

# AP CHEMISTRY

## Chapters 1 & 2: Chemical Foundations

No matter what you are doing, or where you may be going, chemistry is a part of your life. Throughout history, man has pondered what comprises matter and how the world is organized, down to the smallest level. You now live in a time of scanning tunneling microscopes, where atoms can be seen, and much of the quest has been accomplished. However, the study of chemistry continues to help us relate the larger scale world, or macroscopic, to the detailed microuniverse of the microscopic.

### 1.1 An Overview of Chemistry

Fundamentally, chemistry can be summarized with two concepts:

- Matter is composed of various types of atoms
- One substance changes into another by reorganizing the way atoms are attached to one another.

### 1.2 The Scientific Method

We can observe the macroscopic effects of this using the scientific method.

- Make observations and collect data
- Suggest a possible explanation for this data (a hypothesis)
- Do an experiment to test your explanation and repeat as needed
- Create a theory to describe the repeatable results of your experiment
  - Theories are just possible explanations for why a phenomena is occurring.
  - Scientific laws are a summary of an observed natural behavior.
  - A law summarizes *what* happens while a theory is an attempt to explain *why* it happens.

### 1.3 Units of Measurement

Measurements are taken to help observe a phenomena.

- Quantitative measurements are taken with numerical data. (length, mass, density)
  - When measuring mass, be sure to make the distinction between the amount of matter (mass) versus the pull of gravity on that mass (weight).
- Qualitative measurements are taken with the senses (odor, color, sound, taste)
- These measurements are taken using the International System, or SI system. You should be familiar with units of this system.
  - Units of this system can be modified with prefixes to change their meaning. Be sure to know these prefixes and how to use them.

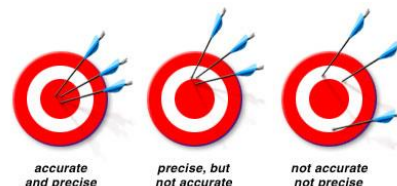
<u>Physical Quantity</u>	<u>Name</u>	<u>Abbreviation</u>
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	Kelvin	K
Electric Current	Ampere	A
Amount of Substance	mole	mol
Luminous Intensity	candela	cd

<u>Prefix</u>	<u>Symbol for Prefix</u>	<u>Symbol for</u>	<u>Scientific Notation</u>
exa	E	1 000 000 000 000 000 000	$10^{18}$
peta	P	1 000 000 000 000 000	$10^{15}$
tera	T	1 000 000 000 000	$10^{12}$
giga	G	1 000 000 000	$10^9$
mega	M	1 000 000	$10^6$
kilo	k	1 000	$10^3$
hecto	h	100	$10^2$
deka	da	10	$10^1$
---	--	1	$10^0$
deci	d	0.1	$10^{-1}$
centi	c	0.01	$10^{-2}$
milli	m	0.001	$10^{-3}$
micro	$\mu$	0.000 001	$10^{-6}$
nano	n	0.000 000 001	$10^{-9}$
pico	p	0.000 000 000 001	$10^{-12}$
femto	f	0.000 000 000 000 001	$10^{-15}$
atto	a	0.000 000 000 000 000 001	$10^{-18}$

### 1.4 Uncertainty in Measurement

Uncertainty results from lab equipment and human differences and should always be taken into account.

- Measurements should include all certain digits plus the first uncertain digit.
  - Ex. reading thermometer, buret, balance, etc.
- Measurements may be close or the same as the accepted value (accurate), or may just be repeated values (precise), both or neither.
  - When measurements are imprecise, they are said to be random.
  - When measurements are precise, but not accurate, they are said to be systematic.



## 1.5 Significant Figures and Calculations

- When taking measurements, the digits present in the measurement that were both read and estimated are called significant digits.
  - Please review by writing in the number of significant digits.  
       \_\_\_\_\_ 7.0023    \_\_\_\_\_ 4.00            \_\_\_\_\_ 0.03000            \_\_\_\_\_ 0.009            \_\_\_\_\_ 1,000
- Significant figures in calculations
  - When adding and subtracting, use the lowest number of decimals.
    - 3.0 + 6.00 = 9.0
  - When multiplying and dividing, use the lowest number of total significant figures.
    - 3.0 x 6.00 = 18
  - Exact numbers like constants have unlimited significant figures and should not be used to determine the significant figures in a calculation.

## 1.7 Temperature

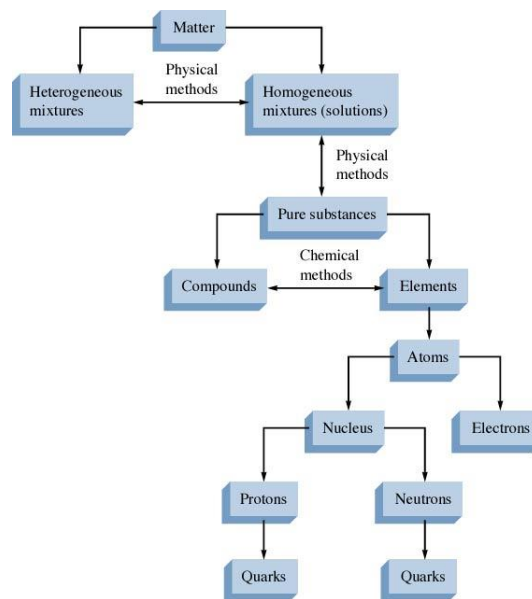
- There are three systems for measuring temperature. We will focus on Kelvin and Celcius.
- Be sure you know how to convert each unit.

Temperature Conversions  
 $^{\circ}\text{C} + 273.15 = \text{K}$   
 $^{\circ}\text{C} (9/5) + 32 = ^{\circ}\text{F}$

## 1.8 and 1.9 Density and Classification of Matter

Matter is what makes up everything. We can classify, measure and convert matter.

- Density is a property of all pure samples of matter. It is a measure of a substances mass per unit volume.
  - $D = m/v$
- The organization of matter is listed in the diagram to the right.
- Be sure you understand this diagram.
- Physical separation of matter can occur through:
  - Distillation-separation based on boiling points
  - Filtration-separation of solids from liquids
  - Chromatography-separation based on intermolecular forces



## Chapter 2: Atoms, Molecules and Ions

### 2.1 The Early History of Chemistry

- Greeks- In 400 BC, the Greek Aristotle determined that there were four fundamental substances (earth, air, fire and water).
  - Although the Greeks thought that matter was composed of particles, they were unable to test these theories due to lack of materials.
- Democritus- stated that matter was composed of small indivisible particles called "atomos"
  - tom = to divide    atom = can't be divided
- Alchemists- Over the next 2000 years, Aristotle's works influenced a branch of science called alchemy that was focused on trying to turn cheap materials into gold.
  - This led to the discovery of some elements and compounds like  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and aqua regia ( $\text{HNO}_3$  and  $\text{HCl}$ ). Many important scientific procedures were developed as well.
- Robert Boyle-1600's
  - The first person to perform quantitative experiments with a focus on gases
  - Wrote a book called *The Skeptical Chymist* in which he described his theory that a substance was an element unless it could be broken down into simpler substances.
  - His research destroyed the notion of only four elements
- Phlogiston theory- (John Becher & George Stahl) postulated that a substance called phlogiston flowed out of burning material during combustion and that materials stopped burning when the phlogiston level became too high.

- Joseph Priestly -1700's
  - Is credited with discovery of oxygen (called it dephlogisticated air)

## 2.2 Fundamental Chemical Laws

- Antoine Lavoisier
  - He determined the nature of combustion with careful quantitative procedures.
  - He developed the law of conservation of mass (mass is neither created nor destroyed)
  - Disproved the phlogiston theory and named oxygen
  - Wrote first chemistry textbook (*Elementary Treatise on Chemistry*)
  - Was executed by guillotine during French Revolution
- Proust- 1800's
  - Developed the Law of Definite Proportion- a given compound always contains exactly the same proportion of elements by weight. If we change the amounts, it changes the identity of the element.
  - Stated that matter is discrete, or particulate, not continuous
- John Dalton- 1800's
  - Created the Law of Multiple Proportions based on the Law of Definite Proportions
  - It stated that when two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.

### Data for compounds of nitrogen and oxygen:

Compound	Percent N	Percent O	Grams of N Reacting With 1.00g of O
I	30.4%	69.6%	0.437
II	46.7%	53.3%	0.876
III	63.6%	36.4%	1.747

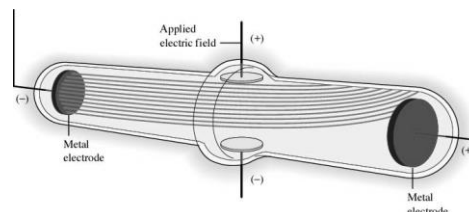
- Unfortunately, you can't deduce absolute formulas from this data.
- Shows that each element consists of a certain type of atom and that compounds were formed from specific combinations of atoms.

## 2.3 Dalton's Atomic Theory

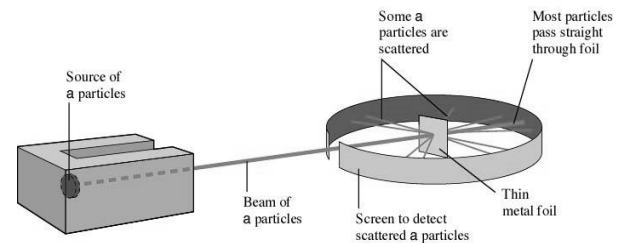
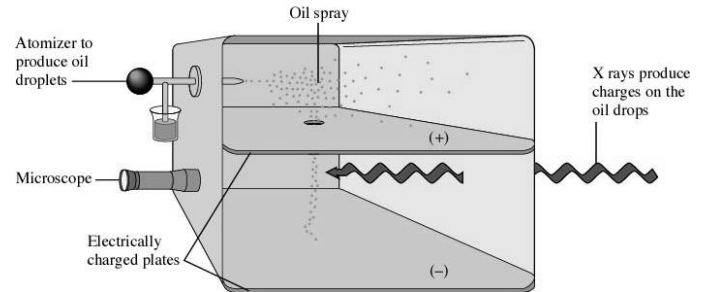
- Dalton's Atomic Theory -1808
  - Each element is made up of particles called atoms.
  - Atoms in an element are all identical and are different than atoms of another element.
  - Compounds are formed when atoms of different elements combine in a constant composition.
  - Atoms are not changed in a chemical reaction, only rearranged.
- Dalton determined the first table of atomic weights. Many were wrong because of incorrect formulas.
  - Ex. OH for water with O having a mass of 8 and H having a mass of 1
- Avogadro's Hypothesis- Gay Lussac and Avogadro studied the volumes of combining gases. This allowed them to determine correct formulas. At the same temperature and pressure, equal volumes of different gases contain the same number of particles.
- It was then determined that various gases are diatomic and correct atomic weights were calculated for them by comparing volumes of reacting gases.
- Gay-Lussac's Law- when gases are involved in chemical reactions, they always react or appear in small whole-number ratios by volume as long as the temperature and pressure remain the same.

## 2.4 Early Experiments to Characterize the Atom

- JJ Thomson 1898-1903
  - discovered electrons using the cathode ray tube
  - The ray is produced at the negative electrode and is repelled by a negative field.

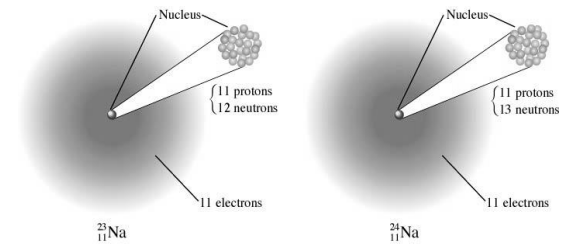


- Thomson assumed that the ray was a stream of negative particles
  - He measured the amount of deflection of the beam by a magnetic field and determined the charge-to-mass ratio of an electron.
  - He found that electrodes made from any metal produced cathode rays so all atoms contain electrons
  - He knew that the atom was neutral, so the rest must be positive
  - He created the Plum Pudding Model to describe the electrons location in the atom.
- Robert Millican -1909
    - Determined the mass of an electron through the use of charged oil droplets. He found the charge of an electron and used this, along with the charge/mass ratio to find the mass.
  - Henri Becquerel -1896
    - Discovered radioactivity when a sample of uranium ore exposed a photographic plate
    - his studies found 3 types of emissions:
      - gamma  $\gamma$  -high energy light (no charge)
      - beta  $\beta$  - high speed electron (1- charge)
      - alpha  $\alpha$  -helium nucleus (2+ charge)
  - Ernest Rutherford- 1911
    - Shot alpha particles (from a sample of radioactive material) through gold foil
    - most went straight through, but a few were deflected
    - This showed that the atom was mostly empty space with a dense, positively charged center.



## 2.5 The Modern View of Atomic Structure

- Nucleus (protons and neutrons) -very tiny
  - Electrons -determine chemical behavior
  - Isotope - atom with the same number of protons but different number of neutrons
- Atomic number = number of protons
  - Mass number = number of protons + number of neutrons
  - Number of protons = Number of electrons in a neutral atom



Mass #  $\rightarrow$  A  
**E**  $\leftarrow$  symbol of element  
 Atomic #  $\rightarrow$  Z

### Review:

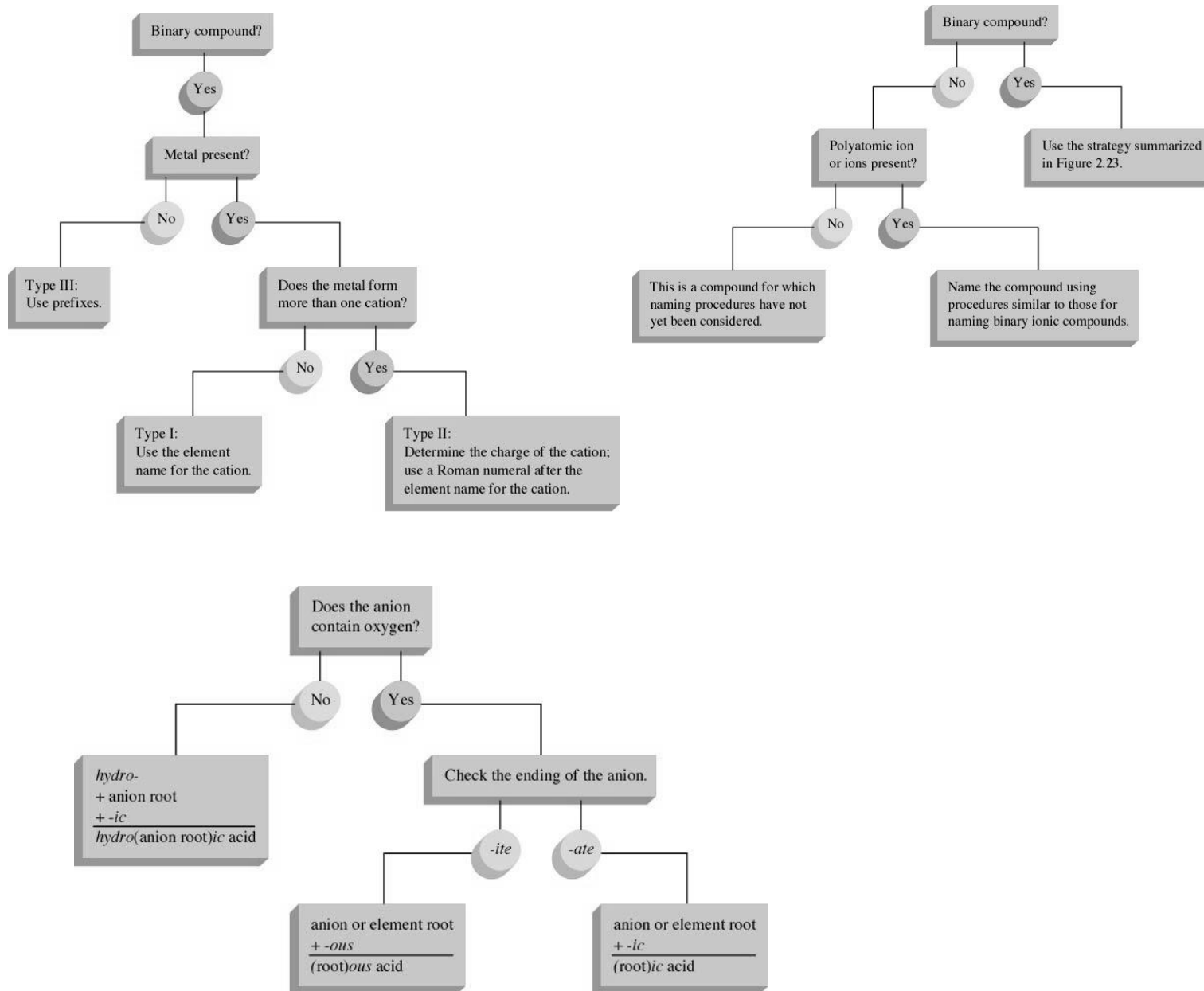
- covalent bonds-created when two or more nonmetals share electrons
- molecule- atoms held together by covalent bonds
- ions- charged particles formed by the loss or gain of electrons
  - ionic bonds- compounds created when one atom loses an electron and another gains it; are held together by electrostatic attraction
- periodic table

Alkali metals																		Transition metals										Halogens										Noble gases			
1	2											13	14	15	16	17	18	3A	4A	5A	6A	7A	8A	1	2																
H	He											B	C	N	O	F	Ne	Al	Si	P	S	Cl	Ar	Li	Be																
3	4											5	6	7	8	9	10	11	12											19	20										
Li	Be											B	C	N	O	F	Ne	Na	Mg											K	Ca										
11	12											13	14	15	16	17	18	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Na	Mg											Al	Si	P	S	Cl	Ar	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
19	20											21	22	23	24	25	26	27	28	29	30	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
K	Ca											Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
37	38											39	40	41	42	43	44	45	46	47	48	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71			
Rb	Sr											Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
55	56											57	58	59	60	61	62	63	64	65	66	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103			
Cs	Ba											La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Fr	Ra	Ac*	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uuc	Uud	Uue	Uuf	Uug			
87	88											89	90	91	92	93	94	95	96	97	98											109	110	111	112						
Fr	Ra											Ac*	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub											Tl	Pb	Bi	Po	At	Rn				

*Lanthanides	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
*Actinides	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

## Naming Compounds: A Review

Be sure that you know how to write and name ionic and molecular compounds, as well as common acids.



## AP Chemistry

### Chapter 3: Stoichiometry

In this chapter, we will look at the quantities of materials consumed and produced in chemical reaction. The study of these quantities is called chemical stoichiometry.

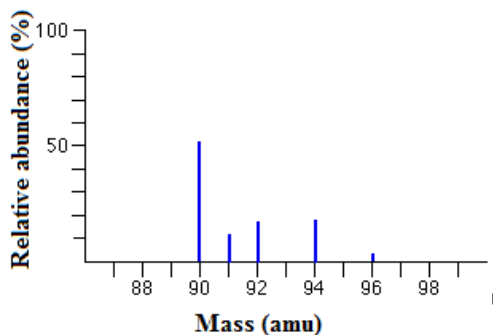
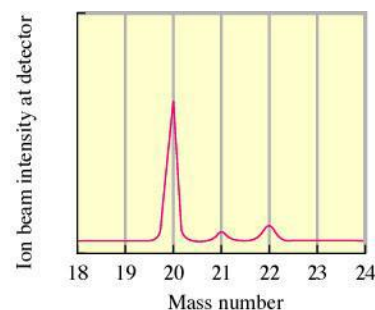
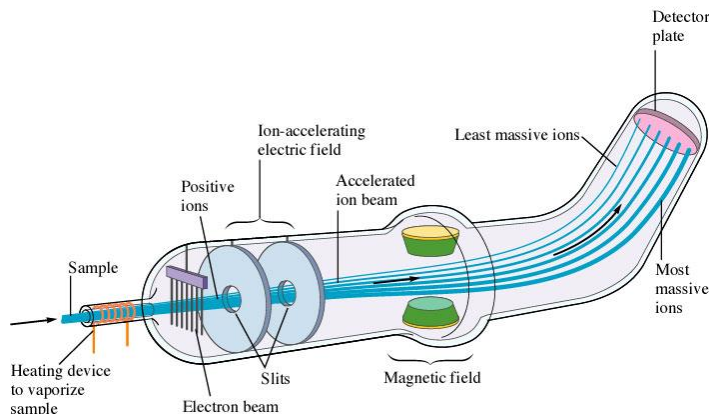
#### 3.1 Counting By Weighing

If we were to take the individual masses of five nails, each nail would probably have a small deviation in mass, but would be relatively the same, let's say an average mass of 2.5g per nail. If someone needed 1,000 nails for a building project, it is easier to take the mass of 1,000 nails, or 2,500g, than to count out all those nails. Objects do not have to have identical masses to be counted by weighing; they behave as if they are all identical. This is very lucky for chemists.

- Just like our nails deviated slightly, atoms of the same element may have different masses. We call these isotopes.
- Average Atomic Mass- an average of each isotope of an element, based on their percent abundance
- To calculate :
  - % Isotope A (mass of A) + % Isotope B (mass of B) + ... = avg. atomic mass
  - Ex. Find the average atomic mass of element "X" if 1.40% of the sample is an isotope with a mass of 203.973 amu, 24.10% is an isotope with a mass of 205.9745 amu, 22.10% is an isotope with a mass of 206.9759 amu and 52.40% is an isotope with a mass of 207.9766 amu.

#### 3.2 Atomic Masses

- So if scientists can't see atoms with their eyes, how do they know all these isotopes exist? They use a mass spectrometer.
- The mass spectrometer heats a sample of atoms into a gas, passes them through a beam of high-speed electrons, which knock off some of the atom's electrons giving them positive charges, and then these positively charged atoms pass through an electric field. The atoms are deflected based on their size, and then detected on a computerized plate.
- Look at the image created for a sample of neon to the right. You can see three "peaks" or bumps on the graph. Each bump represents the amount of particles of that particular mass that were detected, telling us that there are three isotopes of neon in the sample.
- Example. Use the mass spectrum shown on the left to calculate the average atomic mass of this element, then identify the element.



grams.

#### 3.3 The Mole

The mole is the chemist's way of counting atoms. Remember that the mole (or Avogadro's number) is equal to  $6.022 \times 10^{23}$  atoms of any element, which is then equal to the average atomic mass on the periodic table.

- The mole is standardized as the number of carbon atoms in 12.0g of pure carbon-12.
- $6.022 \times 10^{23}$  amu = 1 g
- The mass of one mole of an element is equal to its atomic mass in

- Ex. Cody found a gold nugget that had a mass of 1.250 oz. How many moles was this? How many atoms?

### 3.4 Molar Mass

- mass in grams of one mole of a substance
- may also be called molecular weight
  - Ex. Calculate the molecular mass of cisplatin,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$
  - Ex. How many grams are 3.25 moles of cisplatin?

### 3.6 Percent Composition

- “mass percent” or “percent by mass”
  - Ex. Find the percent composition of all elements in cisplatin,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ .

$$\left( \frac{\text{Total mass of element}}{\text{Total mass of compound}} \right) \times 100 = \% \text{ comp of element}$$

### 3.7 Determining the Formula of a Compound

- Empirical formula- simplest whole number ratio of the various types of atoms in a compound
- Molecular formula- the exact formula or (empirical formula)<sub>x</sub>
  - Ex. A sample of a compound contains 11.66g of iron and 5.01g of oxygen. What is the empirical formula of this compound?

#### Empirical Formula Poem

Percent to mass,  
Mass to moles,  
Divide by smallest,  
And round (or multiply) 'till whole

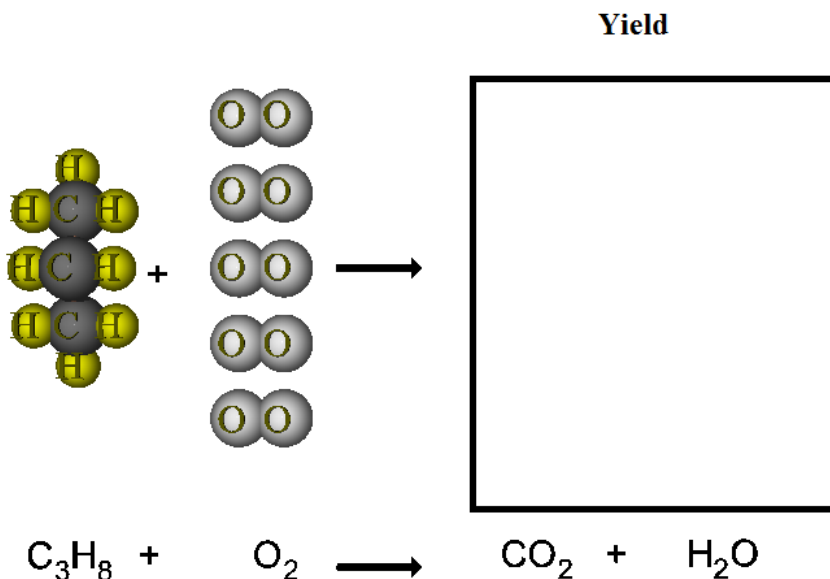
- Ex. What is the empirical formula of hydrazine, which contains 87.5% N and 12.5% H?

### Combustion Analysis

Ex. Suppose you isolate an acid from clover leaves and know that it contains only the elements C, H, and O. Heating 0.513g of the acid in oxygen produces 0.501g of  $\text{CO}_2$  and 0.103g of  $\text{H}_2\text{O}$ . What is the empirical formula of the acid? Given that another experiment has shown that the molar mass of the acid is 90.04g/mol, what is its molecular formula?

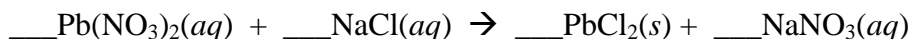
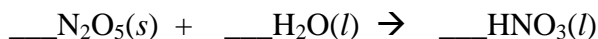
### 3.8 Chemical Equations

- During a chemical reaction, atoms are rearranged when existing bonds are broken and reformed in a different arrangement.
- Since atoms are not lost or gained during a reaction, a balanced equation must have the same number of atoms of each element on each side.
- Symbols representing physical states: (s) (l) (g) (aq)
- Observe the diagram to the left. Balance the equation and then draw in the correct number of expected products.



### 3.9 Balancing Chemical Equations

- We balance equations by adding coefficients, never by changing formulas.
- Most equations can be balanced by inspection. Some redox reactions require a different method.



- You should be able to write and balance an equation when given the reactants and products in words.
  - Ex. Phosphine,  $\text{PH}_3(g)$  is combusted in air to form gaseous water and solid diphosphorus pentoxide.
  - Ex. When ammonia gas is passed over hot liquid sodium metal, hydrogen is released and sodium amide,  $\text{NaNH}_2$ , is formed as a solid product.

### 3.10 Stoichiometric Calculations

Although coefficients in balanced chemical equations tell us how many atoms will react to form products, they do not tell us the actual masses of reactants and products we will use or expect to produce. For this, we need to relate the reactants and products in terms of their mole ratios.

- The mole ratio = moles required/moles given.
  - Ex. What mass of  $\text{NH}_3$  is formed when 5.38g of  $\text{Li}_3\text{N}$  reacts with water according to the equation:  

$$\text{Li}_3\text{N}(s) + 3\text{H}_2\text{O} \rightarrow 3\text{LiOH}(s) + \text{NH}_3(g)$$
?

### 3.11 The Concept of Limiting Reagent

- Limiting reagent- reagent that restricts or determines the amount of product that can be formed
- If in a stoichiometry problem you are given amounts of two or more reactants and asked to determine how much product forms, you must determine which reactant is limiting and use it to work the problem.



- Ex. How many moles of  $\text{Fe}(\text{OH})_3(s)$  can be produced by allowing 1.0 mol  $\text{Fe}_2\text{S}_3$ , 2.0 mol  $\text{H}_2\text{O}$  and 3.0 mol  $\text{O}_2$  to react?  $2\text{Fe}_2\text{S}_3(s) + 6\text{H}_2\text{O}(l) + 3\text{O}_2(g) \rightarrow 4\text{Fe}(\text{OH})_3(s) + 6\text{S}(s)$
  
- Ex. If 17.0g of  $\text{NH}_3(g)$  were reacted with 32.0g of oxygen in the following reaction, how many grams of  $\text{NO}(g)$  would be formed?  $4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(l)$

Once we know how much of a product is formed in a reaction, we can find the percent yield of the reaction.

- Theoretical yield- amount of product that should form according to stoichiometric calculations
- Actual yield- experimental yield

$$\text{Percent yield} = \left( \frac{\text{Actual yield}}{\text{Theoretical yield}} \right) \times 100$$

- Ex. In the reaction of 1.00 mol of  $\text{CH}_4$  with an excess of  $\text{Cl}_2$ , 83.5g of  $\text{CCl}_4$  is obtained. What is the theoretical yield, actual yield and % yield?

**AP Chemistry**  
**Empirical and Molecular Formulas and Percent Composition Worksheet**

1971 AP

1. Water is added to 4.267 grams of  $\text{UF}_6$ . The only products are 3.730 grams of a solid containing only uranium, oxygen, and fluorine and 0.970 gram of a gas. The gas is 95.0% fluorine, and the remainder is hydrogen.

a) From these data, determine the empirical formula of the gas.

b) What fraction of the fluorine of the original compound is in the solid and what fraction in the gas after the reaction?

c) What is the formula of the solid product?

d) Write the balanced equation for the reaction between  $\text{UF}_6$  and  $\text{H}_2\text{O}$ . Assume that the empirical formula of the gas is the true formula.

2. A hydrocarbon mixture consists of 60.0% by mass of  $\text{C}_3\text{H}_8$  and 40% of  $\text{C}_x\text{H}_y$ . When 10.0 grams of this mixture is burned, it yields 29.0 g  $\text{CO}_2$  and 18.8 g  $\text{H}_2\text{O}$  as the only products. What is the formula of the unknown hydrocarbon?

3. A thoroughly dried 1.271 g sample of  $\text{Na}_2\text{SO}_4$  is exposed to the atmosphere and found to gain 0.387 g in mass. What is the percent, by mass, of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in the resulting mixture of hydrate and  $\text{Na}_2\text{SO}_4$ ?
4. A certain brand of lunch meat contains 0.10% sodium benzoate,  $\text{NaC}_7\text{H}_5\text{O}_2$ , by mass as a preservative. If a person eats 2.52 ounces of this meat, how many mg Na will that person consume?
5. Three different brands of "liquid chlorine" for use in purifying water in home swimming pools all cost \$1.00 per gallon and are water solutions of NaOCl. Brand A contains 10% OCl by mass; brand B, 7% available chlorine (Cl) by mass; and brand C, 14% NaOCl by mass. Which of the three brands would you buy?
6. A 0.1510 gram sample of a hydrocarbon produces 0.5008 gram  $\text{CO}_2$  and 0.1282 gram  $\text{H}_2\text{O}$  in combustion analysis. Its molecular weight is found to be 106. For this hydrocarbon, determine (a) its percent composition; (b) its empirical formula; (c) its molecular formula.

## AP<sup>®</sup> EQUATION WRITING

AP equation sets are found in the free-response section of the AP test. You are expected to:

- write balanced net ionic equations for three reactions when given the reactants
- be able to use the equation in terms of a problem
- General point guidelines (they may deviate from this):
  - For each reaction, correct reactants and products should be given and the equation should be balanced.
  - Leaving in the spectator ions will result in the loss of a point.
- The first thing to note is that all AP equations "work". In each case, a reaction will occur.
- These equations need to be written in net ionic form. All spectator ions must be left out and all ions must be written in ionic form.
- All molecular substances and insoluble compounds must be written together (not ionized!). Know your solubility rules!

The best way to prepare for the equation section of the AP test is to practice lots of equations. The equation sets are similar and some equations show up year after year. When you are reading an equation, first try to classify it by type. If the question says anything about acidic or basic solution, it is redox. If you are totally stuck, look up the compounds in the index of your book or other reference books and try to find information that will help you with the equation. All reactions do not fit neatly into the five types of reactions that you learned in Chemistry I. Save the reactions that you write and practice them again before the AP test in May.

\*-----\*

## Reaction Prediction

### 4.4 Types of Chemical Reactions

There are three general types of solution reactions.

- Precipitation reactions (most often include double replacement and complex ion)
- Acid base reactions (also called neutralization)
- Oxidation reduction reactions (most often single replacement, combustion, synthesis and decomposition)
- These equations are written in terms of:
  1. molecular equation –overall reaction stoichiometry
  2. complete ionic equation –all electrolytes are represented as ions
  3. net ionic equation- spectator ions aren't included

### 4.5 Precipitation Reactions

- In a double replacement reaction, two compounds react to form two new compounds.
- No changes in oxidation numbers occur. All double replacement reactions must have a "driving force" that removes a pair of ions from solution.
- Formation of a precipitate: A precipitate is an insoluble substance formed by the reaction of two aqueous substances. Two ions bond together so strongly that water can not pull them apart. You must know your solubility rules to write these net ionic equations to determine which product, if any, will precipitate in a double replacement reaction.
  - Ex. Solutions of silver nitrate and lithium bromide are mixed.
    - $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}(s)$

#### Simple Rules for Solubility

1. Most nitrate ( $\text{NO}_3^-$ ) salts are soluble.
2. Most alkali (group 1A) salts and  $\text{NH}_4^+$  are soluble.
3. Most  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  salts are soluble (NOT  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ )
4. Most sulfate salts are soluble (NOT  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{HgSO}_4$ ,  $\text{CaSO}_4$ )
5. Most  $\text{OH}^-$  salts are only slightly soluble ( $\text{NaOH}$ ,  $\text{KOH}$  are soluble,  $\text{Ba}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  are marginally soluble)
6. Most  $\text{S}^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  salts are only slightly soluble.

- Formation of a gas: Gases may form directly in a double replacement reaction or can form from the decomposition of a product such as  $\text{H}_2\text{CO}_3$  or  $\text{H}_2\text{SO}_3$ .

- Ex. Excess hydrochloric acid solution is added to a solution of potassium sulfite.
  - $2\text{H}^+ + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{SO}_2$
- Ex. A solution of sodium hydroxide is added to a solution of ammonium chloride.
  - $\text{OH}^- + \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}_2\text{O}$

#### Extra Solubility Information

- $\text{Ca}(\text{OH})_2$  and  $\text{Sr}(\text{OH})_2$  are moderately soluble and can be written together or as ions.
- $\text{Ba}(\text{OH})_2$  is soluble and  $\text{Mg}(\text{OH})_2$  is insoluble.
- $\text{CaSO}_4$  and  $\text{SrSO}_4$  are moderately soluble and can be written together or as ions.
- Weak electrolytes, such as acetic acid, are not ionized.
- Solids and pure liquids are written together, also.
- A saturated solution is written in ionic form while a suspension is not ionized.

- Formation of a molecular substance: When a molecular substance such as water or acetic acid is formed, ions are removed from solution and the reaction "works".
  - Ex. Dilute solutions of lithium hydroxide and hydrobromic acid are mixed.
    - $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$  (HBr, HCl, and HI are strong acids)
  - Ex. Gaseous hydrofluoric acid reacts with solid silicon dioxide.
    - $4\text{HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$

Knowing about precipitation reactions allows us to isolate ions in the lab during experiments.

- Qualitative analysis- process of separating and identifying ions
  - Selective precipitation- process by which ions are caused to ppt one by one in sequence to separate mixtures of ions.
    - Ex. Separate  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Fe}^{3+}$
    - Ex. Separate  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$
- Quantitative analysis- determines how much of a component is present.
  - Gravimetric analysis- quantitative procedure where a precipitate containing the substance is formed, filtered, dried & weighed.
    - Ex. The zinc in a 1.2000g sample of foot powder was precipitated as  $\text{ZnNH}_4\text{PO}_4$ . Strong heating of the precipitate yielded 0.4089 g of  $\text{Zn}_2\text{P}_2\text{O}_7$ . Calculate the mass percent of zinc in the sample of the foot powder.
    - Ex. A mixture contains only NaCl and  $\text{Fe}(\text{NO}_3)_3$ . A 0.456g sample of the mixture is dissolved in water, and an excess of NaOH is added, producing a precipitate of  $\text{Fe}(\text{OH})_3$ . The ppt is filtered, dried, & weighed. Its mass is 0.128g.
      - Calculate:
        - a. the mass of the iron
        - b. the mass of  $\text{Fe}(\text{NO}_3)_3$
        - c. the mass percent of  $\text{Fe}(\text{NO}_3)_3$  in the sample

**Precipitation Reaction Practice**

**Write the balanced chemical equation and the net ionic equation in the space provided.**

1. Hydrogen sulfide is bubbled through a solution of silver nitrate.
2. An excess of sodium hydroxide solution is added to a solution of magnesium nitrate.
3. Solutions of sodium iodide and lead nitrate are mixed.
4. A solution of ammonia is added to a solution of ferric chloride.
5. Solutions of silver nitrate and sodium chromate are mixed.
6. Excess silver acetate is added to a solution of trisodium phosphate.
7. Manganese (II) nitrate solution is mixed with sodium hydroxide solution.
8. A saturated solution of calcium hydroxide is added to a solution of magnesium chloride.
9. Hydrogen sulfide gas is added to a solution of cadmium nitrate.
10. Dilute sulfuric acid is added to a solution of barium acetate.
11. A precipitate is formed when solutions of trisodium phosphate and calcium chloride are mixed.
12. A solution of copper (II) sulfate is added to a solution of barium hydroxide.
13. Equal volumes of dilute equimolar solutions of sodium carbonate and hydrochloric acid are mixed.
14. Solid barium peroxide is added to cold dilute sulfuric acid.
15. Excess hydrochloric acid solution is added to a solution of potassium sulfite.
16. Dilute sulfuric acid is added to a solution of barium chloride.
17. A solution of sodium hydroxide is added to a solution of ammonium chloride.

18. Dilute hydrochloric acid is added to a solution of potassium carbonate.
19. Gaseous hydrogen sulfide is bubbled through a solution of nickel (II) nitrate.
20. A solution of sodium sulfide is added to a solution of zinc nitrate.
21. Concentrated hydrochloric acid is added to solid manganese (II) sulfide.
22. Solutions of tri-potassium phosphate and zinc nitrate are mixed.
23. Dilute acetic acid solution is added to solid magnesium carbonate.
24. Gaseous hydrofluoric acid reacts with solid silicon dioxide.
25. Equimolar amounts of trisodium phosphate and hydrogen chloride, both in solution, are mixed.
26. Ammonium chloride crystals are added to a solution of sodium hydroxide.
27. Hydrogen sulfide gas is bubbled through a solution of lead (II) nitrate.
28. Solutions of silver nitrate and sodium chromate are mixed.
29. Solutions of sodium fluoride and dilute hydrochloric acid are mixed.
30. A saturated solution of barium hydroxide is mixed with a solution of iron (III) sulfate.
31. A solution of ammonium sulfate is added to a potassium hydroxide solution.
32. A solution of ammonium sulfate is added to a saturated solution of barium hydroxide.
33. Dilute sulfuric acid is added to solid calcium fluoride.
34. Dilute hydrochloric acid is added to a dilute solution of mercury (I) nitrate.
35. Dilute sulfuric acid is added to a solution of lithium hydrogen carbonate.

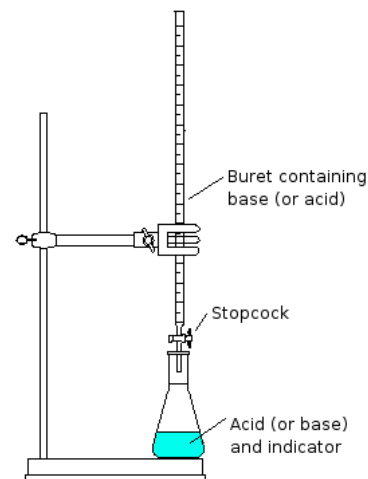
36. Dilute hydrochloric acid is added to a solution of potassium sulfite.
  37. Carbon dioxide gas is bubbled through water containing a suspension of calcium carbonate.
  38. Excess concentrated sulfuric acid is added to solid calcium phosphate.
  39. Hydrogen sulfide gas is bubbled into a solution of mercury (II) chloride.
  40. Solutions of zinc sulfate and sodium phosphate are mixed.
  41. Solutions of silver nitrate and lithium bromide are mixed.
  42. Solutions of manganese (II) sulfate and ammonium sulfide are mixed.
  43. Excess hydrochloric acid solution is added to a solution of potassium sulfite.
- 

#### 4.8 Acid-Base Reactions

- Brønsted-Lowry acid-base definitions:
  - acid- proton donor
  - base- proton acceptor
- When a strong acid reacts with a strong base the net ionic reaction is:  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
- Watch out for information about quantities of each reactant!
- Remember which acids are strong (ionize completely) and which are weak (write as molecule).
- Sulfuric acid solution (strong acid) should be written as  $\text{H}^+$  and  $\text{HSO}_4^-$ .
- Concentrated strong acids must be left together as they do not have enough water to ionize.
  - Ex. A solution of sulfuric acid is added to a solution of barium hydroxide until the same number of moles of each compound has been added.
    - $\text{H}^+ + \text{HSO}_4^- + \text{Ba}^{2+} + 2\text{OH}^- \rightarrow \text{BaSO}_4 + 2\text{H}_2\text{O}$
  - Ex. Hydrogen sulfide gas is bubbled through excess potassium hydroxide solution.
    - $\text{H}_2\text{S} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HS}^-$  \*( $\text{S}^{2-}$  does not exist in water)
- Watch out for substances that react with water before reacting with an acid or a base. These are two step reactions.
  - Ex. Sulfur dioxide gas is bubbled into an excess of a saturated solution of calcium hydroxide.
    - $\text{SO}_2 + \text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$
- When a strong acid reacts with a weak base or a weak acid reacts with a strong base, the reaction is complete (the weak substance ionizes completely.)  $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$ 
  - Neutralization reaction- An acid-base reaction when just enough base ( $\text{OH}^-$ ) is added to react exactly with the acid ( $\text{H}^+$ ) in a solution. This leads to an acid that has been neutralized.



