \ g \ \text{CO}}{1 \ mol \ \text{CO}} \approx \frac{0.816 \ g \ \text{CO}}{1 \ mol \ \text{CO}}$$

Solution 3: When 0.564 g of a liquid compound is vaporized, it fills a volume of 356 mL, at 90 $^{\circ}$ C and 753 mm Hg. What is the molar mass of the compound?

given is m = 0.564 g, V = 356 mL = 0.356 L, T = 90 °C + 273 = 363 K,

$$P = 753 \ mm \ Hg \times \frac{1 \ atm}{760 \ mm \ Hg} \approx 0.9908 \ atm$$

unknown is molar mass, $\mathcal{M} =$?

mass and volume are related as density:

$$\mathcal{A} = \frac{m}{V} = \frac{\mathcal{M} P}{R T}$$

$$\therefore \quad \mathcal{M} = \frac{m R T}{V P}$$

$$= \frac{0.564 \ g \left(0.0821 \ L \cdot atm/mol \cdot K \right) \left(363 \ K \right)}{0.356 \ L \left(0.9908 \ atm \right)}$$

$$\mathcal{M} \approx 47.7 \ g/mol$$

Solution 4: The carbon dioxide exhaled by astronauts is absorbed from the spacecraft air by lithium hydroxide:

$$2 \operatorname{LiOH}_{(s)} + \operatorname{CO}_{2(g)} \longrightarrow \operatorname{Li}_2 \operatorname{CO}_{3(s)} + \operatorname{H}_2 \operatorname{O}_{(l)}$$

A person exhales about 5.8×10^2 L of carbon dioxide (at STP) every day. What mass of lithium hydroxide is required to absorb this carbon dioxide for each astronaut per day?

This is a gas stoichiometry problem.

given is V = $5.8 \times 10^2 \text{ L CO}_{2(g)}$ with STP meaning T = 273 K and P = 1 atm unknown is LiOH_(s) with molar mass = 23.95 g/mol mole ratio is 1 mol CO_{2(g)} = 2 mol LiOH_(s)

step 1: convert given to moles - use Ideal Gas Law

$$P V = n R T$$

$$\therefore \quad n = \frac{P V}{R T}$$

$$n_{CO_2} = \frac{1 \ atm \left(5.8 \times 10^2 \ L\right)}{0.0821 \ L \cdot atm / mol \cdot K \ (273 \ K)}$$

$$n_{CO_2} \approx 25.9 \ mol \ CO_2$$

step 2: convert given to unknown - use mole ratio; step 3: convert unknown from moles - use molar mass

$$25.9 \,mol \,\operatorname{CO}_2 \times \frac{1 \,mol \,\operatorname{LiOH}}{2 \,mol \,\operatorname{CO}_2} \times \frac{23.95 \,g \,\operatorname{LiOH}}{1 \,mol \,\operatorname{LiOH}} \approx 3.1 \times 10^2 \,g \,\operatorname{LiOH}$$

Solution 5: A high explosive is any chemical that undergoes an extremely rapid, exothermic reaction with lots of gas products to produce the blast front. Nitroglycerin is the explosive in dynamite. Its reaction is:

 $4 C_{3}H_{5}(ONO_{2})_{3 (l)} \longrightarrow 6 N_{2 (g)} + 12 CO_{2 (g)} + 10 H_{2}O_{(g)} + O_{2 (g)}$

What is the total volume of gases produced at 400 °C and 2 atm, by the explosion of 200. g of nitroglycerin?

This is a gas stoichiometry problem.

given is 200. g C₃H₅(ONO₂)_{3 (*l*)} with molar mass = 227.1 g/mol; unknown is V = ? of total gas products at T = 400 °C + 273 = 673 K and P = 2 atm; mole ratio is 4 mol C₃H₅(ONO₂)_{3 (*l*)} = 29 mol total gas products

step 1: convert given to moles - use molar mass; step 2: convert given to unknown - use mole ratio:

$$200. g C_{3}H_{5}(ONO_{2})_{3} \times \frac{1 \, mol \, C_{3}H_{5}(ONO_{2})_{3}}{227.1 \, g \, C_{3}H_{5}(ONO_{2})_{3}} \times \frac{29 \, mol \, gas \, prod}{4 \, mol \, C_{3}H_{5}(ONO_{2})_{3}} \approx \frac{6.385 \, mol \, gas \, prod}{6.385 \, mol \, gas \, prod}$$

step 3: convert unknown from moles - use Ideal Gas Law

$$P V = n R T$$

$$\therefore V = \frac{n R T}{P}$$

$$V_{prod} = \frac{6.385 \ mol \left(0.0821 \ L \cdot atm/mol \cdot K\right) \left(673 \ K\right)}{2 \ atm}$$

$$V_{prod} \approx 176 \ L \ total \ gases$$

Solution 6: Propane is the gas burned by gas barbecues. The thermochemical equation for the combustion of proane is:

$$C_{3}H_{8(g)} + 5 O_{2(g)} \longrightarrow 3 CO_{2(g)} + 4 H_{2}O_{(l)} \Delta H^{\circ} = -2219.0 \ kJ/mol$$

If a 5.0 L propane tank at 30.0 °C and under 2.50×10^4 mm Hg pressure is completely burned, how much heat would be produced?

This is a stoichiometry problem.

given is C₃H_{8 (g)} at V = 5.0 L, T = 30.0 °C + 273 = 303 K and P = $2.50 \times 10^4 mm Hg \times \frac{1 atm}{760 mm Hg} \approx 32.89 atm;$

unknown is $\Delta H = ?;$

mole ratio is 1 mol $C_3H_{8(g)} = -2219.0 \text{ kJ}$

step 1: convert given to moles - use Ideal Gas Law:

$$P V = n R T$$

∴ $n = \frac{P V}{R T}$
 $n_{C_3H_8} = \frac{32.89 \ atm (5.0 \ L)}{0.0821 \ L \cdot atm / mol \cdot K (303 \ K)}$
 $n_{C_3H_8} \approx 6.61 \ mol \ C_3H_8$

step 2: convert given to unknown - use mole ratio:

6.61 mol C₃H₈ ×
$$\frac{-2219.0 \ kJ}{1 \ mol \ C_3H_8} \approx -1.5 \times 10^4 \ kJ$$

Chapter 6: Light, subatomic electronic structure

What is light?

This topic begins with a detour into Physics. We start with the question: What is light? Light is an electromagnetic wave. In Chemistry, we don't care about about light's electric and magnetic properties, but we do discuss wave behavior.

A wave is an OSCILLATION (a vibration) that TRAVELS forward and carries ENERGY with it. Light travels at a known CONSTANT SPEED OF LIGHT: $c \approx 2.998 \times 10^8 m/s$. The FREQUENCY is the number of vibrations per second. The abbreviation is the Greek letter, lower case nu - ν ; the unit is called Hertz - Hz. Since a wave travels and vibrates at the same time, the WAVELENGTH is the distance the wave travels during one oscillation. The abbreviation is the Greek letter, lower case lambda - λ , measured in meters.