- Volumetric Analysis
  - Titration- A process in which a solution of known concentration (standard solution) is added to analyze another solution.
    - Titrant- solution of known concentration (in buret)
    - Equivalence point or stoichiometric point- point where just enough titrant has been added to react with the substance being analyzed
    - Indicator- chemical which changes color at or near the equivalence point
    - End point- point at which the indicator changes color
  - Ex. 54.6 mL of 0.100 M  $\text{HClO}_4$  solution is required to neutralize 25.0 mL of a NaOH solution of unknown molarity. What is the concentration of the NaOH solution?



### Acid-Base Neutralization Practice

1. Solutions of ammonia and hydrofluoric acid are mixed.
2. Hydrogen sulfide gas is bubbled through a solution of potassium hydroxide.
3. A solution of sulfuric acid is added to a solution of barium hydroxide until the same number of moles of each compound has been added.
4. A solution of sodium hydroxide is added to a solution of sodium dihydrogen phosphate until the same number of moles of each compound has been added.
5. Dilute nitric acid is added to crystals of pure calcium oxide.
6. Equal volumes of 0.1-molar sulfuric acid and 0.1-molar potassium hydroxide are mixed.
7. A solution of ammonia is added to a dilute solution of acetic acid.
8. Excess sulfur dioxide gas is bubbled through a dilute solution of potassium hydroxide.
9. Sulfur dioxide gas is bubbled into an excess of a saturated solution of calcium hydroxide.
10. A solution of sodium hydroxide is added to a solution of calcium hydrogen carbonate until the number of moles of sodium hydroxide added is twice the number of moles of the calcium salt.
11. Equal volumes of 0.1M hydrochloric acid and 0.1M sodium monohydrogen phosphate are mixed.

12. Hydrogen sulfide gas is bubbled through excess potassium hydroxide solution.
13. Ammonia gas and carbon dioxide gas are bubbled into water.
14. Carbon dioxide gas is bubbled through a concentrated solution of sodium hydroxide.
15. Acetic acid solution is added to a solution of sodium hydrogen carbonate.
16. Excess potassium hydroxide solution is added to a solution of potassium dihydrogen phosphate.

#### 4.9 Oxidation-Reduction Reactions

- Redox reactions involve the transfer of electrons. The oxidation numbers of at least two elements must change. Single replacement, synthesis, decomposition and combustion reactions are redox reactions.
- Oxidation** - loss of electrons
  - increase in oxidation number
- Reduction** - gain of electrons
  - decrease in oxidation number
- Oxidizing agent** - electron acceptor
  - substance that is reduced
- Reducing agent** - electron donor
  - substance that is oxidized
- For the following, write the oxidation states of each element, then decide what is oxidized and reduced.
  - Ex.  $2\text{KI} + \text{F}_2 \rightarrow 2\text{KF} + \text{I}_2$
  - Ex.  $2\text{PbO}_2 \rightarrow 2\text{PbO} + \text{O}_2$
  - In terms of oxidation numbers, non-integer states are rare, but possible. ( $\text{Fe}_3\text{O}_4$ )
- To predict the products of a redox reaction, look at the reagents given to see if there is both an oxidizing agent and a reducing agent. When a problem mentions an acidic or basic solution, it is probably redox. Make sure that charge is balanced!



**LEO the lion goes GER**  
 Lose Electrons = Oxidation,  
 Gain Electrons = Reduction

Oxidation	Reduction
Is	Is
Loss	Gain



Common oxidizing agents	Products formed	Common reducing agents	Products formed
$\text{MnO}_4^-$ in acidic solution	$\text{Mn}^{2+}$	halide ions	free halogen
$\text{MnO}_2$ in acidic solution		free metals	metal ions
$\text{MnO}_4^-$ in neutral or basic solution	$\text{MnO}_2(\text{s})$	sulfite ions or $\text{SO}_2$	sulfate ions
$\text{Cr}_2\text{O}_7^{2-}$ in acidic solution	$\text{Cr}^{3+}$	nitrite ions	nitrate ions
$\text{HNO}_3$ , concentrated	$\text{NO}_2$	free halogens, dilute basic solution	hypohalite ions
$\text{HNO}_3$ , dilute	$\text{NO}$	free halogens, conc. basic solution	halate ions
$\text{H}_2\text{SO}_4$ , hot, concentrated	$\text{SO}_2$	metal-ous ions	metal-ic ions
$\text{Na}_2\text{O}_2$	$\text{NaOH}$	$\text{H}_2\text{O}_2$	$\text{O}_2$
$\text{HClO}_4$	$\text{Cl}^-$	$\text{C}_2\text{O}_4^{2-}$	$\text{CO}_2$
$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}$		
metal-ic ions	metal-ous ions		
free halogens	halide ions		

- Ex. A solution of tin(II) chloride is added to an acidified solution of potassium permanganate.
  - $5\text{Sn}^{2+} + 16\text{H}^+ + 2\text{MnO}_4^- \rightarrow 5\text{Sn}^{4+} + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$

- Ex. A solution of potassium iodide is added to an acidified solution of potassium dichromate.
  - $6\text{I}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$
- Ex. Hydrogen peroxide solution is added to a solution of iron (II) sulfate.
  - $\text{H}_2\text{O}_2 + 2\text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$
- Ex. A piece of iron is added to a solution of iron (III) sulfate.
  - $\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$
- Tricky redox reactions that appear to be ordinary single replacement reactions: Hydrogen reacts with a hot metallic oxide to produce the elemental metal and water.
- Ex. Hydrogen gas is passed over hot copper (II) oxide.
  - $\text{H}_2 + \text{CuO} \rightarrow \text{Cu} + \text{H}_2\text{O}$
- A metal sulfide reacts with oxygen to produce the metallic oxide and sulfur dioxide.
- Chlorine gas reacts with dilute sodium hydroxide to produce sodium hypochlorite, sodium chloride and water. (Disproportionation reaction)
- Copper reacts with concentrated sulfuric acid to produce copper(II) sulfate, sulfur dioxide, and water.
- Copper reacts with dilute nitric acid to produce copper (II) nitrate, nitrogen monoxide and water.
- Copper reacts with concentrated nitric acid to produce copper (II) nitrate, nitrogen dioxide and water.

### **Balancing redox reactions by the half-reaction method**

1. Write skeleton half-reactions.
  2. Balance all elements other than O and H.
  3. Balance O by adding  $\text{H}_2\text{O}$ .
  4. Balance H by adding  $\text{H}^+$ .
  5. Balance charge by adding  $e^-$  to the more positive side.
  6. Make the # of  $e^-$  lost = # of  $e^-$  gained by multiplying each half-rxn by a factor.
  7. Add half-reactions together.
  8. Cancel out anything that is the same on both sides.
  9. If the reaction occurs in basic solution, add an equal number of hydroxide ions to both sides to cancel out the hydrogen ions. Make water on the side with the hydrogen ions. Cancel water if necessary.
  10. Check to see that charge and mass are both balanced.
- Practice these on your own sheet of paper.
    - $\text{Sn}^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Sn}^{4+} + \text{Cr}^{3+}$  (acidic solution)
    - $\text{MnO}_4^{2-} + \text{I}^- \rightarrow \text{MnO}_2 + \text{I}_2$  (basic solution)

### **Oxidation-Reduction Practice**

1. Iron (III) ions are reduced by iodide ions.
2. Potassium permanganate solution is added to concentrated hydrochloric acid.
3. Magnesium metal is added to dilute nitric acid, giving as one of the products a compound in which the oxidation number for nitrogen is -3.
4. A solution of potassium iodide is electrolyzed.
5. Potassium dichromate solution is added to an acidified solution of sodium sulfite.

6. Solutions of potassium iodide, potassium iodate, and dilute sulfuric acid are mixed.
7. A solution of tin (II) sulfate is added to a solution of iron (III) sulfate.
8. Manganese (IV) oxide is added to warm, concentrated hydrobromic acid.
9. Chlorine gas is bubbled into cold dilute sodium hydroxide.
10. Solid iron (III) oxide is heated in excess carbon monoxide.
11. Hydrogen peroxide solution is added to acidified potassium iodide solution.
12. Hydrogen peroxide is added to an acidified solution of potassium dichromate.
13. Sulfur dioxide gas is bubbled through an acidified solution of potassium permanganate.
14. A solution containing tin (II) ions is added to an acidified solution of potassium dichromate.
15. Solid silver sulfide is warmed with dilute nitric acid.
16. A dilute solution of sulfuric acid is electrolyzed between platinum electrodes.
17. Pellets of lead are dropped into hot sulfuric acid.
18. Potassium permanganate solution is added to a solution of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , acidified with a few drops of sulfuric acid.
19. Powdered iron is added to a solution of iron (III) sulfate.
20. A concentrated solution of hydrochloric acid is added to powdered manganese dioxide and gently heated.
21. A strip of copper metal is added to a concentrated solution of sulfuric acid.
22. A solution of copper (II) sulfate is electrolyzed using inert electrodes.


23. A solution of potassium iodide is added to an acidified solution of potassium dichromate.
24. Solid silver is added to a dilute nitric acid (6M) solution.
25. A piece of iron is added to a solution of iron (III) sulfate.
26. An acidified solution of potassium permanganate is added to a solution of sodium sulfite.
27. A solution of tin (II) chloride is added to a solution of iron (III) sulfate.
28. Concentrated hydrochloric acid solution is added to solid manganese (IV) oxide and the reactants are heated.
29. A strip of copper is immersed in dilute nitric acid.
30. Potassium permanganate solution is added to an acidic solution of hydrogen peroxide.
31. Chlorine gas is bubbled into a cold solution of dilute sodium hydroxide.
32. Solid sodium dichromate is added to an acidified solution of sodium iodide.
33. Hydrogen gas is passed over hot iron (III) oxide.
34. Solutions of potassium iodide and potassium iodate are mixed in acid solution.
35. Hydrogen peroxide is added to an acidified solution of sodium bromide.
36. A solution of iron (II) nitrate is exposed to air for an extended period of time.
37. A solution of tin (II) chloride is added to an acidified solution of potassium permanganate.
38. A concentrated solution of hydrochloric acid is added to solid potassium permanganate.
39. A solution of potassium dichromate is added to an acidified solution of iron (II) chloride.

## Single Replacement

- Reaction where one element displaces another in a compound.  
 $A + BC \rightarrow B + AC$
- Active metals replace less active metals or hydrogen from their compounds in aqueous solution.
- Use an activity series or a reduction potential table to determine activity.
- The more easily oxidized metal replaces the less easily oxidized metal.
- The metal with the most negative reduction potential will be the most active.
  - Ex. Magnesium turnings are added to a solution of iron (III) chloride.
    - $3\text{Mg} + 2\text{Fe}^{3+} \rightarrow 2\text{Fe} + 3\text{Mg}^{2+}$
  - Ex. Sodium is added to water.
    - $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{H}_2$
- Active nonmetals replace less active nonmetals from their compounds in aqueous solution. Each halogen will displace less electronegative (heavier) halogens from their binary salts.
  - Ex. Chlorine gas is bubbled into a solution of potassium iodide.
    - $\text{Cl}_2 + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{Cl}^-$

TABLE 4.4 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$
Potassium	$\text{K} \rightarrow \text{K}^+ + \text{e}^-$
Barium	$\text{Ba} \rightarrow \text{Ba}^{2+} + 2\text{e}^-$
Calcium	$\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$
Sodium	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$
Magnesium	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$
Aluminum	$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$
Manganese	$\text{Mn} \rightarrow \text{Mn}^{2+} + 2\text{e}^-$
Zinc	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
Chromium	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$
Iron	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
Cobalt	$\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$
Nickel	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$
Tin	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$
Lead	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$
Hydrogen	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
Copper	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
Silver	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$
Mercury	$\text{Hg} \rightarrow \text{Hg}^{2+} + 2\text{e}^-$
Platinum	$\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$
Gold	$\text{Au} \rightarrow \text{Au}^{3+} + 3\text{e}^-$



## Single Replacement Practice

1. A piece of aluminum metal is added to a solution of silver nitrate.
2. Aluminum metal is added to a solution of copper (II) chloride.
3. Hydrogen gas is passed over hot copper (II) oxide.
4. Small chunks of solid sodium are added to water.
5. Calcium metal is added to a dilute solution of hydrochloric acid.
6. Magnesium turnings are added to a solution of iron (III) chloride.
7. Chlorine gas is bubbled into a solution of sodium bromide.
8. A strip of magnesium is added to a solution of silver nitrate.
9. Solid calcium is added to warm water.
10. Liquid bromine is added to a solution of potassium iodide.

11. Chlorine gas is bubbled into a solution of potassium iodide.
12. Lead foil is immersed in silver nitrate solution.
13. Solid zinc strips are added to a solution of copper (II) sulfate.
15. A bar of zinc metal is immersed in a solution of copper (II) sulfate.
16. A small piece of lithium metal is added to distilled water.

## Decomposition Reactions

- Reaction where a compound breaks down into two or more elements or compounds. Heat, electrolysis, or a catalyst is usually necessary.
- A compound may break down to produce two elements.
  - Ex. Molten sodium chloride is electrolyzed.
    - $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$
- A compound may break down to produce an element and a compound.
  - Ex. A solution of hydrogen peroxide is decomposed catalytically.
    - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
- A compound may break down to produce two compounds.
  - Ex. Solid magnesium carbonate is heated.
    - $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
- Metallic carbonates break down to yield metallic oxides and carbon dioxide.
- Metallic chlorates break down to yield metallic chlorides and oxygen.
- Hydrogen peroxide decomposes into water and oxygen.
- Ammonium carbonate decomposes into ammonia, water and carbon dioxide.
- Sulfurous acid decomposes into water and sulfur dioxide.
- Carbonic acid decomposes into water and carbon dioxide.

## Decomposition Practice

1. A solution of hydrogen peroxide is heated.
2. Solid magnesium carbonate is heated.
3. A solution of hydrogen peroxide is catalytically decomposed.
4. Solid potassium chlorate is heated in the presence of manganese dioxide as a catalyst.

5. Sodium hydrogen carbonate is dissolved in water.

6. Solid ammonium carbonate is heated.

## Addition Reactions

- Two or more elements or compounds combine to form a single product.
- A Group IA or IIA metal may combine with a nonmetal to make a salt.
  - Ex. A piece of lithium metal is dropped into a container of nitrogen gas.
    - $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$
- Two nonmetals may combine to form a molecular compound. The oxidation number of the less electronegative element is often variable depending upon conditions. Generally, a higher oxidation state of one nonmetal is obtained when reacting with an excess of the other nonmetal.
  - Ex.  $\text{P}_4 + 6\text{Cl}_2 \rightarrow 4\text{PCl}_3$       limited Cl
  - Ex.  $\text{P}_4 + 10\text{Cl}_2 \rightarrow 4\text{PCl}_5$       excess Cl
  - Ex.  $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$
- Two compounds combine to form a single product.
  - Ex. Sulfur dioxide gas is passed over solid calcium oxide.
    - $\text{SO}_2 + \text{CaO} \rightarrow \text{CaSO}_3$
  - Ex. The gases boron trifluoride and ammonia are mixed.
    - $\text{BF}_3 + \text{NH}_3 \rightarrow \text{H}_3\text{NBF}_3$
- A metallic oxide plus carbon dioxide yields a metallic carbonate. (Carbon keeps the same oxidation state)
- A metallic oxide plus sulfur dioxide yields a metallic sulfite. (Sulfur keeps the same oxidation state)
- A metallic oxide plus water yields a metallic hydroxide.
- A nonmetallic oxide plus water yields an acid.

## Addition Practice

1. The gases boron trifluoride and ammonia are mixed.
2. A mixture of solid calcium oxide and solid tetraphosphorus decaoxide is heated.
3. Solid calcium oxide is exposed to a stream of carbon dioxide gas.
4. Solid calcium oxide is heated in the presence of sulfur trioxide gas.
5. Calcium metal is heated strongly in nitrogen gas.
6. Excess chlorine gas is passed over hot iron filings.
7. Powdered magnesium oxide is added to a container of carbon dioxide gas.
8. A piece of lithium metal is dropped into a container of nitrogen gas.



9. Magnesium metal is burned in nitrogen gas.

10. Sulfur dioxide gas is passed over solid calcium oxide.

## Combustion Reactions

- Elements or compounds combine with oxygen to form oxides of all elements involved.
  - Hydrocarbons or alcohols combine with oxygen to form carbon dioxide and water. Know your simple organic nomenclature for alkanes, alkenes, alkynes, alcohols, ketones, aldehydes, and esters.
  - Ammonia combines with limited oxygen to produce NO and water and with excess oxygen to produce NO<sub>2</sub> and water.
  - Nonmetallic hydrides combine with oxygen to form oxides and water.
  - Nonmetallic sulfides combine with oxygen to form oxides and sulfur dioxide.
    - Ex. Carbon disulfide vapor is burned in excess oxygen.
      - $\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$
    - Ex. Ethanol is burned completely in air.
      - $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
    - Ex. Diethyl ether is burned in air.
      - $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + 6\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O}$

## Combustion Practice

1. Lithium metal is burned in air.
2. The hydrocarbon hexane is burned in excess oxygen.
3. Gaseous diborane, B<sub>2</sub>H<sub>6</sub>, is burned in excess oxygen.
4. A piece of solid bismuth is heated strongly in oxygen.
5. Solid zinc sulfide is heated in an excess of oxygen.
6. Propanol is burned completely in air.
7. Excess oxygen gas is mixed with ammonia gas in the presence of platinum.
8. Gaseous silane, SiH<sub>4</sub>, is burned in oxygen.
9. Ethanol is completely burned in air.

10. Solid copper (II) sulfide is heated strongly in oxygen gas.

11. Carbon disulfide vapor is burned in excess oxygen.

### SOLUBILITY SONG

To the tune of “ My Favorite Things” from “The Sound of Music”

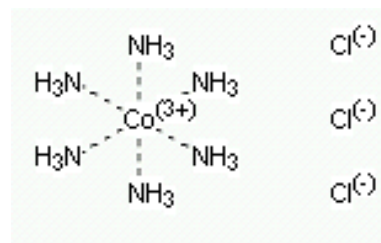
Nitrates and Group One and Ammonium,  
 These are all soluble, a rule of thumb.  
 Then you have chlorides, they're soluble fun,  
 All except Silver, Lead, Mercury I.  
 Then you have sulfates, except for these three:  
 Barium, Calcium and Lead, you see.  
 Worry not only few left to go still.  
 We will do fine on this test. Yes, we will!

Then you have the---  
 Insolubles  
 Hydroxide,  
 Sulfide and Carbonate and Phosphate,  
 And all of these can be dried!

### Other Reactions

#### Complex Ion Reactions

- Complex ion- the combination of a central metal ion and its ligands.
  - Ligand- group bonded to a metal ion
- Coordination compound- a neutral compound containing complex ions
  - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  ( $\text{NH}_3$  is the ligand,  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is the complex ion)



### Common Complex Ions Formed in AP Equations

Complex ion	Name	Formed from
$[\text{Al}(\text{OH})_4]^-$	tetrahydroxoaluminate ion	(Al or $\text{Al}(\text{OH})_3$ or $\text{Al}^{3+} + \text{OH}^-$ )
$[\text{Ag}(\text{NH}_3)_2]^+$	diamminesilver (I) ion	( $\text{Ag}^+ + \text{NH}_3$ )
$[\text{Zn}(\text{OH})_4]^{2-}$	tetrahydroxozincate ion	( $\text{Zn}(\text{OH})_2 + \text{OH}^-$ )
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	tetramminezinc ion	( $\text{Zn}^{2+} + \text{NH}_3$ )
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	tetramminecopper(II) ion	( $\text{Cu}^{2+} + \text{NH}_3$ )
$[\text{Cd}(\text{NH}_3)_4]^{2+}$	tetramminecadmium(II) ion	( $\text{Cd}^{2+} + \text{NH}_3$ )
$[\text{FeSCN}]^{2+}$	thiocyanoiron(III) ion	( $\text{Fe}^{3+} + \text{SCN}^-$ )
$[\text{Ag}(\text{CN})_2]^-$	dicyanoargentate(I) ion	( $\text{Ag}^+$ and $\text{CN}^-$ )
$[\text{Ag}(\text{Cl})_2]^-$	dichloroargentate(I) ion	( $\text{AgCl}$ and $\text{Cl}^-$ )

- Adding an acid to a complex ion will break it up. If HCl is added to a silver complex,  $\text{AgCl}(s)$  is formed. If an acid is added to an ammonia complex,  $\text{NH}_4^+$  is formed.
  - Ex. Excess ammonia is added to a solution of zinc nitrate.

- $\text{NH}_3 + \text{Zn}^{2+} \rightarrow [\text{Zn}(\text{NH}_3)_6]^{2+}$  (other coordination numbers are acceptable as long as correct charge is given.)
- Ex. A solution of diamminesilver(I) chloride is treated with dilute nitric acid.
  - $[\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^- + 2\text{H}^+ \rightarrow \text{AgCl} + 2\text{NH}_4^+$

### Complex Ions Practice

1. Concentrated (15M) ammonia solution is added in excess to a solution of copper (II) nitrate.
2. An excess of nitric acid solution is added to a solution of tetraamminecopper(II) sulfate.
3. Dilute hydrochloric acid is added to a solution of diamminesilver(I) nitrate.
4. Solid aluminum nitrate is dissolved in water.
5. A suspension of copper (II) hydroxide is treated with an excess of ammonia water.
6. A solution of diamminesilver(I) chloride is treated with dilute nitric acid.
7. An excess of concentrated ammonia solution is added to freshly precipitated copper (II) hydroxide.
8. Excess dilute nitric acid is added to a solution containing the tetraamminecadmium(II) ion.
9. An excess of ammonia is bubbled through a solution saturated with silver chloride.
10. A concentrated solution of ammonia is added to a solution of zinc iodide.
11. An excess of sodium hydroxide solution is added to a solution of aluminum chloride.
12. A concentrated solution of ammonia is added to a solution of copper(II) chloride.
13. Excess concentrated sodium hydroxide solution is added to solid aluminum hydroxide.
14. Pellets of aluminum metal are added to a solution containing an excess of sodium hydroxide.
15. A suspension of zinc hydroxide is treated with concentrated sodium hydroxide solution.

16. Silver chloride is dissolved in excess ammonia solution.
17. Sodium hydroxide solution is added to a precipitate of aluminum hydroxide in water.
18. A drop of potassium thiocyanate is added to a solution of iron (III) chloride.
19. A concentrated solution of ammonia is added to a suspension of zinc hydroxide.
20. Excess concentrated potassium hydroxide solution is added to a precipitate of zinc hydroxide.
21. Excess sodium cyanide is added to a solution of silver nitrate.

## Mixed Equation Worksheet #1

**For each of the following reactions, in part (i) write a BALANCED equation and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers.** Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction.

1.

(i) Ethene gas is burned in air.	
(ii) What specific type of hydrocarbon is ethene?	

2.

(i) Solutions of cobalt(II) nitrate and sodium hydroxide are mixed.	
(ii) What are the spectator ions in this reaction?	

3.

(i) A strip of zinc is added to a solution of 6.0-molar hydrobromic acid.	
(ii) What would you observe happening to the zinc strip in this reaction?	

4.

(i) Solutions of tin(II) chloride and iron(III) chloride are mixed.	
(ii) Is this a redox reaction? If so, what is reduced?	

5.

(i) Solid sodium oxide is added to distilled water.	
(ii) Estimate the pH of the final solution.	

6.

(i) Excess hydrochloric acid is added to a solution of diamminesilver(I) nitrate.	
(ii) What would you observe happening in this reaction?	

7.

(i) Solid calcium sulfite is heated in a vacuum.	
(ii) Is this a redox reaction? If so, what is oxidized?	

8.

(i) Equal volumes of equimolar solutions of phosphoric acid and potassium hydroxide are mixed.	
(ii) Estimate the pH of the final solution.	

## Mixed Equation Worksheet #2

**For each of the following reactions, in part (i) write a BALANCED equation and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers.** Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction.

1.

(i) Powdered strontium oxide is added to distilled water.	
(ii) Is the product acidic or basic? How could you test to confirm this?	

2.

(i) Butanol is burned in air.	
(ii) If insufficient air was present, what different product(s) could be formed?	

3.

(i) A solution of copper(II) chloride is added to a solution of sodium sulfide.	
(ii) What color(s) would the two solutions be before the reaction?	

4.

(i) A small piece of calcium metal is added to hot distilled water.	
(ii) What would you observe in this reaction?	

5.

(i) Excess hydrobromic acid solution is added to a solution of potassium hydrogen carbonate.	
(ii) Is this a redox reaction?	

6.

(i) Carbon monoxide gas is passed over hot iron(III) oxide.	
(ii) Name an industrial application of this reaction.	

7.

(i) Excess concentrated ammonia solution is added to a solution of nickel(II) sulfate.	
(ii) Which species acts as a Lewis base in this reaction?	

8.

(i) A solution of tin(II) nitrate is added to a solution of silver nitrate.	
(ii) Name the oxidizing agent in this reaction.	

## Equation Practice Test

There are four sets of equations in this test. Answer all pages!!!

**For each of the following reactions, in part (i) write a BALANCED equation and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers.** Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction.

Example: (i) A strip of magnesium is added to a solution of silver nitrate.

(ii) What would you observe happening to the magnesium?

<b>Ex.</b>	(i.) $\text{Mg} + 2\text{Ag}^+ \rightarrow \text{Mg}^{2+} + 2\text{Ag}$
	(ii.) The Mg strip would become smaller and would become coated with solid silver.

### Set 1

- i. A small piece of sodium metal is added to distilled water.
- ii. Is this reaction endothermic or exothermic?

i.	
ii.	

- i. Solid ammonium carbonate is heated.
- ii. Is this a redox reaction?

i.	
ii.	

- i. A solution of potassium dichromate is added to an acidified solution of iron(II) chloride.
- ii. What color is the solution of potassium dichromate?

i.	
ii.	

### Set 2

- i. Excess sodium cyanide solution is added to a solution of silver nitrate.
- ii. What undesirable product would result if this solution was acidified?

i.	
ii.	

- i. A concentrated solution of hydrochloric acid is added to solid potassium permanganate.

- ii. What color changes, if any, would be observed in this reaction?

i.
ii.

- i. Phosphorus(V) oxide powder is sprinkled over distilled water.  
 ii. Estimate the pH of the resulting solution.

i.
ii.

### Set 3

- i. Sulfur trioxide gas is bubbled through a solution of sodium hydroxide.  
 ii. Is a precipitate formed in this reaction? If so, name it.

i.
ii.

- i. Ethanol is burned in oxygen.  
 ii. What is the oxidizing agent in this reaction? Justify your answer.

i.
ii.

- i. A strip of zinc is placed in a solution of nickel(II) nitrate.  
 ii. What color change, if any, would you observe in this reaction?

i.
ii.

### Set 4

- i. Solid calcium hydride is added to distilled water.  
 ii. Give two laboratory tests that would help to identify the product(s) of this reaction. Describe the results of these tests.

i.
ii.

- i. Chlorine gas is bubbled into a cold, dilute solution of potassium hydroxide.



ii. Give the name for this specific type of redox reaction.

i.

ii.

i. Solid aluminum hydroxide is added to a concentrated solution of potassium hydroxide.

ii. Name the product(s) of this reaction.

i.

ii.

**Practice AP Exam Questions***2010 Version A*

- (a) A 0.2 M potassium hydroxide solution is titrated with a 0.1 M nitric acid solution.
- Balanced equation:
  - What would be observed if the solution was titrated well past the equivalence point using bromthymol blue as the indicator? (Bromthymol blue is yellow in acidic solution and blue in basic solution.)
- 
- (b) Propane is burned completely in excess oxygen gas.
- Balanced equation:
  - When the products of the reaction are bubbled through distilled water, is the resulting solution neutral, acidic, or basic? Explain.
- 
- (c) A solution of hydrogen peroxide is heated, and a gas is produced.
- Balanced equation:
  - Identify the oxidation state of oxygen in hydrogen peroxide.
- 

*2010 Version B*

- (a) Solid copper(II) sulfate pentahydrate is gently heated.
- Balanced equation:
  - How many grams of water are present in 1.00 mol of copper(II) sulfate pentahydrate?
- 
- (b) Excess concentrated aqueous ammonia is added to a solution of nickel(II) nitrate, leading to the formation of a complex ion.
- Balanced equation:
  - Which of the reactants acts as a Lewis acid?
- 
- (c) Methylamine ( $\text{CH}_3\text{NH}_2$ ) is added to a solution of hydrochloric acid.
- Balanced equation:
  - Methylamine dissolves in water to form a solution. Indicate whether this solution is acidic, basic, or neutral.
- 

*2009 Version A*

- (a) A sample of solid iron(III) oxide is reduced completely with solid carbon.
- Balanced equation:
  - What is the oxidation number of carbon before the reaction, and what is the oxidation number of carbon after the reaction is complete?
- 
- (b) Equal volumes of equimolar solutions of ammonia and hydrochloric acid are combined.
- Balanced equation:
  - Indicate whether the resulting solution is acidic, basic, or neutral. Explain.
- 
- (c) Solid mercury(II) oxide decomposes as it is heated in an open test tube in a fume hood.
- Balanced equation:
  - After the reaction is complete, is the mass of the material in the test tube greater than, less than, or equal to the mass of the original sample? Explain.
-

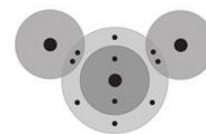
## AP Chemistry

### Chapters 4 & 11: Properties of Solutions

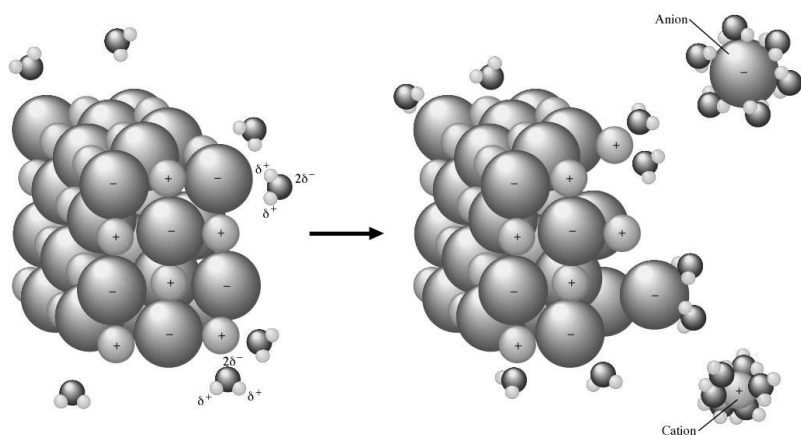
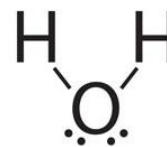
Many common chemical reactions occur in water, or aqueous solution. To understand how chemical species interact in solution, we must first understand water, the universal solvent.

#### 4.1 Water, the Common Solvent

- Water is an excellent solvent due to:
  - Its shape; water is a bent molecule.
  - Electrons aren't shared evenly (oxygen is more electronegative)
  - Electrons spend more time close to O than to H
  - This uneven distribution of charge makes water polar.
- Water is held together by covalent bonds



Water Molecule (H<sub>2</sub>O)



- When water surrounds an ionic crystal, the H end attracts the anion and the O end attracts the cation. This process is called hydration.
- Hydration causes salts to dissolve. H<sub>2</sub>O also dissolves polar covalent substances such as C<sub>2</sub>H<sub>5</sub>OH.
- H<sub>2</sub>O doesn't dissolve nonpolar covalent substances.
- The difference in a substance's ability to dissolve is due to its interaction with itself, and the solvent solution.

#### 4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes

- Review:
  - Solute-the substance that dissolves
  - Solvent-the substance that does the dissolving
  - Electrical conductivity-the ability of a solution to conduct an electrical current
  - Strong electrolyte-a highly ionized solution that easily conducts electrical current
  - Weak electrolyte-a solution with few ions that does not conduct a current very well
  - Nonelectrolyte- a solution made of a soluble compound that does not ionize and thus does not conduct an electrical current.
- Svante Arrhenius determined that the extent to which a solution can conduct an electrical current depends directly on the number of ions present.
  - A solute that ionizes completely conducts very well.
  - He said that the best conductors are:
    - Soluble salts (like sodium chloride or magnesium nitrate)
    - Strong acids like HCl(aq), HNO<sub>3</sub>(aq), H<sub>2</sub>SO<sub>4</sub>(aq)
    - strong bases that contain OH<sup>-</sup> (have a bitter taste, slippery feel and include NaOH and KOH)
  - Ex. Write an equation showing what happens when the salt sodium acetate dissolves in water.
- Arrhenius went on to describe weak electrolytes. He said they only ionize slightly and include weak acids and bases.
  - $\text{HC}_2\text{H}_3\text{O}_2 \rightarrow \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$   
99%                      1%
  - Ammonia (NH<sub>3</sub>) is a weak base.                       $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$
- Solubility- g/given volume solvent or moles/given volume solution

### 4.3 The Composition of Solutions

- In order to perform stoichiometric calculations with solutions, we must know the nature of the solution and the amounts of chemical present.
- Molarity (M) =  $\frac{\text{moles of solute}}{\text{liters of solution}}$
- Ex. Calculate the molarity of a solution made by dissolving 23.4g of sodium sulfate in enough water to form 125 mL of solution.
- Ex. How many grams of  $\text{Na}_2\text{SO}_4$  are required to make 350 mL of 0.50 M  $\text{Na}_2\text{SO}_4$ ?
- Ex. What volume of 1.000 M  $\text{KNO}_3$  must be diluted with water to prepare 500.0 mL of 0.250 M  $\text{KNO}_3$ ? Dilution problem ( $M_1V_1 = M_2V_2$ )
- A standard solution is one where concentration is accurately known.
  - Read procedure for using volumetric flasks and types of pipets. We will be using both in several labs this year.

### 11.1 Solution Composition

- Solutions can generally be described as dilute (very little solute per volume of solvent) or concentrated (a lot of solute per volume of solvent).
- Another way to describe a solution is by looking at the mass of the solute in terms of the mass of the entire solution, or mass percent.
- We can also examine the percent solute to solvent using the mole fraction of the solution, or  $\chi$ .
- Finally, we can look at the amount of solute in moles per amount of solvent in kg to find molality.

$$\text{Mass \%} = \left( \frac{\text{Mass solute}}{\text{Mass of solution}} \right) \times 100$$

$$\text{Mole Fraction } \chi_A = \frac{n_A}{n_A + n_B}$$

$$\text{Molality} = \frac{\text{moles solute}}{\text{Kg solvent}}$$

- Ex. A solution is made using 10.5g ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) in 1,200.0 g of water to make a final volume of 1210.5 ml. Find the molarity, molality, mass % and mole fraction of this solution.

### 11.2 The Energies of Solution Formation

- When a solution forms, it takes place in three distinct steps:
  - Expanding the solute- The solute particles must move away from one another. This may form ions or molecules. ( $\Delta H_1$ )
  - Expanding the solvent- The solvent must break any internal bonds so that it can surround and hydrate the solute. ( $\Delta H_2$ )
  - The solute and solvent begin to interact to form the solution. ( $\Delta H_3$ )
- The heat of solution ( $\Delta H_{\text{soln}}$ ) is equal to the sum of heat produced or consumed in the three steps.

- If the heat of solution is very positive, then energy must come into the system to make the solute dissolve, so the substance is insoluble.
- If the heat of solution is very negative or only slightly positive, then energy is leaving the system as the solute dissolves and the solute is soluble.
- The table below summarizes these interactions.

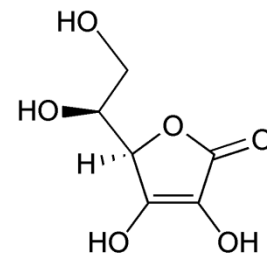
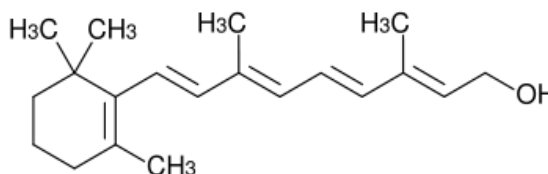
	$\Delta H_1$	$\Delta H_2$	$\Delta H_3$	$\Delta H_{soln}$	Outcome
Polar solute and solvent	Large positive value	Large positive value	Large negative value	Small positive value	Solution forms
Nonpolar solute, polar solvent	Small positive value	Large positive value	Small positive value	Large positive value	No solution forms
Nonpolar solute and solvent	Small positive value	Small positive value	Small positive value	Small positive value	Solution forms
Polar solute, nonpolar solvent	Large positive value	Small positive value	Small positive value	Large positive value	No solution forms

### 11.3 Factors Affecting Solubility

Although we will discuss many of these in other chapters, the following summarizes the reasons for the values of H in the chart above.

- Structural effects- the shape of solute molecules affects their polarity, and thus their ability to dissolve in solvents.

- Ex. Vitamin A vs. Vitamin C



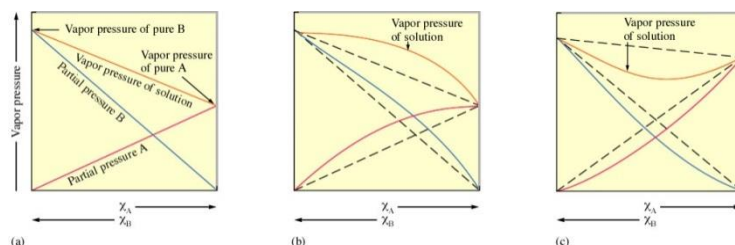
- Pressure effects- as pressure increases on the surface of a solvent, it may increase the rate of dissolution of a solid or liquid solute, but it does not affect the solubility of these solutes. If the solute is a gas, however, increasing pressure on the system will increase the solubility of the gas in the solvent.
- Temperature effects- again, as temperature increases in a solvent, the rate of dissolution will increase. Many solid and liquid solutes will become more soluble, but a few solid and liquid solutes, and almost all gaseous solutes, will become less soluble as temperature increases.

### 11.4 The Vapor Pressure of Solutions

When a solution is created, the properties of the solvent are often changed. For example, adding a solution of water and antifreeze will allow your car to keep running, whether the temperature outside is very high or very low.

- A volatile compound is one that vaporizes easily due to weak internal bonding (ex. Acetone)
- A nonvolatile compound has strong internal bonding and thus does not vaporize easily (ex. water)
- When a volatile solute is added to a solvent like water, the volatile compound will vaporize to some extent, adding to the amount of particles above the surface of the solution. In a closed container, this increases the vapor pressure.
- Nonvolatile solutes, however, will not change the amount of vaporized particles. These types of solutions are called ideal solutions.

- This behavior was described by Francois Raoult, in his law.  $P_{soln} = \chi_{solvent} P_{solvent}$
- You can see that the more solute is added, the smaller the value for the mole fraction of solvent, and thus the smaller the pressure.



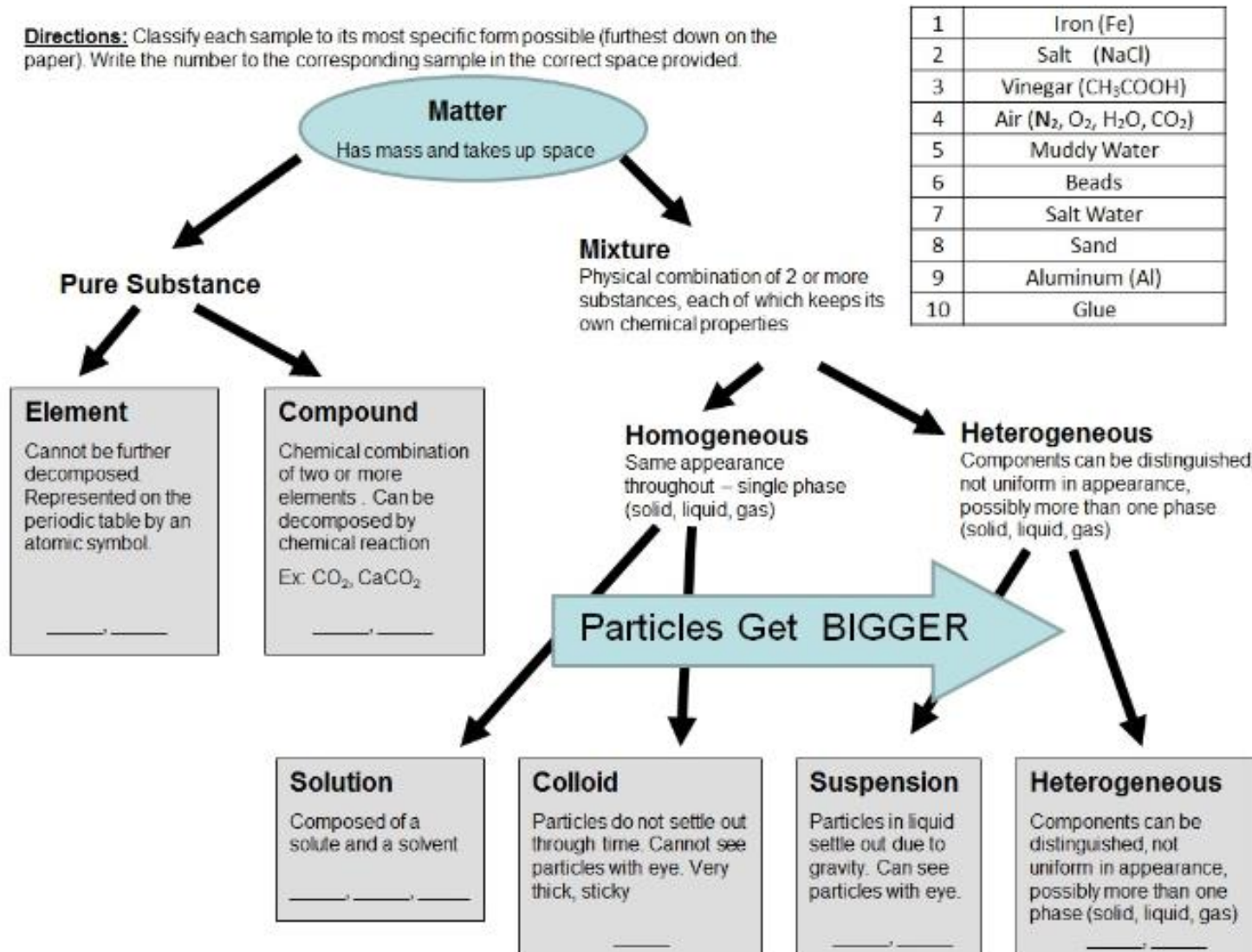
- If a solute is added that actually attracts water molecules, it may lower vapor pressure in a closed container by keeping water in a liquid state. Solutes like salt actually bind to water and keep it from vaporizing, therefore reducing the number of water vapor particles above the surface of the solution.