Since these three thing refer to one wave, the speed of light, the frequency and the wavelength must be related. The wave equation is:

 $c=\lambda\,\nu$

(Be careful, if you search for "wave equation" on the interweb, you will discover a much more complex version of the wave equation, which we don't care about.)

the electromagnetic spectrum

There are different types of light because they have different frequencies and wavelengths.

From longest wavelength/lowest frequency to shortest wavelength/highest frequency, they are: radio/microwave/infrared/visible/ultraviolet/x-rays/gamma rays.

Visible light means light that humans can see (with their eyes). The other spectrum bands require special equipment if humans are to perceive them. There are some animals that can perceive light that humans cannot. Visible light is further separated into the traditional seven major colors of the rainbow - red/orange/yellow/green/ blue/indigo/violet - often abbreviated ROY-G-BIV.

The shorter wavelength/higher frequency side (ultraviolet/x-rays/gamma rays) is dangerous, because it is the high energy side. Energy per quantum (photon) depends on frequency (the Planck-Einstein Equation):

$E = h \nu$

where h is the Planck constant. $h \approx 6.626 \times 10^{-34} \text{ J} \cdot \text{s}.$

the Bohr model of the hydrogen atom

We now come back to Chemistry - specifically the electron structure of atoms.

Remember from CHM 0100: protons and neutrons are packed into the center of an atom called the nucleus, but the electrons are outside the nucleus. Where outside?

The electrons "orbit" the nucleus in different energy shells (levels). Each shell corresponds to the allowed quantized standing "wave function" of the electrons. There is a huge amount of theoretical Physics involved, that we don't care about.

Lower shells have lower energy and are "closer" to the nucleus. More importantly, electrons can transition from lower to higher shells by absorbing energy, and transition from higher to lower shells by emitting photons (light energy). This process explains how LEDs, lasers, neon lights and fluorescent lights produce their light, photoelectric cells produce electricity, and digital cameras capture images.

These electrons shell transitions are valid for all atoms. However, we will only do the calculations for the atomic hydrogen light emission spectrum, because hydrogen has only one electron, making the calculations simpler - even two electrons makes the math a thousand times harder.

For hydrogen, each shell has energy of:

$$E = -R_H \frac{1}{n^2}$$

where $R_H \approx 2.178 \times 10^{-18} J$ and n is the shell number.

therefore, each energy transition is:

$$\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where n_i is the initial shell and n_f is the final shell.

electron configurations

One of the reasons two (or more) electrons is so hard to calculate is that atoms larger than hydrogen need four pieces of information to completely "address" their electrons: SHELL, SUBSHELL, ORBITAL and SPIN. You are only responsible for the known answers.

Use the Periodic Table as the guide to build shell by subshell - the Aufbau principle. Each Period counts the valence shell, Groups 1A and 2A are s-block (s subshell), Groups 3A to 8A are p-block (p subshell) and the transition metal are d-block (d subshell). We usually ignore the actinides and lanthanides, but they are f-block (f subshell). For orbital and spin, remember - two electrons per orbital, differentiated by up versus down spin.



Notice that the transition metal configurations squeeze the d subshell between the s and p subshell, not after the p subshell.

For the electron configurations of ions, remember electrons are gained to or lost from valence, including transition metal ions

Some vocabulary: the VALENCE SHELL is the last or outermost shell; VALENCE ELECTRONS are the electrons in the valence shell; INNER CORE are the shells closer to the nucleus than the valence shell; PARAMAGNETIC means at least one electron is not paired off up spin/down down in the orbitals, DIAMAGNETIC means all the electrons are paired off up spin/down down in the orbitals.

Chapter 6: Light, electronic structure Problems

Problem 1: The top radio station in New York is usually the sports talk station WFAN. It broadcasts at a frequency of 660 kHz. What are the wavelength and energy per photon of the station? Since WFAN broadcasts with a power of 50,000 Joules per second, how many photons does the station transmitter produce every second?

Problem 2: What is the wavelength of light (in nanometers) emitted when an electron transitions from n = 5 to n = 3 in a hydrogen atom?

Problem 3: Of the following electron configurations:



which is the ground-state configuration for an element (a) in Group 2A, (b) in Period 3, (c) that is a transition metal, (d) that is paramagnetic? (e) Which electron configuration is an excited state?

There is only one correct answer to each question, each choice is used once, and all questions have answers.

Problem 4: What is the electron configuration of the iron (III) ion?

Chapter 6: Light, electronic structure Solutions

Solution 1: The top radio station in New York is usually the sports talk station WFAN. It broadcasts at a frequency of 660 kHz. What are the wavelength and energy per photon of the station? Since WFAN broadcasts with a power of 50,000 Joules per second, how many photons does the station transmitter produce every second?

given: $\nu = 660 \, kHz = 660 \times 10^3 \, Hz$, $c \approx 2.998 \times 10^8 \, m/s$, $h \approx 6.626 \times 10^{-34} \, J \cdot s$

power = 50,000 J/s

$$c = \lambda \nu$$

$$\therefore \quad \lambda = \frac{c}{\nu}$$

$$= \frac{2.998 \times 10^8 \text{ m/s}}{660 \times 10^3 \text{ Hz}}$$

$$\lambda \approx 454 \text{ m}$$

$$E = h \nu$$

$$= 6.626 \times 10^{-34} \text{ J} \cdot s (660 \times 10^3 \text{ Hz})$$

$$E \approx 4.37 \times 10^{-28} \text{ J/photon}$$

$$\frac{50,000 J}{s} \times \frac{photon}{4.37 \times 10^{-28} J} \approx 1.14 \times 10^{32} \ photons/s$$

Solution 2: What is the wavelength of light (in nanometers) emitted when an electron transitions from n = 5 to n = 3 in a hydrogen atom?

given: $n_i = 5$, $n_f = 3$ unknown: $\lambda = ?$ in nanometers.

$$c = \lambda \nu$$

$$\therefore \quad \lambda = \frac{c}{\nu}$$

$$= \frac{2.998 \times 10^8 \ m/s}{2.339 \times 10^{14} \ Hz}$$

$$\lambda \approx 1.282 \times 10^{-6} \ m$$

$$1.282 \times 10^{-6} \ m \times \frac{nm}{10^{-9} \ m} = 1.282 \times 10^3 \ nm$$

Solution 3: Of the following electron configurations:



which is the ground-state configuration for an element (a) in Group 2A, (b) in Period 3, (c) that is a transition metal, (d) that is single-electron paramagnetic? (e) Which electron configuration is an excited state?

There is only one correct answer to each question, each choice is used once, and all questions have answers.



Solution 4: What is the electron configuration of the iron (III) ion?

This is the iron atom configuration:

		 	, ↑↓ ↑	`↓ ↑↓ ↑↓	, ↑↓↑	↓↑ ↑	Î	↑
Fe	$1s^2 2s^2$	2p ⁶	$3s^2$	3p ⁶	$4s^2$	30	1^{6}	

Since, iron is a transition metal, the 3d electrons are not valence. The iron (III) ion loses two (2) electrons from 4s first - making it empty, and then one (1) electron from 3d.