## 11.8 Colloids

Matter can be separated as shown in the diagram below.

- One of the ways we can classify solutions is to look at the particles they are made of.
  - Homogenous solutions are made up of relatively small particles that are permanently suspended in solvent.
  - Heterogeneous solutions are made up of relatively large particles that will settle out of solution over time.
  - Colloids fall into a special category because they are made up of intermediately sized particles that stay suspended due to interactions with the surrounding solvent.
    - The only way to distinguish between a colloid and a solution is to shine a light through them. Colloid particles are large enough that they bounce light, creating a “beam” you can see (called the Tyndall effect). Solutions will not show a “beam” effect.

**Directions:** Classify each sample to its most specific form possible (furthest down on the paper). Write the number to the corresponding sample in the correct space provided.



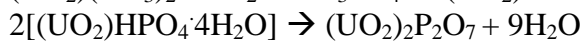
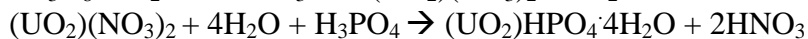
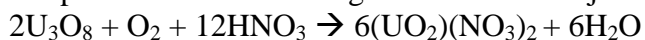
**AP Chemistry: Chapter 4 Worksheet**  
AP Chemistry Worksheet

- Complete and balance the reactions resulting from the mixing of the following aqueous solutions. Write a net ionic equation for each reaction. If no reaction occurs, write NR on the right side of the equation.
  - beryllium nitrate and sodium acetate
  - barium nitrate and sodium sulfate
  - lead(II) nitrate and potassium iodide
  - cesium hydroxide and hydrochloric acid
- Selenic acid ( $\text{H}_2\text{SeO}_4$ ) is a powerful oxidizing acid that dissolves gold through the reaction:  
$$2\text{Au(s)} + 6\text{H}_2\text{SeO}_4\text{(aq)} \rightarrow \text{Au}_2\text{(SeO}_4\text{)}_3\text{(aq)} + 3\text{H}_2\text{SeO}_3\text{(aq)} + 3\text{H}_2\text{O(l)}$$
Determine the oxidation numbers of the atoms in this equation. Which species is oxidized and which is reduced?
- Identify the oxidizing agent and the reducing agent in each of the following reactions:
  - $\text{Zn(s)} + 2\text{HCl} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$ , a simple way for preparing  $\text{H}_2$  gas in the laboratory
  - $2\text{H}_2\text{S(g)} + \text{SO}_2\text{(g)} \rightarrow 3\text{S(s)} + 2\text{H}_2\text{O(l)}$ , a reaction used to produce sulfur from hydrogen sulfide, the “sour gas” in natural gas.
  - $\text{B}_2\text{O}_3\text{(s)} + 3\text{Mg(s)} \rightarrow 2\text{B(s)} + 3\text{MgO(s)}$ , a preparation of elemental boron
- A 100.0 mL sample of 0.2516 M aqueous barium chloride was treated with an excess of sulfuric acid. The resulting barium sulfate precipitate was filtered, dried, and found to have a mass of 4.9852 g. Compute the percentage yield of barium sulfate in this process.

5. A chemist studying the properties of photographic emulsions needed to prepare 25.00 mL of 0.155M  $\text{AgNO}_3(\text{aq})$ . What mass of silver nitrate must be placed into a 25 mL volumetric flask and dissolved and diluted to the mark with water?
6. A 12.56 mL sample of 1.345 M  $\text{K}_2\text{SO}_4(\text{aq})$  is diluted to 250.0 mL. What is the concentration of  $\text{K}_2\text{SO}_4$  in the diluted solution?
7. The iron content in an ore can be determined by titrating a sample with a  $\text{KMnO}_4$  solution. The ore is dissolved in hydrochloric acid, forming iron(II) ions; the latter react with  $\text{MnO}_4^-$  in the following **unbalanced** equation:  
$$\text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
  
A sample of ore of mass 0.202 g needed 16.7 mL of 0.0108 M  $\text{KMnO}_4(\text{aq})$  to reach the stoichiometric point. What is the mass percentage of iron in the ore sample?
8. What volume of 0.0125 M HBr solution is required to titrate 125 mL of a 0.0100 M  $\text{Ca}(\text{OH})_2$  solution?

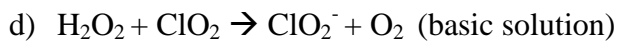
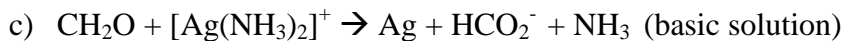
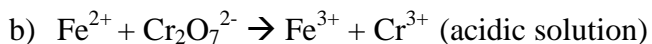
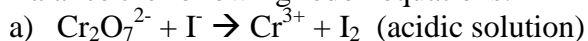


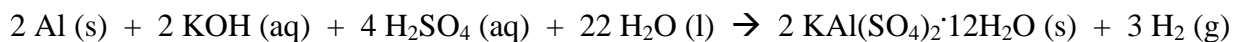
9. Uranium may be isolated from the mineral pitchblende, which contains  $\text{U}_3\text{O}_8$ . The pitchblende in a 6.235g sample of an ore containing uranium was subjected to the following sequence of reactions:



What is the percentage of  $\text{U}_3\text{O}_8$  in the ore by mass if 1.607 g of  $(\text{UO}_2)_2\text{P}_2\text{O}_7$  is isolated?

10. Balance the following redox equations:



**2005 AP<sup>®</sup> Chemistry Free Response Question #5 (Form B)**

5. In an experiment, a student synthesizes alum,  $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O (s)}$ , by reacting aluminum metal with potassium hydroxide and sulfuric acid, as represented in the balanced equation above.

a) In order to synthesize alum, the student must prepare a 5.0 M solution of sulfuric acid. Describe the procedure for preparing 50.0 mL of 5.0 M  $\text{H}_2\text{SO}_4$  using any of the chemicals and equipment listed below. Indicate specific amounts and equipment where appropriate.

- 10.0 M  $\text{H}_2\text{SO}_4$
- Distilled water
- 100 mL graduated cylinder
- 100 mL beaker
- 50.0 mL volumetric flask
- 50.0 mL buret
- 25.0 mL pipet
- 50 mL beaker

b) Calculate the minimum volume of 5.0 M  $\text{H}_2\text{SO}_4$  that the student must use to react completely with 2.7 g of aluminum metal.

c) As the reaction solution cools, alum crystals precipitate. The student filters the mixture and dries the crystals, then measures their mass.

a. If the student weighs the crystals before they are completely dry, would the calculated percent yield be greater than, less than, or equal to the actual percent yield? Explain.

b. Cooling the reaction solution in an ice bath improves the percent yield obtained. Explain.

d) The student heats crystals of pure alum,  $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O (s)}$ , in an open crucible to a constant mass. The mass of the sample after heating is less than the mass before heating. Explain.

## AP Chemistry: Chapter 5

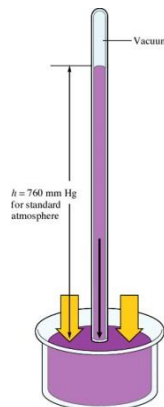
### Gases

We live in a solution of gases; nitrogen, oxygen and other gases surround and support us. In this chapter we will focus on the behavior of gases and the laws that govern that behavior.

#### 5.1 Pressure

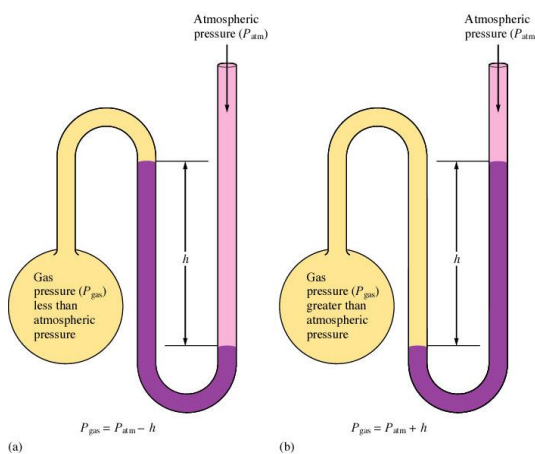
##### Properties of Gases

- Gases are compressible
- Gases uniformly fill any container
- Gases mix easily with other gases
- In 1643, Evangelista Torricelli invented the barometer, an instrument for measuring atmospheric pressure. Atmospheric pressure results from gravity's pull on air masses.
  - dish filled with mercury with a closed tube
  - outside pressure causes mercury level to rise and fall
- Manometer- instrument used for measuring pressure
  - Gas pressure less than atmospheric pressure
    - gas pressure = atm pressure – h
  - Gas pressure greater than atmospheric pressure
    - gas pressure = atm pressure + h



##### Units of Pressure

- mm Hg is also called torr
  - 760mm Hg = 760 torr = 1 atm
- SI unit of pressure is N/m<sup>2</sup> or Pascal (Pa)
  - 1 atm = 101,325 Pa or 101.325 kPa



#### 5.2 The Gas Laws

##### 1. Boyle's Law

- Robert Boyle performed the first quantitative study of gases in the 1600s
- He found that pressure and volume are inversely related.
- Ideal gas- gas that obeys Boyle's law

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \quad P_1 V_1 = P_2 V_2$$

##### 2. Charles' Law

- Jacques Charles, a French scientist, determined in the late 1700's that the volume of a gas is directly proportional to Kelvin temperature
- The temperature must be in Kelvin!
- The volume of a gas at absolute zero is zero.

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

##### 3. Avogadro's Law

- Amadeo Avogadro determined in 1811 that equal volumes of gases at the same temperature and pressure contain the same # of particles
- for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas

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

##### 4. Combined Gas Law

- Combines all the gas laws

- “Peas and Vegetables on the Table”

### 5.3 The Ideal Gas Law

- The Ideal Gas Law combined Boyle’s, Charles’, and Avogadro’s laws into  $PV = nRT$ .
  - $R = 0.08206 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$  (proportionality constant)
  - $n$  = the number of moles of gas present
- Most gases behave ideally at pressures less than 1 atm.
- We can use the ideal gas law for all gas law problems by putting changing variables on one side and the constant on the other.

Ex. If P&V change w/ others constant:

$$PV = nRT$$

$$P_1V_1 = nRT \text{ and } P_2V_2 = nRT \text{ so } P_1V_1 = P_2V_2$$

If V&T change with others constant:

$$PV = nRT$$

$$\frac{V_1}{T_1} = \frac{nR}{P} \text{ and } \frac{V_2}{T_2} = \frac{nR}{P} \text{ so } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Ex. The gas pressure inside an aerosol can is 1.5 atm at 25°C. Assuming that the gas is ideal, what would the pressure be if the can were heated to 450°C?

Ex. A quantity of helium gas occupies a volume of 16.5 L At 78°C and 45.6 atm. What is the volume at STP?

Ex. Many gases are shipped in high-pressure containers. If a steel tank whose volume is 50.0L contains O<sub>2</sub> gas at a total pressure of 1500 kPa at 23°C, what mass of oxygen does it contain?

### 5.4 Gas Stoichiometry

- Molar Volume = 22.42 L of an ideal gas at STP (Some gases behave more ideally than others.)
  - STP Conditions = 0°C and 1 atmosphere of pressure

Ex. CaH<sub>2</sub> reacts with H<sub>2</sub>O to produce H<sub>2</sub> gas.  $\text{CaH}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$   
 This rxn is used to generate H<sub>2</sub> to inflate life rafts and for similar uses where a simple, compact means of H<sub>2</sub> generation is desired. Assuming complete rxn with water, how many grams of CaH<sub>2</sub> are required to fill a balloon to a total pressure of 1.12 atm at 15°C if its volume is 5.50 L?

Ex. How many liters of  $N_2$  is required to produce 115 g of  $NH_3$  at STP?

- Molecular Weight and Density of a Gas

- The molar mass of a gas can be determined from the measured density of a gas

$$n = \frac{\text{mass (g)}}{\text{MW (g/mol)}} \quad \text{so } P = \frac{nRT}{V(\text{MW})}$$

$$\text{Since } m/v = \text{density (g/L), } P = \frac{dRT}{\text{MW}}$$



Ex. Calculate the molecular weight of a gas if 0.608g occupies 750 mL at 385 mm Hg and 35°C.

### 5.5 Dalton's Law of Partial Pressures

- For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.

$$P_{\text{tot}} = P_1 + P_2 + P_3 + \dots \quad \text{OR} \quad P_{\text{tot}} = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \dots = n_{\text{total}} \left( \frac{RT}{V} \right)$$

(It doesn't matter what the gas is.)

- Mole Fraction- the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

- $\chi$  is used to symbolize mole fraction.

$$\chi_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$

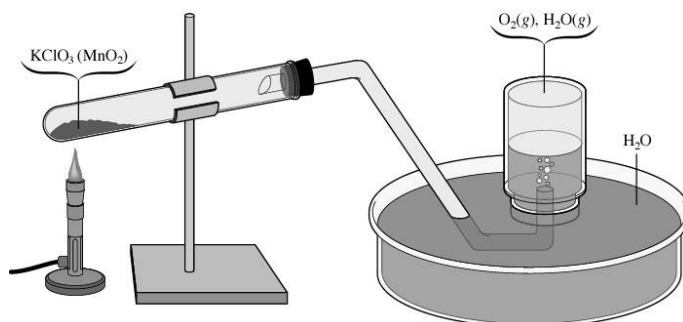
- The partial pressure of a particular component of a gaseous mixture is the mole fraction of that component times the total pressure.

- $P_1 = \chi_1 \times P_{\text{total}}$

- When gases are collected over water, we must adjust for the pressure of the water vapor.

- $P_{H_2O} + P_{\text{gas}} = P_{\text{total}}$

Ex. If a 0.20 L sample of  $O_2$  at 0°C and 1.0 atm pressure and a 0.10 L sample of  $N_2$  at 0°C and 2.0 atm pressure are both placed in a 0.40 L container at 0°C, what is the total pressure in the container?



## 5.6 Kinetic Molecular Theory of Gases

- The Kinetic Molecular Theory of Gases is a simple model that attempts to explain properties of an ideal gas. It states that gases consist of particles which have the following properties:
  1. The particles are so small compared to the distances between them that the volume of the individual particles can be assumed to be negligible (zero).
  2. The particles are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.
  3. The particles are assumed to exert no forces on each other; they are assumed neither to attract nor to repel each other.
  4. The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.
- Real gases don't conform to these assumptions!
- Kelvin temperature is an index of the random motions of the particles of a gas, with higher temperatures meaning greater motion.
  - $KE_{\text{avg}} = 3/2 RT$ 
    - $R = 8.3148 \text{ J/K mol}$
    - Units are J/mol
- Root mean square velocity
  - $\overline{u^2}$  = is the average of the squares of the particle's velocities
  - $\sqrt{\overline{u^2}}$  = root mean square velocity =  $u_{\text{rms}}$
  - At any given temperature, lighter molecules have higher root mean square velocities.

“You are a Mess”

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

Where  $M$  = mass of a mole of gas in kg  
The units of  $u_{\text{rms}}$  are m/s.

Ex. Calculate the root mean square velocity in m/s of  $O_2$  molecules at  $27^\circ\text{C}$ .

Calculate the avg. KE of the same molecules.

- Real gases have many collisions between particles. The average distance a particle travels between collisions in a particular gas sample is called the mean free path. These collisions produce a huge variation in velocities. As temperature increases, the range of velocities is greater.

## 5.7 Effusion and Diffusion

- Diffusion- the mixing of gases
- Effusion- the passage of a gas through a tiny orifice into an evacuated chamber
- Graham's Law of Effusion- The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles.
  - $\frac{\text{Rate of Effusion for Gas 1}}{\text{Rate of Effusion for Gas 2}} = \frac{\sqrt{MW_2}}{\sqrt{MW_1}}$
  - $MW_1$  and  $MW_2$  represent the molar masses of the gases.
  - Diffusion rates can be calculated the same way
  - Lighter gases effuse & diffuse faster than heavier gases

## 5.8 Real Gases

- No gas exactly follows the ideal gas law.
- A real gas exhibits behavior closest to ideal behavior at low pressures and high temperatures.
  - At high temperatures, there is less interaction between particles because they are moving too fast.
  - At high concentrations, gases have much greater attractive forces between particles. This causes particles to hit the walls of the container with less force (producing less pressure than expected).
  - At high pressure (small volume), the volume of the particles becomes significant, so that the volume available to the gas is significantly less than the container volume.
  - Attractive forces are greatest for large, complex molecules.
- We can use the Van der Waals equation to adjust for departures from ideal conditions.
  - $PV = nRT$  becomes:  $[P_{\text{obs}} + a(n/V)^2]V - nb = nRT$ 
    - $a$  = correction for pressure that takes into account the intermolecular attractions between molecules. It increases with an increase in MW and an increase in molecular complexity.
    - $b$  = correction for the finite volume of the gas molecules. It is a measure of the actual volume occupied by the gas molecules. It increases with an increase in mass of the molecule or in the complexity of the structure.
    - We can look up values of  $a$  &  $b$  for common gases in Table 5.3.

## 5.10 Chemistry in the Atmosphere

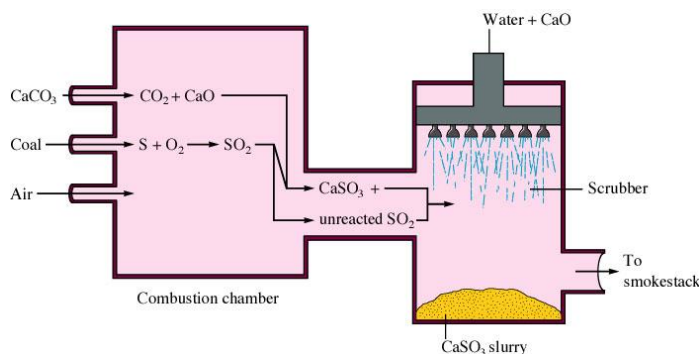
- The major gases in the atmosphere are  $N_2$  and  $O_2$ 
  - Other gases include Ar,  $CO_2$ , Ne, He,  $CH_4$ , Kr,  $H_2$ , NO and Xe.
  - The heaviest gases are concentrated closest to the surface while lighter molecules tend to drift upward toward space.
- The lower layer of the atmosphere is the troposphere.
  - The troposphere is strongly affected by human activities. Most air pollution centers around NO, Nitric oxide, which is emitted into the air from exhaust of engines.
  - Ozone reacts with unburned hydrocarbons in polluted air to produce irritating chemicals. This process is called photochemical smog.
 
$$NO + O_2 \rightarrow NO_2$$

$$NO_2(g) \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3$$
  - The ozone produced in the troposphere is converted to nitric acid vapor, which can affect human respiratory systems.
- The upper layer contains the ozone layer. The ozone layer is affected by incoming radiation from the sun and serves to block these particles from the lower layers.
- Another source of atmospheric pollution comes from the burning of coal to create energy.
  - The burning of coal releases sulfur dioxide which eventually produces sulfuric acid or acid rain.
 
$$S \text{ (from coal)} + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow SO_3$$

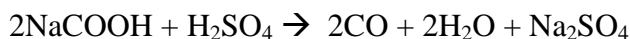
$$SO_3 + H_2O \rightarrow H_2SO_4$$
- Some of the harmful sulfur can be removed through a process called “scrubbing”.



**AP Chemistry: Gas Law Worksheet**

1. A 2.000 gram sample containing graphite (carbon) and an inert substance was burned in oxygen and produced a mixture of carbon dioxide and carbon monoxide in the mole ratio 2.00:1.00. The volume of oxygen used was 747.0 milliliters at 1092 K and 12.00 atmospheres pressure. Calculate the percentage by weight of graphite in the original mixture.

2. A 0.964 gram sample of a mixture of sodium formate and sodium chloride is analyzed by adding sulfuric acid. The equation for the reaction of sodium formate with sulfuric acid is shown below. The carbon monoxide formed measures 242 milliliters when collected over water at 752 torr and 22.0°C. Calculate the percentage of sodium formate in the original mixture. (partial pressure of H<sub>2</sub>O = 20.0 torr)



3. A 5.00 gram sample of a dry mixture of potassium hydroxide, potassium carbonate, and potassium chloride is reacted with 0.100 liter of 2.0 molar HCl solution.

a) A 249 milliliter sample of dry CO<sub>2</sub> gas, measured at 22°C and 740 torr, is obtained from the reaction. What is the percentage of potassium carbonate in the mixture?

b) The excess HCl is found by titration to be chemically equivalent to 86.6 milliliters of 1.50 molar NaOH. Calculate the percentages of potassium hydroxide and of potassium chloride in the original mixture.



4. A 6.19 gram sample of  $\text{PCl}_5$  is placed in an evacuated 2.00 liter flask and is completely vaporized at  $252^\circ\text{C}$ .

a) Calculate the pressure in the flask if no chemical reaction were to occur.

b) Actually at  $252^\circ\text{C}$  the  $\text{PCl}_5$  is partially dissociated according to the following equation:



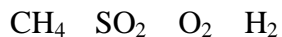
The observed pressure is found to be 1.00 atmospheres. In view of this observation, calculate the partial pressure of  $\text{PCl}_5$  and  $\text{PCl}_3$  in the flask at  $252^\circ\text{C}$ .

5. When the molecular weight of a volatile liquid is calculated from the weight, volume, temperature, and pressure of a sample of that liquid when vaporized, the assumption is usually made that the gas behaves ideally. In fact at a temperature not far above the boiling point of the liquid, the gas is not ideal. Explain how this would affect the results of the molecular weight determination.

6. Discuss the following.

a) From the standpoint of the kinetic molecular theory, discuss briefly the properties of gas molecules that cause deviations from ideal behavior.

b) At  $25^\circ\text{C}$  and 1 atmosphere pressure, which of the following gases shows the greatest deviation from ideal behavior? Give two reasons for your choice.



c) Real gases approach ideality at low pressure, high temperature, or both. Explain these observations.

7. Three volatile compounds, X, Y, and Z each contain element Q. The percent by weight of element Q in each compound was determined. Some of the data obtained are given below.

<i>Compound</i>	<i>Percent by Weight of Element Q</i>	<i>Molecular Weight</i>
X	64.8 %	?
Y	73.0 %	104.
Z	59.3 %	64.0

a) The vapor density of compound X at 27°C and 750 mm Hg was determined to be 3.53 grams per liter. Calculate the molecular weight of compound X.

b) Determine the mass of element Q contained in 1.00 mole of each of the three compounds.

c) Calculate the most probable value of the atomic weight of element Q.

d) Compound Z contains carbon, hydrogen, and element Q. When 1.00 gram of compound Z is oxidized and all of the carbon and hydrogen are converted to oxides, 1.37 grams of CO<sub>2</sub> and 0.281 gram of water are produced. Determine the most probable molecular formula of compound Z.

## AP Chemistry: Chapter 7

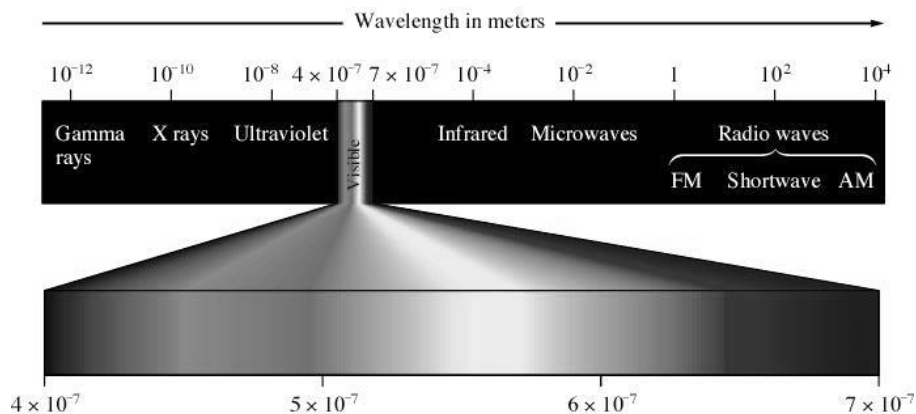
### Atomic Structure and Periodicity

In this unit, we will ask ourselves the same question that scientists asked once they believed in the atom; “What is the nature of the atom?” We will look not only at how the atom is structured, but also how this relates to the arrangement of the periodic table.

**7.1 Electromagnetic radiation-** radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum.

Waves have three Primary Characteristics:

- Wavelength ( $\lambda$ ) -distance between two consecutive peaks or troughs in a wave.
- Frequency ( $\nu$ ) -number of waves per second that pass a given point in space.
- Speed – all EM radiation travels at the speed of light in a vacuum
  - As the wavelength decreases, frequency increases.
  - Ex. The yellow light given off by a sodium lamp has a wavelength of 589 nm. What is the frequency of the radiation?



$$\lambda \nu = c$$

$\lambda$  measured in m  
 $\nu$  measured in cycles/s  
 (written as 1/s) or Hz  
 $c$  speed of light  $3.00 \times 10^8$  m/s

### 7.2 The Nature of Matter

Until the early 1900's, it was believed that matter and energy were very different. Matter was composed of particles and energy was composed of waves. In 1901, Max Planck found that when solids were heated strongly, they absorbed and emitted energy. He determined that energy can be gained or lost only in integer multiples of  $h\nu$ .

- $h$  is Planck's constant =  $6.626 \times 10^{-34}$  J's
- This showed that energy was quantized or made of “packets”.
  - Ex. Calculate the smallest increment of energy (the quantum of energy) that an object can absorb from yellow light whose wavelength is 589 nm.

$$\Delta E = h\nu$$

$\nu$  measured in  $s^{-1}$  or Hz

Einstein studied the photoelectric effect whereby light of sufficient frequency shining on a metal causes current to flow (electrons to be expelled). The amplitude of the radiation was not important, the frequency was. This told him that the light must be in particles, each having a given energy.

Einstein proposed that electromagnetic radiation can be viewed as a stream of particles called photons.

- Einstein's special theory of relativity:  $E = mc^2$
- Matter and energy are different forms of the same special entity.
- Energy of a photon:  $E = h\nu$

$$\lambda = h/mv$$

$m$  = mass in kg  
 $v$  = velocity in m/s  
 $h$  = Planck's constant =  $6.626 \times 10^{-34}$  J's

We can combine this equation with the equation for waves to determine the mass of a photon. This is called the DeBroglie equation.

DeBroglie's equation is used to find the wavelength of a particle. It was determined that matter behaves as though it were moving in a wave.

$$E_{\text{photon}} = hc/\lambda$$

$\lambda$  measured in m  
 $c$  speed of light  $3.00 \times 10^8$  m/s  
 $h$  = Planck's constant =  $6.626 \times 10^{-34}$  J's

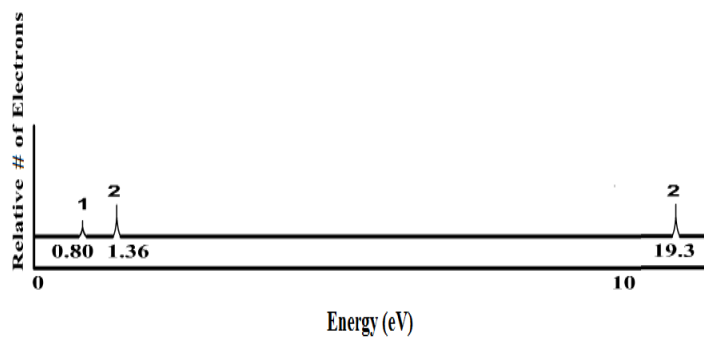
This is important in small objects such as electrons but is negligible in larger objects such as baseballs. Since mass is in the denominator of the equation, the larger the mass, the shorter the wavelength. Heavy objects have *very* short wavelengths.

Einstein's photoelectric effect is now being utilized in another manner for chemists. This is called photoelectron spectroscopy, or PES.

- PES uses the energy from electrons emitted via the photoelectric effect to gain information about the electronic structure of a substance.
- When light of a certain frequency is shone onto a sample, there are a limited number of electrons emitted. The energy of these emissions reflect the energy (and energy levels) in an atom
  - When the kinetic energy of the emitted electron is subtracted from the energy of the light photons, the resulting value is the ionization energy of that particular electron.
- The photons used for photoelectron spectroscopy range from ultraviolet light to X-rays. Analysis of photoelectron spectra for a single element can give us information about the shells and subshells of electrons and the number of electrons in each.

The diagram to the right is a PES image for the element boron.

- The x-axis has units of ionization energy or binding energy of the electron.
- Electrons closer to the nucleus have greater Coulombic attraction and thus have a higher ionization energy.
- The energy scale at the bottom may change and units vary, so all that is needed is interpretation of the diagram, not details.
- The height of the peak indicates the number of electrons in the atom having that energy (the number of electrons in a sublevel).



### 7.3 The Atomic Spectrum

When EM radiation is separated into its single wavelength components a spectrum is produced. White light produces a continuous spectrum (rainbow) when passed through a prism.

- Some emitters of light radiate only certain colors and wavelengths. This produces a **bright line spectrum**.
- When various gases at low pressures are put in tubes and a high voltage is applied, they glow in various colors. If this light is passed through a prism, a series of lines of color is produced. This series identifies the element.

### 7.4 The Bohr Model

- Niels Bohr found that the absorptions and emissions of light by hydrogen atoms correspond to energy changes of electrons within the atom. Bohr proposed that the electron in hydrogen travels only in certain allowed orbits.
- Bohr calculated the energy differences between these orbits and predicted the wavelengths at which lines would be found.
- Bohr determined that when an electron moved from an outer orbital to an inner orbital, or to its ground state (lowest energy level of an electron), it would release a predictable amount of energy.
- His research worked great with the hydrogen atom but did not work correctly for polyelectronic atoms.
  - Polyelectronic atoms- atoms with more than one electron (anything beyond hydrogen)
- Bohr developed an equation that could be used to find the change in energy of a hydrogen electron as it goes from one energy level to another:

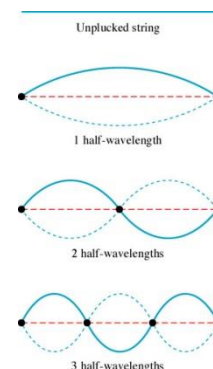
$\Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$  \* $2.178 \times 10^{-18}$  is called the Rydberg constant.

- Example: Calculate the wavelength of light emitted when an electron falls from  $n=4$  to  $n=2$  in the hydrogen atom.

## 7.5 The Quantum Mechanical Model of the Atom

By the mid-1920's de Broglie realized that the Bohr model was not able to be used with other atoms. Thus he, Erwin Schrödinger and Werner Heisenberg began work on a wave mechanical model of the atom.

- The electron is visualized as a standing wave (opposite of a traveling wave- like a vibrating guitar string instead of an ocean wave).
- This model assumes that the electrons must exist in half-wave increments, thus there are finite positions for each electron.
- A specific wave function  $-\psi$ -(function of the x, y and z coordinates of the electron's location in space) became known as an orbital. The orbital represents the mathematically calculated area of probability in which an electron can expect to be found at least 90% of the time.
- Warner von Heisenberg put forth in his uncertainty principle that there is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time. This is negligible with macroscopic objects such as a baseball but very important with an electron.



## 7.6 Quantum Numbers

- Defines the "address" of an electron.

Principle Quantum Number (n) *Energy level or "shell" *as n increases, energy increases	Azimuthal Quantum Number (l) *shape of the orbital *s = sphere (2 e <sup>-</sup> ), p = peanut (6 e <sup>-</sup> ), d = donut or daisy (10 e <sup>-</sup> ), f = fancy (14 e <sup>-</sup> )	Magnetic Quantum Number (m <sub>l</sub> ) *orientation of orbitals in space (x, y, or z)	Spin Quantum Number (m <sub>s</sub> ) *direction of electron spin (clockwise or counterclockwise)
1	0 = s	0	+1/2 or -1/2
2	0 = s, 1 = p	-1, 0, 1	+1/2 or -1/2
3	0 = s, 1 = p, 2 = d	-2, -1, 0, 1, 2	+1/2 or -1/2
4	0 = s, 1 = p, 2 = d, 3 = f	-3, -2, -1, 0, 1, 2, 3	+1/2 or -1/2
5	0 = s, 1 = p, 2 = d, 3 = f	-3, -2, -1, 0, 1, 2, 3	+1/2 or -1/2

Practice: Determine if these quantum numbers are possible for the outer electrons in these elements.

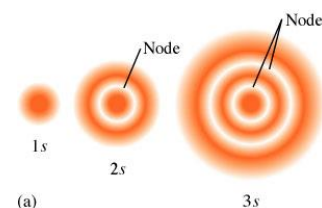
Vanadium (4, 0, 0, +1/2)

Sulfur (3, 1, 2, +1/2)

Cerium (5, 0, 0, -1/2)

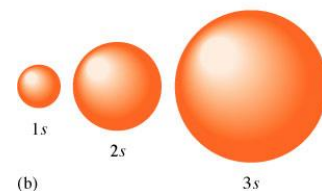
## 7.7 Orbital Shapes and Energies

- Orbitals have regions of high electron probability and regions of zero electron probability. Areas of zero electron probability are called nodes.
- Degenerate -orbitals that are equal in energy. Ex. All three 2 p orbitals are degenerate.



## 7.8 Electron Spin and the Pauli Exclusion Principle

- In a given atom, no two electrons can have the same set of four quantum numbers. An orbital can only hold two electrons, and they must have opposite spins (creating two magnetic moments).



## 7.9 Polyelectronic Atoms

- When an atom has more than one electron, these electrons tend to repel each other. The effect of the electron repulsions is to reduce the nuclear charge (pull of the nucleus on the electron).
- The apparent nuclear charge or effective nuclear charge,  $Z_{\text{eff}}$ , is the charge felt by a particular electron. Electrons in inner shells shield the electrons in higher shells quite effectively from the nuclear charge (shielding effect). Electrons in the same shell are much less effective at shielding each other.
  - $Z_{\text{eff}} = Z_{\text{actual}} - \text{effect of } e^- \text{ repulsions}$
  - Each electron in an atom has its own value of  $Z_{\text{eff}}$  which can be calculated from the experimental energy required to remove that electron from the atom.
  - Shielding- the effect by which the other electrons screen or shield a given electron from some of the nuclear charge.
    - Ex.  $Z_{\text{eff}}$  for the 3s electron in Na is 1.84, the  $Z_{\text{eff}}$  for a 1s electron is 10.3.
- Penetration effect- the effect whereby a valence electron penetrates the core electrons, thus reducing the shielding effect and increasing  $Z_{\text{eff}}$ .
  - A 3s electron has a small but significant chance of being close to the nucleus.
  - Most penetration  $ns > np > nd > nf$  least penetration
- Electrons fill orbitals in order of increasing energy. Because of the penetration effect, electrons fill (n+1)s before nd ((n+1)s has lower energy).
- Electrons sharing an orbital do not shield each other as well as core electrons shield outer electrons.
  - $Z_{\text{eff}}$  increases for a 1s electron going from H to He but decreases from He to Li because 1s electrons are effective in shielding the 2s electron.
  - $Z_{\text{eff}}$  increases from Li to Be
  - $Z_{\text{eff}}$  decreases from Be to B
  - $Z_{\text{eff}}$  increases from B to N
  - $Z_{\text{eff}}$  decreases from N to O because one 2p orbital is doubly occupied
  - $Z_{\text{eff}}$  increases from O to Ne

## 7.10 The History of the Periodic Table

- Originally, four elements were suggested by the Greeks; earth, air, fire and water.
- Mendeleev, a Russian chemist, was the first to organize elements by their atomic mass and to organize them by their physical characteristics.
- Moseley later organized the periodic table by atomic number instead of mass.

## 7.11 The Aufbau Principle and the Periodic Table

Aufbau principle- As protons are added one by one to the nucleus, electrons enter orbitals of lowest energy first.

- In its ground state, atoms have electrons in the lowest energy orbitals. The order that the orbitals fill is: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d

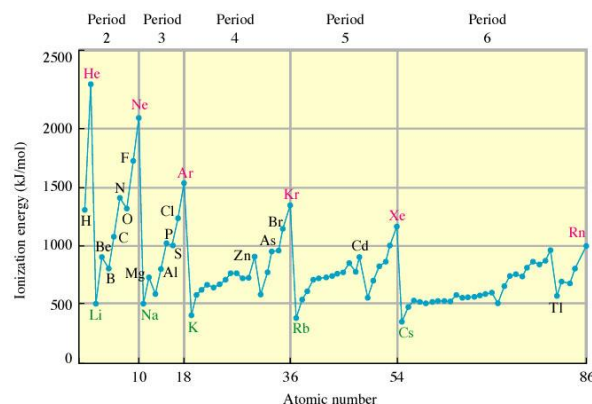
Hund's rule- All orbitals in a sublevel must be half-filled with electrons having parallel spins before any may be completely filled.

- Valence electrons- electrons in the outermost principle quantum number
- Core electrons- inner electrons

Write the electron configuration for the following:

Mn \_\_\_\_\_  
 Sn \_\_\_\_\_  
 Cl<sup>-</sup> \_\_\_\_\_

- Exceptions to Aufbau principle: Cu and Cr are two



elements that have exceptional electron configurations. Cu has a configuration that ends in  $4s^1 3d^{10}$  instead of  $4s^2 3d^9$ . Cr is  $4s^1 3d^5$  instead of  $4s^2 3d^4$ . This gives half-filled sublevels. It is more stable because of decreased electron repulsion.

## 7.12 Periodic Trends in Atomic Properties

Ionization energy (IE)- energy required to remove an electron from a gaseous atom or ion.

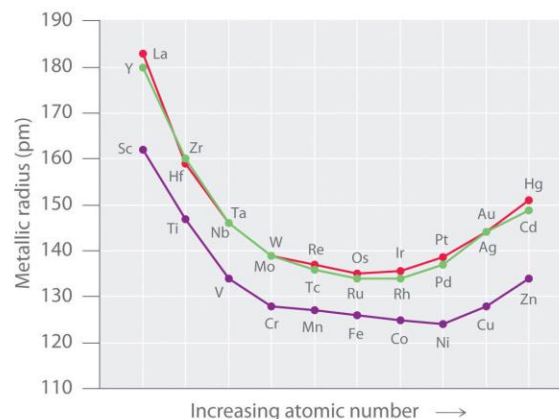
- $X(g) \rightarrow X^+(g) + e^-$
- A measure of how much work it is to remove an electron or how tightly the electron is held by the nucleus.
- Units are usually kJ/mol
- Ionization Energy depends mainly on two factors:
  - The effective nuclear charge
  - The average distance of the electron from the nucleus
- Ionization energy takes a large jump going from a valence electron to a core electron. The second ionization energy of sodium is much higher than the first. The third ionization energy of magnesium is much higher than that of the first and second electron. Core electrons are much more tightly held than valence electrons.
- The first ionization energy generally increases going from left to right across a period (very similar to  $Z_{\text{eff}}$ ). It decreases going down a group because electrons being removed are farther from the nucleus.
- Exceptions to these general trends occur at group 3 (shielding of p electron by s electrons) and group 6 (paired electron repulsion).
- Atoms with a low  $IE_1$  tend to form cations during reactions, whereas those with a high  $IE_1$  (except noble gases) tend to form anions.
- Metals have low IE. Nonmetals have high IE and very negative EA. Density generally increases going down the periodic table because the atomic number increases faster than the atomic size.

Electron Affinity (EA)- the energy associated with the addition of an electron to a gaseous atom

- If the addition is exothermic, EA is negative. The more negative, the greater the energy released.
- In going down a group, EA generally becomes more positive (less energy released) because the electron is farther from the nucleus. There are many exceptions. EA generally becomes more negative going across a period (again, many exceptions)

Atomic Radius- obtained by measuring the distances between atoms in chemical compounds.

- Decreases going from left to right across a period because  $Z_{\text{eff}}$  increases from left to right.
- Increases going down a group because of larger orbitals.  $Z_{\text{eff}}$  stays about the same because of shielding.
- Transition Metal Size and Lanthanide Contractions
  - The variation in size as we go across a row of transition metals is much less than among the representative elements. This is because electrons are being added to an inner shell as the nuclear charge gets larger. The inner shell electrons are almost completely effective at shielding the outer shell from the nuclear charge, so the outer electrons experience only a small, gradual increase in  $Z_{\text{eff}}$ . Therefore, only small size decreases occur.
  - A similar phenomenon occurs among the inner transition metals (Ex. lanthanides) The lanthanides fall between La and Hf, La last fills the  $5d^1$  electron, Ce ends in  $5d^1 4f^1$ . In this 6th period we have a much larger decrease in size occurring



between La and Hf because of the intervening lanthanide elements. This additional decrease in size is known as the **lanthanide contraction**. It causes Hf to be the same size as Zr, even though Hf is below Zr.

- All of the rest of the transition elements in the 6th period are nearly the same size as the elements above them in the fifth period. This causes the 6th period transition metals to be extremely dense. This even influences lead and bismuth beyond the transition metals.

IA												VIII A					
H 1													He 2				
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
21	19											Ga 29	Ge 30	As 31	Se 32	Br 33	Kr 34
K 19	Ca 20											In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
23	21											Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Rb 37	Sr 38																
25	23																
Cs 55	Ba 56																
27	25																
Fr 87	Ra 88																

## AP Chemistry: Atomic Theory and Periodicity Worksheet

- Write the ground state electron configuration for an arsenic atom, showing the number of electrons in each subshell.
  - Give one permissible set of four quantum numbers for each of the outermost electrons in a single As atom when it is in its ground state.
  - Explain how the electron configuration of the arsenic atom in the ground state is consistent with the existence of the following known compounds:  $\text{Na}_3\text{As}$ ,  $\text{AsCl}_3$ , and  $\text{AsF}_5$ .
- Use the details of modern atomic theory to explain each of the following experimental observations.
  - Within a family such as the alkali metals, the ionic radius increases as the atomic number increases.



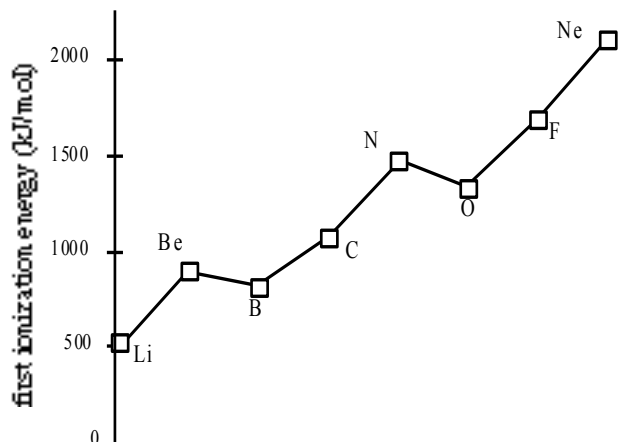
(b) The radius of the chlorine atom is smaller than the radius of the chloride ion.

(c) The first ionization energy of aluminum is lower than the first ionization energy of magnesium.

(d) For magnesium, the difference between the second and third ionization energies is much larger than the difference between the first and second ionization energies.

3. The diagram shows the first ionization energies for the elements from Li to Ne. Briefly explain each of the following in terms of atomic structure.

(a) In general, there is an increase in the first ionization energy from Li to Ne.



(b) The first ionization energy of B is lower than that of Be.

(c) The first ionization energy of O is lower than that of N.

(d) Predict how the first ionization energy of Na compares to those of Li and of Ne. Explain.

4. Account for each of the following in terms of principles of atom structure, including the number, properties, and arrangements of subatomic particles.

- (a) The second ionization energy of sodium is about three times greater than the second ionization energy of magnesium.
- (b) The difference between the atomic radii of Na and K is relatively large compared to the difference between the atomic radii of Rb and Cs.

5. Using principles of atomic and molecular structure and the information in the table below, answer the following questions about atomic fluorine, oxygen, and xenon, as well as some of their compounds.

Atom	First Ionization Energy (kJ mol <sup>-1</sup> )
F	1,681.0
O	1,313.9
Xe	?

- (a) Write the equation for the ionization of atomic fluorine that requires 1,681.0 kJ mol<sup>-1</sup>
- (b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss both atoms in your response.)
- (c) Predict whether the first ionization energy of atomic xenon is greater than, less than, or equal to the first ionization energy of atomic fluorine. Justify your prediction.

## AP Chemistry: Chapter 7 Practice Test

## Multiple Choice (3 pts each):

1. A local radio station has a frequency of 92.1 megahertz (MHz). What is the wavelength of this station in centimeters?  
A. 326 cm B.  $2.76 \times 10^{18}$  cm C. 0.307 cm D. 0.00307 cm
2. Which of the following has the longest wavelength?  
A. blue light B. red light C. yellow light D. green light
3. If the frequency of ultraviolet light is  $5.0 \times 10^{13}$  Hz, what is the energy of one quantum of this radiation?  
A.  $3.3 \times 10^{48}$  J B.  $5.7 \times 10^{-6}$  J C.  $3.3 \times 10^{-20}$  J D.  $4.0 \times 10^{-39}$  J
4. Which of the following electronic transitions in a hydrogen atom would have the highest energy?  
A.  $n = 4$  to  $n = 1$  B.  $n = 4$  to  $n = 2$  C.  $n = 2$  to  $n = 1$  D.  $n = 4$  to  $n = 3$
5. When  $n = 3$ , which of the following is a possible value for  $l$ ?  
A. -1 B. 0 C. 3 D. 6
6. When  $l = 2$ , what set of orbitals is designated?  
A. p B. d C. f D. g
7. Which of the following is NOT a valid set of quantum numbers?  
A.  $n = 4, l = 1$ , and  $m_l = -1$  C.  $n = 2, l = 2$ , and  $m_l = +1$   
B.  $n = 6, l = 5$ , and  $m_l = 0$  D.  $n = 3, l = 2$ , and  $m_l = -2$
8. What element has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ ?  
A. Zn B. Ge C. Ca D. Ni
9. Which of the following best describes the variation of atomic radii of the elements with respect to their position on the periodic table?  
A. increases across a period, increases down a group  
B. increases across a period, decreases down a group  
C. decreases across a period, increases down a group.  
D. decreases across a period, decreases down a group.
10. The energy needed to remove an electron from an atom in the gas phase is called \_\_\_\_\_.  
A. electron affinity B. electronic configuration C. atomic radius D. ionization energy
11. Which of the following groups of elements is arranged correctly in order of increasing first ionization energy?  
A. Mg < C < N < F B. N < Mg < C < F C. Mg < N < C < F D. F < C < Mg < N
12. Which of the following groups of elements is arranged correctly in order of increasing affinity for electrons (that is, electron affinity becomes more negative)?  
A. Mg < S < Al < Cl B. Al < Mg < S < Cl C. Mg < Al < S < Cl D. Cl < S < Mg < Al
13. Which of the following groups of elements is arranged correctly in order of increasing atomic radius?  
A. Mg < S < Al < Cl B. Al < Mg < S < Cl C. Mg < Al < S < Cl D. Cl < S < Mg < Al

14. Which of the following elements would have the greatest difference between the first and the second ionization energy?  
A. lithium B. carbon C. fluorine D. nitrogen
15. The maximum number of electrons that may be associated with the set of quantum numbers  $n = 5$  and  $l = 3$  is:  
A. 2 B. 6 C. 10 D. 14
16. The shape of an atomic orbital is associated with:  
A. the principal quantum number ( $n$ ) C. the azimuthal quantum number ( $l$ )  
B. the magnetic quantum number ( $m_l$ ) D. the spin quantum number ( $m_s$ )
17. "Electrons added to atomic orbitals of the same energy will remain unpaired with parallel spins until the subshell is more than half-filled" is a statement of:  
A. the aufbau principle C. the Pauli exclusion principle  
B. Hund's rule D. the periodic law
18. "Each electron in an atom must have its own unique set of quantum numbers" is a statement of:  
A. the aufbau principle C. the Pauli exclusion principle  
B. Hund's rule D. the periodic law
19. If a sample oxide has the formula  $X_2O_5$ , the most likely electron configuration for the element X is:  
A.  $1s^2 2s^2 2p^6 3s^2 3p^3$  C.  $1s^2 2s^2 2p^6$  E.  $1s^2 2s^2 2p^6 3s^2 3p^4$   
B.  $1s^2 2s^2 2p^6 3s^2$  D.  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
20. Which of the following is not a correct equation?  
A.  $Al + \text{energy} \rightarrow Al^{3+} + 3e^-$  C.  $F + e^- \rightarrow F^- + \text{energy}$  E.  $Ca^+ + \text{energy} \rightarrow Ca^{2+} + e^-$   
B.  $S + \text{energy} \rightarrow S^{2-} + 2e^-$  D.  $He + e^- + \text{energy} \rightarrow He^-$
21. Which of the following sets of quantum numbers describes the highest energy electron in a ground state atom of bromine?  
A. 4,0,0,1/2 B. 4,0,1, 1/2 C. 4,1,1,1/2 D. 4,1,3,1/2 E. 4,2,5,1/2
22. Which of the following statements is TRUE?  
A. The exact location of an electron can be determined if we know its energy.  
B. An electron in a 2s orbital can have the same  $n$ ,  $l$ , and  $m_l$  quantum numbers as an electron in a 3s orbital.  
C. Ni has 2 unpaired electrons in its 3d orbitals.  
D. In the build-up of atoms, electrons occupy the 4f orbitals before the 3s orbitals.  
E. Only three quantum numbers are needed to uniquely describe an electron.
23. How many electrons can be described by the quantum numbers  $n = 3, l = 3, m_l = 1$ ?  
A. 0 B. 2 C. 6 D. 10 E. 14
24. An element E has the electron configuration  $[Kr]4d^{10}5s^2 5p^2$ . The formula for the fluoride of E is most likely:  
A.  $EF_{14}$  B.  $EF_4$  C.  $EF$  D.  $EF_6$  E.  $EF_8$

25. Consider the ionization energy (I.E.) of the magnesium atom. Which of the following is NOT true?
- A. The I.E. of Mg is lower than that of sodium.
  - B. The I.E. of Mg is lower than that of neon.
  - C. The I.E. of Mg is lower than that of beryllium.
  - D. The I.E. of Mg is higher than that of calcium.
  - E. The I.E. of Mg is lower than that of  $\text{Mg}^+$ .
26. For a neutron (mass =  $1.675 \times 10^{-27}$  kg) moving with a velocity of 4.20 m/s, what is the de Broglie wavelength in nanometers? (5 pts)
27. Radiation in the ultraviolet region of the electromagnetic spectrum is quite energetic. It is this radiation that causes dyes to fade and your skin to burn. If you are bombarded with one mole of photons with a wavelength of 300 nm, what amount of energy are you being subjected to? (5 pts)
28. Account for each of the following in terms of principles of atom structure, including the number, properties and arrangements of subatomic particles.
- (a) The second ionization energy of sodium is about three times greater than the second ionization energy of magnesium. (4 pts)
  
  - (b) The difference between the atomic radii of Na and K is relatively large compared to the difference between the atomic radii of Rb and Cs. (4 pts)
29. State the Heisenberg uncertainty principle as it related to the determining the position and momentum of an object. (3 pts)
30. Write the electron configuration for the following elements: (4 pts)
- A. Cr
  
  - B. Pb

## AP Multiple Choice Questions

### 1984 MULTIPLE CHOICE

1. Which of the following represents a pair of isotopes?

Answer Choice	A		B		C		D		E	
Atomic #	6	7	6	14	6	14	7	7	8	16
Mass #	14	14	7	14	14	28	13	14	10	20

2.  $1s^2 2s^2 2p^6 3s^2 3p^3$   
 Atoms of an element, X, have the electronic configuration shown above. The compound most likely formed with magnesium.  
 (A) MgX (B) Mg<sub>2</sub>X (C) MgX<sub>2</sub> (D) Mg<sub>2</sub>X<sub>3</sub> (E) Mg<sub>3</sub>X<sub>2</sub>
3. Which of the following represents the ground state electron configuration for the Mn<sup>3+</sup> ion? (Atomic number Mn = 25)  
 (A)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$  (B)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$   
 (C)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$  (D)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$  (E)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^1$
4. Ca, V, Co, Zn, As  
 Gaseous atoms of which of the elements above are paramagnetic?  
 (A) Ca and As only (B) Ca, V, and Co only (C) Zn and As only (D) V, Co, and As only (E) V, Co, and Zn only
5. One of the outer most electrons in a strontium atom in the ground state can be described by which of the following sets of four quantum numbers?  
 (A) 5, 2, 0, 1/2 (B) 5, 1, 1, 1/2 (C) 5, 1, 0, 1/2 (D) 5, 0, 1, 1/2 (E) 5, 0, 0, 1/2

### 1989 MULTIPLE CHOICE

Use the box to the right to answer questions 6-9

6. An impossible electron configuration  
 7. The ground-state configuration for the atoms of a transition element  
 8. The ground-state configuration of a negative ion of a halogen  
 9. The ground-state configuration of a common ion of an alkaline earth element

(A)  $1s^2 2s^2 2p^5 3s^2 3p^5$   
 (B)  $1s^2 2s^2 2p^6 3s^2 3p^6$   
 (C)  $1s^2 2s^2 2p^6 2d^{10} 3s^2 3p^6$   
 (D)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$   
 (E)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

10. Which of the following conclusions can be drawn from J.J. Thomson's cathode ray experiments?  
 (A) Atoms contain electrons.  
 (B) Practically all the mass of an atom is contained in its nucleus.  
 (C) Atoms contain protons, neutrons, and electrons.  
 (D) Atoms have a positively charged nucleus surrounded by an electron cloud.  
 (E) No two electrons in one atom can have the same four quantum numbers.

(A) Heisenberg uncertainty principle  
 (B) Pauli exclusion principle  
 (C) Hund's rule (principle of maximum multiplicity)  
 (D) Shielding effect  
 (E) Wave nature of matter

### 1994 MULTIPLE CHOICE QUESTIONS

Use the box to the right to answer questions 11-14

11. Can be used to predict that a gaseous carbon atom in its ground state is paramagnetic.  
 12. Explains the experimental phenomenon of electron diffraction.  
 13. Indicates that an atomic orbital can hold no more than two electrons.  
 14. Predicts that it is impossible to determine simultaneously the exact position and the exact velocity of an electron.

## AP Chemistry: Chapter 8 & 9

### Ionic and Covalent Bonding & Orbitals

#### 8.1 Types of Chemical Bonds

To study chemical bonds, we can look at physical or chemical properties like melting point, hardness, conductivity, solubility and bond energy.

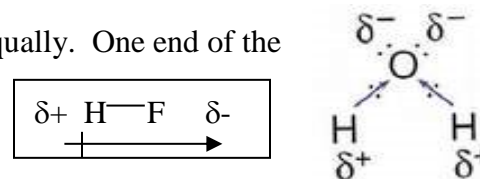
- bond energy- energy required to break a chemical bond
  - we can measure bond energy to determine the strength of interaction between particles

Ionic compound- product when a metal reacts with a nonmetal

- Ionic bonds form when an atom that loses electrons easily reacts with an atom that has a high affinity for electrons. The charged ions are held together by their mutual attraction.
- Ionic bonds form because the ion pair has lower energy than the separated ions. All bonds form in order to reach a lower energy level.
- The strength of an ionic bond can be predicted using Coulomb's law.  $E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left( \frac{Q_1 Q_2}{r} \right)$

Bonding occurs as atoms try to achieve their lowest possible energy state.

- Bond length is the distance where the energy is at a minimum.
- When two like atoms form a bond, there is a balance among proton-proton repulsion, electron-electron repulsion, and proton-electron attraction.
  - In  $\text{H}_2$ , the two  $e^-$  will usually be found between the two H atoms because they are spontaneously attracted to both protons. Therefore, electrons are shared by both nuclei. This is called covalent bonding.
  - Polar covalent bonds occur when electrons are not shared equally. One end of the molecule may have a partial charge. This is called a dipole.

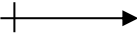


#### 8.2 Electronegativity

Electronegativity- the ability of an atom in a molecule to attract shared electrons to itself

- Electronegativity generally increases across a period and decreases down a group. It ranges from 0.79 for cesium to 4.0 for fluorine.

#### 8.3 Bond Polarity and Dipole Moments

- As stated earlier, particles may have a positive area and a negative area due to unequal sharing of electrons.
- These particles are said to be dipolar or to have a dipole moment.
  - This is represented by an arrow with a positive end and a negative end. 
  - Dipole moments may cancel themselves out, as in the case of  $\text{CO}_2$  and  $\text{CCl}_4$ .
  - Dipole moments can be shown by looking at differences in electronegativity of the bonding pairs, or by examining an electrostatic potential diagram.



#### 8.4 Ions: Electron Configurations and Sizes

- Stable compounds usually have atoms with noble gas electron configurations.
- Two nonmetals react to form a covalent bond by sharing electrons to obtain noble gas electron configurations.
- When a nonmetal and a group A metal react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal is completed and the valence orbitals of the metal are emptied to give both noble gas configurations.
- Ions form to obtain noble gas configurations.
  - Exceptions in Group A metals:  $\text{Sn}^{2+}$  &  $\text{Sn}^{4+}$   $\text{Pb}^{2+}$  &  $\text{Pb}^{4+}$      $\text{Bi}^{3+}$  &  $\text{Bi}^{5+}$      $\text{Tl}^+$  &  $\text{Tl}^{3+}$

- Metals with d electrons will lose their highest numerical energy level electrons before losing their inner d electrons.

### Size of Ions

- Positive ions (cations) are smaller than their parent atoms since they are losing electrons.
- Negative ions (anions) are larger than their parent atoms since they are gaining electrons.
- Ion size increases going down a group.

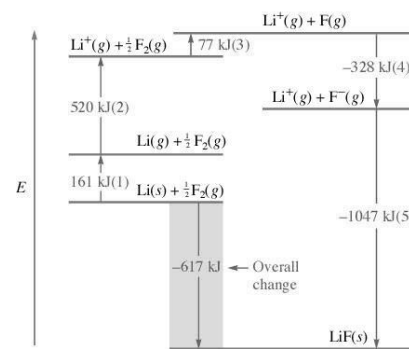
### Isoelectronic ions

- Ions that contain the same number of electrons.
- $O^{2-}$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Al^{3+}$  all have the electron configuration of neon. They are isoelectronic.
  - For an isoelectronic series, size decreases as  $Z$  increases.

## 8.5 Energy Effects in Binary Ionic Compounds

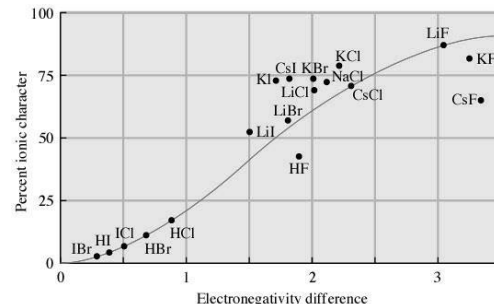
### Lattice energy

- The change in energy that takes place when separated gaseous ions are packed together to form an ionic solid.  $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ 
  - If exothermic, the sign will be negative and the ionic solid will be the stable form.
  - We can use a variety of steps to determine the heat of formation of an ionic solid from its elements. This is called the Born-Haber cycle.
- Lattice energy can be calculated using the following:
 
$$Lattice\ energy = k \left( \frac{Q_1 Q_2}{r} \right)$$
  - where  $k$  is a proportionality constant that depends on the structure of the solid and the electron configuration of the ions.
  - $Q_1$  &  $Q_2$  are the charges on the ions.
  - $r$  is the distance between the center of the cation and the anion.
- Since the ions will have opposite charges, lattice energy will be negative (exothermic).
- The attractive force between a pair of oppositely charged ions increases with increased charge on the ions or with decreased ionic sizes.
  - There is far more energy released when  $Mg^{2+}$  and  $O^{2-}$  combine than when  $Na^+$  and  $F^-$  combine.



## 8.6 Partial Ionic Character of Covalent Bonds

- There are probably no totally ionic bonds. Percent ionic character in binary compounds can be calculated. Percent ionic character increases with electronegativity difference.
- Compounds with more than 50% ionic character are considered to be ionic (electronegativity difference of about 1.7).
- Polyatomic ions are held together by covalent bonds. We call  $Na_2SO_4$  ionic even though it has 4 covalent bonds and 2 ionic bonds.
- Ionic compound- any solid that conducts an electrical current when melted or dissolved in water.



## 8.7 The Covalent Chemical Bond: A Model

A chemical bond is a model “invented” by scientists to explain stability of compounds. A bond really represents an amount of energy. The bonding model helps us understand and describe molecular structure. It is supported by much research data. To fully understand a model, we must understand the data that prompted its description. However, models are not always correct and we can learn from their faults.



Bond energies and bond lengths are given on page 362 and 363.

## 8.8 Covalent Bond Energies and Chemical Reactions

- Single bond- one pair of shared electrons; long bond length
- Double bond- two pair of shared electrons; intermediate bond length
- Triple bond- three pair of shared electrons; short bond length
- We can use bond energies to calculate heats of reaction.
  - $\Delta H = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})$ 
    - $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
    - Ex.  $\Delta H = [2(432) + 495] - [4(467)] = -509 \text{ kJ}$   
 $2 \text{H-H} \quad \text{O}=\text{O} \quad 4\text{H-O} \quad \text{exothermic}$
  - Practice! Use the table of bond energies to find the  $\Delta H$  of the following reaction.
  - $\text{CH}_4(\text{g}) + 2\text{Cl}_2(\text{g}) + 2\text{F}_2(\text{g}) \rightarrow \text{CF}_2\text{Cl}_2(\text{g}) + 2\text{HF}(\text{g}) + 2\text{HCl}(\text{g})$

## 8.9 The Localized Electron Bonding Model

Molecular Orbital Model-

- electrons occupy orbitals in a molecule in much the same way as they occupy orbitals in atoms
- electrons do not belong to any one atom
- very complex

Localized electron model-

- molecules are composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms
- traditional model
  - lone pair- pair of electrons localized on an atom (nonbonding)
  - shared pair or bonding pair- electrons found in the space between atoms

## 8.10 Lewis Structures

Lewis structures show how the valence electrons are arranged among the atoms in the molecule

- The most important requirement for the formation of a stable compound is that the atoms achieve noble gas configurations
    - ionic- only valence electrons are included
    - molecular  $\text{H}_2\text{O}$
- $$\begin{array}{c} \text{H} \\ \vdots \\ \text{:O:} \\ \vdots \\ \text{H} \end{array}$$

$$\cdot\text{Mg}\cdot + \cdot\cdot\text{O}\cdot\cdot \longrightarrow \text{Mg}^{2+} + \cdot\cdot\text{O}^{2-}\cdot\cdot$$

$$\text{H}\cdot + \cdot\text{H} \longrightarrow \text{H:H}$$
- duet rule- formation of stable molecules when two electrons are shared ( $\text{H}_2$ )
  - octet rule- filled valence shells of all other elements
    - Why does He not form bonds? Its valence orbitals are already filled.
- $$\cdot\ddot{\text{Cl}}\cdot + \cdot\ddot{\text{Cl}}\cdot \longrightarrow \text{:}\ddot{\text{Cl}}\text{:}\ddot{\text{Cl}}\text{:}$$

Rules for writing Lewis structures

1. Add up the number of valence electrons from all atoms.
2. Use 2 electrons to form a bond between each pair of bound atoms.
3. Arrange the remaining electrons to satisfy the duet rule for H and the octet rule for most others.

Practice!

H <sub>2</sub> S	# Valence Electrons =		HCN	# Valence Electrons =	
CO <sub>2</sub>	# Valence Electrons =		NO <sup>+</sup>	# Valence Electrons =	

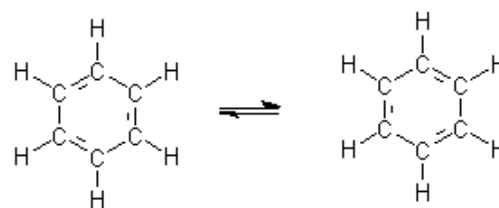
NH <sub>3</sub>	# Valence Electrons =		CO <sub>3</sub> <sup>2-</sup>	# Valence Electrons =	
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### 8.11 Exceptions to the Octet Rule

- Boron and beryllium tend to form compounds where the B or Be atom have fewer than 8 electrons around them. Ex. BF<sub>3</sub>
  - Common AP equation: NH<sub>3</sub> + BF<sub>3</sub> → H<sub>3</sub>NBF<sub>3</sub>
- C, N, O, F always obey the octet rule.
- Some elements in Period 3 and beyond exceed the octet rule. Ex. SF<sub>6</sub> S has 12 e<sup>-</sup> around it.
  - d orbitals are used to accommodate the extra electrons.
- Elements in the 1<sup>st</sup> or 2<sup>nd</sup> period of the table can't exceed the octet rule because there is no d sublevel.
- If the octet rule can be exceeded, the extra electrons are placed on the central atom.
  - See examples of exceptions on pg 372. Ex. I<sub>3</sub><sup>-</sup>, ClF<sub>3</sub>, RnCl<sub>2</sub>

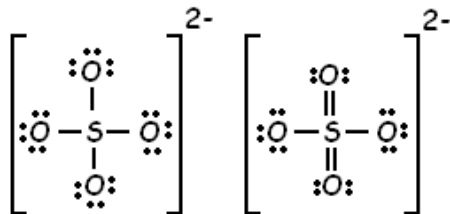
### 8.12 Resonance

- occurs when more than one valid Lewis structure can be written for a particular molecule
- actual structure is an average of all resonance structures
- this concept is needed to beat the localized electron model (electrons are really delocalized)
  - Ex. Benzene, C<sub>6</sub>H<sub>6</sub>
  - All bond lengths and angles are the same.
  - Ex. SO<sub>3</sub>



### Formal Charge

- Formal charge is the charge on an atom in a compound that is used to determine the most accurate Lewis structure.
- It is the difference between the # of valence electrons on the free atom and the # of valence electrons assigned to the atom in the molecule
- atoms try to achieve formal charges as close to zero as possible
- any negative formal charges are expected to reside on the most electronegative atoms
- Sum of the formal charges must equal the overall charge on the molecule (zero) or ion.
  - Ex. SO<sub>4</sub><sup>2-</sup>



### 8.13 Molecular Structure: The VSEPR Model

- Stands for Valence Shell Electron Pair Repulsion
- allows us to use electron dot structures to determine molecular shapes
- the structure around a given atom is determined primarily by minimizing electron repulsions
- bonding and nonbonding pairs of electrons around an atom position themselves as far apart as possible
  - Steps:
    - Draw Lewis structure
    - Count effective electron pairs on central atom (double and triple bonds count as one)
    - Arrange the electron pairs as far apart as possible

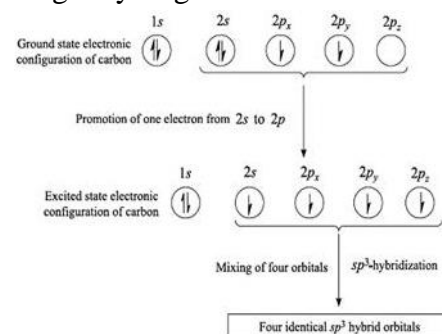
## VSEPR Structures for Molecules and Ions

Effective Electron Pairs	Bonding Electron Pairs	Nonbonding Electron Pairs	VSEPR Formula	Approx. Bond Angles	Hybridization	3-D Structure	Examples
2	2	0	AX <sub>2</sub>	180°	sp	linear	CO <sub>2</sub> , BeCl <sub>2</sub>
3	3	0	AX <sub>3</sub>	120°	sp <sup>2</sup>	trigonal planar	BF <sub>3</sub> , CO <sub>3</sub> <sup>2-</sup>
3	2	1	AX <sub>2</sub> E	<120°	sp <sup>2</sup>	bent	SnCl <sub>2</sub> , PbBr <sub>2</sub>
4	4	0	AX <sub>4</sub>	109.5°	sp <sup>3</sup>	tetrahedral	CH <sub>4</sub> , SnCl <sub>4</sub>
4	3	1	AX <sub>3</sub> E	<109.5°	sp <sup>3</sup>	trigonal pyramidal	NH <sub>3</sub> , PCl <sub>3</sub> , H <sub>3</sub> O <sup>+</sup>
4	2	2	AX <sub>2</sub> E <sub>2</sub>	<109.5°	sp <sup>3</sup>	bent	H <sub>2</sub> O, OF <sub>2</sub> , SCl <sub>2</sub>
5	5	0	AX <sub>5</sub>	90°, 120°	sp <sup>3</sup> d	trigonal bipyramidal	PCl <sub>5</sub> , NbCl <sub>5</sub>
5	4	1	AX <sub>4</sub> E	<90°, <120°	sp <sup>3</sup> d	see-saw	SF <sub>4</sub> , TeCl <sub>4</sub>
5	3	2	AX <sub>3</sub> E <sub>2</sub>	<90°	sp <sup>3</sup> d	T-shaped	ClF <sub>3</sub>
5	2	3	AX <sub>2</sub> E <sub>3</sub>	180°	sp <sup>3</sup> d	linear	ICl <sub>2</sub> <sup>-</sup> , I <sub>3</sub> <sup>-</sup> , XeF <sub>2</sub>
6	6	0	AX <sub>6</sub>	90°	sp <sup>3</sup> d <sup>2</sup>	octahedral	SF <sub>6</sub>
6	5	1	AX <sub>5</sub> E	<90°	sp <sup>3</sup> d <sup>2</sup>	square pyramidal	BrF <sub>5</sub>
6	4	2	AX <sub>4</sub> E <sub>2</sub>	90°	sp <sup>3</sup> d <sup>2</sup>	square planar	ICl <sub>4</sub> <sup>-</sup> , XeF <sub>4</sub>

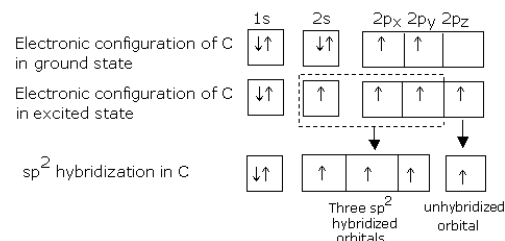
### 9.1 Hybridization and the Localized Electron Model

When drawing Lewis structures to explain bonding, we have been using the Localized Electron Model of bonding.

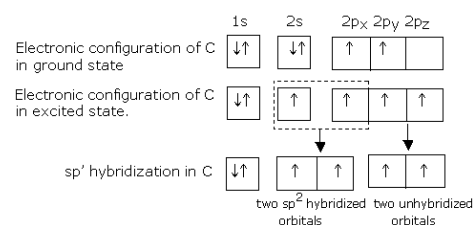
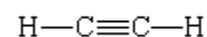
- This assumes that the electrons stay with (or close to) the atoms from which they originated and that bonds are formed by the overlap of atomic orbitals. This model needs to be developed a little further to explain experimental data.
- In methane, CH<sub>4</sub>, carbon has one 2s and three 2p orbitals available for bonding. Hydrogen has one 1s orbital available.
- We could imagine that one of the bonds in methane would be formed from the overlap of a hydrogen 1s orbital and a carbon 2s orbital and the other three bonds would be formed from the overlap of a hydrogen 1s orbital and a carbon 2p orbital. This would make 2 different kinds of bonds.
- Experimental data shows that all four bonds are identical, so how do we resolve this?
- If the bonds instead were an overlap of the hydrogen's 1s and a new kind of orbital from the carbon, then the bonds would all be equal in length.
  - The "new" orbital from the carbon is created by utilizing carbon's 2s and all three of its 2p orbitals. These orbitals are blended (hybridized) into a mixture that produces four orbitals that look a lot like p orbitals, with a hint of s.
  - These are called sp<sup>3</sup> orbitals, to indicate what they are made from.
  - The hybrid sp<sup>3</sup> orbitals each overlap with the 1s orbitals from each hydrogen atom and make four identical bonds having 109.5° bond angles. These overlapping single bonds are called sigma bonds (σ).
  - Atoms with four effective electron pairs have sp<sup>3</sup> hybridization, even if they have unshared pairs as in H<sub>2</sub>O and NH<sub>3</sub>. The electron pairs have a tetrahedral arrangement.



- We can look at the hybridization in the bonding of ethene ( $C_2H_4$ ).
- These bonds are going to happen when a 1s orbital from hydrogen overlaps with an orbital from carbon.
  - This time, each carbon has to form three bonds, one with the other carbon, and two with hydrogen. We will discuss the double bond in a moment.
  - This time, each carbon will use one s and two p orbitals to make these three bonds. This forms an  $sp^2$  hybrid orbital.
  - This type of hybridization results in trigonal planar electron pair arrangements and  $120^\circ$  bond angles.
  - Notice that when this occurs, one p orbital from each carbon is not used to form the hybrid orbitals. These p orbitals actually have one promoted electron in each that form areas of stability above and below the molecule.
  - This is what makes up the double bond. A double bond is called a pi bond ( $\pi$ ).
  - Because the electrons in a pi bond are not directly between the nuclei, a pi bond is weaker than a sigma bond. A double bond contains one sigma plus one pi bond and is thus stronger and shorter than a single bond.



- Let's look at the hybridization and bonding in ethyne (acetylene),  $C_2H_2$ .
  - In ethyne, each carbon is forming two bonds, one with hydrogen, one with the other carbon. We will discuss the triple bond in a moment.
  - Carbon will utilize one s and one p to form these bonds, so the hybrid orbitals are called  $sp$ .
  - Linear molecules and  $180^\circ$  bond angles result from  $sp$  hybridization.
  - The two p orbitals and their electrons interact around the C-C sigma bond above and below the plane of the molecule to form two pi bonds. This completes the triple bond.
  - A triple bond is one sigma and two pi bonds and is thus stronger and shorter than either a single or a double bond.



- We learned that certain elements can exceed the octet rule by utilizing unfilled d orbitals. These d orbitals are also involved in hybridization. For example,  $PF_5$  has five effective electron pairs. These five pairs require five equal bonds. We must throw one s, three p and 1 d orbital into the blender to get five  $dsp^3$  (or  $sp^3d$ ) orbitals.
  - This form of hybridization results in trigonal bipyramidal shapes and  $90^\circ$  and  $120^\circ$  bond angles.
- With  $SF_6$  we have six effective electron pairs. We must hybridize one s, three p, and two d orbitals to get six  $d^2sp^3$  or  $sp^3d^2$  orbitals.
  - This results in the octahedral shape with  $90^\circ$  bond angles.

Practice! For each of the following, determine:

a) hybridization of each atom

and # of pi bonds

b) bond angles

c)

molecula

r shape

d) # of

sigma

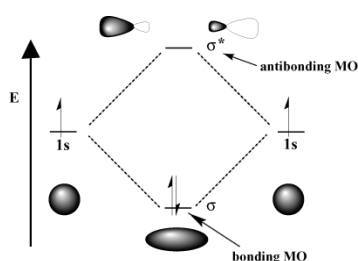
bonds

	$SbCl_5$	$NO_3^-$	$CHCl_3$

## 9.2 The Molecular Orbital Model (MO)

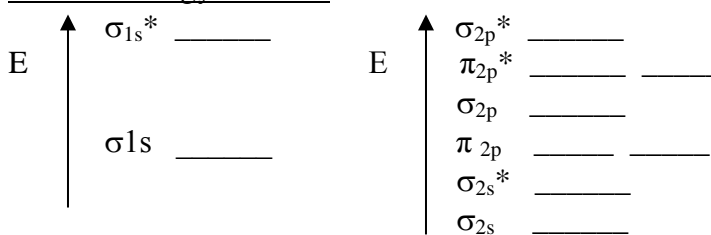
- The molecule is assumed to be a new entity consisting of positively charged nuclei and electrons.
- Molecular orbitals (MOs) are constructed from the valence orbitals of the atoms. (Some texts use core electrons also)
- Like atomic orbitals, MOs can hold two electrons with opposite spins
- MOs fall into two classes: bonding & antibonding
  - A bonding MO is lower in energy than the atomic orbitals of which it is composed.
  - An antibonding MO is higher in energy than the atomic orbitals of which it is composed.
  - In a bonding orbital, electrons have the greatest probability of being between the nuclei. In an antibonding orbital, electrons are mainly outside the space between the nuclei.
  - We can have  $\sigma$  and  $\pi$  MOs. Orbitals are conserved. The number of MOs will be the same as the number of AOs used to construct them.

Ex.  $H_2$



The MO configuration for  $H_2$  is:  $\sigma_{1s}^2$

### Order of energy for MOs



- For  $O_2$  through  $Ne_2$ , the order of the  $\sigma_{2p}$  and the  $\pi_{2p}$  orbitals are reversed.
- Bond order may be determined as a measure of the stability of a molecule.
- Bond order =  $\frac{\# \text{ of bonding } e^- - \# \text{ antibonding } e^-}{2}$

- A bond order equal to zero means that the molecule has equal numbers of electrons in bonding MOs and in antibonding MOs. Such a molecule would be no more stable than separate atoms, so it would not exist. The greater the bond order, the more stable we predict the molecule or ion to be. As bond order increases, the bond energy increases and the bond length decreases.

### Paramagnetism and Diamagnetism

- Most substances are not magnetic unless they are placed in a magnetic field. Substances that contain unpaired electrons are weakly attracted into magnetic fields and are said to be paramagnetic. Those whose electrons are paired are very weakly repelled by magnetic fields and are called diamagnetic.
- Ferromagnetism is exhibited by Fe, Co, and Ni and is much stronger than paramagnetism.

	$B_2$	$C_2$	$N_2$	$O_2$	$F_2$
$\sigma_{2p}^*$	—	—	—	$\sigma_{2p}^*$ —	—
$\pi_{2p}^*$	— —	— —	— —	$\pi_{2p}^*$ ↑ ↑	— —
$\sigma_{2p}$	—	—	—	$\pi_{2p}$ — —	— —
$\pi_{2p}$	↑ ↑	— —	— —	$\sigma_{2p}$ —	— —
$\sigma_{2s}^*$	— —	— —	— —	$\sigma_{2s}^*$ — —	— —
$\sigma_{2s}$	— —	— —	— —	$\sigma_{2s}$ — —	— —
Magnetism	Para-magnetic	Dia-magnetic	Dia-magnetic	Para-magnetic	Dia-magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

### Resonance

- To eliminate the need for resonance we can use the localized electron model to describe the  $\sigma$  bonding and the MO model to describe the  $\pi$  bonding.
- In benzene, each C is  $sp^2$  hybridized. The 6 additional p orbitals perpendicular to the ring are used to form  $\pi$  MOs. The electrons in these  $\pi$  MOs are delocalized above and below the plane of the ring.



4.                     $\text{CF}_4$                      $\text{XeF}_4$                      $\text{ClF}_3$
- a) Draw a Lewis electron-dot structure for each of the molecules above and identify the shape of each.
- b) Use the valence shell electron-pair repulsion (VSEPR) model to explain the geometry of each of these molecules.
- 
5. Use simple structure and bonding models to account for each of the following.
- a) The bond length between the two carbon atoms is shorter in  $\text{C}_2\text{H}_4$  than in  $\text{C}_2\text{H}_6$ .
- b) The H-N-H bond angle is  $107.5^\circ$ , in  $\text{NH}_3$ .
- c) The bond lengths in  $\text{SO}_3$  are all identical and are shorter than a sulfur-oxygen single bond.
- d) The  $\text{I}_3^-$  ion is linear
- 
6.     $\text{NO}_2$                      $\text{NO}_2^-$                      $\text{NO}_2^+$
- Nitrogen is the central atom in each of the species given above.
- a) Draw the Lewis electron-dot structure for each of the three species.
- b) List the species in order of increasing bond angle. Justify your answer.
- c) Select one of the species and give the hybridization of the nitrogen atom in it.
- d) Identify the only one of the species that dimerizes and explain what causes it to do so.

## AP Chemistry: Chapter 10

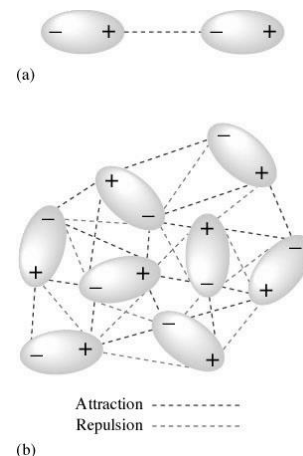
### Liquids and Solids

Liquids and solids are unique from gases in that they have very similar compressibility, density and behavior of particles. In this chapter, we will study how liquids and solids behave.

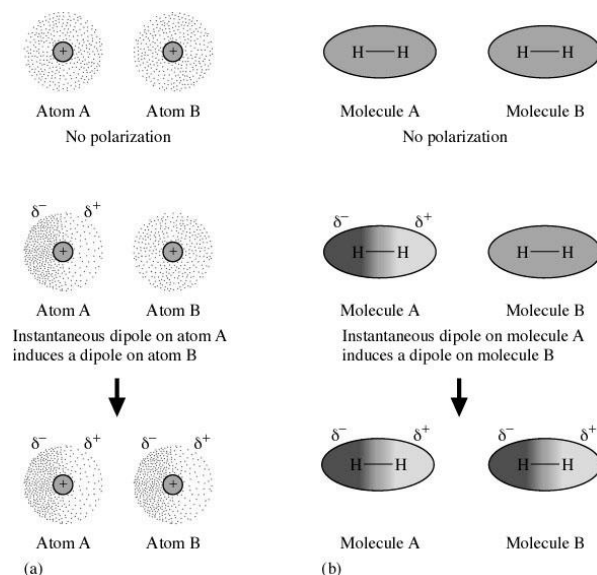
#### 10.1 Intermolecular Forces

Molecules interact in many ways. Forces inside of molecules are different than those outside.

- Intramolecular bonding- bonding that occurs inside of covalently bonded compounds.
- Intermolecular bonding- interactions between particles (atoms, molecules or ions)
  - Intermolecular forces act on the condensed states of matter (liquids and solids), but less often on gases
  - Changes in state are due to changes in intermolecular bonding, not intramolecular bonding.
- Dipole-dipole attraction- attraction of molecules having dipole moments for each other. (negative-positive)
  - About 1% as strong as covalent or ionic bonds.
  - Molecules orient themselves to minimize repulsion and maximize attractions
  - A particularly strong form of dipole-dipole attraction is hydrogen bonding- unusually strong dipole-dipole attractions involving hydrogen atoms which are covalently bonded to a very electronegative atom (F,O,N) with unshared electrons.
  - There are two reasons for strength of hydrogen bonds:
    1. Small size of H atom allows closeness
    2. Large variation in polarity
  - Substances with large amounts of H-bonding have high boiling points compared to similar substances. Ex.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , HF



- London dispersion forces (LDFs) -relatively weak forces (usually) that exist between noble gas atoms and nonpolar molecules. LDFs also exist in compounds that have dipole-dipole and/or hydrogen bonding. LDFs may be the most important force in large molecules of these types.
  - LDFs occur because of momentary electron imbalance (temporary dipole) which can induce the same in adjacent molecules.
  - This force is often very weak, thus the low freezing point of noble gases. The freezing point of noble gases gets higher as we go down the group because heavier atoms have more electrons and are thus more *polarizable* because they can develop temporary dipoles.
  - **This causes London dispersion forces to increase down a group.**



- The boiling point of covalent hydrides increases with molecular weight in Group 4. In other groups, the first hydride has a high boiling point because of hydrogen bonding.
- Metallic bonding, ionic bonding, and network covalent bonding will be discussed later. They are much stronger attractions.