Chapter 7: Periodic properties

RECALL: The Periodic Table lists all of the elements in a grid of 7 Periods and 18 Groups, arranged by their valence. Since the arrangement of the elements is not random, this has important consequences for chemical behavior.

The top, right corner of the Periodic Table, and the bottom, left corner the Table are opposites. Along the diagonal between francium and helium (or fluorine, if the inert, noble gases are ignored), the differences between elements increase if they are further apart (or similarities increase if they are closer together).

There are several PERIODIC PROPERTIES of the elements. These are general trends of certain physical and chemical properties of the elements based on their position on the Periodic Table. In other words, you know things about elements and can compare them just by locating where they are on the Table, in relation to francium and helium (or fluorine). You are not expected to memorize exact numbers; only the trends.

The major periodic properties are:

• ATOMIC RADIUS (AR) - the spherical size of an atom measured as the "distance" from the center to valence shell. Note, AR is not directly related to atomic mass or weight.

Francium has the largest AR. Helium (or fluorine) has the smallest AR. In comparing elements: moving from left to right across a Period, AR decreases because of decreasing shielding effect (or increasing effective nuclear charge), and moving from top to bottom of a Group, AR increases because of increasing valence. Elements closer to francium have larger AR, and elements closer to helium have smaller AR.

• IONIC RADIUS (IR) - the spherical size of an ion measured as the "distance" from the center to valence shell. IR is proportional to AR. The IR of an anion (negative ion) is always larger than the original AR, and the higher the negative charge the larger the IR. The IR of a cation (positive ion) is always smaller than the original AR, and the higher the positive charge the smaller the IR.

• IONIZATION ENERGY (IE) - the energy (per mole) required to remove the "last" electron from an atom - producing a 1+ cation. More electrons can be removed, one at a time, so the second ionization energy (IE₂) is the energy (per mole) required to remove a second electron from a 1+ ion to producing a 2+ cation, etc. IE₂ is always higher than IE₁, and IE₃ is is always higher than IE₂, etc.

In addition, the IE to "reach into" the inner core is always much, much higher than the IE to remove from valence.

Francium has the lowest IE. Helium (or fluorine) has the highest IE. In comparing elements: moving from left to right across a Period, IR increases, and moving from top to bottom of a Group, IR decreases. Elements closer to francium have lower IE, and elements closer to helium have higher IE.

• ELECTRON AFFINITY (EA) - the energy (per mole) gained when an electron is added to an atom - producing a -1 anion.

Francium has the lowest EA. Fluorine has the highest EA. In comparing elements: moving from left to right across a Period, EA increases, and moving from top to bottom of a Group, EA decreases. Elements closer to francium have lower EA, and elements closer to fluorine have higher EA. The EA trend has important exceptions.

• ELECTRONEGATIVITY (e.n.) - a number on a scale of zero (0) to four (4) that measures how strongly an atom attracts electrons to itself when it forms chemical bonds

Francium has the lowest e.n.. Fluorine has the highest e.n., with a perfect 4.0. In comparing elements: moving from left to right across a Period, e.n. increases, and moving from top to bottom of a Group, e.n. decreases. Elements closer to francium have lower e.n., and elements closer to fluorine have higher e.n..

Chapter 7: Periodic properties Problems

- Problem 1: Arrange the following atoms in order of increasing atomic radius: Al, Na, Si, Ar, P
- Problem 2: Arrange the following atoms in order of decreasing first ionization energy: Te, Se, O, S, Po
- Problem 3: Arrange the following atoms in order of increasing second ionization energy: Na, Mg, Al
- Problem 4: Arrange the following species in order of decreasing radius: S, S⁺, S²⁺, S⁻, S²⁻
- Problem 5: Arrange the following ions in order of increasing ionic radius: Ca^{2+} , Mg^{2+} , Ba^{2+} , Be^{2+}

Chapter 7: Periodic properties Solutions

Solution 1: Arrange the following atoms in order of increasing atomic radius: Al, Na, Si, Ar, P

increasing order means smallest AR first and largest AR last. These elements are all in Period 3 - AR increases moving from right to left across a Period:

 $Ar \ < \ P \ < \ Si \ < \ Al \ < \ Na$

Solution 2: Arrange the following atoms in order of decreasing first ionization energy: Te, Se, O, S, Po

decreasing order means highest IE first and lowest IR last. These elements are all in Group 6A - IE decreases moving from top to bottom down a Group:

Solution 3: Arrange the following atoms in order of increasing second ionization energy: Na, Mg, Al

increasing order means lowest IE_2 first and highest IE_2 last. Normally, IR increases moving from left to right across a Period. However, Na is in Group 1A - therefore IE_2 would remove an electron from the inner core, which has a huge increase in IE:

Solution 4: Arrange the following species in order of decreasing radius:

$$S, S^+, S^{2+}, S^-, S^{2-}$$

decreasing order means largest radius first and smallest radius last. Negative ions are always larger than the original atom, while positive ions are always smaller than the original atom:

 $S^{2-} > S^{-} > S > S^{+} > S^{2+}$

Solution 5: Arrange the following ions in order of increasing ionic radius: Ca^{2+} , Mg^{2+} , Ba^{2+} , Be^{2+}

increasing order means smallest IR first and largest IR last. Since these ions have the same charge, and are all in the same Group, only the Period matters - radius increases moving down a Group:

 $Be^{2+} < Mg^{2+} < Ca^{2+} < Ba^{2+}$

Chapter 8: Chemical bonding

Lewis diagrams

Lewis (electron dot) diagrams/structures are pictures that Chemists draw of a molecule to show the bonding between the atoms. It is most useful for covalent bonding - the diagram for ionic compounds is usually considered trivial (too simple to worry about).

Covalent bonding is a sharing of electrons. One atom contributes one electron, another atom contributes another electron, and the two electrons end up being shared between the two atoms. It is usually possible to draw the diagrams for two atoms and immediately see how single (unpaired) electrons for each atom would pair off to form the bond, and redraw the molecule.

However, it is usually faster to draw the molecule, without drawing the atoms. I recommend a five-step procedure:

step 1: COUNT the total valence electrons. Remember only valence electrons are used by atoms to form bonds. (The shortcut is to check the Group number of each atom.)

step 2: SYMMETRY. For most molecules, put one atom in the center and surround it with the other atoms. The atom closer to Group 4 is usually the center atom. If atoms are in the same Group, the center atom is usually lower in the Group (larger Period). Sometimes the formula gives a hint for the center atom, by writing it in the center of the formula.

step 3: SINGLE BONDS. Connect the center atom to each of the surrounding atoms with one dash each. Remember: one dash represents one bond, but represents two electrons. Two atoms only expected to bond once with each other. There are common molecules with double or triple bonds, but single bonds are the first choice - unless there is evidence to the contrary.

step 4: OCTET RULE. Give each atom more electrons, if necessary, using pairs of dots, representing two electrons not being shared in a bond (lone pairs), so that each atom has a total of eight electrons. Atoms are only expected to bond because they are most stable with eight valence electrons (are isoelectronic with the noble gases). There are some exceptions to the octet rule, but obeying the octet rule is the first choice - unless there is evidence to the contrary. Carbon (4 bonds, zero lone), nitrogen (3 bonds, 1 lone), oxygen (2 bonds. 2 lone) and fluorine (1 bond, 3 lone) should always obey the octet rule. Hydrogen is too small to obey the octet rule; it only needs two electrons.

Real Chemists often omit the lone pairs when they are in a rush. As students, you are not allowed to skip the lone pairs, because the diagram is incomplete without them.

step 5: CHECK. Count the electrons in your diagram and check that matches the count from step 1. If it matches, you're done. If it doesn't match, you need to try a different structure using double or triple bonds, or with a center atom that disobeys the octet rule.

Carbon, nitrogen and oxygen (and rarely, silicon, phosphorus, sulfur and chlorine) can form double bonds - but only with each other. Carbon and nitrogen can form triple bonds - and only with each other. Beryllium, boron and aluminum usually have an incomplete octet (Be = 4 e-, B = 6 e-, Al = 6 e-). Phosphorus, sulfur and chlorine may have an expanded octet (P = 10 e-, S = 10 or 12 e-, Cl = 10, 12 or 14e-).

Drawing Lewis diagrams is an extremely important Chemistry skill. Chemists are always drawing Lewis diagrams, even if it's just in their heads, because understanding the bond structure naturally leads to much other chemical knowledge.

formal charge

Sometimes, it is possible to draw two (or more) Lewis diagrams for one molecule that seem to be valid. But, which one is the "best" one? A way to double-check your diagram is to account for each atoms's valence electrons by calculating its formal charge. A simple way to compute the formal charge for each atom is:

(# of valance e^-) - (# of lone e^-) - (bonds) = formal charge

rule 1: the total formal charge of a molecule must equal zero. The total formal charge of a polyatomic ion must equal its charge. Otherwise the diagram is just plain wrong.

rule 2: the individual formal charges should be zero, or a close as possible to zero. Positive or negative one is OK. However, positive or negative two is most likely unstable - the molecule would fall apart.

rule 3: any negative formal charge should belong to the atom with higher electronegativity. Zero or positive formal charge belongs to the atom with lower electronegativity.

polar versus nonpolar bonds

As stated before: covalent bonding is a sharing of electrons. However, the sharing does not have to be fair or equal. If the sharing is equal, it is called a NONPOLAR COVALENT BOND. If the sharing is unequal, it is called a POLAR COVALENT BOND. Chemists use the word "polar" to say that one side of an unequal bond is slightly negative (δ –) in charge. It is the negative pole (because the negative electrons are more on that side). The other side is slightly positive (δ +) in charge. It is the positive pole (because the negative electrons are less on that side). δ – and δ + is called DELTA NOTATION - δ is the Greek lower-case letter delta. An arrow is often drawn pointing toward the negative pole.

The simplest way to determine whether a bond is polar or nonpolar covalent bond, is to compare the ELECTRONEGATIVITY of the two atoms. Electronegativity is a number from zero (0) to four (4), that measures how strongly an atom attracts electrons to itself when it bonds. A nonpolar covalent bond has a very small electronegativity difference; while a polar covalent bond has a large electronegativity difference. (Ionic bonds have a very large electronegativity difference.)

Check with your professor, but a 0.0 to 0.4 e.n. difference should indicate a nonpolar covalent bond. A 0.5 to 1.8 e.n. difference indicates a polar covalent bond. A 1.9 or greater difference indicates an ionic bond. Remember, the diatomic elements must have a nonpolar covalent bond, because the atoms are identical.

Remember also that electronegativity is a periodic property; there is a Periodic Table pattern to electronegativity. The electronegativity increases toward the top, right corner of the Table, and electronegativity decreases toward the bottom, left corner of the Table. Therefore, atoms closer to each other on the Table are less polar, while atoms further apart on the Table are more polar.

You are not expected to memorize exact electronegativity numbers; except that fluorine (F) is the highest, with a perfect 4.0. Oxygen (O) is second highest. The periodic property trend is often enough.

bond energy

One interesting application of Lewis diagrams is the use of bond energy to estimate the enthalpy change of a chemical reaction. The "strength" of a chemical bond can be measured by the amount of energy required to "break" the chemical bond (completely separate the atoms). Since a chemical reaction requires breaking chemical bonds in the

reactants and the formation of new bonds in the products, the bond energy (BE) difference is equivalent to the enthalpy change.

$$\Delta H_{rxn}^{\circ} \approx \sum n_r \ BE \ (reactants) - \sum n_p \ BE \ (products)$$

Notice: this formula is similar to the enthalpy of formation formula, except this is reactants subtract products.

Bond energies have been measured and published in tables. But, a table is useless if you don't know what bonds to look up. You need to draw Lewis diagrams of all the chemicals in the reaction to identify the bonds.

Chapter 8 and Chapter 9 problems are grouped together.

Chapter 9: Molecular geometry

VSEPR geometry

See attached table.

The Lewis diagram is extremely useful in Chemistry. They are a 99% accurate practical representation of the bonding in a molecule - impressive, since they're just simple dotsand-dashes pencil-and-paper drawings. This knowledge can be extended to determine many other properties of a molecule - including VSEPR geometry, the 3-dimensional shape of a molecule. We do not expect you to draw the 3-D geometry, because we do not expect you to be an artist. Instead, we want you to remember the shape name. Remember, the Lewis diagram is not an accurate representation of the molecular 3-D geometry, because it is 2-D (flat), but you need it to count the bond and lone domains.

Geometry also determines whether a molecule is polar or nonpolar. Polar bonds can result in a nonpolar molecule, and nonpolar bonds can still exist in a polar molecule. The general rule is that perfectly symmetric molecules (that both bond and lone domains cancel out in 3-dimensions) are nonpolar; while non-symmetric molecules are polar.

hybridization

In covalent bonding, one atom contributes one electron in one atomic orbital, another atom contributes another electron in another atomic orbital, and the two orbital HYBRIDIZE (merge) into one MOLECULAR ORBITAL so that the two electrons end up orbiting both atoms.

Lewis diagrams can also be used to determine the atomic orbitals used for hybridization, simply by counting an atom's bonds and lone pairs. Remember, double and triple bonds count only once for hybridization.

The unusual hybridization for double and triple bonds also means that multiple bonds are not equivalent. A sigma (σ) bond directly joins the atoms. A pi (π) bond involves orbitals that need to "twist" to connect the atoms. A single bond is always a sigma bond. A double bond has one sigma and one pi bond. A triple bond has one sigma and two pi bonds.

Chapter 8 & 9: Chemical bonding and geometry Problems

Problem 1: Using these electronegativity values: P = 2.1, As = 2.0, Cl = 3.0, Br = 2.8, arrange the following bonds in order of increasing polarity:

Problem 2: Using these electronegativity values: C = 2.5, N = 3.0, O = 3.5, F = 4.0, arrange the following bonds in order of decreasing polarity:

Problem 3: Use an arrow and delta notation to indicate the polarity of the following bonds: (a) C—N, (b) O—S, (c) Cl—Si, (d) Br—F. Hint: the arrow points toward the negative pole.

Problem 4: Draw Lewis structures for the following species that obey the octet rule. State their VSEPR geometry name. What is the center atom's hybridization? Is the species polar or nonpolar?