## General trends in strength of attraction

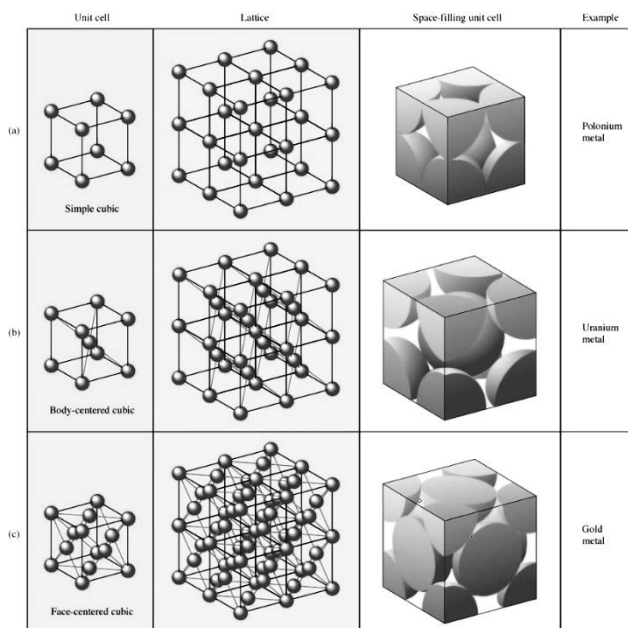
LDF < Dipole-dipole < H-bonding < Metallic Bonding < Ionic Bonding < Covalent Network Solid

- Surface tension- resistance of a liquid to an increase in its surface area.
  - Liquids with relatively large intermolecular forces have high surface tensions.
    - Ex.  $\text{H}_2\text{O}$ . Polar molecules have more surface tension than nonpolar molecules.
- Capillary action- spontaneous rising of a polar liquid in a narrow tube.
  - Caused by 2 forces:
    - Cohesive forces: intermolecular forces among the liquid molecules
    - Adhesive forces: forces between the liquid molecules and their container. The container must be made of polar material such as glass.
    - A concave meniscus forms because the water's adhesive forces toward the glass are stronger than its cohesive forces.
    - A nonpolar liquid can produce a convex meniscus (cohesive > adhesive)
- Viscosity- resistance of a liquid to flow.
- Liquids with large intermolecular forces tend to be highly viscous. Ex. glycerol (AKA glycerine)
  - More complex molecules are more viscous because they tangle up. (gasoline vs. grease)



### 10.3 An Introduction to Structures and Types of Solids

- Amorphous solids- very disordered, usually long chain-like molecules twisted up like spaghetti. (plastics, asphalt, rubber)
- Crystalline solids- highly regular arrangement of components
  - lattice- a 3-D system of points designating the centers of the components (atoms, ions or molecules)
  - unit cell - smallest repeating unit of the lattice. (Learn the 3 common cubic unit cells pg 446!)
- X-ray diffraction- method of determining crystal structure.
  - X-rays of a single wavelength are directed at a crystal and are scattered by it, producing a diffraction pattern which can be used to determine the crystal structure.
- Types of Cubic Unit Cells
  - Simple cubic- 1 net sphere (8  $\cdot$  1/8 spheres) The coordination number of each particle is six.
  - Body-centered cubic - 2 net spheres (1 complete and 8  $\cdot$  1/8 spheres) The coordination number is eight.
  - Face-centered cubic- 4 net spheres (6  $\cdot$  1/2 spheres and 8  $\cdot$  1/8 spheres). The coordination number is twelve.
  - NaCl and other alkali halides are face-centered cubic (fcc).



### Types of crystalline solids

- Ionic solids (NaCl)- have ions at lattice points, held together by strong ionic forces.

- Molecular solids (sucrose)- have molecules at lattice points, held together by LDF, dipole-dipole, &/or hydrogen bonding (Ice has H<sub>2</sub>O molecules at each point of the lattice)
- Metallic solids (gold)- have a metal atom at lattice points, held together by metallic bonds.
- Atomic solids (argon)- have a noble gas atom at lattice points, held together by LDF
- Covalent network solid (diamond and silicon compounds) (essentially one giant molecule) covalently bonded, have an atom at each lattice point, held together by very strong covalent bonds.
  - The properties of a solid depend on the nature of the forces that hold the solid together. Diamond has very strong, covalent network forces.

#### 10.4 Structure and Bonding in Metals

- Metallic crystals
  - Have nondirectional covalent bonding that leads to properties like conductivity, malleability and ductility
  - Spherical atoms packed together and bonded to each other equally-called metallic bonding
  - Types of bonding include closest-packed (with hexagonal or face centered cubic unit cells) and body centered cubic unit cells
- Bonding in Metals
  - Strong and nondirectional which means they are difficult to separate, but easy to move.
- Two models are used to describe metallic bonding. They are:
  - Electron sea model- This is the simplest model. The metal cations are in a sea of valence electrons. The mobile electrons can conduct heat and electricity. The cations can be easily moved around (lead to properties of ductility and malleability).
  - Band model (MO model)- This is a more detailed model. The electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal ions. The MOs that result are very closely spaced in energy levels, thus they form a continuous band. Some MOs are empty. Mobile electrons are excited into these empty MOs. The electrons are free to move throughout the metal crystal.
- Metal alloy - substance that contains a mixture of elements and has metallic properties. There are two types of metal alloys.
  - Substitutional alloy- some of the host metal atoms are replaced by other metal atoms of similar size. Ex. brass, sterling silver, pewter
  - Interstitial alloy -holes in closest packed metal structure are filled by small atoms. Ex. steel (carbon in iron)

#### 10.5 Carbon and Silicon: Network Atomic Solids

- Network solids- atomic solids with strong directional covalent bonds
  - Brittle and don't conduct heat or electricity Ex. C and Si
    - Allotropes- different forms of the same element Ex. diamond, graphite, and buckminsterfullerene are allotropes of carbon.
    - Sulfur has several allotropes
  - Strongest type of bonding
  - Diamond has a tetrahedral sp<sup>3</sup> arrangement. Its MOs are far apart in energy, thus no conduction of electricity.
  - Graphite has layers of six member rings (sp<sup>2</sup>). The pi molecular orbitals allow it to conduct electricity. It has strong bonding within its layers. We can convert graphite to diamond at a pressure of 150,000 atm and a temperature of 2800°C.
- Silicon compounds are to geology as carbon compounds are to biology. Most important Si compounds contain Si and O. Silica, SiO<sub>2</sub> (empirical formula) is the fundamental Si-O compound. Quartz and some types of sand are silica. Silica is a network of SiO<sub>4</sub> tetrahedra. The bonds are single because the 3p orbitals are too big to bond strongly with oxygen. Silicates are anions of Si and O. Ex. SiO<sub>4</sub><sup>4-</sup>, Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>, Si<sub>3</sub>O<sub>9</sub><sup>6-</sup>

- Glass is formed when silica is melted and cooled rapidly. Other substances are added to glass to vary its properties. Glass is amorphous and can be called a “supercooled liquid”. Ceramics contain tiny crystals of silica in a glassy cement.
- Semiconductors- Elemental silicon has the same structure as diamond but the energy gap between filled and empty MOs is much smaller. Thus, a few electrons can cross this gap at room temperature, making Si a semiconductor.
  - At higher temperatures, where more energy is available to excite electrons into the conduction bands, the conductivity of Si increases. Most metals have decreased conductivity at higher temperatures.
  - Doping is a process which increases the conductivity of silicon. A very few of the Si atoms are replaced by other atoms such as arsenic.
    - Arsenic has one more valence electron than carbon. This gives more electrons for conduction and produces an n-type semiconductor (n stands for negative). If we instead replace a few Si atoms with atoms with one fewer electron (such as boron), we produce holes that electrons can travel into (producing a chain effect). This produces a p-type semiconductor.

### 10.6 Molecular Solids

- Molecular solids have molecules at lattice points instead of atoms or ions.
  - Ex. ice, dry ice, sulfur (S<sub>8</sub>), phosphorus (P<sub>4</sub>)
  - Strong covalent bonding within molecules but relatively weak forces between molecules.
  - The atoms within the molecule are closer to each other than atoms from adjacent molecules are. This indicates stronger bonding.
  - CO<sub>2</sub>, S<sub>8</sub>, I<sub>2</sub>, and P<sub>4</sub> have no dipole-dipole forces. The last three are solids at room temperature because London dispersion forces are stronger in larger molecules.

### 10.7 Ionic Solids

- Ionic solids have ions at lattice points.
  - Stable, high melting point, held together by strong electrostatic forces
  - Structure of most binary ionic solids can be explained by the closest packing of spheres
  - The smaller ions (usually cations) fit into the holes between the larger ions (anions). Attractions are maximized and repulsions are minimized.

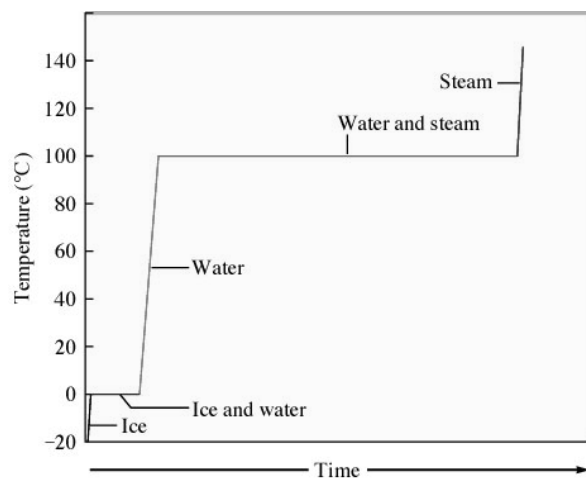
*Summary of Types and Properties of Solids*

Type of Solid	Atomic			Molecular	Ionic
	Covalent Network	Metallic	Group 8A		
Structural Unit (at lattice point)	Atom	Atom	Atom	Molecule	Ion
Type of Bonding	Directional covalent bonding	Nondirectional covalent bonding; electrons are delocalized throughout the crystal	LDF	Polar molecules have dipole-dipole interactions Nonpolar molecules have LDF	Ionic bonding
Properties	Hard with high mp, good insulators	Range of hardness and mp, good conductors, malleable, ductile	Low mp but increases with LDF	Soft with low mp, good insulators	Hard with high mp and good insulator
Ex.	Diamond, Si cmpds	Fe, Ag, Brass	Ar	Ice, CO <sub>2</sub> (s)	NaCl, CaF <sub>2</sub>

### 10.8 Vapor Pressure and Changes in State

We will now consider how the properties of matter we have discussed thus far affect state changes in that same matter.

- Vaporization (evaporation)- endothermic process because we add energy to break intermolecular bonding.
  - Heat (enthalpy) of vaporization- energy required to vaporize 1 mole of a liquid at a pressure of 1 atm ( $\Delta H_{\text{vap}}$ )
  - $\Delta H_{\text{vap}}$  of water is 40.7 kJ/mol
- Evaporation is a cooling process and is the opposite process of vaporization (uses the same value of  $\Delta H$ )
  - Condensation- process by which vapor molecules reform a liquid
  - dynamic equilibrium occurs when the rate of condensation = rate of vaporization
  - vapor pressure- pressure of the vapor present at equilibrium
    - measured by a barometer
    - $P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$
  - volatile -liquids which evaporate rapidly and have high vapor pressure
- Vapor pressure is affected by two factors:
  1. Molecular weight- At a given temperature, heavy molecules have lower velocities than light molecules and thus have a lower tendency to escape from the liquid surface. A liquid with a high molecular weight tends to have a small vapor pressure.
  2. Intermolecular forces- molecules with strong intermolecular forces also tend to have low vapor pressure because they need lots of energy to escape.
- Vapor pressure increases with temperature (higher KE) but it is not a direct relationship.
  - You do not need to be able to solve VP-temp problems.
  - Below 0°C, The VP of ice is less than the VP of liquid water.
- Sublimation is a direct change of a solid to a gas
  - Ex. dry ice, freeze drying, iodine
- Heating curve- a plot of temperature versus time for a process where energy is added at a constant rate.
  - Temperature remains constant as a phase changes.
- Heat (enthalpy) of fusion- enthalpy change that occurs when a solid melts,  $\Delta H_{\text{fus}}$ 
  - This is an endothermic process as well
  - The  $\Delta H_{\text{fus}}$  of water is 6.02 kJ/mol
- Normal melting point- the temperature at which the solid and liquid have the same vapor pressure at 1 atm total pressure.
- Boiling -occurs when VP of the liquid = external pressure
  - Normal boiling point - the temperature at which the VP of the liquid is exactly 1 atm.



Ex. How many joules are needed to convert 5.0 g of ice at -15°C to steam at 130°C?

## AP Chemistry: Chapter 10 Worksheet

1988 D

Discuss some differences in physical and chemical properties of metals and nonmetals. What characteristic of the electronic configurations of atoms distinguishes metals from nonmetals? On the basis of this characteristic, explain why there are many more metals than nonmetals.

1974 D

The boiling points of the following compounds increase in the order in which they are listed below:



Discuss the theoretical considerations involved and use them to account for this order.

1977 D

The state of aggregation of solids can be described as belonging to the following four types:

(1) ionic                      (2) metallic                      (3) covalent network                      (4) molecular

For each of these types of solids, indicate the kinds of particles that occupy the lattice points and identify forces among these particles. How could each type of solid be identified in the laboratory?

1985 D

- a. Discuss how the trend in the melting points of the substances tabulated above can be explained in terms of the types of attractive forces and/or bonds in these substances.
- b. For any pairs of substances that have the same kind(s) of attractive forces and/or bonds, discuss the factors that cause variations in the strengths of the forces and/or bonds.

Substance	Melting Point (°C)
H <sub>2</sub>	-259
C <sub>3</sub> H <sub>8</sub>	-190
HF	-92
CsI	621
LiF	870
SiC	>2,000

1988 D

Using principles of chemical bonding and/or intermolecular forces, explain each of the following.

- Xenon has a higher boiling point than neon has.
- Solid copper is an excellent conductor of electricity, but solid copper chloride is not.
- $\text{SiO}_2$  melts at a very high temperature, while  $\text{CO}_2$  is a gas at room temperature, even though Si and C are in the same chemical family.

1986 D

Give a scientific explanation for each of the following observations. Use equations or diagrams if they seem relevant.

- Graphite is used to make electrodes, while diamond, another allotrope of carbon, is a very poor conductor of electricity.

1975

Alcohol dissolves in water to give a solution that boils at a lower temperature than pure water. Salt dissolves in water to give a solution that boils at a higher temperature than pure water. Explain these facts from the standpoint of vapor pressure.

1984 C

Give a scientific explanation for the following observations. Use equations or diagrams if they are relevant.

- It takes longer to cook an egg until it is hard-boiled in Denver (altitude 1 mile above sea level) than it does in New York City (near sea level).
- Perspiring is a mechanism for cooling the body.
- The addition of antifreeze to water in a radiator decreases the likelihood that the liquid in the radiator will either freeze or boil.

## AP Chemistry: Chapter 10 Practice Test

*Multiple Choice: Choose the best answer. (3 pts each)*

For questions 1-5, select from the list of intermolecular forces the one which best accounts for the following phenomena.

1. Accounts for the electrical conductivity of silver.
2. NaCl has a very high heat of vaporization.
3. The high volatility of helium.
4. Hydrogen chloride has a smaller molar volume than predicted by the Ideal Gas Law.
5. Water has a much higher boiling point than the heavier hydrogen sulfide.
6. Which of the following will have the highest melting point?  
A. F<sub>2</sub>    B. OF<sub>2</sub>    C. CF<sub>4</sub>    D. CsF    E. NaF
7. Which of the following would have the highest boiling point?  
A. H<sub>2</sub>    B. HF    C. H<sub>2</sub>O    D. C<sub>3</sub>F<sub>8</sub>    E. NaF

A. London dispersion forces
B. dipole-dipole attractions
C. hydrogen bonding
D. ionic bonding
E. metallic bonding

Use the diagram to answer the questions below.

Answer the questions below that relate to the five aqueous solutions at 25°C shown above.

8. Which solution has the highest boiling point?

a. 1    b. 2    c. 3    d. 4    e. 5

9. Identify a pair of the solutions that would produce a precipitate when mixed together.

a. 1&2    b. 2&3    c. 3&5    d. 1&5

10. Which solution would be the least effective conductor of electricity?

a. 1    b. 2    c. 3    d. 4    e. 5

11. If the molar heat of fusion of water is 6.01 kJ/mol, how much heat is needed to turn a 30.0g block of ice at 0°C to liquid water at 37°C? (The specific heat of water is 4.18J/g°C).

A. 14.66 kJ    B. 11.13 kJ    C. 10.26 kJ    D. 10.02 kJ    E. 4.64 kJ

12. Which of the following would have the highest boiling point?

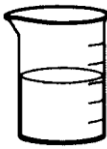
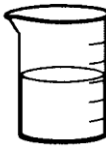



A. ammonia    B. water    C. lithium fluoride    D. ethanol    E. octane

13. Graphite and diamonds are forms of carbon which are called:

A. azeotropes    D. structural isomers  
B. allotropes    E. geometric isomers  
C. optical isomers

14. Polystyrene plastic is an example of:

A. a network solid    D. a crystalline solid

Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
				
0.10 M Pb(NO <sub>3</sub> ) <sub>2</sub>	0.10 M NaCl	0.10 M KMnO <sub>4</sub>	0.10 M C <sub>2</sub> H <sub>5</sub> OH	0.10 M KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>

- B. an ionic solid                      E. a molecular solid  
C. an amorphous solid

15. Which of the following has the highest melting point?  
A.  $\text{CCl}_4$               B.  $\text{Cl}_2$               C.  $\text{LiCl}$               D.  $\text{Cl}_2\text{O}$               E.  $\text{HCl}$
16. Which of the following types of chemical forces are usually strongest?  
A. hydrogen bond                      C. London dispersion  
B. dipole-dipole                      D. covalent
17. Which of the following would you expect to have the highest vapor pressure at any given temperature?  
A.  $\text{C}_2\text{H}_6$               B.  $\text{C}_3\text{H}_8$               C.  $\text{C}_4\text{H}_{10}$               D.  $\text{C}_5\text{H}_{12}$
18. What is the net number of particles in a simple cubic unit cell?  
A. 1                      B. 2                      C. 3                      D. 4
19. The elements of group 5A, the nitrogen family, form compounds with hydrogen having the boiling points listed below:  
 $\text{SbH}_3 -17^\circ\text{C}$ ,  $\text{AsH}_3 -55^\circ\text{C}$ ,  $\text{PH}_3 -87^\circ\text{C}$ ,  $\text{NH}_3 -33^\circ\text{C}$   
The first three compounds illustrate a trend where the boiling point decreases as the mass decreases; however, ammonia ( $\text{NH}_3$ ) does not follow the trend because of  
A) dipole-dipole attraction                      D) London dispersion forces  
B) metallic bonding                      E) ionic bonding  
C) hydrogen bonding
20. Which of the following compounds has the lowest viscosity?  
A)  $\text{CCl}_4(l)$                       C)  $\text{H}_2\text{O}(l)$                       E)  $\text{HCl}(g)$   
B)  $\text{N}_2(g)$                       D)  $\text{CH}_3-(\text{CH}_2)_{25}-\text{CH}_3(l)$
21. What is responsible for capillary action, a property of liquids?  
A) surface tension                      C) adhesive forces                      E) two of these  
B) cohesive forces                      D) viscosity
22. Doping Se with B would produce a(n) \_\_\_\_\_ semiconductor with \_\_\_\_\_ conductivity compared to pure Se.  
A) *p*-type, increased  
B) *n*-type, decreased  
C) *n*-type, increased  
D) *p*-type, decreased  
E) intrinsic, identical
23. The boiling points of four different liquid substances are given below. Which one is likely to have the largest heat of vaporization?  
A. 373K              B. 353K              C. 332K              D. 184K
24. A gas will condense to a liquid when:  
A. its pressure exceeds the vapor pressure  
B. its pressure exceeds the critical pressure below the critical temperature  
C. the triple point is reached  
D. any of the above



25. A vacuum pump attached to a container of water will cause the water to boil because:
- the vapor pressure of the water is increased
  - the heat of vaporization of the water is decreased
  - the temperature of the water is increased
  - the boiling point of the water is decreased at the lower pressure
26. In which of the following substances is the smallest unit of structure the molecule?
- BaO<sub>2</sub>
  - CO<sub>2</sub>
  - SiO<sub>2</sub>
  - all of the above
27. In order to boil the molecular substance methyl alcohol, forces between molecules have to be overcome, including:
- hydrogen bonds
  - dispersion forces
  - dipole forces
  - all of these
28. Which of these substances is most likely to exist as a gas under ordinary conditions?
- AgCl
  - Cl<sub>2</sub>
  - I<sub>2</sub>
  - KCl
29. Which of these substances has the lowest boiling point?
- CH<sub>4</sub>
  - SiH<sub>4</sub>
  - GeH<sub>4</sub>
  - SnH<sub>4</sub>
30. The melting point of ice:
- is decreased by increasing temperature
  - is decreased by increasing pressure
  - is increased by increasing pressure
  - is independent of pressure
31. This bond forms the strongest hydrogen-bonded interactions?
- N-H
  - O-H
  - F-H
  - S-H
32. The repeating unit in a crystal lattice is called:
- a molecule
  - an ionic center
  - the unit cell
  - two dimensional
33. The melting points of the alkali metals decrease from Li to Cs. In contrast, the melting points of the halogens increase from F<sub>2</sub> to I<sub>2</sub>. (3 pts each)
- Using bonding principles, account for the decrease in the melting points of the alkali metals.
  - Using bonding principles, account for the increase in the melting points of the halogens.
  - What is the expected trend in the melting points of the compounds LiF, NaCl, KBr, and CsI? Explain this trend using bonding principles.

34. How much heat is required to convert 40.0 g of ice at  $-10.0^{\circ}\text{C}$  to steam at  $120.0^{\circ}\text{C}$ ? The heat capacity of ice is  $2.1 \text{ J/g}^{\circ}\text{C}$ . The heat capacity of liquid water is  $4.2 \text{ J/g}^{\circ}\text{C}$ . The heat capacity of steam is  $1.8 \text{ J/g}^{\circ}\text{C}$ . The heat of vaporization of water is  $41.2 \text{ kJ/mol}$ . The heat of fusion of water is  $6.0 \text{ kJ/mol}$ . (10 pts)

35. In each case indicate which liquid will have the higher boiling point and explain why. (2 pts each)

A.  $\text{CO}_2$  or  $\text{SO}_2$

B.  $\text{Cl}_2$  or  $\text{Br}_2$

C.  $\text{C}_2\text{H}_5\text{SH}$  or  $\text{C}_2\text{H}_5\text{OH}$

D. 
$$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{H-C} - \text{C-H} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

## AP Chemistry: Chapter 12

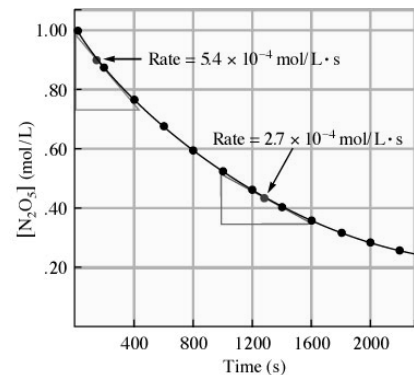
### Chemical Kinetics

Although we can know a lot of things about a chemical reaction, including the reactants and expected products, the stoichiometry and the energy, we must understand the rate of the reaction to truly grasp what is occurring. Although graphite can be compressed into a diamond, the reaction is so slow that we cannot view this in our lifetime. Therefore, we must choose to examine only those reactions that occur at a reasonable rate.

#### 12.1 Reaction Rates

- Reaction Rate- change in concentration of a reactant or product per unit time.
  - We will write the concentration in mol/L as [A] where “A” is the substance
  - If the rate expression involves a reactant:
    - Rate =  $-\frac{\Delta[A]}{\Delta t}$  (negative because [ ] decreases)
    - The above gives the average rate.
  - To get an instantaneous rate, we can compute the slope of a line tangent to the curve at that point.
    - Rate = -(slope of the tangent line)
  - The rate of a reaction is not constant but changes with time because concentrations change with time. We will only work with reaction rates that are “initial rates” (reverse reaction is negligible)

$$\text{Rate} = \frac{\Delta[A]}{\Delta t}$$



#### 12.2 Rate Laws: An Introduction

- Rate laws can express how quickly a reactant is consumed or the rate at which a product is produced. In this chapter, however, we will focus on the consumption of reactants.
  - We will make the assumption that only the forward reaction is occurring; this means that calculations of the reverse reaction do not have to be considered here.
- Differential Rate Law or Rate Equation- a rate law that expresses how the rate depends on concentration.
- For the reaction  $aA + bB + \dots \rightarrow gG + hH + \dots$ 
  - Rate =  $k[A]^m[B]^n \dots$  where [A] & [B] represent molarities
  - The exponents are positive or negative, integers or fractions.
  - Usually positive integers (small whole numbers)
  - k = rate constant
    - The value of k depends on the type of reaction, temperature and presence of a catalyst
    - The faster the reaction, the larger the k value
  - The exponents determine the **order** of the reactants. The sum of the exponents is the order of the reaction.
    - $R = k[A][B]^2$  is first order in A, second order in B and third order overall.
    - The units of k can be calculated by reaction orders and units of concentration and rate. For example, if rate is in mol/L.s in the above rate law, we can find the units for k as follows:

$$\left( \frac{\text{Rate}}{[A][B]^2} \right) = k \text{ so } k = \left( \frac{\frac{\text{mol}}{\text{L} \cdot \text{s}}}{\frac{\text{mol}}{\text{L}} \frac{\text{mol}^2}{\text{L}^2}} \right) \quad \text{This simplifies to: } k = \left( \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}} \right)$$

- The “shortcut” to determining units of k is as follows:  $k = \text{L}^x/\text{mol}^x \cdot \text{time}$ .
  - The value of x will be one less than the order of the reaction.
  - If the reaction is 3rd order,  $k = \text{L}^2/\text{mol}^2 \cdot \text{time}$ .
  - If the reaction is 2nd order,  $k = \text{L}/\text{mol} \cdot \text{time}$

- If the reaction is 1st order,  $k = 1/\text{time}$

### 12.3 Determining the Form of the Rate Law

- Determining Differential Rate Laws from Experimental Data
  - If doubling the initial [ ] of a reactant causes the initial rate to double, the reaction is first order in that reactant.
  - If doubling the initial [ ] of a reactant causes the initial rate to quadruple, the reaction is second order in that reactant.
  - If doubling the initial [ ] of a reactant causes the initial rate to increase 8 times, the reaction is third order in that reactant.
  - If doubling the initial [ ] of a reactant does not change the initial rate, the reaction is zero order in that reactant and that reactant is removed from the rate law.
  - Let's Practice!

Ex. $2A + B \rightarrow 2C$		
[A]	[B]	Rate
0.40	0.20	0.10
0.40	0.40	0.20
0.80	0.40	0.80

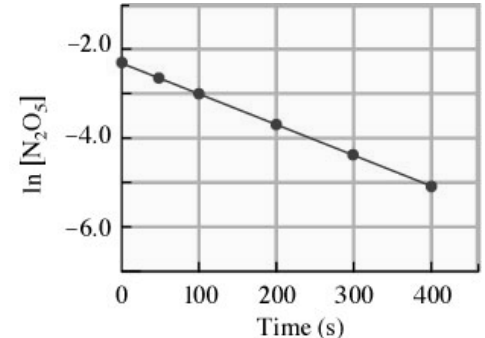
Rate = \_\_\_\_\_  
overall reaction order is \_\_\_\_

Ex. $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$		
$[\text{NH}_4^+]$	$[\text{NO}_2^-]$	Rate
0.100	0.0050	$1.35 \times 10^{-7}$
0.100	0.010	$2.70 \times 10^{-7}$
0.200	0.010	$5.40 \times 10^{-7}$

Rate = \_\_\_\_\_  
overall reaction order is \_\_\_\_

### 12.4 The Integrated Rate Law

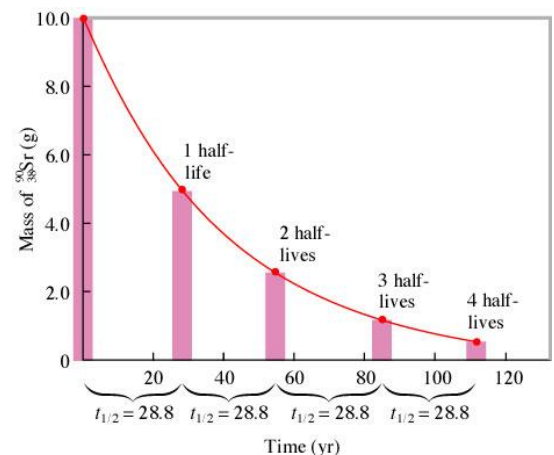
- Integrated Rate Law- expresses how the concentration of the reactant depends on time
  - Instead of changing initial concentrations and using multiple experiments, one experiment is done and concentration changes over time are measured.
  - *Note: The rate law we choose to determine by experiment often depends on what types of data are easiest to collect. If we can conveniently measure how the rate changes as the concentrations are changed, we can readily determine the differential rate law. On the other hand, if it is more convenient to measure the concentration as a function of time, we can determine the form of the integrated rate law.*
  - 1<sup>st</sup> order integrated rate law  $\ln \left( \frac{[A]_0}{[A]_t} \right) = kt$
  - A plot of  $\ln[A]$  vs  $t$  always gives a straight line for a 1<sup>st</sup> order reaction. The slope =  $-k$ .
  - Ex. At 400°C, the 1<sup>st</sup> order conversion of cyclopropane into propylene as a rate constant of  $1.16 \times 10^{-6} \text{ s}^{-1}$ . If the initial concentration of cyclopropane is  $1.00 \times 10^{-2} \text{ mol/L}$  at 400°C, what will its concentration be 24.0 hrs after the reaction begins?



### 21.2 The Kinetics of Radioactive Decay

Every radioactive sample has a decay rate, or amount of particles that will decay over time.

- This is a first-order process
- This a derivative of the “naughty katy” equation
  - $\text{Rate} = -(\Delta N/\Delta t) = kN$
- Half-life ( $t_{1/2}$ ) is the length of time required for the concentration of a reactant to decrease to half of its initial value.



- $t_{1/2} = 0.693/k$
- A fast reaction with a short  $t_{1/2}$  has a large  $k$ .
- A slow reaction with a long  $t_{1/2}$  has a small  $k$ .
- Example: The decomposition of  $\text{SO}_2\text{Cl}_2$  and  $\text{Cl}_2$  is a first order reaction with  $k = 2.2 \times 10^{-5} \text{s}^{-1}$  at  $320^\circ\text{C}$ . Determine the half-life of this reaction.
- Example: The decomposition of  $\text{N}_2\text{O}_5$  dissolved in  $\text{CCl}_4$  is a first order reaction. The chemical change is:  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$   
At  $45^\circ\text{C}$  the reaction was begun with an initial  $\text{N}_2\text{O}_5$  concentration of  $1.00 \text{ mol/L}$ . After  $3.00$  hours the  $\text{N}_2\text{O}_5$  concentration had decreased to  $1.21 \times 10^{-3} \text{ mol/L}$ . What is the half-life of  $\text{N}_2\text{O}_5$  expressed in minutes at  $45^\circ\text{C}$ ?
- More Advanced Half-life Problems
  - Ex. The radioactive decay of thallium-206 to lead-206 has a half-life of  $4.20 \text{ min}$ . Starting with  $5.00 \times 10^{22}$  atoms of thallium-206, calculate the number of such atoms left after  $42.0 \text{ min}$ .
  - Ex. A freshly isolated sample of  $^{90}\text{Y}$  was found to have an activity of  $9.8 \times 10^5$  disintegrations per minutes at 1:00 PM on December 3, 1995. At 2:15 PM on December 17, 1995, its activity was redetermined and found to be  $2.6 \times 10^4$  disintegrations per minute. Calculate the half-life of  $^{90}\text{Y}$ .

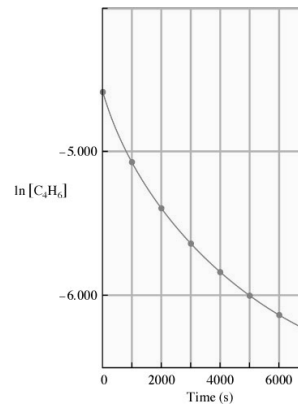
- Second order integrated rate law      Rate =  $k[\text{A}]^2$

$$\left( \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} \right) = kt$$

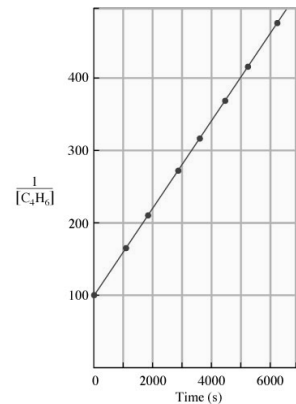
- A plot of  $1/[\text{A}]_t$  versus  $t$  produces a straight line with slope  $k$ .

- Zero Order      Rate =  $k$

- $[\text{A}]_t - [\text{A}]_0 = -kt$
- A plot of  $[\text{A}]$  versus  $t$  produces a straight line with slope  $-k$ .



(a)

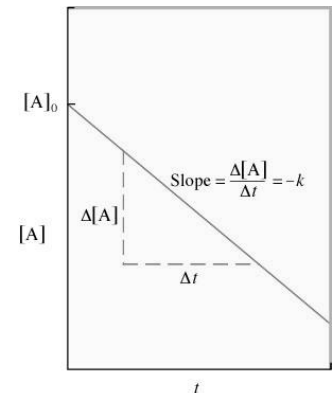


(b)

## 12.5 Reaction Mechanisms

Reaction mechanisms diagram a series of steps in which a chemical reaction occurs.

- Intermediate- a species that is neither a product nor a reactant in the overall equation
  - Is used up in a subsequent step
- Elementary step- a reaction whose rate law can be written from its molecularity (balanced equation)
  - Molecularity- the number of species that must collide to produce the reaction represented by the elementary step.
- Unimolecular step- a reaction step involving only one molecule.
- Bimolecular step- a reaction step involving the collision of two molecules (Rate law always  $2^{\text{nd}}$  order)



- Rate-determining step -slowest step
- Elementary Reaction -agrees with the balanced equation
- Reaction mechanisms must:
  1. Add up to the overall balanced equation.
  2. Agree with the rate law
    - We can't prove a mechanism absolutely. We can only come up with a possible mechanism.
    - Ex. Elementary Rxn :  $\text{NO} + \text{N}_2\text{O} \rightarrow \text{NO}_2 + \text{N}_2$       Rate Law:  $R = k[\text{NO}][\text{N}_2\text{O}]$
    - Ex. The reaction  $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}$  is thought to proceed via the following two-step mechanism:
 

$\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F}$	slow
$\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$	fast

Determine the rate law for the reaction:

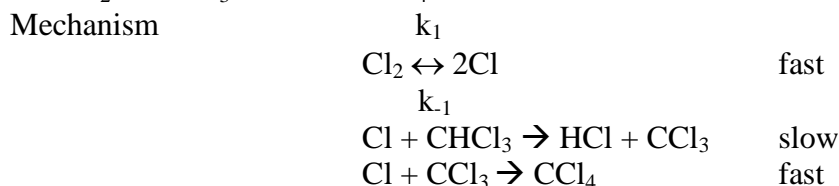
- When an intermediate is a reactant in the rate-determining step, the derivation of the rate law is more difficult.
  - Ex.  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ 

$\text{NO}_2 + \text{NO}_2 \xrightleftharpoons[k_1]{k_1} \text{NO}_3 + \text{NO}$	Fast
$\text{NO}_3 + \text{CO} \xrightarrow{k_1} \text{CO}_2 + \text{NO}_2$	Slow

Slow step determines rate law (rate-determining step)

Rate law:  $R = k[\text{NO}_3][\text{CO}]$  But,  $\text{NO}_3$  was an intermediate. We must come up with something equal to  $\text{NO}_3$  to substitute.

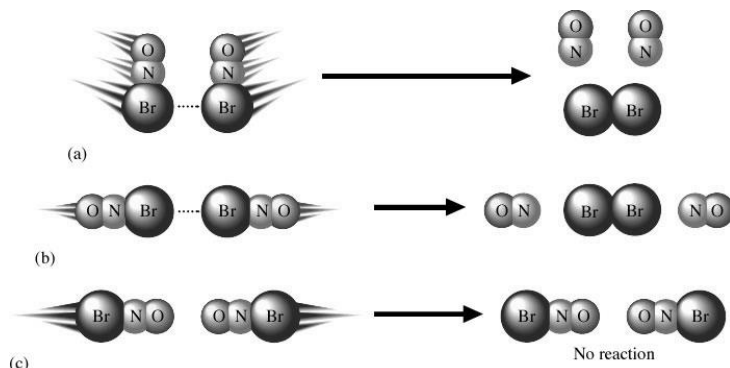
Ex.  $\text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_4$



Rate Law:

## 12.6 A Model for Chemical Kinetics

- Molecules must collide to react. Only a small portion of collisions produce a reaction.
- Increasing temperature increases reaction speed. Rate and rate constants often double for every  $10^\circ$  increase in temperature.
- Activation energy ( $E_A$ )- energy that must be overcome to produce a chemical reaction.
- Rate of reaction depends on  $E_A$ , not  $\Delta E$ .  $\Delta E$  has no effect on rate of reaction.
  - The higher the  $E_A$ , the slower the reaction at a given temperature.



- Molecules and collisions have varying energies. As temperature increases, more collisions will have sufficient energy to overcome the activation energy. As temperature doubles, the fraction of effective collisions increases exponentially.
- Reaction rate is smaller than would be predicted from the number of collisions having sufficient energy to react. This is because of molecular orientations.
- **2 factors: 1. Sufficient energy and 2. Proper molecular orientation**

- Arrhenius Equation- can be used to calculate  $E_A$ 
  - As  $E_A$  increases,  $k$  decreases.
  - The Arrhenius equation describes a line. We can plot  $1/T$  vs  $\ln k$  and get a straight line whose slope is equal to  $-E_A/R$ .
  - A variation of the Arrhenius equation can be used to calculate  $E_A$  or to find  $k$  at another temperature if  $E_A$  is known:

$$\ln k = \ln A - \frac{E_A}{RT}$$

$k$  = rate constant

$R = 8.314 \text{ J/K mol}$

$T$  = Kelvin temperature

$A$  = frequency factor (constant as temperature changes)

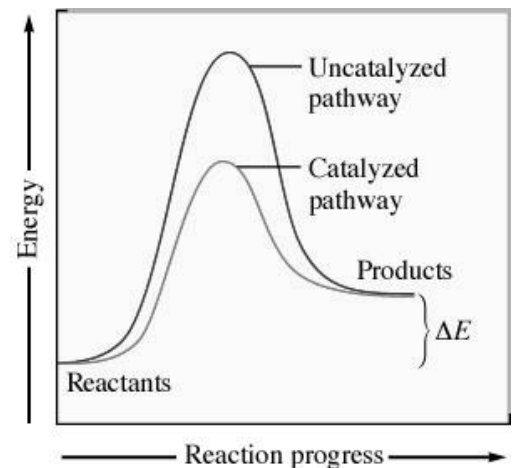
$E_A$  = activation energy

$$\ln \frac{k_1}{k_2} = \frac{E_A}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Ex. The rate constant of a first order reaction is  $3.46 \times 10^{-2} \text{ s}^{-1}$  at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

## 12.8 Catalysis

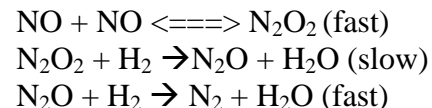
- Catalyst- substance that speeds up a reaction without being consumed.
  - produces a new reaction pathway with a lower activation energy
  - A catalyst lowers the  $E_A$  for both the forward and reverse reaction.
    - enzymes- biological catalysts
    - homogeneous catalyst- present in the same phase as the reacting molecules (usually liquid phase)
    - heterogeneous catalyst- exists in a different phase
      - Usually involves gaseous reactants being adsorbed on the surface of a solid catalyst (such as a car's catalytic converter)
      - Absorption involves penetration.



## AP Chemistry: Rate Law Worksheet

### #1

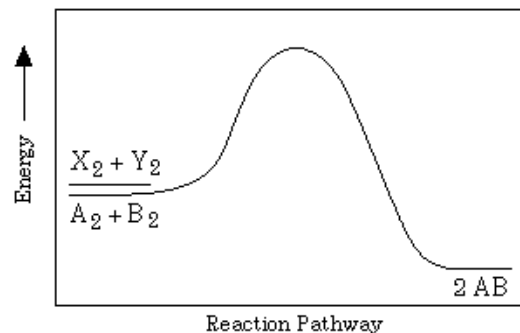
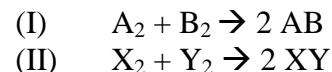
The reaction between NO and H<sub>2</sub> is believed to occur in the following three-step process.



- a) Write a balanced equation for the overall reaction.
  
- b) Identify the intermediates in the reaction. Explain your reasoning.
  
- c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is  $\text{rate} = k[\text{NO}]^2[\text{H}_2]$ . The student then concludes that:
  - (1) the reaction is third-order and
  - (2) the mechanism involves the simultaneous collision of two NO molecules and an H<sub>2</sub> molecule.
 Are conclusions (1) and (2) correct? Explain.
  