- (a) CH₄
- (b) NH₃
- (c) OF₂
- (d) BF₄
- (e) CH₃Cl
- (f) HF
- (g) PCl_3
- (h) PCl_2^-
- (i) H_2CO
- (j) HCN
- (k) HOCl
- (1) CO₂

- (m) CO
- (n) C_2H_4
- (o) CH₃OH
- (p) CH₃CHO

Problem 5: Draw two resonance Lewis structures for the nitrite ion, NO_2^- :

Problem 6: Draw Lewis structures for the following species that have incomplete octets. State their VSEPR geometry name. What is the center atom's hybridization? Is the species polar or nonpolar?

- (a) $AlCl_3$
- (b) $GeCl_2$

Problem 7: Draw Lewis structures for the following species that have expanded octets. State their VSEPR geometry name. What is the center atom's hybridization? Is the species polar or nonpolar?

- (a) PCl_5
- (b) POCl₃
- (c) SO_2F_2
- (d) SF₄
- (e) ICl_5
- (f) SO_4^{2-}
- (g) XeF_2

Problem 8: Draw three resonance Lewis structures for the cyanate ion OCN⁻ (carbon is the center atom). Compute each atom's formal charge for the three diagrams. Which structure is the most stable?

Problem 9: Use bond energies to estimate the enthalpy change for the reaction:

$$HCN_{(g)} + 2 H_{2(g)} \longrightarrow CH_3NH_{2(g)}$$

Problem 10: This is a Lewis diagram for aspirin:



How many sigma (σ) and pi (π) bonds does this molecule have?

Chapter 8 & 9: Chemical bonding and geometry Solutions

Solution 1: Using these electronegativity values: P = 2.1, As = 2.0, Cl = 3.0, Br = 2.8, arrange the following bonds in order of increasing polarity:

Increasing order means least polar first and most polar last.

$$P-Br < As-Br < P-Cl < As-Cl$$

 $\Delta e.n. = 0.7 \quad \Delta e.n. = 0.8 \quad \Delta e.n. = 0.9 \quad \Delta e.n. = 1.0$

Solution 2: Using these electronegativity values: C = 2.5, N = 3.0, O = 3.5, F = 4.0, arrange the following bonds in order of decreasing polarity:

C—N, C—O, C—C, C—F.

Decreasing order means most polar first and least polar last.

$$C-F > C-O > C-N > C-C$$

$$\Delta e.n. = 1.5 \quad \Delta e.n. = 1.0 \quad \Delta e.n. = 0.5 \quad \Delta e.n. = 0.0$$

Solution 3: Use an arrow and delta notation to indicate the polarity of the following bonds: (a) C—N, (b) O—S, (c) Cl—Si, (d) Br—F. Hint: the arrow points toward the negative pole.

The exact electronegativity values are not needed, because it is a periodic property.

(a) Nitrogen is to the right of carbon on the Periodic Table; it must be the negative pole.

$$\delta + \overrightarrow{C - N} \delta -$$

(b) Oxygen is above sulfur on the Periodic Table; it must be the negative pole.

$$\delta - \overleftarrow{O - S} \delta +$$

(c) Chlorine is to the right of silicon on the Periodic Table; it must be the negative pole.

$$\delta^{-} \overleftarrow{\text{Cl} - \text{Si}} \delta^{+}$$

(d) Fluorine is above bromine on the Periodic Table; it must be the negative pole.

$$\delta + \overrightarrow{\mathrm{Br} - \mathrm{F}} \delta -$$

Solution 4: Draw Lewis structures for the following species that obey the octet rule. State their VSEPR geometry name. What is the center atom's hybridization? Is the species polar or nonpolar?

(a) CH_4 has 8 valence electrons



The C has 4 bond + 0 lone = 4 total domains.

VSEPR is tetrahedral, sp³ hybridization, nonpolar molecule.

(b) NH_3 has 8 valence electrons



The N has 3 bond + 1 lone = 4 total domains.

VSEPR is trigonal pyramidal, sp³ hybridization, polar molecule.

(c) OF_2 has 20 valence electrons



The O has 2 bond + 2 lone = 4 total domains.

VSEPR is bent (at less than 109.5°), sp³ hybridization, polar molecule.

(d) BF_4^- has 32 valence electrons



The B has 4 bond + 0 lone = 4 total domains.

VSEPR is tetrahedral, sp³ hybridization, nonpolar ion.

(e) CH₃Cl has 14 valence electrons



The C has 4 bond + 0 lone = 4 total domains.

VSEPR is tetrahedral, sp³ hybridization, polar molecule.

(f) HF has 8 valence electrons

The F has 1 bond + 3 lone = 4 total domains.

VSEPR is linear, sp³ hybridization (for F), polar molecule.

(g) PCl₃ has 26 valence electrons



The P has 3 bond + 1 lone = 4 total domains.

VSEPR is trigonal pyramidal, sp³ hybridization, polar molecule.

(h) PCl_2^- has 20 valence electrons



The P has 2 bond + 2 lone = 4 total domains.

VSEPR is bent (at less than 109.5°), sp³ hybridization, polar ion.





The C has 3 bond + 0 lone = 3 total domains.

VSEPR is trigonal planar, sp² hybridization, polar molecule.
(j) HCN has 10 valence electrons

 $H - C \equiv N$:

The C has 2 bond + 0 lone = 2 total domains. VSEPR is linear, sp hybridization, polar molecule.

(k) HOCl has 14 valence electrons



The O has 2 bond + 2 lone = 4 total domains.

VSEPR is bent (at less than 109.5°), sp³ hybridization, polar molecule.

(l) CO_2 has 16 valence electrons

The C has 2 bond + 0 lone = 2 total domains.

VSEPR is linear, sp hybridization, nonpolar molecule.

(m) CO has 10 valence electrons

The C and the O both have 1 bond + 1 lone = 2 total domains. VSEPR is linear, sp hybridization, polar molecule.

7/8/20 version

(n) C_2H_4 has 12 valence electrons



Both C have 3 bond + 0 lone = 3 total domains.

VSEPR is trigonal planar (for both C), sp² hybridization (for both C), nonpolar molecule (in whole).

(o) CH₃OH has 14 valence electrons



The C has 4 bond + 0 lone = 4 total domains. The O has 2 bond + 2 lone = 4 total domains.

VSEPR is tetrahedral (for C) and bent at less than 109.5° (for O), sp³ (for C) and sp³ (for O) hybridization, polar molecule (in whole).

(p) CH₃CHO has 18 valence electrons



The left C has 4 bond + 0 lone = 4 total domains. The right C has 3 bond + 0 lone = 3 total domains.

VSEPR is tetrahedral (for left C) and trigonal planar (for right C), sp³ (for left C) and sp² (for right C) hybridization, polar molecule (in whole).

Solution 5: Draw two resonance Lewis structures for the nitrite ion, NO₂⁻:

NO₂⁻ has 18 valence electrons



Solution 6: Draw Lewis structures for the following species that have incomplete octets. State their VSEPR geometry name. What is the center atom's hybridization? Is the species polar or nonpolar?

(a) AlCl₃ has 24 valence electrons



The Al has 3 bond + 0 lone = 3 total domains.

VSEPR is trigonal planar, sp² hybridization, nonpolar molecule.

(b) GeCl₂ has 18 valence electrons



The Ge has 2 bond + 1 lone = 3 total domains.

VSEPR is bent (at less than 120°), sp² hybridization, polar molecule.

Solution 7: Draw Lewis structures for the following species that have expanded octets. State their VSEPR geometry name. What is the center atom's hybridization? Is the species polar or nonpolar?

(a) PCl₅ has 40 valence electrons



The P has 5 bond + 0 lone = 5 total domains.

VSEPR is trigonal bipyramidal, sp³d hybridization, nonpolar molecule.

(b) $POCl_3$ has 32 valence electrons



The P has 4 bond + 0 lone = 4 total domains.

VSEPR is tetrahedral, sp³ hybridization, polar molecule.

(c) SO_2F_2 has 32 valence electrons



The S has 4 bond + 0 lone = 4 total domains.

VSEPR is tetrahedral, sp³ hybridization, nonpolar molecule.

(d) SF_4 has 34 valence electrons



The S has 4 bond + 1 lone = 5 total domains.

VSEPR is seesaw, sp³d hybridization, polar molecule.

(e) ICl₅ has 42 valence electrons



The I has 5 bond + 1 lone = 6 total domains.

VSEPR is square pyramidal, sp³d² hybridization, polar molecule.

(f) SO_4^{2-} has 32 valence electrons



The S has 4 bond + 0 lone = 4 total domains. VSEPR is tetrahedral, sp^3 hybridization, nonpolar ion. (g) XeF_2 has 22 valence electrons



The Xe has 2 bond + 3 lone = 5 total domains.

VSEPR is linear, sp³d hybridization, nonpolar molecule.

Solution 8: Draw three resonance Lewis structures for the cyanate ion OCN⁻ (carbon is the center atom). Compute each atom's formal charge for the three diagrams. Which structure is the most stable?

OCN⁻ has 16 valence electrons



Solution 9: Use bond energies to estimate the enthalpy change for the reaction:

$$HCN_{(g)} + 2 H_{2(g)} \longrightarrow CH_3NH_{2(g)}$$

The reaction rewritten as Lewis structures is:



$$\Delta H_{rxn}^{\circ} \approx \sum n_r BE \text{ (reactants)} - \sum n_p BE \text{ (products)}$$

$$C - H = 413 \ kJ/mol$$

$$C \equiv N = 891 \ kJ/mol$$

$$2 (H - H) = 2 (435 \ kJ/mol) = 870 \ kJ/mol$$

$$react = \overline{2174 \ kJ/mol}$$

$$3 (C - H) = 3 (413 \ kJ/mol) = 1239 \ kJ/mol$$

$$C - N = 305 \ kJ/mol$$

$$2 (N - H) = 2 (391 \ kJ/mol) = 782 \ kJ/mol$$

$$prod = \overline{2326 \ kJ/mol}$$

$$\Delta H_{rxn}^{\circ} \approx \sum n_r \ BE \text{ (reactants)} - \sum n_p \ BE \text{ (products)}$$
$$\approx 2174 \ kJ/mol \ - \ 2326 \ kJ/mol$$
$$\Delta H_{rxn}^{\circ} \approx -152 \ kJ/mol$$

Solution 10: This is a Lewis diagram for aspirin:



How many sigma (σ) and pi (π) bonds does this molecule have?



There are twenty-one (21) sigma (σ) bonds and five (5) pi (π) bonds.

Chapter 11: Solids and liquids

intermolecular forces

Recall: a gas has neither a definite volume nor shape, while solids have definite volume and shape, and liquids has a definite volume, but no definite shape. What holds solids and liquids into their shapes or volumes?

Solids and liquids have INTERMOLECULAR FORCES. (Intermolecular means between one molecule (or atom) and other molecules (or atoms. Intramolecular means inside a molecule - chemical bonds.) We will not worry much about the electrical Physics of the forces. We want to recognize the kinds of intermolecular forces in different chemicals.

• nonpolar molecules (or monatomic elements) have London DISPERSION FORCES only. Dispersion forces are very weak, and these chemicals are expected to be gases (have low melting and boiling points, and high vapor pressure) under normal conditions, unless the molar mass is high.

• polar molecules have DIPOLE-DIPOLE FORCES and London dispersion forces. Dipole-dipole forces are strong, and these chemicals are expected to not be gases (with high melting and boiling points, and low vapor pressure) under normal conditions, because the molecules will be harder to "loosen" or "separate".

• very polar molecules have HYDROGEN BONDING and London dispersion forces. Hydrogen bonding is very strong, and these chemicals are almost never gases (with very high melting and boiling points, and very low vapor pressure) under normal conditions., because these molecules will be very hard to "loosen" or "separate" What is considered very polar? - hydrogen with fluorine, oxygen or nitrogen - FON. Note, although we say "bonding," hydrogen bonds are not chemical bonds. They are much weaker than real chemical bonds.

• ionic compounds have ELECTROSTATIC/IONIC FORCES and London dispersion forces. Electrostatic forces are extremely strong, and these chemicals are almost always solids (with extremely high melting and boiling points, and extremely low vapor pressure) under normal conditions.

Notice, all substances are expected to have dispersion forces. Pay attention to any additional forces. Also, all else being equal, a larger molar mass should have higher melting and boiling points, and lower vapor pressure.

the heating curve

Recall: calorimetry says that when heat is added to a solid, its temperature will increase.

However, the temperature will not increase forever - at some point the solid will melt at a fixed melting point temperature. The HEAT OF FUSION (ΔH_{fus}) accounts for the "loosening" of the atoms/molecules in the solid-to-liquid PHASE CHANGE.

After the solid completely liquifies, the temperature of the liquid will increase again if heat continues to be added, but once again, the temperature increase will not continue forever. At some point, the temperature will plateau at a fixed boiling point as the liquid vaporizes (boils), before the temperature increase can continue. The HEAT OF VAPORIZATION (ΔH_{vap}) accounts for the "separation" of the atoms/molecules in the liquid-to-gas phase change.

A HEATING CURVE is the five-step graph of heat added (x-axis) versus temperature change (y-axis) showing the five-step solid/melt/liquid/boil/gas process. Note, the process is reversible - removing heat reverses the process - a cooling curve.



Heat added at a constant rate

The heat for a temperature change is still calculated using the calorimetry equation:

$$q = m s \Delta T$$

The heat for a phase change is calculated:

$$q = m \,\Delta H$$

Be careful, the heats of fusion and vaporization are listed in both kJ/mol and kJ/g.

phase diagrams

When Chemists say that the freezing point of water is 0 °C and the boiling point is 100 °C, this is only correct at a pressure of 1 atm. The freezing and boiling points of chemicals changes - sometimes a lot - at different external pressures.

The PHASE DIAGRAM plots temperature (x-axis) versus pressure (y-axis), showing the freezing and boiling points of chemicals at different pressures. It shows a "Y" shape, that separates the solid, liquid and gas phases into different zones. Be aware: some substances have much more complex phase diagrams because of their allotropes.