- d) Explain why an increase in temperature increases the rate constant,  $k$ , given the rate law in (c).

### #2

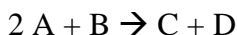
Two reactions are represented to the right. The potential-energy diagram for reaction I is shown below. The potential energy of the reactants in reaction II is also indicated on the diagram. Reaction II is endothermic, and the activation energy of reaction I is greater than that of reaction II.



- a) Complete the potential-energy diagram for reaction II on the graph.
- b) For reaction I, predict how each of the following is affected as the temperature is increased by 20°C. Explain the basis for each prediction.
  - i. Rate of reaction
  
  - ii. Heat of reaction
  
- c) For reaction II, the form of the rate law is  $\text{rate} = k[\text{X}_2]^m[\text{Y}_2]^n$ . Briefly describe an experiment that can be conducted in order to determine the values of  $m$  and  $n$  in the rate law for the reaction.
  
- d) From the information given, determine which reaction initially proceeds at the faster rate under the same conditions of concentration and temperature. Justify your answer.



## #3



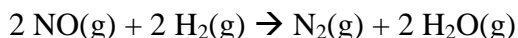
The following results were obtained when the reaction represented above was studied at 25 °C

Experiment	Initial[A]	Initial[B]	Initial Rate of Formation of C (mol L <sup>-1</sup> min <sup>-1</sup> )
1	0.25	0.75	4.3 x 10 <sup>-4</sup>
2	0.75	0.75	1.3 x 10 <sup>-3</sup>
3	1.50	1.50	5.3 x 10 <sup>-3</sup>
4	1.75	??	8.0 x 10 <sup>-3</sup>

- Determine the order of the reaction with respect to A and B. Justify your answer.
- Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.
- Determine the initial rate of change of [A] in Experiment 3.
- Determine the initial value of [B] in Experiment 4.
- Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.

1. A + B → C + M    Fast M + A → D            Slow	2. B <====> M        Fast equilibrium M + A → C + X    Slow A + X → D            Fast	3. A <====> M        Fast equilibrium M + A → C + X    Slow X → D                Fast
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## #4

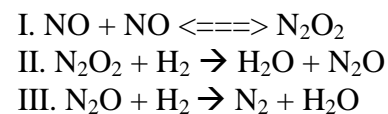


Experiments conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table.

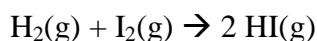
Experiment	Initial Concentration (mol/L)		Initial Rate of Formation of N <sub>2</sub> (mol/L min)
	[NO]	[H <sub>2</sub> ]	
1	0.0060	0.0010	1.8 x 10 <sup>-4</sup>
2	0.0060	0.0020	3.6 x 10 <sup>-4</sup>
3	0.0010	0.0060	0.30 x 10 <sup>-4</sup>
4	0.0020	0.0060	1.2 x 10 <sup>-4</sup>

- Determine the order for each of the reactants, NO and H<sub>2</sub>, from the data given and show your reasoning.
  - Write the overall rate law for the reaction.
- Calculate the value of the rate constant, k, for the reaction. Include units.
- For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H<sub>2</sub> has been consumed.

- d) The following sequence of elementary steps is a proposed mechanism for the reaction. Based on the data present, which of the above is the rate-determining step? Show that the mechanism is consistent with:
- the observed rate law for the reaction, and
  - the overall stoichiometry of the reaction.



#5



For the exothermic reaction represented above, carried out at 298 K, the rate law is as follows. Rate =  $k [\text{H}_2] [\text{I}_2]$

Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

- Addition of hydrogen gas at constant temperature and volume.
- Increase in volume of the reaction vessel at constant temperature.
- Addition of a catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate.
- Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy

#6

Consider the following general equation for a chemical reaction.  $\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{D}(\text{g})$

- Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.
- How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
- Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.  
 $\text{A} + \text{B} \rightleftharpoons [\text{AB}]$  (fast)  
 $[\text{AB}] + \text{B} \rightarrow \text{C} + \text{D}$  (slow)
- Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

### Practice AP Problems

2003

1. In a study of the kinetics of the reaction represented below, the following data were obtained at 298K.



Experiment	Initial $[\text{Br}^-]$	Initial $[\text{BrO}_3^-]$	Initial $[\text{H}^+]$	Rate of Disappearance of $\text{BrO}_3^-$ (mol/L·s)
1	0.00100	0.00500	0.100	$2.50 \times 10^{-4}$
2	0.00200	0.00500	0.100	$5.00 \times 10^{-4}$
3	0.00100	0.00750	0.100	$3.75 \times 10^{-4}$
4	0.00100	0.01500	0.200	$3.00 \times 10^{-3}$

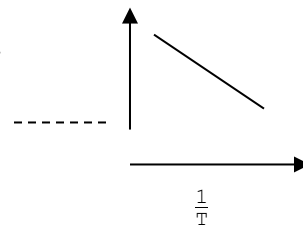
- From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.
  - $\text{Br}^-$
  - $\text{BrO}_3^-$
  - $\text{H}^+$
- Write the rate law for the overall reaction.
- Determine the value of the specific rate constant for the reaction at 298K. Include correct units.

2004

2. The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in the absorbance over time. Species X has a molar absorptivity constant of  $5.00 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$  and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table to the right.

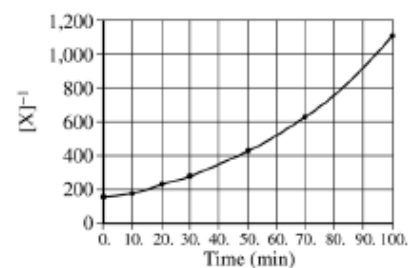
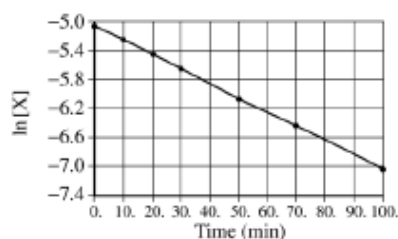
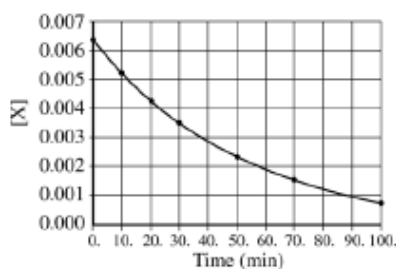
$[\text{X}]$ (M)	Absorbance	Time (min)
?	0.600	0.0
$4.00 \times 10^{-5}$	0.200	35.0
$3.00 \times 10^{-5}$	0.150	44.2
$1.50 \times 10^{-5}$	0.075	?

- Calculate the initial concentration of the colored species. (Hint: Absorptivity = molar absorptivity constant  $\times$  path length  $\times$  concentration)
- Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.
- Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.
- Calculate the half-life of the reaction. Include units with your answer.
- Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph shown, where T is temperature. This graph can be used to determine the activation energy, EA, of the reaction.
  - Label the vertical axis of the graph.
  - Explain how to calculate the activation energy from this graph.



3. The decomposition of gas X to produce gases Y and Z is represented by the equation:  $X \rightarrow 2Y + Z$   
 In a certain experiment, the reaction took place in a 5.00L flask at 428K. Data from this experiment were used to produce the information in the table shown. This information is plotted in the graphs that follow.

Time (min)	[X] (mol L <sup>-1</sup> )	ln [X]	[X] <sup>-1</sup> (L mol <sup>-1</sup> )
0	0.00633	-5.062	158
10.	0.00520	-5.259	192
20.	0.00427	-5.456	234
30.	0.00349	-5.658	287
50.	0.00236	-6.049	424
70.	0.00160	-6.438	625
100.	0.000900	-7.013	1,110



- How many moles of X were initially in the flask?
- How many molecules of Y were produced in the first 20. minutes of the reaction?
- What is the order of this reaction with respect to X? Justify your answer.
- Write the rate law for this reaction.
- Calculate the specific rate constant for this reaction. Specify units.
- Calculate the concentration of X in the flask after a total of 150. minutes of reaction.

## AP Chemistry: Chapter 13

### Chemical Equilibrium

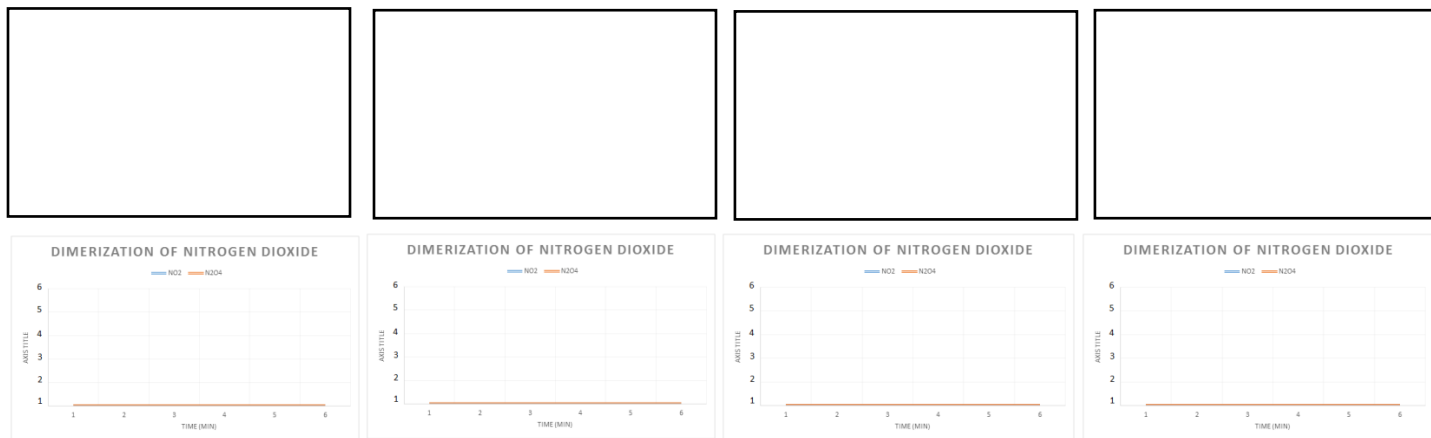
#### 13.1 The Equilibrium Condition

As we have learned stoichiometry, we have assumed that chemical reactions proceed to completion and that all reactants are converted to products. Many chemical reactions stop short of completion, however, and we will now learn to examine and calculate the progress of these reactions.

Chemical equilibrium- state where concentrations of products and reactants remain constant over time

- Equilibrium is dynamic- particles are constantly forming products and then reforming reactants.
  - If mostly products are formed, the reaction is said to lie to the right.
  - If mostly reactants are present, the reaction is said to lie to the left.
- Any chemical reaction in a closed vessel will reach equilibrium.
- At equilibrium, forward reaction rate = reverse reaction rate.

Example: Draw in the diagrams from the powerpoint, then graph the progress of the reaction in the graph provided.



*Points to take away...*

- *Molecules react by colliding, so high concentrations of reactants lead to the formation of products.*
- *When product concentrations increase, the reverse reaction is favored.*
- *All equilibrium systems are working to increase entropy while decreasing free energy; the final system should have the lowest energy.*
- *A system will remain at equilibrium unless disturbed.*

#### 13.2 The Equilibrium Constant

Law of Mass Action

- The equilibrium constant,  $K$ , can be denoted by any of the following:  $K_c = K = K_{eq}$
- For the reaction:  $jA + kB \rightleftharpoons lC + mD$        $K_c = \frac{[C]^l[D]^m}{[A]^j[B]^k}$ 
  - [ ] = concentration = mol/L
  - Ex. Write the equilibrium expression for the following reaction:  
 $4 \text{NH}_3(g) + 7 \text{O}_2(g) \rightleftharpoons 4 \text{NO}_2(g) + 6 \text{H}_2\text{O}(g)$
  - If we know equilibrium concentrations, we can calculate the equilibrium constant,  $K$ .
    - Only gases and aqueous solutions are used to write the equilibrium expression.
    - $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$        $K_{eq} =$

- If an equilibrium reaction is composed of reactants and products all in the same state, it is said to be a homogeneous system. If they are different, it is termed heterogeneous.
- K changes with temperature (not with concentration or pressure).

- The value of K can be calculated easily if the original equation is manipulated, as shown in the table below.

Reaction	$jA + kB \rightleftharpoons lC + mD$	$lC + mD \rightleftharpoons jA + kB$	$njA + nkB \rightleftharpoons nlC + nmD$
Expression	$K_c = \frac{[C]^l[D]^m}{[A]^j[B]^k}$	$K_c' = \frac{[A]^j[B]^k}{[C]^l[D]^m}$	$K_c'' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}}$
To Solve	Plug in equilibrium concentrations	Take the inverse of K. $K_c' = \frac{1}{K_c}$	Raise K to the power of the coefficient. $K_c^n$

- For a 2-step reaction with  $K_1$  and  $K_2$  as K values for each step, the K for the overall reaction is  $K_3 = K_1 \times K_2$ .
  - The units for K depend on the reaction and take into account “non-ideal” behavior. They will not be used.
- Practice! The following equilibrium concentrations were observed for the synthesis of ammonia from its elements.  $[N_2] = 8.5 \times 10^{-1}$ ,  $[H_2] = 3.1 \times 10^{-3}$ ,  $[NH_3] = 3.1 \times 10^{-2}$ 
  - Write the balanced equation for the reaction \_\_\_\_\_
  - Write the equilibrium expression \_\_\_\_\_
  - Solve for K.
  - If the reaction is reversed and the coefficients are doubled, solve for K.
- Equilibrium position - a set of equilibrium concentrations.
  - Depends on initial concentrations. (K doesn't)

### 13.3 and 13.4 Equilibrium Expressions Involving Pressures and Heterogeneous Equilibria

Pressures can be used in equilibrium expressions. The equilibrium constant is called  $K_p$ .

- Using the same mass action equation as above, the  $K_p$  expression becomes:  $K_p = \frac{(P_C)^l(P_D)^m}{(P_A)^j(P_B)^k}$ 
  - P = partial pressure at equilibrium in atm.
- $K_c$  involves concentrations while  $K_p$  involves pressures.
- $K_p$  and  $K_c$  can be interconverted using the following relationship:
- $K_c = K_p$  if # moles gaseous product = # moles gaseous reactant
- A value for K greater than one means that the equilibrium is far to the right (mostly products).
- A value for K less than one means that the equilibrium is far to the left (mostly reactants).
- The size of K and the time needed to reach equilibrium are not directly related.
- K values can not always be directly compared because stoichiometry differs.

$$K_p = K_c(RT)^{\Delta n}$$

R = 0.0821 L·atm/mol·K  
 T = Kelvin temperature  
 $\Delta n$  = #moles gaseous product - # moles gaseous reactant

#### Practice Problem!

Consider the reaction  $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$  at  $35^\circ C$ , when 3.00 mol  $NOCl(g)$ , 1.00 mol  $NO(g)$ , and 2.00 mol  $Cl_2(g)$  are mixed in a 10.0 L flask. After the system has reached equilibrium the

concentrations are observed to be:  $[\text{Cl}_2] = 1.52 \times 10^{-1} \text{ M}$ ,  $[\text{NO}] = 4.00 \times 10^{-3} \text{ M}$ , and  $[\text{NOCl}] = 3.96 \times 10^{-1} \text{ M}$ .

- Calculate the value of  $K$  for this system at  $35^\circ\text{C}$ .
- Calculate the value of  $K$  for the reaction  $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \leftrightarrow 2\text{NOCl}(\text{g})$ .
- Calculate the value of  $K$  for the reaction  $4\text{NOCl}(\text{g}) \leftrightarrow 4\text{NO}(\text{g}) + 2\text{Cl}_2(\text{g})$ .
- Calculate  $K_p$  for the first reaction.

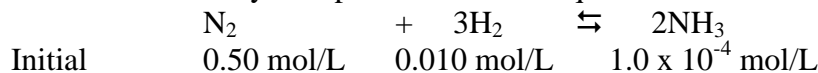
### 13.5 Application of the Equilibrium Constant

When working equilibrium problems, it is not always obvious which way that equilibrium is going to shift. Obviously, if the initial concentration of products is zero, we will shift to form products. However, if there are reactants and products present in the reaction, you must solve for the reaction quotient,  $Q$ , to determine which way the reaction will shift to obtain equilibrium.

- $Q$  = reaction quotient
  - Calculated like  $K_c$ , but using initial concentrations instead of equilibrium concentrations
    - If  $K = Q$ , then system is at equilibrium (no shift occurs)
    - If  $K < Q$ ,  $[\text{product}]/[\text{reactant}]$  is too large (system shifts to left)
    - If  $K > Q$ ,  $[\text{product}]/[\text{reactant}]$  is too small (system shifts to the right)

#### Practice Problem!

For the synthesis of ammonia, the value of  $K$  is  $6 \times 10^{-2}$  at  $500.^\circ\text{C}$ . In an experiment,  $0.50 \text{ mol}$  of  $\text{N}_2(\text{g})$ ,  $1.0 \times 10^{-2} \text{ mol}$  of  $\text{H}_2(\text{g})$ , and  $1.0 \times 10^{-4} \text{ mol}$  of  $\text{NH}_3(\text{g})$  are mixed at  $500.^\circ\text{C}$  in a  $1.0 \text{ L}$  flask. In which direction will the system proceed to reach equilibrium?



Since \_\_\_\_\_, the reaction will shift to the \_\_\_\_\_ to reach equilibrium.

### 13.6 Solving Equilibrium Problems

When solving equilibrium problems, it is very important to follow a series of steps. Skipping these can lead to problems (and fewer points on your AP exam).

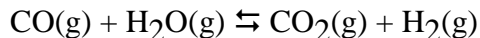
#### Steps for Solving Equilibrium Problems

- Write a balanced equation. If a chemical reaction occurs, work out the stoichiometry and then write a second equation for the equilibrium reaction. Always do stoichiometry (in moles) first!
  - Set up the equilibrium expression. (No numbers yet!)
  - If you can't tell which way the reaction is going to shift, solve for  $Q$ .
  - Set up a chart that includes the equation, initial concentrations, changes in concentration in terms of  $X$ , and final concentrations.
  - Substitute these final concentrations into the equilibrium expression and solve for  $X$ .
  - Check your answer to make sure that it is logical!
- When solving an equilibrium problem, some  $+X$  and  $-X$  values can be treated as negligible.  $X$  is considered negligible if it is less than 5% of the number that it was to be subtracted from or added to.

- The value of  $X$  is considered negligible when the value of  $K$  is very small. If  $K$  is small, very few products are formed, so  $X$  is going to be a very small value.
- *For most of the problems you will encounter,  $X$  will be negligible, but always check your answer to be sure it makes sense.*

### Practice Problem!

At 700 K, carbon monoxide reacts with water to form carbon dioxide and hydrogen:



The equilibrium constant for this reaction at 700 K is 5.10. Consider an experiment in which 1.00 mol of  $\text{CO(g)}$  and 1.00 mol of  $\text{H}_2\text{O(g)}$  are mixed together in a 1.00 L flask at 700 K. Calculate the concentrations of all species at equilibrium.

<b>Reaction</b>	$\text{CO}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CO}_2$	+	$\text{H}_2$
<b>Initial</b>							
<b>Change</b>							
<b>Equil.</b>							

Phosphorus pentachloride gas decomposes to form chlorine gas and phosphorus trichloride gas. At a certain temperature, a 2.00L flask initially contained 0.298 mol  $\text{PCl}_3$  and 0.00870 mol  $\text{PCl}_5$ . After the system had reached equilibrium, 0.00200 mol  $\text{Cl}_2$  gas was found in the flask. Calculate the equilibrium constant for this reaction.

Consider the reaction  $2\text{HF(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{F}_2\text{(g)}$  where  $K = 1.0 \times 10^{-2}$  at some very high temperature. In an experiment, 5.00 mol of  $\text{HF(g)}$ , 0.500 mol of  $\text{H}_2\text{(g)}$ , and 0.750 mol of  $\text{F}_2\text{(g)}$  are mixed in a 5.00 L flask and allowed to react to equilibrium. Solve for the equilibrium concentrations.

Gaseous  $\text{NOCl}$  decomposes to form nitrogen monoxide and chlorine gases. If 0.650 mol of  $\text{NOCl}$  is placed into a 2.0L flask, what will be the equilibrium concentrations for each species in the reaction?  $K = 1.6 \times 10^{-5}$ .

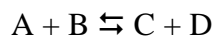
## 13.7 LeChâtelier's Principle

When a stress is applied to a system, the equilibrium will shift in the direction that will relieve the stress. This is what we will call the "Bathtub Hypothesis". ☺ There are four changes that can happen to a system at equilibrium.

- Changes in concentration



- An increase in concentration of a reactant will cause equilibrium to shift to the right to form more products. An increase in concentration of a product will cause equilibrium to shift to the left to form more reactants.
- A decrease in concentration of a product will cause equilibrium to shift to the right to form more products. A decrease in the concentration of a reactant will cause equilibrium to shift to the left to make more reactants.
  - A change in concentration of reactant or product will not affect the value of  $K$ .



Add A or B \_\_\_\_\_

Remove A or B \_\_\_\_\_

Add C or D \_\_\_\_\_

Remove C or D \_\_\_\_\_



b. Changes in temperature

- Changes in temperature may easily be treated as changes in concentration if you think of heat as a product (exothermic rxn) or a reactant (endothermic rxn).
- An increase in temperature of an exothermic reaction will cause equilibrium to shift to the left.  $K$  will decrease. A decrease in temperature of an exothermic reaction will cause equilibrium to shift to the right.  $K$  will increase.
- An increase in temperature of an endothermic reaction will cause equilibrium to shift to the right.  $K$  will increase. A decrease in temperature of an endothermic reaction will cause equilibrium to shift to the left.  $K$  will decrease.

c. Changes in pressure

- Changes in pressure only affect equilibrium systems having gaseous products and/or reactants.
- Increasing the pressure of a gaseous system will cause equilibrium to shift to the side with fewer gas particles. Decreasing the pressure of a gaseous system will cause equilibrium to shift to the side with more gas particles.
- If the system has the same number of moles of gas on each side, changes in pressure do not affect equilibrium. Adding an inert gas does not affect equilibrium since the partial pressures of the gases in the reaction are not affected.
- Changing pressure does not affect the value of the equilibrium constant.

d. Addition of a catalyst

- Adding a catalyst does not affect equilibrium.

Consider the reaction  $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$  which is exothermic. A vessel contains  $NO_2(g)$ ,  $N_2(g)$ , and  $O_2(g)$  at equilibrium. Predict how each of the following stresses will affect the concentration of  $O_2$  and the value of  $K$ .

- $NO_2$  is added
- $N_2$  is removed
- The volume is halved
- $He(g)$  is added
- The temperature is increased
- A catalyst is added



- c. Determine  $K_p$ , in terms of  $K_c$  for this system.
- d. When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the  $\text{CO}(g)$  is converted back to  $\text{CO}_2(g)$ . Calculate the value of  $K_c$  at this lower temperature.
- e. In a different experiment, 0.50 mole of  $\text{H}_2(g)$  is mixed with 0.50 mole of  $\text{CO}_2(g)$  in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of  $\text{CO}(g)$  at this temperature.

**#3**

Sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , is a highly reactive gaseous compound. When heated, it decomposes as follows:

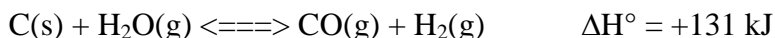


This decomposition is endothermic. A sample of 3.509 grams of  $\text{SO}_2\text{Cl}_2$  is placed in an evacuated 1.00 liter bulb and the temperature is raised to 375°K.

- a. What would be the pressure in atmospheres in the bulb if no dissociation of the  $\text{SO}_2\text{Cl}_2(g)$  occurred?
- b. When the system has come to equilibrium at 375 K, the total pressure in the bulb is found to be 1.43 atmospheres. Calculate the partial pressures of  $\text{SO}_2$ ,  $\text{Cl}_2$ , and  $\text{SO}_2\text{Cl}_2$  at equilibrium at 375K.
- c. Give the expression for the equilibrium constant (either  $K_p$  or  $K_c$ ) for the decomposition of  $\text{SO}_2\text{Cl}_2(g)$  at 375°K. Calculate the value of the equilibrium constant you have given, and specify its units.
- d. If the temperature raised to 500 K, what effect would this have on the equilibrium constant? Explain briefly.

## AP Chemistry: Equilibrium Worksheet #2

**#1**



A rigid container holds a mixture of graphite pellets (C(s)), H<sub>2</sub>O(g), CO(g), and H<sub>2</sub>(g) at equilibrium. State whether the number of moles of CO(g) in the container will increase, decrease, or remain the same after each of the following disturbances is applied to the original mixture. For each case, assume that all other variables remain constant except for the given disturbance. Explain each answer with a short statement.

- a. Additional H<sub>2</sub>(g) is added to the equilibrium mixture at constant volume.
  
- b. The temperature of the equilibrium mixture is increased at constant volume.
  
- c. The volume of the container is decreased at constant temperature.
  
- d. The graphite pellets are pulverized.

**#2**



The equilibrium above is established by placing solid NH<sub>4</sub>HS in an evacuated container at 25°C. At equilibrium, some solid NH<sub>4</sub>HS remains in the container. Predict and explain each of the following:

- a. The effect on the equilibrium partial pressure of NH<sub>3</sub> gas when additional solid NH<sub>4</sub>HS is introduced into the container.
  
- b. The effect on the equilibrium partial pressure of NH<sub>3</sub> gas when additional H<sub>2</sub>S gas is introduced into the container.
  
- c. The effect on the mass of solid NH<sub>4</sub>HS present when the volume of the container is decreased.
  
- d. The effect on the mass of solid NH<sub>4</sub>HS present when the temperature is increased.

**#3**

For the system  $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)}$ ,  $\Delta H$  is negative for the production of SO<sub>3</sub>. Assume that one has an equilibrium mixture of these substances. Predict the effect of each of the following changes on the value of the equilibrium constant and on the number of moles of SO<sub>3</sub> present in the mixture at equilibrium. Briefly account for each of your predictions. (Assume that in each case all other factors remain constant.)

- a. Decreasing the volume of the system

b. Adding oxygen to the equilibrium mixture

c. Raising the temperature of the system



Suppose the substances in the reaction above are at equilibrium at 600°K in volume V and at pressure P. State whether the partial pressure of  $\text{NH}_3(g)$  will have increased, decreased, or remained the same when equilibrium is reestablished after each of the following disturbances of the original system. *Some solid  $\text{NH}_4\text{Cl}$  remains in the flask at all times.* Justify each answer with a one or two sentence explanation.

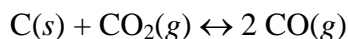
- A small quantity of  $\text{NH}_4\text{Cl}$  is added.
- The temperature of the system is increased.
- The volume of the system is increased.
- A quantity of gaseous  $\text{HCl}$  is added.
- A quantity of gaseous  $\text{NH}_3$  is added.

**#5**

Ammonium hydrogen sulfide is a crystalline solid that decomposes as follows:  $\text{NH}_4\text{HS}(s) \rightarrow \text{NH}_3(g) + \text{H}_2\text{S}(g)$

- Some solid  $\text{NH}_4\text{HS}$  is placed in an evacuated vessel at 25°C. After equilibrium is attained, the total pressure inside the vessel is found to be 0.659 atmosphere. Some solid  $\text{NH}_4\text{HS}$  remains in the vessel at equilibrium. For this decomposition, write the expression for  $K_p$  and calculate its numerical value at 25°C.
- Some extra  $\text{NH}_3$  gas is injected into the vessel containing the sample described in part (a). When equilibrium is reestablished at 25°C, the partial pressure of  $\text{NH}_3$  in the vessel is twice the partial pressure of  $\text{H}_2\text{S}$ . Calculate the numerical value of the partial pressure of  $\text{NH}_3$  and the partial pressure of the  $\text{H}_2\text{S}$  in the vessel after the  $\text{NH}_3$  has been added and the equilibrium has been reestablished.
- In a different experiment,  $\text{NH}_3$  gas and  $\text{H}_2\text{S}$  gas are introduced into an empty 1.00 liter vessel at 25°C. The initial partial pressure of each gas is 0.500 atmospheres. Calculate the number of moles of solid  $\text{NH}_4\text{HS}$  that is present when equilibrium is established.

#6



Solid carbon and carbon dioxide gas at 1,160 K were placed in a rigid 2.00 L container, and the reaction represented above occurred. As the reaction proceeded, the total pressure in the container was monitored.

When equilibrium was reached, there was still some C(s) remaining in the container. Results are recorded in the table shown.

<i>Time (hours)</i>	<i>Total Pressure of Gases in Container at 1,160 K (atm)</i>
0.0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

- Write the expression for the equilibrium constant,  $K_p$ , for the reaction.
- Calculate the number of moles of  $\text{CO}_2(g)$  initially placed in the container. (Assume that the volume of the solid carbon is negligible.)
- For the reaction mixture at equilibrium at 1,160 K, the partial pressure of the  $\text{CO}_2(g)$  is 1.63 atm. Calculate
  - The partial pressure of  $\text{CO}(g)$ , and
  - The value of the equilibrium constant,  $K_p$ .
- If a suitable solid catalyst were placed in the reaction vessel, would the final total pressure of the gases at equilibrium be greater than, less than, or equal to the final total pressure of the gases at equilibrium without the catalyst? Justify your answer. (Assume that the volume of the solid catalyst is negligible.)

In another experiment involving the same reaction, a rigid 2.00 L container initially contains 10.0 g of C(s), plus  $\text{CO}(g)$  and  $\text{CO}_2(g)$ , each at a partial pressure of 2.00 atm at 1,160 K.

- Predict whether the partial pressure of  $\text{CO}_2(g)$  will increase, decrease, or remain the same as this system approaches equilibrium. Justify your prediction with a calculation.

## AP Chemistry: Chapter 13 Practice Test

Multiple Choice: 3 pts each

- The equilibrium constant expression for the reaction  $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$  would be written:
 

(a)  $K_c = [\text{NH}_3][\text{HCl}]$       (b)  $K_c = \frac{[\text{NH}_4\text{Cl}][\text{NH}_3]}{[\text{HCl}]}$       (c)  $K_c = \frac{[\text{NH}_3][\text{HCl}]}{[\text{NH}_4\text{Cl}]}$       (d)  $K_c = \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3][\text{HCl}]}$       (e)  $K_c = \frac{[\text{NH}_3]}{[\text{HCl}]}$
- In a 1.0-liter container there are, at equilibrium, 0.10 mole  $\text{H}_2$ , 0.20 mole  $\text{N}_2$ , and 0.40 mole  $\text{NH}_3$  in the system  $\text{N}_2(g) + 3\text{H}_2(g) \leftrightarrow 2\text{NH}_3(g)$  What is the value of  $K_c$  for this reaction at this temp.?
 

(a) 0.0012      (b) 20      (c)  $8.0 \times 10^2$       (d) 0.050      (e) 8.0
- The equilibrium constant,  $K_c$ , for the following gas phase reaction is 0.50 at  $600^\circ\text{C}$ . A mixture of  $\text{HCHO}$ ,  $\text{H}_2$ , and  $\text{CO}$  is introduced into a flask at  $600^\circ\text{C}$ . After a short time, analysis of a small amount of the reaction mixture shows the concentrations to be  $[\text{HCHO}] = 1.5\text{ M}$ ,  $[\text{H}_2] = 1.2\text{ M}$ , and  $[\text{CO}] = 1.0\text{ M}$ . Which of the following statements about this reaction mixture is true?  $\text{HCHO} \leftrightarrow \text{H}_2 + \text{CO}$ 

(a) The reaction mixture is at equilibrium.  
 (b) The reaction mixture is not at equilibrium, but no further reaction will occur.  
 (c) The reaction mixture is not at equilibrium, and will move toward equilibrium by forming more  $\text{HCHO}$ .  
 (d) The reaction mixture is not at equilibrium, and will move toward equilibrium by using up more  $\text{HCHO}$ .  
 (e) The forward rate of this reaction is the same as the reverse rate.
- If the system below is at equilibrium in a closed vessel and a small amount of nitrous acid is added, what would be expected to happen?  $\text{HN}_3(l) + 2\text{H}_2\text{O}(l) \leftrightarrow \text{N}_2\text{H}_4(l) + \text{HNO}_2(l)$   $\Delta H^\circ = +641\text{ kJ}$ 

hydrazoic acid
hydrazine
nitrous acid

(a) Some  $\text{HN}_3$  would be used up in re-establishing equilibrium.  
 (b) Some  $\text{HNO}_2$  would be formed in re-establishing equilibrium.  
 (c) Some  $\text{HNO}_2$  would be formed, and some  $\text{N}_2\text{H}_4$  would be lost.  
 (d) More  $\text{HN}_3$  and  $\text{H}_2\text{O}$  would be formed.  
 (e) The temperature would decrease, and the forward reaction would be favored.
- Suppose the following reaction is at equilibrium at a given temperature and pressure. The pressure is then increased at constant temperature, by compressing the reaction mixture, and the mixture is allowed to re-establish equilibrium. At the new equilibrium \_\_\_\_\_.  $\text{N}_2(g) + 3\text{H}_2(g) \leftrightarrow 2\text{NH}_3(g)$ 

(a) there is more ammonia than there was originally  
 (b) there is less ammonia than there was originally  
 (c) there is the same amount of ammonia present as there was originally  
 (d) the nitrogen is used up completely  
 (e) the amount of ammonia may be either larger or smaller than it was originally, depending on the value of  $K$

6. Which of the numbered responses lists all of the following stresses that would shift the equilibrium to the left, and no other stresses?  $2\text{NOCl}(\text{g}) + 75 \text{ kJ} \leftrightarrow 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$
- Add a catalyst.
  - Heat the mixture.
  - Decrease the volume at constant temperature.
  - Increase the partial pressure of NOCl by adding NOCl.
- (a) I, II, and IV                      (b) II, III, and IV                      (c) II and III  
(d) III                                      (e) a different one or a different combination
7. Consider the system shown at equilibrium at  $200^\circ\text{C}$ .  $2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{heat} \leftrightarrow 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$   
Which response contains all the stresses listed that will result in a shift of the equilibrium so that more HCl is produced when equilibrium is re-established, and no stresses that will not?
- adding some  $\text{Cl}_2$
  - raising the temperature at constant pressure
  - decreasing the volume at constant temperature
- (a) I and II                                      (b) II and III                                      (c) III  
(d) I and II                                      (e) another one or another combination
8. For the **gas phase** reaction  $\text{SO}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{SO}_3$   $\Delta H^0 = -1.6 \times 10^2 \text{ kJ}$  for the forward reaction. In order to increase the yield of  $\text{SO}_3$ , the reaction should be run
- (a) at high P, high T.                                      (b) at high P, low T.  
(c) at low P, high T.                                      (d) at low P, low T.  
(e) at high P, but is independent of T.
9.  $K_{\text{C}} = 4.6 \times 10^{-3}$  for the reaction shown at  $25^\circ\text{C}$ . Evaluate  $K_{\text{P}}$  at  $25^\circ\text{C}$ .  $\text{N}_2\text{O}_4(\text{g}) \leftrightarrow 2\text{NO}_2(\text{g})$
- (a) 0.086                                      (b) 0.11                                      (c)  $6.2 \times 10^{-3}$   
(d)  $1.9 \times 10^{-4}$                                       (e)  $3.2 \times 10^{-1}$
10. Which one of the following would force the forward reaction to completion?  
 $\text{CaCO}_3(\text{s}) + 2\text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
- Removing some  $\text{H}_3\text{O}^+$  from the reaction mixture, by neutralizing it with base.
  - Adding more  $\text{Ca}^{2+}$  to the mixture.
  - Removing  $\text{CO}_2$  as it is formed.
  - Adding  $\text{CO}_2$  to the reaction mixture.
  - None of the preceding would have any effect on the amount of  $\text{CaCO}_3$  consumed.
11. The numerical value of the equilibrium constant,  $K_{\text{C}}$ , for the following gas phase reaction is 0.50 at a certain temperature. When a certain reaction mixture reaches equilibrium, the concentration of  $\text{O}_2$  is found to be 2.0 M, while the concentration of  $\text{SO}_3$  is found to be 10.0 M. What is the equilibrium concentration of  $\text{SO}_2$  in this mixture?  $2\text{SO}_2 + \text{O}_2 \leftrightarrow 2\text{SO}_3$  (6 pts)
12. At  $25^\circ\text{C}$ ,  $K_{\text{C}}$  for the following reaction is  $4.66 \times 10^{-3}$ . If 0.800 mol of  $\text{N}_2\text{O}_4$  is injected into a closed 1.00-liter glass container at  $25^\circ\text{C}$ , what will be the equilibrium concentration of  $\text{N}_2\text{O}_4$ ? (12 pts)
- $$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$



13. Phosgene is a potent chemical warfare agent that was outlawed by the Geneva Convention. It decomposes by the reaction:  $\text{COCl}_2(g) \leftrightarrow \text{CO}(g) + \text{Cl}_2(g)$   
 $K_c = 8.3 \times 10^{-4}$  at  $360^\circ\text{C}$ . Calculate  $[\text{CO}]$ ,  $[\text{Cl}_2]$ , and  $[\text{COCl}_2]$ , when 0.100 mol  $\text{COCl}_2$  decomposes and reaches equilibrium in a 10.0 L flask. (14 pts)
14. For the reaction shown,  $K_p = 6.70 \times 10^{-3}$  at  $25^\circ\text{C}$ .  $\text{COCl}_2(g) \leftrightarrow \text{CO}(g) + \text{Cl}_2(g)$   
A sample of  $\text{COCl}_2$  is placed in a closed 15.0-liter vessel at  $25^\circ\text{C}$ , and it exerts a pressure of 4.65 atm before decomposition begins. What will be the total pressure at equilibrium? (10 pts)
15. The extent of the change from  $\text{CO}$  and  $\text{H}_2\text{O}$  to  $\text{CO}_2$  and  $\text{H}_2$  is used to regulate the proportions in syngas fuel mixtures. If 0.250 mol  $\text{CO}$  and 0.250 mol  $\text{H}_2\text{O}$  are placed in a 125-mL flask at 900K, what is the composition of the equilibrium mixture?  $K_c = 1.56$ .  $\text{CO}(g) + \text{H}_2\text{O}(g) \leftrightarrow \text{CO}_2(g) + \text{H}_2(g)$  (12 pts)
16. The following reaction is exothermic:  $3\text{NO}(g) \leftrightarrow \text{N}_2\text{O}(g) + \text{NO}_2(g)$   
Explain the effect of each of the following stresses on the concentration of  $\text{NO}_2$ . (4 pts each)
- $\text{N}_2\text{O}(g)$  is added to the equilibrium mixture without change of volume or temperature.
  - The volume of the equilibrium mixture is reduced at constant temperature.
  - The temperature of the equilibrium mixture is decreased.
  - Gaseous argon is added to the equilibrium mixture without changing the volume.

## AP Chemistry: Chapter 14

### Acid and Base Equilibria

#### 14.1 The Nature of Acids and Bases

In review:

- |  |  |
|--|--|
| <ul style="list-style-type: none"> <li>• Acids           <ul style="list-style-type: none"> <li>○ Taste sour</li> <li>○ Have pH values of less than 7</li> <li>○ Typically have a hydrogen in front of the formula or a COOH group (carboxylic acids)</li> </ul> </li> </ul> | <ul style="list-style-type: none"> <li>• Bases           <ul style="list-style-type: none"> <li>○ Referred to as alkali</li> <li>○ Taste bitter and feel slippery</li> <li>○ Have pH values of greater than 7</li> <li>○ Tend to have a hydroxide (OH<sup>-</sup>) at the back of the formula</li> </ul> </li> </ul> |
|--|--|

There are three general definitions for acids and bases:

- Arrhenius concept- acids produce hydrogen ions in aqueous solution while bases produce hydroxide ions.
  - Bronsted-Lowry model- acids are proton (H<sup>+</sup>) donors and bases are proton acceptors.
    - Hydronium ion (H<sub>3</sub>O<sup>+</sup>) - formed on reaction of a proton with a water molecule.
    - H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> are used interchangeably in most situations.
- Ex.    HA(aq) + H<sub>2</sub>O(l) ↔ H<sub>3</sub>O<sup>+</sup>(aq) + A<sup>-</sup>(aq)
- |      |      |                |                |
|------|------|----------------|----------------|
| Acid | Base | Conjugate Acid | Conjugate Base |
|------|------|----------------|----------------|
- Conjugate base- everything that remains of the acid molecule after a proton is lost
  - Conjugate acid- the base after the addition of a proton
- Lewis model- acids are electron pair acceptors while bases are electron pair donors

According to these models, the acid has a weaker hold on the hydrogen ion than the base's attraction for it. Therefore, the base takes the hydrogen ion and becomes the conjugate acid. The amount of conjugate acid and base formed from the exchange of the hydrogen ion in relation to the amount of acid remaining can be described by the equilibrium position of the reaction.

- Acid dissociation constant (K<sub>a</sub>)                       $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$                       or  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ 
  - A large K<sub>a</sub> value would indicate that the acid had strongly dissociated and formed a lot of conjugate acid and base. This would indicate a strong acid. *Very strong acids DO NOT have K<sub>a</sub> values because the amount of undissociated reactant is too small to measure accurately.*
  - A small K<sub>a</sub> value would indicate that the acid had stayed together for the most part and did not form a lot of conjugate acid and base. This would indicate a weak acid.
    - Strong acid - mostly dissociated
      - Equilibrium lies far to the right
      - A strong acid yields a weak conjugate base (much weaker than H<sub>2</sub>O)
    - Weak acid- mostly undissociated
      - Equilibrium lies far to the left
      - Has a strong conjugate base (stronger than water)
  - Sulfuric acid is a diprotic acid which means that it has two acidic protons. The first (H<sub>2</sub>SO<sub>4</sub>) is strong and the second (HSO<sub>4</sub><sup>-</sup>) is weak.