The phase diagram also shows the triple point - the one pressure and temperature, where solid, liquid and gas coexist in equilibrium. You have probably never seen this, because the triple point of most substances is at such a low pressure, you would be unable to breathe - you'd be long since dead.

Remember: solid to liquid is melting; liquid to solid is freezing; liquid to gas is boiling; gas to liquid is condensing

Special note: it is possible for a solid to directly change into a gas, without ever passing through the liquid phase. This is called SUBLIMATION. You may have never seen this either, because sublimation occurs at a very low temperature and pressure for most common substances. The only sublimation that most non-Chemists have ever seen is "dry ice". Solid carbon dioxide will sublimate to gas at normal conditions, which is why it's called "dry" - there's never any liquid. Also: gas directly to solid is called deposition.

Chapter 11: Solids and liquids Problems

Problem 1: Which of the following pair of substances, has the given property. Explain your answer.

- (a) higher boiling point: HBr, or Kr.
- (b) higher freezing point: H₂O, or NaCl.
- (c) lower vapor pressure at 258°C: Cl₂, or I₂ .
- (d) lowest melting point: CO, or CO_2 .

Problem 2: What mass of water ice originally at -20°C can be heated to hot liquid water at 90°C by the burning of one gallon (3785 mL) of gasoline (isooctane $C_8H_{18(l)}$)? The density of gasoline is 0.740 g/mL and the enthalpy of combustion of gasoline is -5461 kJ/mol. The heat of fusion of H₂O is 333 J/g, the specific heat of solid H₂O is 2.10 J/g · °C and the specific heat of liquid H₂O is 4.18 J/g · °C.

Problem 3: In this phase diagram:



Which letter indicates (a) the solid region, (b) the liquid region, (c) the gas region, (d) the triple point, and (e) a sublimation? Some of the letters are not correct answers.

Chapter 11: Solids and liquids Solutions

Solution 1: Which of the following pair of substances, has the given property. Explain your answer.

(a) higher boiling point: HBr, or Kr.

HBr has the higher boiling point. HBr is a polar compound, with dipole-dipole forces (plus dispersion forces), stronger than Kr, a nonpolar noble gas with only dispersion forces.

(b) higher freezing point: H₂O, or NaCl.

NaCl has the higher freezing point. H₂O is a very polar molecule with has hydrogen bonding (plus dispersion forces), but NaCl is an ionic compound that has stronger ionic forces.

(c) lower vapor pressure at 258°C: Cl₂, or I₂ .

 I_2 has the lower vapor pressure. CI_2 , or I_2 are both diatomic halogen elements, both are nonpolar, but I_2 has the larger molar mass.

(d) lowest melting point: CO, or CO_2 .

 CO_2 has the lower melting point. CO is a polar molecule with dipole-dipole forces (plus dispersion forces), while CO_2 is a nonpolar molecule with weak dispersion forces only.

Solution 2: What mass of water ice originally at -20.°C can be heated to hot liquid water at 90.°C by the burning of one gallon (3785 mL) of gasoline (isooctane $C_8H_{18(l)}$)? The density of gasoline is 0.740 g/mL and the enthalpy of combustion of gasoline is -5461 kJ/mol. The heat of fusion of H₂O is 333 J/g, the specific heat of solid H₂O is 2.10 J/g · °C and the specific heat of liquid H₂O is 4.18 J/g · °C.

given: the gasoline is the system and the water is the surroundings, that obey conservation of energy - heat transfers from the gasoline to the water.

$$V_{gas} = 3785 \ mL, \ d_{gas} = 0.740 \ g/mL, \ \Delta H_{gas} = -5461 \ kJ/mol, \ \mathcal{M} = 114.2 \ g/mol$$

$$s_{ice} = 2.10 \ J/g \cdot ^{\circ} C, \ T_{i \ ice} = -20.^{\circ}C, \ s_{water} = 4.18 \ J/g \cdot ^{\circ} C, \ T_{f \ water} = 90.^{\circ}C,$$

$$H_{fusion} = 333 \ J/g, \ T_{melt} = 0^{\circ}C$$
unknown: $m_{water} = ?$

Note: the combustion reaction is not important, because this is not stoichiometry.

$$\Delta H_{gas} = 3785 \ \text{mL} \times \frac{0.740 \ \text{g}}{\text{mL}} \times \frac{1 \ \text{mol}}{114.2 \ \text{g}} \times \frac{-5461 \ \text{kJ}}{\text{mol}} \approx -1.339 \times 10^5 \ \text{kJ}$$
$$\Delta H_{gas} \approx -1.339 \times 10^5 \ \text{kJ} \times \frac{1000 \ \text{J}}{\text{kJ}} \approx -1.339 \times 10^8 \ \text{J}$$

$$q_{water} = q_{solid} + q_{melt} + q_{liquid}$$

$$= (m \ s_{ice} \ \Delta T) + (m \ \Delta H_{fus}) + (m \ s_{water} \ \Delta T)$$

$$= m \left(\left(s_{ice} \ \Delta T \right) + \Delta H_{fus} + (m \ s_{water} \ \Delta T) \right)$$

$$= m \left(\left(2.10 \ \frac{J}{g \cdot {}^{\circ}C} \right) (20.{}^{\circ}C) + 333 \ \frac{J}{g} + \left(4.18 \ \frac{J}{g \cdot {}^{\circ}C} \right) (90.{}^{\circ}C) \right)$$

 $q_{water} \approx m_{water} \left(751 \ J/g\right)$

$$q_{system} + q_{surroundings} = 0$$

$$\Delta H_{gas} + q_{water} = 0$$

$$q_{water} = -\Delta H_{gas}$$

$$m_{water} (751 \ J/g) \approx -(-1.339 \times 10^8 \ J)$$

$$\therefore m_{water} \approx \frac{1.339 \times 10^8 \ J}{751 \ J/g}$$

$$m_{water} \approx 1.78 \times 10^5 \ g$$

Solution 3: In this phase diagram:



Which letter indicates (a) the solid region, (b) the liquid region, (c) the gas region, (d) the triple point, and (e) a sublimation? Some of the letters are not correct answers.

- a) the solid region = B
- (b) the liquid region = D
- (c) gas region = F
- (d) the triple point = C
- (e) a sublimation = A

Chapter 12: Properties of solutions

Recall: A solute is dissolved into a solvent to make a solution. However, not every solute will dissolve into any solvent.

A easy-to-use rule on what solutes and solvents are MISCIBLE (mixable) and IMMISCIBLE (not mixable) is "Like dissolves like." Usually, two polar chemicals OR two nonpolar chemicals will mix together to make a solution, but if one is polar and one is nonpolar, they will not make a solution. The saying "Oil and water don't mix" is true, chemistry-wise, because, oil molecules are nonpolar hydrocarbons, while water is highly polar.

Also recall: the concentration of the solute in a solution is measured by Molarity, defined:

$$Molarity = \frac{moles \ solute}{Liters \ solution}$$
$$M = \frac{mol}{L}$$

However, just like any other measurement, there are other ways to measure the concentration of a solution. We have already mentioned mole fraction, introduced for gas mixtures. Percent of solute in solution is commonly used in medicine.

We now introduce molality:

$$molality = \frac{moles \ solute}{kilograms \ solvent}$$
$$m = \frac{mol}{kg}$$

Be careful, "m" abbreviates for molality, not mass in this topic.

colligative properties

A solution of any solute in a liquid solvent has properties related to, but the same as, the solvent by itself. These COLLIGATIVE PROPERTIES of solutions include boiling point elevation (BPE), freezing point depression (FPD), vapor pressure depression (VPD), and osmotic pressure.

BOILING POINT ELEVATION (BPE) says the boiling point of a solution is always higher than the boiling point of the original solvent:

$$\Delta T_b = m K_b$$

FREEZING POINT DEPRESSION (BPE) says the freezing point of a solution is always lower than the freezing point of the original solvent:

$$\Delta T_f = m K_f$$

These formulae assume nonelectrolyte solutions. Ionic compounds produce more than one particle per unit formula in solution - they produce a number of electrolyte ions in solution, which increases the colligative effect on the solution. The van't Hoff factor (i) counts the ions and the increase in effect:

$$\Delta T_b = i m K_b$$
$$\Delta T_f = i m K_f$$

"I have attempted to give you a glimpse ... of what there may be of soul in chemistry. But it may have been in vain. Perchance the chemist is already damned and the guardian the blackest. But if the chemist has lost his soul, he will not have lost his courage and as he descends into the inferno, sees the rows of glowing furnaces and sniffs the homey fumes of brimstone, he will call out: 'Asmodeus, hand me a testtube.'" [Gilbert Newton] G. N. Lewis (1875 – 1946)

Chapter 12: Properties of solutions Problems

Problem 1: The concentration of industrial grade hydrochloric acid (sometimes called muriatic acid) is 12.4 M, with a density of 1.18 g/mL. What is the molality of this solution?

Problem 2: Calcium chloride is the chemical in "sno-melt." It is more effective than the cheaper rock salt because its van't Hoff factor is higher. What would be the freezing point of the electrolytic solution prepared by dissolving 125 g of calcium chloride in 500. mL of water? The freezing point constant of water is $1.86 \,^{\circ}\text{C} \cdot \text{kg/mol}$.

Problem 3: A 1.07 mg sample of a nonelectrolyte compound is dissolved in 78.1 mg of camphor. The resulting solution melts at 176.0 °C. What is the molecular weight of the compound? The freezing point of pure camphor is 179.5 °C and its freezing point constant is 40. °C \cdot kg/mol.

Chapter 12: Properties of solutions Solutions

Solution 1: The concentration of industrial grade hydrochloric acid (sometimes called muriatic acid) is 12.4 M, with a density of 1.18 g/mL. What is the molality of this solution?

solute = 12.4 mol HCl, $\mathcal{M} = 36.46 \text{ g/mol}$ given is: <u>+ solvent = water</u> = solution = 1 L, d = 1.18 g/mL

unknown is: solution molality (m = ?)

$$d = \frac{mass}{V}$$

$$\therefore \quad mass = d \ V$$

$$= \left(\frac{1.18 \ g}{mL} \times \frac{1000 \ mL}{L}\right) 1 \ L$$

$$mass = 1180 \ g \times \frac{kg}{1000 \ g}$$

$$mass = 1.18 \ kg \ solution$$

 $12.4 \ mol \ HCl \times \frac{35.46 \ g \ HCl}{1 \ mol \ HCl} \times \frac{1 \ kg}{1000 \ g} = 0.4397 \ kg \ HCl$ $1.18 \ kg \ solution - 0.4397 \ kg \ HCl \approx 0.74 \ kg \ water$

$$m = \frac{mol}{kg}$$
$$= \frac{12.4 \ mol}{0.74 \ kg}$$
$$m \approx 16.8 \ mol/kg$$

Solution 2: Calcium chloride is the chemical in "sno-melt." Is is more effective than the cheaper rock salt because its van't Hoff factor is higher. What would be the freezing point of the electrolytic solution prepared by dissolving 125 g of calcium chloride in 500. mL of water? The freezing point constant of water is 1.86 °C \cdot kg/mol.

$$solute = 125 \ g \ CaCl_2, \ \mathcal{M} = 110.98 \ g/mol \\ + \ solvent = 500. \ mL \ water \ (= 500. \ g = 0.500 \ kg, since \ d = 1 \ g/mL) \\ K_f = 1.86^{\circ}C \cdot kg/mol, \ T_f = 0^{\circ}C$$

= solution

unknown is solution freezing point ($T_f = ?$)

The problem is done in three steps:

step 1: convert to moles

$$125 g \operatorname{CaCl}_2 \times \frac{1 \ mol \ \operatorname{CaCl}_2}{110.98 \ g \ \operatorname{CaCl}_2} = 1.126 \ mol \ \operatorname{CaCl}_2$$

step 2: calculate molality

$$m = \frac{mol}{kg}$$
$$m = \frac{1.126 \ mol \ CaCl_2}{0.500 \ kg}$$
$$m \approx 2.252 \ mol \ CaCl_2/kg$$

step 3: find temperature depression

$$0^{\circ}C \quad water$$

$$-12.6^{\circ}C \quad depression$$

$$T_{f} \approx -12.6^{\circ}C \quad solution$$

Solution 3: A 1.07 mg sample of a nonelectrolyte compound is dissolved in 78.1 mg of camphor. The resulting solution melts at 176.0 °C. What is the molecular weight of the compound? The freezing point of pure camphor is 179.5 °C and its freezing point constant is 40. °C \cdot kg/mol.

solute = 1.07 mg nonelectrolyte (=
$$1.07 \times 10^{-3}$$
 g), i = 1
solute = 78.1 mg camphor (= 7.81×10^{-5} kg)
 $K_f = 40.^{\circ}C \cdot kg/mol, T_f = 179.5^{\circ}C$
 $\overline{K_f} = 176.0^{\circ}C$

unknown is molar mass of solute ($\mathcal{M} = ?$).

The is also a three step problem, but sort-of backwards:

step 1: use temperature depression to calculate molality

$$\Delta T_f = i m K_f$$

$$T_{f \, solvent} - T_{f \, solution} = m K_f$$

$$\therefore m = \frac{T_{f \, solvent} - T_{f \, solution}}{K_f}$$

$$= \frac{179.5 \,^{\circ}C - 176.0 \,^{\circ}C}{40. \,^{\circ}C \cdot kg/mol}$$

$$m \approx 0.0875 \, mol/kg$$

step 2: use molality definition to calculate moles

$$m = \frac{mol}{kg}$$

$$\therefore \quad mol = m \times kg$$

$$= 0.0875 \; mol/kg \times (7.81 \times 10^{-5} \; kg)$$

$$mol \approx 6.833 \times 10^{-6} \; mol$$

step 3: calculate molar mass as grams divided by moles

$$\mathcal{M} = \frac{mass}{mol}$$
$$= \frac{1.07 \times 10^{-3} g}{6.833 \times 10^{-6} mol}$$
$$\mathcal{M} \approx 157 g/mol$$