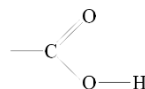
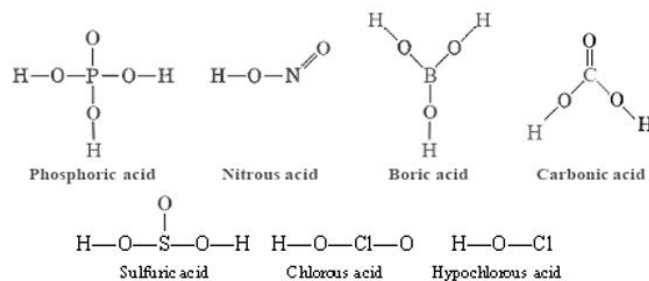
**Common strong acids-  
all aqueous solutions  
(Know these!)**

H<sub>2</sub>SO<sub>4</sub> (sulfuric)  
 HNO<sub>3</sub> (nitric)  
 HClO<sub>4</sub> (perchloric)  
 H<sub>2</sub>CrO<sub>4</sub> (chromic)  
 HMnO<sub>4</sub> (permanganic)  
 HCl (hydrochloric)  
 HBr (hydrobromic)  
 HI (hydroiodic)

#### 14.2 Acid Strength

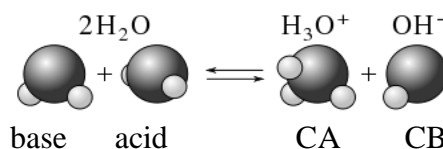
- Oxyacids- Formed when a covalent oxide (like CO<sub>2</sub>) dissolves in water to make an acid (like H<sub>2</sub>CO<sub>3</sub>)

- Most acids are oxyacids
- The acidic proton is attached to O
  - Weak oxyacids:
    - $\text{H}_3\text{PO}_4$  (phosphoric)
    - $\text{HNO}_2$  (nitrous)
    - $\text{HOCl}$  (hypochlorous)
- Within a series, acid strength increases with increasing numbers of oxygen atoms. For example:  $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$  and  $\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$  (Electronegative O draws electrons away from O-H bond)
- Acid strength also increases with increasing electronegativity of oxyacids.
  - For example:  $\text{HOCl} > \text{HOBr} > \text{HOI} > \text{HOCH}_3$
- Organic acids- have a carboxyl group
  - Usually are weak acids
    - Ex.  $\text{CH}_3\text{COOH}$  (acetic) &  $\text{C}_6\text{H}_5\text{COOH}$  (benzoic)
- Hydrohalic acids- H is attached to a halogen ( $\text{HCl}$ ,  $\text{HI}$ , etc.)
  - $\text{HF}$  is the only weak hydrohalic acid. Although the H-F bond is very polar, the bond is so strong (due to the small F atom) that the acid does not completely dissociate.
- Effects of Electronegativity on Acid-Base Strength
  - In terms of polarity:  $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$ 
    - Because of the strong HF bond (small F atom), HF is a weak acid.
  - In terms of electronegativity and acid strength:  $\text{HOCl} > \text{HOBr} > \text{HOI} > \text{HOCH}_3$



Some substances have the ability to both gain and lose protons. We call these amphoteric substances.

- Amphoteric substance- Substance that can act as an acid or as a base. Ex.  $\text{H}_2\text{O}$
- Autoionization of water



**Ion product constant for water ( $K_w$ )**

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

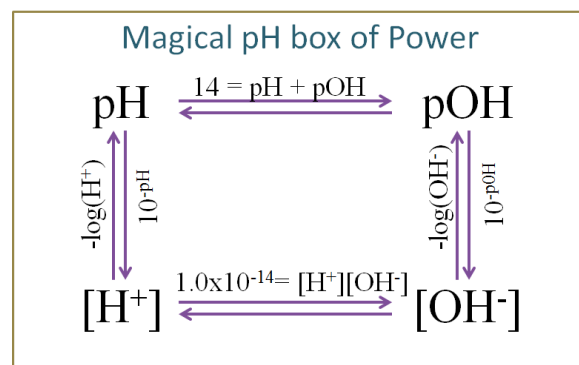
$$K_w = [\text{H}^+][\text{OH}^-]$$

- At  $25^\circ\text{C}$ ,  $K_w = 1 \times 10^{-14} \text{ mol}^2/\text{L}^2$  because  $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$ 
  - No matter what an aqueous solution contains, at  $25^\circ\text{C}$   $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$ 
    - Neutral solution  $[\text{H}^+] = [\text{OH}^-]$
    - Acidic solution  $[\text{H}^+] > [\text{OH}^-]$
    - Basic solution  $[\text{H}^+] < [\text{OH}^-]$
  - $K_w$  varies with temperature

### 14.3 The pH Scale

Because  $[\text{H}^+]$  in a solution is typically very small, we can use the pH scale, which is based on the logarithm of molarity, to help us relate acids and bases of differing strengths.

- Significant figures in pH and other log values: The number of decimal places in the log value should equal the number of significant digits in the original number (concentration).
- pH and pOH are logarithmic functions. The pH changes by 1 for every power of 10 change in  $[\text{H}^+]$ .
- pH decreases as  $[\text{H}^+]$  increases.



### 14.4 Calculating the pH of Strong Acid Solutions

Calculating pH of strong acid solutions is generally very simple. The pH is simply calculated by taking the negative logarithm of concentration of a monoprotic strong acid. For example, the pH of 0.1 M HCl is 1.0. However, if the acid concentration is less than  $1.0 \times 10^{-7}$ , the water becomes the important source of  $[H^+]$  and the pH is 7.00. *The pH of an acidic solution can not be greater than 7 at 25°C!*

Another exception is calculating the pH of an  $H_2SO_4$  solution that is more dilute than 1.0 M. At this concentration, the  $[H^+]$  of the  $HSO_4^-$  must also be calculated.

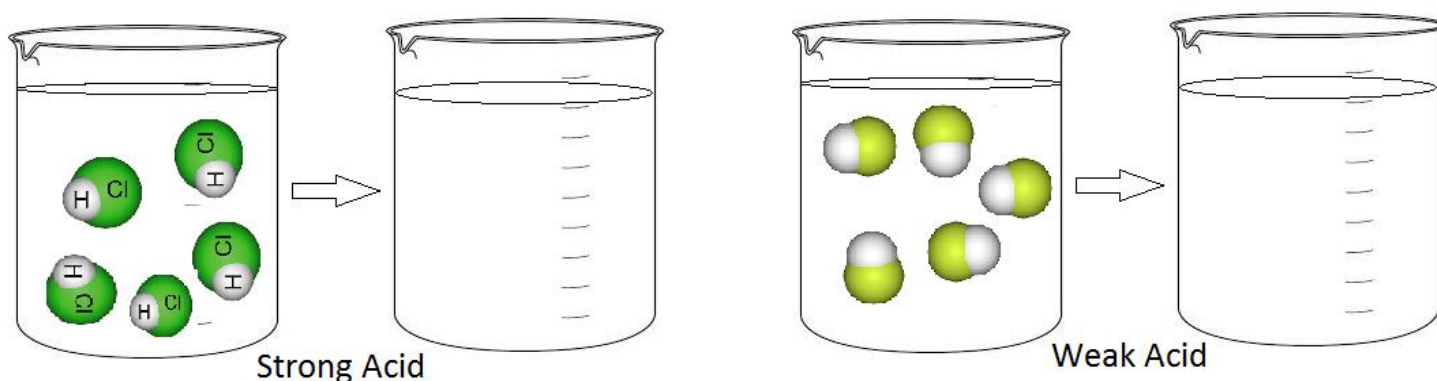
- Ex. Calculate the  $[H^+]$  and pH in a 1.0 M solution of HCl.

- Ex. Calculate the pH of  $1.0 \times 10^{-10}$  M HCl.

### 14.5 Calculating the pH of Weak Acid Solutions

As we stated earlier, weak acids are weak because they are mostly undissociated.

In the space below, draw in the result of a strong acid dissolving and a weak acid dissolving.



The following table contains equilibrium constants for many common weak monoprotic acids. Note that as the value of  $K$  gets smaller, the fewer molecules have dissociated and the stronger the conjugate base.

Formula	Name	$K_a$	Formula	Name	$K_a$
$HSO_4^-$	Bisulfate ion	$1.2 \times 10^{-2}$	$HC_2H_3O_2$	Acetic acid	$1.8 \times 10^{-5}$
$HClO_2$	Chlorous acid	$1.2 \times 10^{-2}$	$HOCl$	Hypochlorous acid	$3.5 \times 10^{-8}$
$HC_2H_2ClO_2$	Monochloroacetic acid	$1.35 \times 10^{-3}$	$HCN$	Hydrocyanic acid	$6.2 \times 10^{-10}$
$HF$	Hydrofluoric acid	$7.2 \times 10^{-4}$	$NH_4^+$	Ammonium ion	$5.6 \times 10^{-10}$
$HNO_2$	Nitrous acid	$4.0 \times 10^{-4}$	$HOC_6H_5$	phenol	$1.6 \times 10^{-10}$

Practice:

1. Arrange the following according to their strengths as bases: HI,  $H_2O$ , HF,  $HNO_2$ , HCN
2. Write the following as acids AND in order of increasing percent ionization:  $OCl^-$ ,  $F^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $NH_3$

Calculating the pH of weak acids involves setting up an equilibrium. Follow these steps for success.

1. Always start by writing the equation and identifying the major species involved. Use a RICE table!!
2. Next, set up the acid equilibrium expression ( $K_a$ )
3. Now, define initial concentrations, changes, and final concentrations in terms of X in the RICE table.
4. Finally, substitute values and variables into the  $K_a$  expression and solve for X.

- Ex. Calculate the pH of a 0.250 M solution of hypochlorous acid.

- When you assume that  $x$  is negligible, you must check the validity of this assumption. To be valid,  $x$  must be less than 5% of the number that it was to be subtracted from. In this example  $9.35 \times 10^{-5}$  is less than 5% of 0.250. This means that the assumption that  $x$  was negligible was valid.

Practice:

Propanoic acid,  $\text{HC}_3\text{H}_5\text{O}_2$ , ionizes in water and has a  $K_a$  value of  $1.34 \times 10^{-5}$ .

- Write the equation and equilibrium expression for this reaction.
- What is the pH of a 0.0500 M sample of this solution at equilibrium?

Calculating the pH of polyprotic acids (material from section 14.7)

- All polyprotic acids dissociate stepwise. Each dissociation has its own  $K_a$  value. As each H is removed, the remaining acid gets weaker and therefore has a smaller  $K_a$ . As the negative charge on the acid increases, it becomes more difficult to remove the positively charged proton.
- *Except for  $\text{H}_2\text{SO}_4$* , polyprotic acids have  $K_{a2}$  and  $K_{a3}$  values so much weaker than their  $K_{a1}$  value that the 2nd and 3rd (if applicable) dissociation can be ignored. The  $[\text{H}^+]$  obtained from this 2nd and 3rd dissociation is negligible compared to the  $[\text{H}^+]$  from the 1st dissociation.
- *Because  $\text{H}_2\text{SO}_4$  is a strong acid in its first dissociation and a weak acid in its second, we need to consider both if the concentration is more dilute than 1.0 M.* The quadratic equation is needed to work this type of problem.

Ex. Calculate the pH of a 0.0150 M  $\text{H}_2\text{SO}_4$  solution.

Since  $\text{H}_2\text{SO}_4$  is strong,  $[\text{H}^+] = 1.00 \times 10^{-2} + x$ , where  $x$  is the  $\text{H}^+$  contributed from the second dissociation.

Determination of the pH of a Mixture of Weak Acids

- Only the acid with the largest  $K_a$  value will contribute an appreciable  $[\text{H}^+]$ .
- Determine the pH based on this acid and ignore any others.

Determination of the Percent Dissociation of a Weak Acid

- Percent dissociation =  $\left( \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \right) \times 100 = \left( \frac{\text{final } [\text{H}^+]}{\text{initial } [\text{HA}]} \right) \times 100$

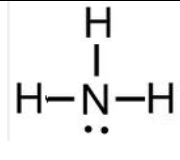
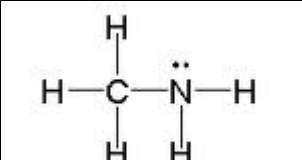
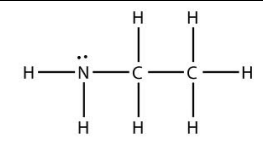
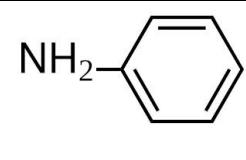
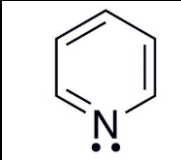
- For a weak acid, percent dissociation (or ionization) increases as the acid becomes more dilute. Equilibrium shifts to the right.

## 14.6 Bases

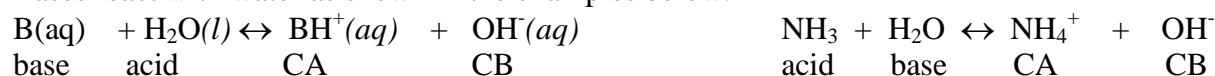
- The hydroxides of Group I and IIA metals are all strong bases.
- The Group IIA hydroxides are not very soluble, especially  $\text{Mg}(\text{OH})_2$ . This property allows some of them to be used effectively as stomach antacids.
  - Ex. Calculate the  $[\text{OH}^-]$ ,  $[\text{H}^+]$ , and pH of a 0.0100 M solution of NaOH.

Weak bases (bases without  $\text{OH}^-$ ) react with water to produce a hydroxide ion. This means that when you write these reactions, you must add water to the equation!

- Common examples of weak bases, which you need to know, are shown in the table below.

Name	Ammonia	Methylamine	Ethylamine	Aniline	Pyridine
Formula	$\text{NH}_3$	$\text{CH}_3\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_5\text{H}_5\text{N}$
$K_b$	$1.8 \times 10^{-5}$	$4.38 \times 10^{-4}$	$5.6 \times 10^{-4}$	$3.8 \times 10^{-10}$	$1.7 \times 10^{-9}$
Structure					

- Bases react with water as shown in the examples below.



- The lone pair on N or the base forms a bond with a  $\text{H}^+$ . Most weak bases involve N.
- Base dissociation constant ( $K_b$ )
 
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \qquad K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$
- Determination of the pH of a weak base is very similar to the determination of the pH of a weak acid. Follow the same steps. Remember, however, that  $x$  is the  $[\text{OH}^-]$  and taking the negative log of  $x$  will give you the pOH and not the pH!
- Ex. Calculate the  $[\text{OH}^-]$  and the pH for a 15.0 M  $\text{NH}_3$  solution.

## 14.8 Acid-Base Properties of Salts

- Neutral Salts- Salts that are formed from the cation of a strong base and the anion from a strong acid form neutral solutions when dissolved in water. Ex.  $\text{NaCl}$ ,  $\text{KNO}_3$ 
  - Acid Salts- Salts that are formed from the cation of a weak base and the anion from a strong acid form acidic solutions when dissolved in water.
  - Ex.  $\text{NH}_4\text{Cl}$  The cation hydrolyzes the water molecule to produce hydronium ions and thus an acidic solution.
 
$$\text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{NH}_3$$

strong acid      weak base
  - Basic Salts- Salts that are formed from the cation of a strong base and the anion from a weak acid

from basic solutions when dissolved in water.

- Ex.  $\text{NaC}_2\text{H}_3\text{O}_2$ ,  $\text{KNO}_2$  The anion hydrolyzes the water molecule to produce hydroxide ions and thus a basic solution.
 
$$\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{HC}_2\text{H}_3\text{O}_2$$

strong base      weak acid

- When determining the exact pH of salt solutions, we can use the  $K_a$  of the weak acid formed to find the  $K_b$  of the salt or we can use the  $K_b$  of the weak base formed to find the  $K_a$  of the salt.  $K_a \times K_b = K_w$
- Ex. Calculate the pH of a 0.15 M solution of sodium acetate.
  - a. Ask yourself, "What type of salt is sodium acetate?" \_\_\_\_\_
  - b. Use the weakest part of the salt and water to write an equation. \_\_\_\_\_
  - c. Use this equation and a RICE table to solve for the pH.

#### 14.10 Acid-Base Properties of Oxides

- When metallic (ionic) oxides dissolve in water they produce a metallic hydroxide (basic solution).
  - $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
- When nonmetallic (covalent) oxides dissolve in water they produce a weak acid (acidic solution).
  - $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$
- Salts of Highly Charged Metals
  - Salts that contain a highly charged metal ion produce an acidic solution.
    - $\text{AlCl}_3 + 6\text{H}_2\text{O} \rightarrow \text{Al(H}_2\text{O)}_6^{3+} + 3\text{Cl}^-$
    - $\text{Al(H}_2\text{O)}_6^{3+} \rightarrow \text{Al(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}^+$
    - The higher the charge on the metal ion, the stronger the acidity of the hydrated ion. The electrons are pulled away from the O-H bond and toward the positively charged metal ion, leaving the hydrogen ion free to dissociate.  $\text{FeCl}_3$  and  $\text{Al(NO}_3)_3$  also behave this way.

## Chapter 14 Practice Worksheet #1

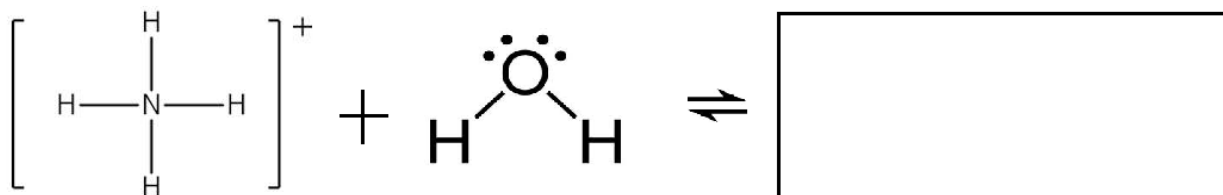
1. Ammonia reacts with water to create a 0.150 M solution.
- Write the equation for this solution formation and the equilibrium constant for this reaction.

b. Calculate the pH of the solution at equilibrium.

c. Determine the percent ionization of the weak base.

d. Calculate the hydronium ion concentration in the above solution.

- e. Ammonium ions react with water to form a solution with a pH of 4.827. Complete the reaction below by drawing in the Lewis structures for *both* products of the reaction.



f. Determine the number of moles of ammonium ions in 250 ml of the solution in part “e”.

2. Hydrocyanic acid is a weak acid with a dissociation constant of  $6.2 \times 10^{-10}$ .

a. Write the equation for the dissociation of hydrocyanic acid as well as the equilibrium expression.

b. Calculate the hydronium ion concentration of a 0.250 M solution of HCN.

c. Lithium cyanide, a salt, is dissolved in water to produce a basic solution. Write the net ionic equation that illustrates why the resulting solution is basic.

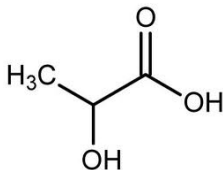
d. Calculate the equilibrium constant for the reaction in part “c”.



3. Carbonic acid, a diprotic acid, is dissolved in water.
- Write a balanced chemical equation showing both the first and second dissociation reactions for this acid.
  - The equilibrium constant,  $K_{eq}$ , for this reaction is  $2.4 \times 10^{-17}$ . The dissociation constant for the second dissociation,  $K_{a2} = 5.6 \times 10^{-11}$ . Calculate the equilibrium constant for the first dissociation, or  $K_{a1}$ .
  - Based on  $K_{a1}$  and  $K_{a2}$ , which dissociation yields more hydrogen ions? If you were calculating the pH of this solution, would the second dissociation contribute significantly toward that value? Explain your answer.
- 
- 
- 

4. Solid potassium lactate,  $KC_3H_5O_3$ , is dissolved in enough water to make a 0.24 M solution with a pH of 12.25 at  $25^\circ\text{C}$ .
- Explain why the solution produced by dissolving  $KC_3H_5O_3$  is basic. Use an equation as part of your justification.
  - Calculate the hydroxide ion concentration of the solution described above.
  - Calculate the value of the equilibrium constant for the reaction in part "a".
  - Calculate the acid dissociation constant,  $K_a$ , for lactic acid.

- e. The structural formula for lactic acid is shown below. Circle the hydrogen lost when lactic acid ionizes.



- f. A student needs to dilute a 0.240 M solution of potassium lactate to make 50.0 mL of 0.100 M potassium lactate solution. Describe the steps and lab equipment needed to make this solution.

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**Chapter 14 Practice Worksheet #2**

For each of the following problems, write the equilibrium expression without values, a RICE table and the final answer for full credit. Show all work!

1. What is the pH of the resulting solution when 0.500 moles of acetic acid are dissolved in water and diluted to 1.00 L?
2. What is the pH of a 2.50 M solution of nitric acid?
3. What is the pH of a solution formed when 100.0 mL of 0.500 M of hypochlorous acid is mixed with 100.0 mL water?
4. 250.0 mL of a 0.300 M solution of ammonia is added to 750.0 mL of water. What is the pH of the resulting solution?
5. Calculate  $K_b$  for methylamine if a solution prepared by dissolving 0.100 moles of methylamine in 1.00 L of water has a measured pH of 11.80.
6. 0.500 moles of nitrous acid are dissolved in water and diluted to 1.00 L. What is the pH of the resulting solution?
7. What is the pH of a 0.500 M solution of  $\text{NH}_4\text{Cl}$  in water?
8. What is the pH of a solution created by diluting 25.00 mL of 8.0 M KOH to 100.00 mL?
9. What is the pH of household bleach, which is 5.25% sodium hypochlorite,  $\text{NaClO}$ , by weight? The  $K_a$  of hypochlorous acid is  $3.0 \times 10^{-8}$ . (Useful information: MW  $\text{NaClO} = 74.44$  g/mol)
10. What is the pH of a 0.320 M solution of sodium bicarbonate,  $\text{NaHCO}_3$ ? Carbonic acid has the following  $K_a$  values:  $K_a^1 = 4.45 \times 10^{-7}$ ,  $K_a^2 = 4.70 \times 10^{-11}$

## AP Chemistry: Chapter 14 Practice Test

## Multiple Choice: 3 pts each

\_\_\_\_ 1. For the equilibrium that exists in an aqueous solution of nitrous acid ( $\text{HNO}_2$ , a weak acid), the equilibrium constant expression is:

A)  $K = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$

B)  $K = \frac{[\text{H}^+][\text{N}][\text{O}]^2}{[\text{HNO}_2]}$

C)  $K = [\text{H}^+][\text{NO}_2^-]$

D)  $K = \frac{[\text{H}^+]^2[\text{NO}_2^-]}{[\text{HNO}_2]}$

E) none of these

\_\_\_\_ 2. Which of the following is a conjugate acid/base pair?

A)  $\text{HCl}/\text{OCl}^-$

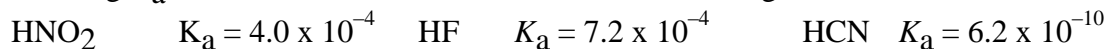
D)  $\text{H}_3\text{O}^+/\text{OH}^-$

B)  $\text{H}_2\text{SO}_4/\text{SO}_4^{2-}$

E) none of these

C)  $\text{NH}_4^+/\text{NH}_3$

\_\_\_\_ 3. Using the following  $K_a$  values, indicate the correct order of base strength.



A)  $\text{CN}^- > \text{NO}_2^- > \text{F}^- > \text{H}_2\text{O} > \text{Cl}^-$

D)  $\text{H}_2\text{O} > \text{CN}^- > \text{NO}_2^- > \text{F}^- > \text{Cl}^-$

B)  $\text{Cl}^- > \text{H}_2\text{O} > \text{F}^- > \text{NO}_2^- > \text{CN}^-$

E) none of these

C)  $\text{CN}^- > \text{F}^- > \text{NO}_2^- > \text{Cl}^- > \text{H}_2\text{O}$

\_\_\_\_ 4. The conjugate base of a weak acid is

A) a strong base

C) a strong acid

E) none of these

B) a weak base

D) a weak acid

\_\_\_\_ 5. Calculate the  $[\text{H}^+]$  in a solution that has a pH of 2.30.

A) 2.3 M

C)  $5.0 \times 10^{-3}$  M

E) none of these

B) 11.7 M

D)  $2.0 \times 10^{-12}$  M

\_\_\_\_ 6. The pH of a solution at  $25^\circ\text{C}$  in which  $[\text{OH}^-] = 3.4 \times 10^{-5}$  M is:

A) 4.5

C) 9.5

E) none of these

B) 10.5

D) 6.3

\_\_\_\_ 7. Consider the reaction  $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+ + \text{NO}_2^-$ . Which species is the conjugate base?

A)  $\text{HNO}_2(\text{aq})$

C)  $\text{H}_3\text{O}^+(\text{aq})$

E) Two of these

B)  $\text{H}_2\text{O}(\text{l})$

D)  $\text{NO}_2^-(\text{aq})$

\_\_\_\_ 8. Which of the following is not true for a solution at  $25^\circ\text{C}$  in which the  $[\text{OH}^-] = 2.5 \times 10^{-6}$  M?

A)  $K_w = 1 \times 10^{-14}$

D) The  $[\text{H}^+]$  is  $4 \times 10^{-9}$  M.

B) The solution is acidic.

E) The  $K_w$  is independent of what the

C) The solution is basic.

solution contains.

\_\_\_\_ 9. Calculate the  $[\text{H}^+]$  in a solution that has a pH of 9.7.

A)  $2.0 \times 10^{-10}$  M

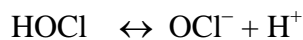
C)  $3.6 \times 10^{-9}$  M

E)  $6.3 \times 10^{-10}$  M

B)  $5.0 \times 10^{-5}$  M

D)  $9.7 \times 10^{-9}$  M





19. Hypochlorous acid, HOCl, is a weak acid commonly used as a bleaching agent. The acid-dissociation constant,  $K_a$ , for the reaction represented above is  $3.2 \times 10^{-8}$ .

- (a) Calculate the  $[\text{H}^+]$  of a 0.14-molar solution of HOCl. (8 pts)
- (b) Write the correctly balanced net ionic equation for the reaction that occurs when NaOCl is dissolved in water and calculate the numerical value of the equilibrium constant for the reaction. (6 pts)

20. A 0.025M solution of hydroxylamine has a pH of 9.11. What is the value of  $K_b$  for this weak base?



21. Ascorbic acid (vitamin C,  $\text{C}_6\text{H}_8\text{O}_6$ ) is a diprotic acid ( $K_{a1} = 6.8 \times 10^{-5}$  and  $K_{a2} = 2.7 \times 10^{-12}$ ). What is the pH of a solution that contains 5.0 mg of acid per milliliter of solution?(10 pts)

22. Calculate the pH of a 0.20 M solution of  $\text{NaC}_2\text{H}_3\text{O}_2$  (for  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $K_a = 1.8 \times 10^{-5}$ ). (10pts)

23. What is the percent ionization of the solution in #19a? (4 pts)

## Chapter 15 & 16: Applications of Aqueous Equilibria

### 15.1 Solutions of Acids or Bases Containing a Common Ion

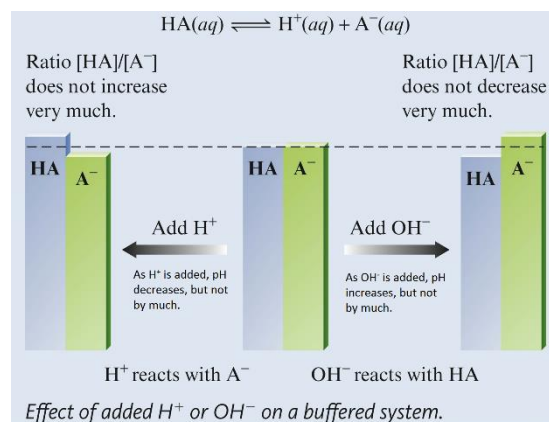
Common ion effect- The addition of an ion already present (common) in a system causes equilibrium to shift away from the common ion.

- For example, the addition of NaF to a solution of HF. The HF is dissolved and at equilibrium. Adding a common ion, in this case,  $F^-$ , to the solution, shifts the equilibrium and makes the HF less soluble.
  - This can be explained by the use of LeChatelier's Principle.
  - *The addition of a common ion to a solution of a weak acid makes the solution less acidic.*
    - $HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$  If we add  $NaC_2H_3O_2$ , equilibrium shifts to undissociated  $HC_2H_3O_2$ , raising pH.
    - The new pH can be calculated by putting the concentration of the anion into the  $K_a$  equation and solving for the new  $[H^+]$ .
    - Ex 1. A solution contains 1.0 M HF and 1.5 M KF. What is the pH of the solution?
- If the pH of 1.0 M HF is originally 1.57, what did the addition of the salt do to the pH and why?

### 15.2 Buffered Solutions

Buffered solution- A solution that resists changes in pH when hydroxide ions or protons are added. A buffer solution usually consists of a solution of a weak acid and its salt or a weak base and its salt.

- Ex.  $HC_2H_3O_2/C_2H_3O_2^-$  buffer system
  - Addition of strong acid: \_\_\_\_\_
  - Addition of strong base: \_\_\_\_\_
- Ex.  $NH_3/NH_4^+$  buffer system
  - Addition of strong acid: \_\_\_\_\_
  - Addition of strong base: \_\_\_\_\_
- So, how does a buffer work? As you can see above, when hydrogen ions are added to a buffer system, they react with the basic portion of the buffer. This drives the production of the weak acid portion of the system. If hydroxide ions are added to the buffer system, they react with the acidic portion of the buffer, producing the conjugate base.
- Buffer capacity- The amount of acid or base that can be absorbed by a buffer system without a significant change in pH.
  - In order to have a large buffer capacity, a solution should have large concentrations of both buffer components.
  - A buffer should maintain a system at a desired pH. To find what acids are best for a certain buffer, look at their  $K_a$  values. A buffer with a pH of 4.0 can be obtained from an acid with a  $pK_a$  of 4.0.



- Hints for Solving Buffer System Problems:

1. Write an equation for the dissociation of the acid or base into your RICE table.
  2. Write the concentration of the acid and conjugate base or base and conjugate acid. You will have two values in the “initial” section of your table.
  3. Solve for  $x$  just as you always would, but subtracted and added  $x$  values will probably be negligible in your expression.
  4. Solve and check your answer to see that it makes sense.
- Ex 2. A solution is 0.120 M in acetic acid and 0.0900 M in sodium acetate. Calculate the  $[H^+]$  at equilibrium. The  $K_a$  of acetic acid is  $1.8 \times 10^{-5}$ .
  - Once a buffered solution is set up, the ions are at equilibrium. However, addition of common ions can shift that equilibrium.
  - Here are some hints for working with this kind of problem:
    1. Determine major species involved initially.
    2. If a base is added, react it with the acid part of the buffer. If an acid is added, react it with the basic part of the buffer. Show all stoichiometry for this process in a before, change, after (BCA) table.
    3. Find the molarity of the major species after the reaction, and use them in a RICE table.
    4. Set up equilibrium expression ( $K_a$  or  $K_b$ ) and solve.
    5. Check the logic of your answer.
  - Ex 3. Calculate the pH of the buffer system in example 2 when 100.0 mL of 0.100 M HCl is added to 455 mL of solution.

### The Henderson-Hasselbach Equation

- One way to calculate the pH of a buffer system in which the ratio  $[HA]/[A^-]$  is known is with the Henderson-Hasselbach equation.
  - For a particular buffering system, all solutions that have the same ratio of  $[A^-]/[HA]$  have the same pH.
  - Optimum buffering occurs when  $[HA] = [A^-]$  and the  $pK_a$  of the weak acid used should be as close as possible to the desired pH of the buffer system.
  - This equation comes from the equilibrium expression.
- $K_a = \frac{[H^+][A^-]}{[HA]}$  which can be rearranged to  $[H^+] = K_a \frac{[HA]}{[A^-]}$  This means that if you know the concentration of the acid and conjugate base, you can find the hydrogen ion concentration. This can be used to find pH. The simplified version of this equation is shown below.

$$\boxed{\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} \qquad \text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}}$$

- *The Henderson-Hasselbach (HH) equation needs to be used cautiously. It is sometimes used as a quick, easy equation to plug numbers into. A  $K_a$  or  $K_b$  problem requires a greater understanding of the factors involved and can always be used instead of the HH equation.*
- Ex. 4 A buffer is prepared by adding 0.25 M  $NH_3$  ( $K_b = 1.8 \times 10^{-5}$ ) and 0.40 M  $NH_4Cl$ .

- A. Calculate the pH of this solution.
  
- B. calculate the pH that results when 0.10 mole of gaseous HCl is added to 1.0 L of the buffered solution.
  
- Use the Henderson-Hasselbach equation to calculate part B of this problem.

### 15.4 Titrations and pH Curves

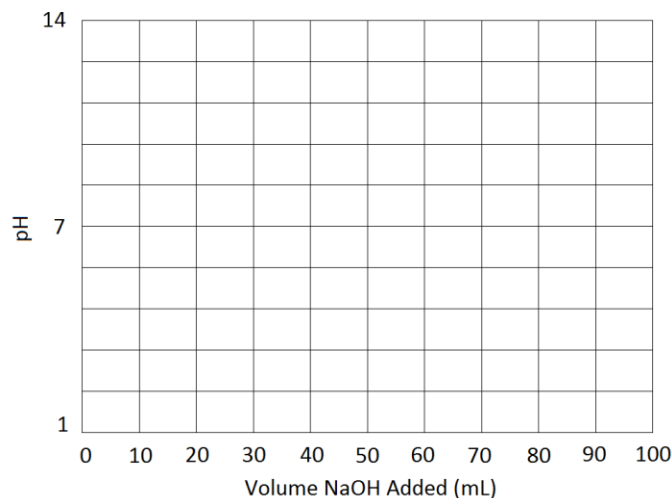
In an acid/base titration, the titrant (commonly a base) is added to a solution of unknown concentration until the substance being analyzed is just consumed (stoichiometric point or equivalence point).

- Titrant-solution of known concentration (in buret)
- pH or titration curve -plot of pH as a function of the amount of titrant added.

*There are three main types of acid/base titrations. We will examine each one and discuss how to calculate the concentration of species during the titration.*

#### I. Strong Acid-Strong Base:

- Simple reaction  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
- The pH is easy to calculate because all reactions go to completion.
- At the equivalence point, the solution is neutral.
  
- Ex. 5 12.5 mL of 0.200 M  $\text{HNO}_3$  is titrated with 0.100 M NaOH.
  - Calculate the pH at the start of the titration. Write this point on the graph.



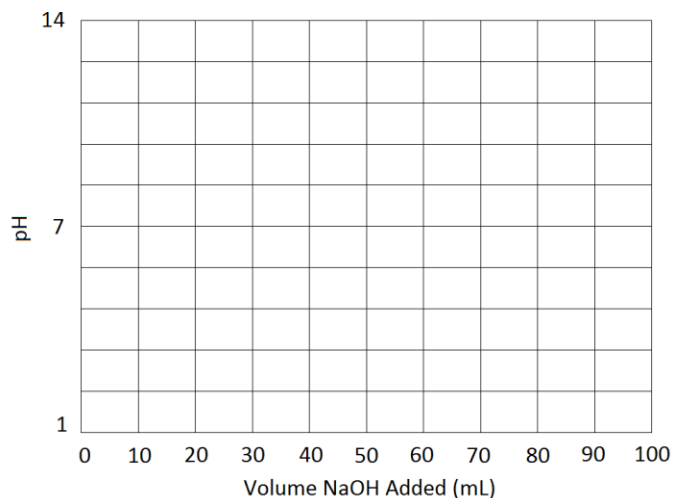
- Calculate the pH of the solution after 2.5 mL of NaOH has been added. Add this point to the graph.



- Calculate the pH of the solution after 5.0 mL of NaOH has been added. Add this point to the graph.
  
- Calculate the pH of the solution after 25.0 mL of NaOH has been added. Add this point to the graph.
  
- Calculate the pH of the solution after 35.0 mL of NaOH has been added. Add this point to the graph.
  
- Calculate the pH of the solution after 50.0 mL of NaOH has been added. Add this point to the graph.

## II. Weak Acid - Strong Base

- The reaction of a strong base with a weak acid is assumed to go to completion.
- Before the equivalence point, the concentration of weak acid remaining and the conjugate base formed are determined.
- At halfway to the equivalence point,  $\text{pH} = \text{pK}_a$ .
- At the equivalence point, a basic salt is present and the pH will be greater than 7. After the equivalence point, the strong base will be the dominant species and a simple pH calculation can be made after the stoichiometry is done.

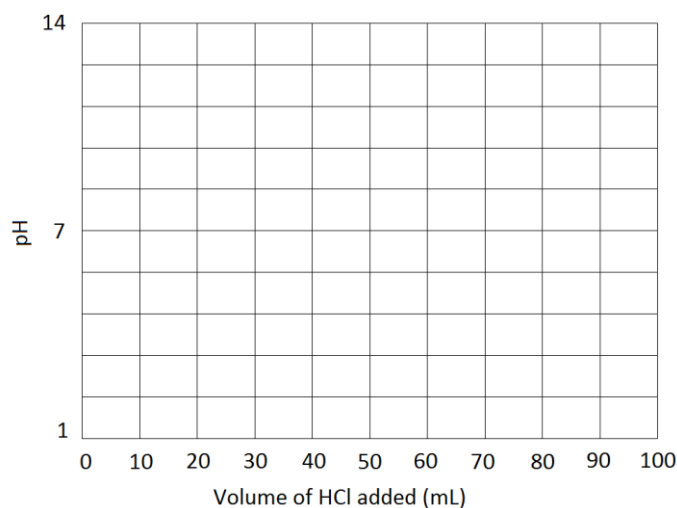


- Ex. 6 A 25.0 mL sample of 0.10 M acetic acid is titrated with 0.10 M NaOH.
  - Calculate the pH at the start of the titration. Write this point on the graph.
  
  - Calculate the pH of the solution after 5.0 mL of NaOH has been added. Add this point to the graph.

- Calculate the pH of the solution after 12.5 mL of NaOH has been added. Add this point to the graph.
  
- Calculate the pH of the solution after 20.0 mL of NaOH has been added. Add this point to the graph.
  
- Calculate the pH of the solution after 25.0 mL of NaOH has been added. Add this point to the graph.
  
- Calculate the pH of the solution after 40.0 mL of NaOH has been added. Add this point to the graph.

### III. Weak Base - Strong Acid

- Before the equivalence point, a weak base equilibria exists. Calculate the stoichiometry and then the weak base equilibria.
- At the equivalence point, an acidic salt is present and the pH is below 7. After the equivalence point, the strong acid is the dominant species. Use the  $[H^+]$  to find the pH.
- Ex. Calculate the pH when 50.0 mL of 0.050 M  $NH_3$  is titrated with 0.10 M HCl. ( $K_b$  of  $NH_3 = 1.8 \times 10^{-5}$ )
  - Calculate the pH at the start of the titration. Write this point on the graph.



- Calculate the pH of the solution after 7.5 mL of HCl has been added. Add this point to the graph.

- Calculate the pH of the solution after 12.5 mL of HCl has been added. Add this point to the graph.
- Calculate the pH of the solution after 25.0 mL of HCl has been added. Add this point to the graph.
- Calculate the pH of the solution after 35.0 mL of HCl has been added. Add this point to the graph.
- Calculate the pH of the solution after 50.0 mL of HCl has been added. Add this point to the graph.

### 15.5 Acid-Base Indicators

- End point- the point in a titration where the indicator changes color
- Indicators are usually weak acids, HIn. They have one color in their acidic (HIn) form and another color in their basic (In<sup>-</sup>) form.
- A very common indicator, phenolphthalein, is colorless in its HIn form and pink in its In<sup>-</sup> form. It changes color in the range of pH 8-10.
- When choosing an indicator, we want the indicator end point and the titration equivalence point to be as close as possible.
- Since strong acid-strong base titrations have a large vertical area, color changes will be sharp and a wide range of indicators can be used. For titrations involving weak acids or weak bases, we must be more careful in our choice of indicator.
- Usually 1/10 of the initial form of the indicator must be changed to the other form before a new color is apparent.
  - The following equations can be used to determine the pH at which an indicator will change color:
    - For titration of an acid:  $\text{pH} = \text{pK}_a + \log 1/10 = \text{pK}_a - 1$
    - For titration of a base:  $\text{pH} = \text{pK}_a + \log 10/1 = \text{pK}_a + 1$
  - The useful range of an indicator is usually its  $\text{pK}_a \pm 1$ .
  - When choosing an indicator, determine the pH at the equivalence point of the titration and then choose an indicator with a  $\text{pK}_a$  close to that.

## Chapter 16: Solubility Equilibrium

### 16.1 Solubility Equilibria and the Solubility Product

Saturated solutions of salts are another type of chemical equilibria.

- For a saturated solution of AgCl, the equation would be:  $\text{AgCl}(s) \leftrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$
- The solubility product expression would be:  $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$

- The  $\text{AgCl(s)}$  is left out since solids are left out of equilibrium expressions (constant concentrations).
  - For  $\text{Ag}_2\text{CO}_3$ ,  $\text{Ag}_2\text{CO}_3 \leftrightarrow 2\text{Ag}^+ + \text{CO}_3^{2-}$   $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$
- The  $K_{\text{sp}}$  of  $\text{AgCl}$  is  $1.6 \times 10^{-10}$ .
  - This means that if the product of  $[\text{Ag}^+][\text{Cl}^-] < 1.6 \times 10^{-10}$ , the solution is unsaturated and no solid would be present.
  - If the product =  $1.6 \times 10^{-10}$ , the product is exactly saturated and no solid would be present.
  - If the product  $> 1.6 \times 10^{-10}$ , the solution is saturated and a solid (precipitate) would form.
  - The product of the ions (raised to the power of their coefficients) is called the ion product constant or  $Q$ .
    - If  $K_{\text{sp}} > Q$ , no ppt forms.
    - If  $K_{\text{sp}} < Q$ , ppt forms.
- Ex. The molar solubility of silver sulfate is  $1.5 \times 10^{-2}$  mol/L. Calculate the solubility product of the salt.

Remember that molar solubility is “x”!

- Ex. Calculate the molar solubility of calcium phosphate. The  $K_{\text{sp}}$  of calcium phosphate is  $1.2 \times 10^{-26}$ .

Remember that molar solubility is “x”!

- Ex. What is the molar solubility of lead(II) iodide in a 0.050 M solution of sodium iodide?  
(Common ion effect problem)

Don't forget to put in the initial concentration of the common ion!

- The molar solubility of  $\text{PbI}_2$  in pure water is  $1.5 \times 10^{-3}$  M. This shows the decreased solubility of a salt in the presence of a common ion.
- Ex. Exactly 200 mL of 0.040 M  $\text{BaCl}_2$  are added to exactly 600 mL of 0.080 M  $\text{K}_2\text{SO}_4$ . Will a precipitate form?  
 $\text{BaCl}_2 + \text{K}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{KCl}$



3. A 0.682 gram sample of an unknown weak monoprotic organic acid, HA, was dissolved in sufficient water to make 50 milliliters of solution and was titrated with a 0.135 molar NaOH solution. After the addition of 10.6 milliliters of base, a pH of 5.65 was recorded. The equivalence point (end point) was reached after the addition of 27.4 milliliters of the 0.135 molar NaOH.

- a) Calculate the number of moles of acid in the original sample.
  
  
  
  
  
  
  
  
  
  
- b) Calculate the molecular weight of the acid, HA.
  
  
  
  
  
  
  
  
  
  
- c) Calculate the number of moles of unreacted HA remaining in solution when the pH was 5.65.
  
  
  
  
  
  
  
  
  
  
- d) Calculate the  $[H_3O^+]$  at pH = 5.65.
  
  
  
  
  
  
  
  
  
  
- e) Calculate the value of the ionization constant,  $K_a$ , of the acid HA.

4. If 0.050 mole of crystalline lanthanum nitrate is added to 1.00 liter of a solution containing 0.20 mole of  $CH_3NH_2$  and 0.20 mole of its salt  $CH_3NH_3Cl$  at  $25^\circ C$ , and the solution is stirred until equilibrium is attained, will any  $La(OH)_3$  precipitate? Show the calculations that prove your answer. (The solubility constant for  $La(OH)_3$ ,  $K_{sp} = 1 \times 10^{-19}$  at  $25^\circ C$ . The base dissociation constant for  $CH_3NH_2$  is  $4.38 \times 10^{-4}$ .)

5. Given a solution of ammonium chloride. What additional reagent or reagents are needed to prepare a buffer from the ammonium chloride solution?



- c) An aqueous solution of  $\text{Sr}(\text{NO}_3)_2$  is added slowly to 1.0 liter of a well stirred solution containing 0.020 mole  $\text{F}^-$  and 0.10 mole  $\text{SO}_4^{2-}$  at  $25^\circ\text{C}$  (You may assume that the added  $\text{Sr}(\text{NO}_3)_2$  solution does not materially affect the total volume of the system). Which salt precipitates first? What is the concentration of strontium ion,  $\text{Sr}^{+2}$ , in the solution when the first precipitate begins to form?
- d) As more  $\text{Sr}(\text{NO}_3)_2$  is added to the mixture in (c), a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?
8. A saturated solution of lead iodate in pure water has a lead ion concentration of  $4.0 \times 10^{-5}$  mole per liter at  $20^\circ\text{C}$ .
- a) Calculate the value for the solubility product constant of  $\text{Pb}(\text{IO}_3)_2$  at  $25^\circ\text{C}$ .
- b) Calculate the molar solubility of  $\text{Pb}(\text{IO}_3)_2$  in a 0.10 molar  $\text{Pb}(\text{NO}_3)_2$  solution at  $25^\circ\text{C}$ .
- c) To 333 milliliters of a 0.120-molar  $\text{Pb}(\text{NO}_3)_2$  solution, 667 milliliters of 0.435-molar  $\text{KIO}_3$  is added. Calculate the concentrations of  $\text{Pb}^{2+}$  and  $\text{IO}_3^-$  in the solution at equilibrium at  $25^\circ\text{C}$ .



## AP Chemistry: Aqueous Equilibria Worksheet #2



Benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150M NaOH.

a) After addition of 15.0 mL of the 0.150 M NaOH, the pH of the resulting solution is 4.37. Calculate each of the following.

(i)  $[\text{H}^+]$  in the solution

(ii)  $[\text{OH}^-]$  in the solution

(iii) The number of moles of NaOH added

(iv) The number of moles of  $\text{C}_6\text{H}_5\text{COO}^-(aq)$  in the solution

(v) The number of moles of  $\text{C}_6\text{H}_5\text{COOH}$  in the solution

b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

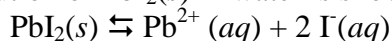
c) In a different titration, a 0.7529 g sample of a mixture of solid  $\text{C}_6\text{H}_5\text{COOH}$  and solid NaCl is dissolved in water and titrated with 0.0150M NaOH. The equivalence point is reached when 24.78 mL of the base solution is added. Calculate each of the following.

(i) The mass, in grams, of benzoic acid in the solid sample

(ii) The mass percentage of benzoic acid in the solid sample

2. Answer the following questions that relate to solubility of salts of lead and barium.

a) A saturated solution is prepared by adding excess  $\text{PbI}_2(s)$  to distilled water to form 1.0 L of solution at  $25^\circ\text{C}$ . The concentration of  $\text{Pb}^{2+}(aq)$  in the saturated solution is found to be  $1.3 \times 10^{-3}\text{M}$ . The chemical equation for the dissolution of  $\text{PbI}_2(s)$  in water is shown below.



(i) Write the equilibrium-constant expression for the equation.

(ii) Calculate the molar concentration of  $\text{I}^{-}(aq)$  in the solution.

(iii) Calculate the value of the equilibrium constant,  $K_{sp}$ .

b) A saturated solution is prepared by adding  $\text{PbI}_2(s)$  to distilled water to form 2.0L of solution at  $25^{\circ}\text{C}$ . What are the molar concentrations of  $\text{Pb}^{2+}(aq)$  and  $\text{I}^{-}(aq)$  in the solution? Justify your answer.

c) Solid  $\text{NaI}$  is added to a saturated solution of  $\text{PbI}_2$  at  $25^{\circ}\text{C}$ . Assuming that the volume of the solution does not change, does the molar concentration of  $\text{Pb}^{2+}(aq)$  in the solution increase, decrease, or remain the same? Justify your answer.

d) The value of  $K_{sp}$  for the salt  $\text{BaCrO}_4$  is  $1.2 \times 10^{-10}$ . When a 500.mL sample of  $8.2 \times 10^{-6} \text{ M Ba}(\text{NO}_3)_2$  is added to 500. mL of  $8.2 \times 10^{-6} \text{ M Na}_2\text{CrO}_4$ , no precipitate is observed.

(i) Assuming that volumes are additive, calculate the molar concentration of  $\text{Ba}^{2+}(aq)$  and  $\text{CrO}_4^{2-}(aq)$  in the 1.00L of solution.

(ii) Use the molar concentrations of  $\text{Ba}^{2+}(aq)$  ions and  $\text{CrO}_4^{2-}(aq)$  ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer.

$$3. \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = 3.2 \times 10^{-8}$$

Hypochlorous acid,  $\text{HOCl}$ , is a weak acid in water. The  $K_a$  expression for  $\text{HOCl}$  is shown above.

a) Write a chemical equation showing how  $\text{HOCl}$  behaves as an acid in water.

b) Calculate the pH of a 0.175M solution of  $\text{HOCl}$ .

c) Write the net ionic equation for the reaction between the weak acid  $\text{HOCl}(aq)$  and the strong base  $\text{NaOH}(aq)$ .

- d) In an experiment, 20.00 mL of 0.175M HOCl(aq) is placed in a flask and titrated with 6.55 mL of 0.435M NaOH(aq).
- Calculate the number of moles of NaOH(aq) added.

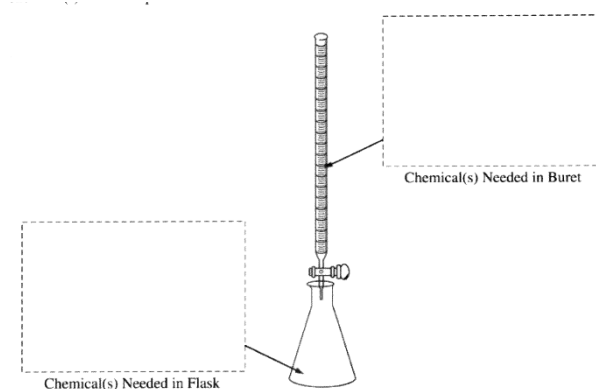
b. Calculate  $[H_3O^+]$  in the flask after the NaOH(aq) has been added.

(iii) Calculate  $[OH^-]$  in the flask after the NaOH(aq) has been added.

4. An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

- What measurement(s) must be made to determine the number of moles of NaOH used in the titration?
- Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.
- How can the number of moles of HA consumed in the titration be determined?
- In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA?
- Write the mathematical expression that is used to determine the molar mass of HA.

f) The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.

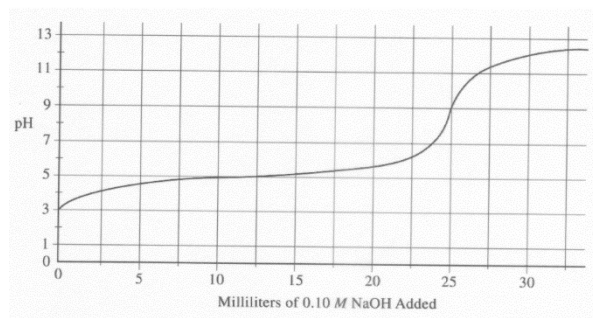


g) Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.

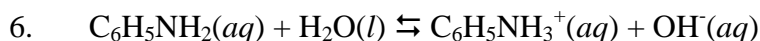
(i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

(ii) The procedure called for 25 mL of H<sub>2</sub>O in the Erlenmeyer flask, but a student used 35 mL of H<sub>2</sub>O.

5. The graph below shows the result of the titration of a 25 mL sample of a 0.10 M solution of a weak acid, HA, with a strong base, 0.10M NaOH.



- a) Describe two features of the graph above that identify HA as a weak acid.
- b) Describe one method by which the value of the acid-dissociation constant for HA can be determined using the graph above.
- c) On the graph above, sketch the titration curve that would result if 25 mL of 0.10M HCl were used instead of 0.10M HA.
- d) A 25 mL sample of 0.10M HA is titrated with 0.20M NaOH.
- (i) What volume of base must be added to reach the equivalence point?
- (ii) The pH at the equivalence point for this titration is slightly higher than the pH at the equivalence point in the titration using 0.10M NaOH. Explain.



Aniline, a weak base, reacts with water according to the reaction represented above.

- a) Write the equilibrium constant expression,  $K_b$ , for the reaction represented above.
- b) A sample of aniline, is dissolved in water to produce 25.0 mL of a 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant,  $K_b$ , for this reaction.
- c) The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.
- d) Calculate the pH at the equivalence point of the titration in part (c).
- e) The  $\text{p}K_a$  values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	$\text{p}K_a$
Erythrosine	3
Litmus	7
Thymolphthalein	10

## AP Chemistry: Chapters 6 & 17 Notes

### Thermochemistry

#### 6.1 The Nature of Energy

In this chapter, we will study energy in terms of chemical potential energy and how that energy can change form to accomplish work. We will focus specifically on heat and energy transfer.

- Energy- the capacity to do work or to produce heat
- Work- force acting over a distance
  - It involves a transfer of energy
- 1st Law of Thermodynamics- also known as the Law of Conservation of Energy. States that energy can be converted from one form to another but it can be neither created nor destroyed.
  - The total amount of energy in the universe is constant.
- Energy can be classified in two ways:
  - Potential energy- energy due to position or composition (included chemical potential energy)
  - Kinetic energy- energy due to the motion of an object
    - Kinetic energy is dependent on the mass and velocity of an object
- Heat- involves a transfer of energy between two objects due to a temperature difference.
  - Heat always moves from warmer matter to cooler matter.
- Temperature- a property that reflects random motions of the particles of a particular substance
  - Exothermic- reaction which releases heat
    - Energy flows out of the system
    - Potential energy is changed to thermal energy
    - Products have lower potential energy than reactants
  - Endothermic- reaction which absorbs heat
    - Energy flows into the system
    - Thermal energy is changed into potential energy
    - Products have higher PE than reactants
- In terms of a chemical reaction, the system is our reaction. The surroundings are everything else, including things like the container the reaction occurs in, the room it sits in, etc.
- Internal energy (E) of a system is the sum of the kinetic and potential energies of all the particles in a system.
- Thermodynamic quantities always consist of a number and a sign (+ or -). The sign represents the systems point of view. (Engineers use the surroundings point of view)
  - Exothermic -q (systems energy is decreasing)
  - Endothermic +q (systems energy is increasing)
  - Example: Calculate  $\Delta E$  if  $q = -50 \text{ kJ}$  and  $w = +35 \text{ kJ}$ .

$$KE = \frac{1}{2} mv^2$$

- m = mass in kg
- v = velocity in m/s
- units are J, since  $J = (\text{kg m}^2)/\text{s}^2$

$$\Delta E = q + w$$

- $\Delta E$  is the change in the system's internal energy
- q represents heat
- w represents work usually in J or kJ

- For a gas that expands or is compressed, work can be calculated by:
  - $w = -P\Delta V$
  - units: L·atm
  - Example: Calculate the work if the volume of a gas is increased from 15 mL to 2.0 L at a constant pressure of 1.5 atm.

## 6.2 Enthalpy and Calorimetry

- Enthalpy (H) concerns the heat energy in a system.
- $\Delta H = q$  at constant pressure only
- At constant pressure, the terms heat of reaction and change in enthalpy are used interchangeably.
- The change in the enthalpy of a system can be calculated using:
  - $\Delta H = H_{\text{products}} - H_{\text{reactants}}$ 
    - For an exothermic reaction,  $\Delta H$  is negative
    - For an endothermic reaction,  $\Delta H$  is positive
  - Example: For the reaction  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$ ,  $\Delta H = -368 \text{ kJ}$  Calculate the heat change that occurs when 3.5 g of Na reacts with excess water.

$$H = E + PV$$

- E is internal energy
- P is pressure
- V is volume

- Calorimetry- the science of measuring heat flow in a chemical reaction.
  - It is based on observing the temperature change when a body absorbs or discharges heat.
  - The instrument used to measure this change is the calorimeter.

### Heat Capacity (C)

$$C = \frac{\text{heat absorbed}}{\text{Increase in temp.}}$$

$$C = \text{J/g}^\circ\text{C} \quad \text{or} \quad \text{J/mol}^\circ\text{C}$$

- The heat capacity of  $\text{H}_2\text{O}$  is  $4.18 \text{ J/g}^\circ\text{C}$
- Constant pressure calorimetry- pressure remains constant during the process
- Simple calorimetry- used to determine heats of reaction
- The primary reaction to calculate heat changes in a system is the "Mcat" equation.

- Energy released as heat = (heat capacity) (mass of solution) (increase in temp)

- Example: A coffee cup calorimeter contains 150 g  $\text{H}_2\text{O}$  at  $24.6^\circ\text{C}$ . A 110 g block of molybdenum is heated to  $100^\circ\text{C}$  and then placed in the water in the calorimeter. The contents of the calorimeter come to a temperature of  $28.0^\circ\text{C}$ . What is the heat capacity per gram of molybdenum?

$$q = mC\Delta T$$

$$\text{J} = (\text{J/g}^\circ\text{C})(\text{g})(\Delta^\circ\text{C})$$

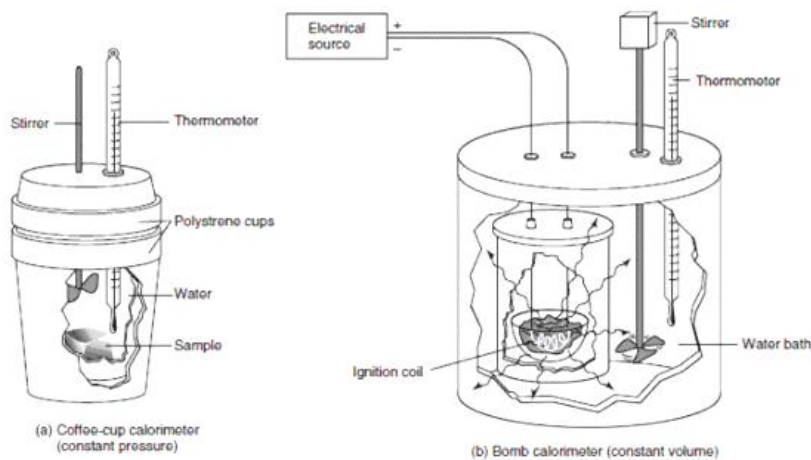


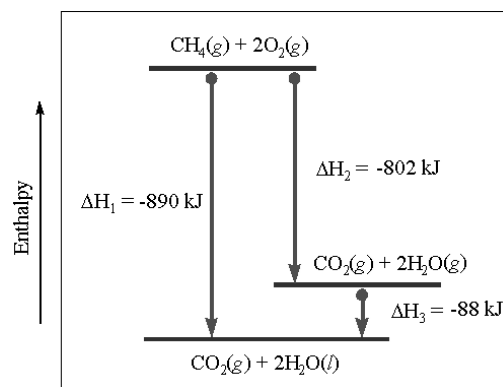
Figure 9.1 Two types of calorimeters.



- In terms of calorimetry, we can describe certain properties of the reaction as an:
  - Extensive property- this depends on the amount of substance (ex. Heat of reaction)
  - Intensive property- doesn't depend on the amount of substance (ex. Temperature)
- Calorimetry can be done in a closed, rigid container. This is called constant volume calorimetry
  - Ex. Flashbulb in a camera or a bomb calorimeter
  - No work can be done since the volume doesn't change
  - Heat evolved =  $\Delta T \times$  heat capacity of calorimeter (energy required to change the temp  $1^\circ\text{C}$ )

### 6.3 Hess's Law

- Hess's Law- States that the change in enthalpy from products to reactants, or  $\Delta H$ , is the same whether the reaction occurs in one step or in several steps.
  - $\Delta H$  is not dependent on the reaction pathway.
  - The sum of the  $\Delta H$  for each step equals the  $\Delta H$  for the total reaction.
  - If a reaction is reversed, the sign of  $\Delta H$  is reversed.
  - If the coefficients in a reaction are multiplied by an integer, the value of  $\Delta H$  is multiplied by the same integer.
  - Example: Given the following reactions and their respective enthalpy changes, calculate  $\Delta H$  for the reaction:  $2\text{C} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2$ .



$\text{C}_2\text{H}_2 + 5/2 \text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$	$\Delta H = -1299.6 \text{ kJ/mol C}_2\text{H}_2$
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$\Delta H = -393.5 \text{ kJ/mol C}$
$\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$	$\Delta H = -285.9 \text{ kJ/mol H}_2$

- Example: The heat of combustion of C to  $\text{CO}_2$  is  $-393.5 \text{ kJ/mol}$  of  $\text{CO}_2$ , whereas that for combustion of CO to  $\text{CO}_2$  is  $-283.0 \text{ kJ/mol}$  of  $\text{CO}_2$ . Calculate the heat of combustion of C to CO.

### 6.4 Standard Enthalpies of Formation

- Standard enthalpy of formation ( $\Delta H_f^\circ$ ) – The change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states at  $25^\circ\text{C}$ .
- The degree sign on a thermodynamics function indicates that the process it represents has been carried out at standard state conditions.
  - Standard States
    - for gases, pressure is 1 atm
    - for a substance in solution, the concentration is 1 M
    - for a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
    - for an element, the standard state is the form in which the element exists under conditions of 1 atm and  $25^\circ\text{C}$ .
    - Values of  $\Delta H_f^\circ$  are found in Appendix 4

$$\bullet \Delta H_{\text{reaction}}^{\circ} = \sum \Delta H_{\text{f products}}^{\circ} - \sum \Delta H_{\text{f reactants}}^{\circ}$$

- Example: The standard enthalpy change for the reaction  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO} + \text{CO}_2(\text{g})$  is 178.1 kJ. Calculate the  $\Delta H_{\text{f}}^{\circ}$  for  $\text{CaCO}_3(\text{s})$ .

## 6.5 Present Sources of Energy

In this section, we will discuss some sources of energy, including fossil fuels, and their effects on the environment.

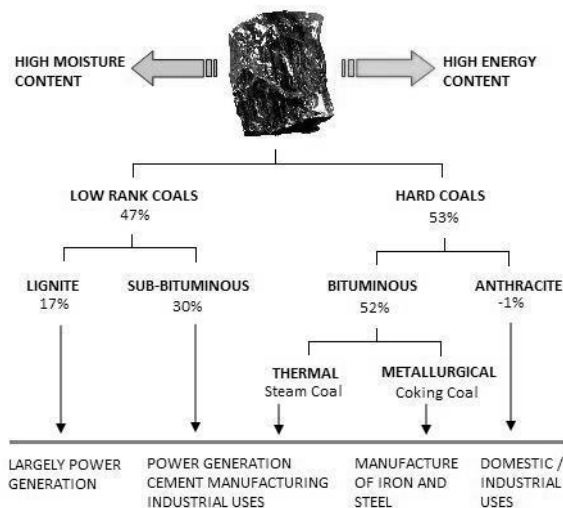
- Petroleum- A thick, dark liquid composed of hydrocarbons chains of 5-25 carbons
  - Refining petroleum involves the process of pyrolytic cracking, or distilling the fractions of petroleum from the main sample based on their molecular mass and boiling point.
  - Gasoline  $\text{C}_5\text{-C}_{12}$ 
    - Gasoline, when first used in car engines, caused a dramatic knocking sound and was thus treated with tetraethyl lead,  $(\text{C}_2\text{H}_5)_4\text{Pb}$ , an antiknock agent. This introduced lead into the atmosphere as the fuel was spent and increased the amount of ingested lead in the human and animal populations until 1960 when “leaded” gas was finally phased out.
    - kerosene & jet fuel  $\text{C}_{10}\text{-C}_{18}$
    - heating and lubricating oil and diesel fuel  $\text{C}_{15}\text{-C}_{25}$
    - asphalt  $>\text{C}_{25}$
  - Natural gas- This substance is usually found alongside petroleum and is composed mostly of methane. It also contains ethane, propane, and butane.
  - Coal- formed from the remains of plants buried under pressure for many years. Cellulose,  $\text{CH}_2\text{O}_x$ , gradually loses its H and O.
  - Coal develops through 4 stages:
    - lignite (least valuable)
    - subbituminous
    - bituminous (high sulfur)
    - anthracite (most valuable)
  - Coal provides 20% of our energy in the U.S.

### Effects of $\text{CO}_2$ on the Climate

- Greenhouse effect -  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules in the atmosphere reflect IR radiation and send it back to earth thus raising the earth’s temperature. The  $\text{CO}_2$  concentration has increased by about 16% in the past 100 years because of increase in the use of fossil fuels.

### New Energy Sources

- Coal gasification- treating coal with oxygen and steam at high temperatures to break down many of the C-C bonds and form C-O and C-H bonds. The products are syngas ( $\text{CO} + \text{H}_2$ ) and methane gas. Syngas may be converted to methanol.  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$
- Hydrogen as a Fuel  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H^{\circ} = -286 \text{ kJ}$ 
  - ~2.5 times that of natural gas
  - 3 problems: production (too expensive), transport (too volatile), and storage (large volume, decomposes to H atoms on metal surfaces, makes metal brittle-forms metal hydrides)
- Other Alternatives: oil shale, ethanol, gasohol, seed oil (sunflower)





## Chapter 17: Thermochemistry

### 17.1 & 17.2 Spontaneous Processes and Entropy and the Second Law of Thermodynamics

The first Law of Thermodynamics states that energy is neither created nor destroyed; it is constant in the universe. We can measure energy changes in chemical reactions to help determine exactly what is happening and how it is occurring.

Keep in mind that thermodynamics deals with the reactants and products while kinetics deals with how reactants become products.

- Spontaneous process- occurs without outside intervention (ex. Rusting)
  - This may be fast or slow (CO<sub>2</sub> sublimates vs. iron rusting)
- Entropy (S)- a measure of randomness or disorder
  - This is associated with probability. (there are more ways for something to be disorganized than organized)
  - Entropy increases going from a solid to a liquid to a gas and when solutions are formed.
  - Entropy increases in a reaction when more atoms or molecules are formed.
  - Entropy increases with increasing temperature.
- 2nd Law of Thermodynamics- In any spontaneous process there is always an increase in the entropy of the universe. The energy of the universe is constant but the entropy of the universe is increasing.

### 17.3 and 17.4 Free Energy

- Free energy (G)- the amount of energy available to do work.
  - Free energy change is a measure of the spontaneity of a reaction. It is the maximum work available from the system.
  - A spontaneous reaction carried out as constant temperature and pressure has a negative  $\Delta G$ . For example, when ice melts  $\Delta H$  is positive (endothermic),  $\Delta S$  is positive and  $\Delta G = 0$  at 0°C.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta S$	$\Delta H$	$\Delta G$	Spontaneous?
+	-	-	Yes, always
+	+	?	Yes, at high T
-	-	?	Yes, at low T
-	+	+	No, never

### 17.5 Entropy Changes in Chemical Reactions

- Third Law of Thermodynamics- The entropy of a perfect crystal at 0 K is zero.
  - $\Delta S^{\circ}_{\text{reaction}} = \Sigma S^{\circ}_{\text{products}} - \Sigma S^{\circ}_{\text{reactants}}$
  - Ex. Given the following standard molar entropies, calculate  $\Delta S^{\circ}$  for the reaction:
 

$2\text{Al}(s) + 3\text{MgO}(s) \rightarrow 3\text{Mg}(s) + \text{Al}_2\text{O}_3(s)$	$S^{\circ}(\text{Al}(s)) = 28.0 \text{ J/K}$	$S^{\circ}(\text{MgO}(s)) = 27.0 \text{ J/K}$
	$S^{\circ}(\text{Mg}(s)) = 33.0 \text{ J/K}$	$S^{\circ}(\text{Al}_2\text{O}_3(s)) = 51.0 \text{ J/K}$

### 17.6 Free Energy and Chemical Reactions

- Standard free energy change ( $\Delta G^{\circ}$ ) -The change in free energy that occurs if the reactants in their standard states are converted to products in their standard states.
  - $\Delta G^{\circ} = \Sigma \Delta G^{\circ}_{\text{f products}} - \Sigma \Delta G^{\circ}_{\text{f reactants}}$  at standard conditions
  - $\Delta G^{\circ}_{\text{f}}$  for a free element in its standard state is zero.
  - Ex. Given the equation  $\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$  and the following data, calculate  $\Delta G^{\circ}$ .
 

$G^{\circ}_{\text{f}}$ for $\text{N}_2\text{O}_4(g) = 97.82 \text{ kJ/mol}$ ,	$G^{\circ}_{\text{f}}$ for $\text{NO}_2(g) = 51.30 \text{ kJ/mol}$
---	--

- The Gibbs-Helmholtz equation works like the Gibbs Free Energy equation, just at standard state conditions.
  - $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  (When working this, change the units for S to kJ).
  - Ex. For the given reaction and the following information, calculate  $\Delta G^\circ$  at 25°C.  
 $2\text{PbO}(s) + 2\text{SO}_2(g) \rightarrow 2\text{PbS}(s) + 3\text{O}_2(g)$

	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol·K)
PbO (s)	-218.0	70.0
SO <sub>2</sub> (s)	-297.0	248.0
PbS (s)	-100.0	91.0
O <sub>2</sub> (g)	?	205.0

### 17.7 The Dependence of Free Energy on Pressure

In an ideal gas, enthalpy does not depend on pressure. Entropy, however, does depend on pressure because it depends upon volume. Gases in large volumes have greater entropy than in a small volume. Gases at a low pressure have greater entropy than at a high pressure. Because entropy depends on pressure,  $\Delta G$  of an ideal gas depends on its pressure.

- If we incorporate  $PV = nRT$  with the equation for free energy, we end up with an equation to calculate free energy in relation to temperature and pressure variables.

- Ex. Calculate  $\Delta G$  at 298K for the following reaction if the reaction mixture consists of 1.0 atm N<sub>2</sub>, 3.0 atm H<sub>2</sub>, and 1.0 atm NH<sub>3</sub>.  
 $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \quad \Delta G^\circ = -33.32 \text{ kJ/mol}$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

Q = reaction quotient (partial pressure of products/reactants raised to the power of their coefficients)-only pressures of gases are included.

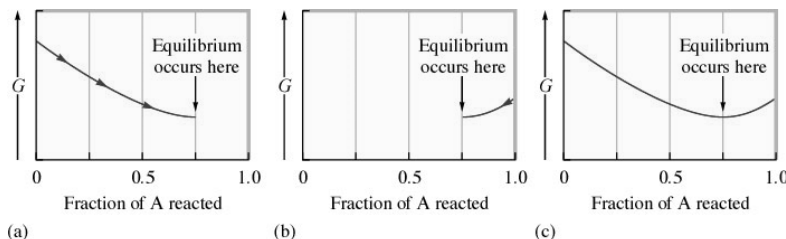
T = temperature in Kelvin

R = gas constant 8.314 J/K·mol

$\Delta G^\circ$  = free energy change at 1 atm (be sure to change to Joules!)

### 17.8 Free Energy and Equilibrium

- The equilibrium point in terms of kinetics occurs when the forward and reverse reactions were occurring at an equal rate. In terms of free energy, the equilibrium point occurs at the lowest value of free energy available to the reaction system.
- These two definitions are the same!
  - $\Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$
  - Ex. Given for the reaction  $\text{Hg}(l) \rightarrow \text{Hg}(g)$  that  $\Delta H^\circ = 61.3 \text{ kJ/mol}$  and  $\Delta S^\circ = 100.0 \text{ J/mol·K}$ , calculate the normal boiling point of Hg.



- We can utilize the previous two equations ( $\Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$  and  $\Delta G = \Delta G^\circ + RT \ln(Q)$ ) to form an equation that describes the relationship between free energy and the value of the equilibrium constant.
- $\Delta G^\circ = -RT \ln(K)$  (the “rat link” equation)
  - When  $\Delta G^\circ = 0$ , free energy of reactants and products are equal when all components are in their standard states. During a phase change,  $\Delta G = 0$ .
  - When  $\Delta G^\circ < 0$ ,  $G^\circ_{\text{products}} < G^\circ_{\text{reactants}}$  The reaction is not at equilibrium,  $K > 1$  since pressure of products is  $> 1$  and the pressure of reactants is  $< 1$ .
  - When  $\Delta G^\circ > 0$ ,  $G^\circ_{\text{reactants}} < G^\circ_{\text{products}}$  The reaction is not at equilibrium,  $K < 1$  since pressure of products is  $< 1$  and the pressure of reactants is  $> 1$ .
  - Ex. Calculate the approximate standard free energy for the ionization of hydrofluoric acid, HF ( $K_a = 1.0 \times 10^{-3}$ ), at 25°C.

- We can use  $\Delta G = \Delta G^\circ + RT \ln(Q)$  to calculate the direction that a reaction will shift to reach equilibrium.
  - Free energy is energy available to do useful work.  $W_{\max} = \Delta G$

### AP Chemistry: Thermochemistry Worksheet #1

#1

When 1.000 gram of propane gas,  $C_3H_8$ , is burned at  $25^\circ C$  and 1.00 atmosphere,  $H_2O(l)$  and  $CO_2(g)$  are formed with the evolution of 50.29 kilojoules.

Compound	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/Kmol)
$H_2O(l)$	-286	70
$CO_2(g)$	-393.5	214.5
$O_2(g)$	0.0	205
$C_3H_8(g)$	?	270

- Write a balanced equation for the combustion reaction.
- Calculate the molar enthalpy of combustion,  $\Delta H_{\text{combustion}}^\circ$ , of propane.
- Calculate the standard molar enthalpy of formation,  $\Delta H_f^\circ$ , of propane gas.
- Calculate the entropy change,  $\Delta S_{\text{comb}}^\circ$ , for the reaction and *account for the sign of  $\Delta S_{\text{comb}}^\circ$* .

2. From each of the following pairs of substances, choose the one expected to have the greater absolute entropy. *Explain your choice in each case.* Assume 1 mole of each substance.

- $Pb(s)$  or  $C(\text{graphite})$  at the same temperature and pressure
- $He(g)$  at 1 atmosphere or  $He(g)$  at 0.05 atmosphere, both at the same temperature
- $H_2O(l)$  or  $CH_3CH_2OH(l)$  at the same temperature and pressure
- $Mg(s)$  at  $0^\circ C$  or  $Mg(s)$  at  $150^\circ C$ , both at the same pressure

3. For the reaction shown,  $\Delta H^\circ = +22.1$  kilocalories per mole at  $25^\circ C$ .  $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

- Does the tendency of reactions to proceed to a state of minimum energy favor the formation of products of this reaction? Explain.

- b) Does the tendency of reactions to proceed to a state of maximum entropy favor the formation of the products of this reaction? Explain.
- c) State whether an increase in temperature drives this reaction to the right, to the left, or has no effect. Explain.
- d) State whether a decrease in the volume of the system at constant temperature drives this reaction to the right, to the left or has no effect. Explain.

4.  $\text{CO(g)} + 2\text{H}_2\text{(g)} \leftrightarrow \text{CH}_3\text{OH(l)}$   $\Delta H^\circ = -128.1 \text{ kJ}$   
 The data in the table shown were determined at  $25^\circ\text{C}$ .

a) Calculate  $\Delta G^\circ$  for the reaction above at  $25^\circ\text{C}$ .

	$\Delta H_f^\circ (\text{kJ/mol})$	$\Delta G_f^\circ (\text{kJ/mol})$	$S^\circ (\text{J/K}\cdot\text{mol})$
CO(g)	-110.5	-137.3	+197.9
CH <sub>3</sub> OH(l)	-238.6	-166.2	+126.8

b) Calculate  $K_{\text{eq}}$  for the reaction above at  $25^\circ\text{C}$ .

c) Calculate  $\Delta S^\circ$  for the reaction above at  $25^\circ\text{C}$ .

d) In the table above, there are no data for  $\text{H}_2$ . What are the values of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ , and of the absolute entropy,  $S^\circ$ , for  $\text{H}_2$  at  $25^\circ\text{C}$ ?

5. The enthalpy change for the combustion of butyric acid at  $25^\circ\text{C}$ ,  $\Delta H_{\text{comb}}^\circ$ , is  $-2183.5 \text{ kJ/mole}$ . The combustion reaction is:  
 $\text{C}_3\text{H}_7\text{COOH(l)} + 5\text{O}_2\text{(g)} \leftrightarrow 4\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(l)}$

a) From the data above, calculate the standard heat of formation,  $\Delta H_f^\circ$ , for butyric acid at  $25^\circ\text{C}$ .

Substance	Standard Heat of Formation, $\Delta H_f^\circ$ , in kJ/mol	Absolute Entropy, $S^\circ$ , in J/K·mol
C(s)	0.00	5.69
CO <sub>2</sub> (g)	-393.5	213.6
H <sub>2</sub> (g)	0.00	130.6
H <sub>2</sub> O(l)	-285.85	69.96
O <sub>2</sub> (g)	0.00	205.0
C <sub>3</sub> H <sub>7</sub> COOH(l)	?	226.3

b) Write a correctly balanced equation for the formation of butyric acid from its elements.

c) Calculate the standard entropy change,  $\Delta S_f^\circ$ , for the formation of butyric acid at 25°C. The entropy change,  $\Delta S^\circ$ , for the combustion reaction above is -117.1 J/K at 25°C.

d) Calculate the standard free energy of formation,  $\Delta G_f^\circ$ , for butyric acid at 25°C.

6.

a) Write a separate balanced chemical equation for the combustion of each of the following: C(s), H<sub>2</sub>(g), and C<sub>2</sub>H<sub>5</sub>OH(l). Consider the only products to be CO<sub>2</sub>(g) and/or H<sub>2</sub>O(l).

<i>Substance</i>	<i>Enthalpy of Combustion, <math>\Delta H^\circ</math>, (kJ/mol)</i>	<i>Absolute Entropy, <math>S^\circ</math>, (J/mol·K)</i>
C(s)	-393.5	5.740
H <sub>2</sub> (g)	-285.8	130.6
C <sub>2</sub> H <sub>5</sub> OH(l)	-1366.7	160.7
H <sub>2</sub> O(l)	?	69.91

b) In principle, ethanol can be prepared by the following reaction.  $2\text{C(s)} + 2\text{H}_2\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{C}_2\text{H}_5\text{OH(l)}$   
Calculate the standard enthalpy change,  $\Delta H^\circ$ , for the preparation of ethanol, as shown in the reaction above.

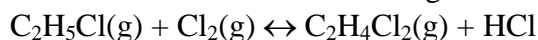
c) Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction given in part (b).

d) Calculate the value of the equilibrium constant at 25°C for the reaction represented by the equation in part (b).

**AP Chemistry: Thermochemistry Worksheet #2**

1. The reaction shown is a reversible reaction.  $\text{BaCl}_2(\text{g}) + \text{NH}_3(\text{g}) \leftrightarrow \text{Cl}_3\text{BNH}_3(\text{s})$
- Predict the sign of the entropy change,  $\Delta S$ , as the reaction proceeds to the right. Explain your prediction.
  - If the reaction spontaneously proceeds to the right, predict the sign of the enthalpy change,  $\Delta H$ . Explain your prediction.
  - The direction in which the reaction spontaneously precedes changes as the temperature is increased above a specific temperature. Explain.
  - What is the value of the equilibrium constant at the temperature referred to in part c; that is, the specific temperature at which the direction of the spontaneous reaction changes? Explain.
2.  $\text{ClF}_3$  can be prepared by the reaction represented by this equation:  $\text{Cl}_2(\text{g}) + 3 \text{F}_2(\text{g}) \rightarrow 2 \text{ClF}_3(\text{g})$  For  $\text{ClF}_3$  the standard enthalpy of formation,  $\Delta H_f^\circ$ , is  $-163.2 \text{ kJ/mol}$  and the standard free energy of formation,  $\Delta G_f^\circ$ , is  $-123.0 \text{ kJ/mol}$ .
- Calculate the value of the equilibrium constant for the reaction at 298K.
  - Calculate the standard entropy change,  $\Delta S^\circ$ , for the reaction at 298K.
  - If  $\text{ClF}_3$  were produced as a liquid rather than as a gas, how would the sign and the magnitude of  $\Delta S$  for the reaction be affected? Explain.
  - At 298K the absolute entropies of  $\text{Cl}_2(\text{g})$  and  $\text{ClF}_3(\text{g})$  are  $222.96 \text{ J/mol}\cdot\text{K}$  and  $281.50 \text{ J/mol}\cdot\text{K}$ , respectively.
    - Account for the larger entropy of  $\text{ClF}_3(\text{g})$  relative to that of  $\text{Cl}_2(\text{g})$ .
    - Calculate the value of the absolute entropy of  $\text{F}_2(\text{g})$  at 298K.

3. The tables below contain information for determining thermodynamic properties of the reaction shown.

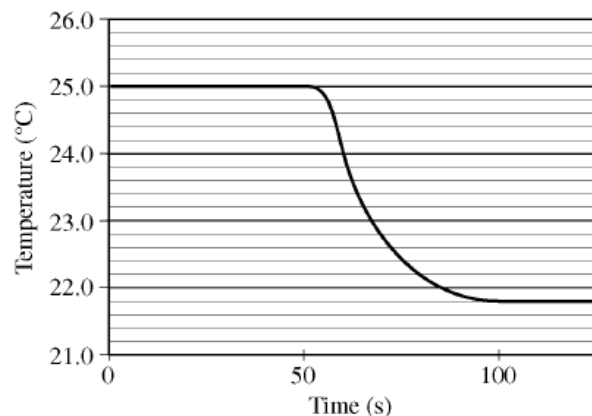


Substance	Standard Free Energies of Formation at 298K, $\Delta G^\circ_f$ at 298K (kJ/mol)
$\text{C}_2\text{H}_4\text{Cl}_2(\text{g})$	-80.3
$\text{C}_2\text{H}_5\text{Cl}(\text{g})$	-60.5
$\text{HCl}(\text{g})$	-95.3
$\text{Cl}_2(\text{g})$	0

Bond	Average Bond Dissociation Energies at 298K, (kJ/mol)
C-H	414
C-C	347
C-Cl	377
Cl-Cl	243
H-Cl	431

- Calculate the  $\Delta H^\circ$  for the reaction above, using the table of average bond dissociation energies.
- Calculate the  $\Delta S^\circ$  for the reaction at 298 K, using data from either table as needed.
- Calculate the value of  $K_{\text{eq}}$  for the reaction at 298K.
- What is the effect of an increase in temperature on the value of the equilibrium constant? Explain your answer.

4. A student performs an experiment to determine the molar enthalpy of solution of urea,  $\text{H}_2\text{NCONH}_2$ . The student places 91.95 g of water at  $25^\circ\text{C}$  into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at  $25^\circ\text{C}$ , to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown to the right.



- Determine the change in temperature of the solution that results from the dissolution of the urea.
- According to the data, is the dissolution of urea in water an endothermic process or an exothermic process?

Justify your answer.

- c. Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is  $4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$  throughout the experiment.
- Calculate the heat of dissolution of the urea in joules.

ii. Calculate the molar enthalpy of solution,  $\Delta H_{\text{soln}}$ , of urea in  $\text{kJ mol}^{-1}$ .

- d. Using the information in the table shown, calculate the value of the molar entropy of solution,  $\Delta S_{\text{soln}}$ , of urea at 298 K. Include units with your answer.

	Accepted Value
$\Delta H_{\text{soln}}$ of urea	$14.0 \text{ kJ mol}^{-1}$
$\Delta G_{\text{soln}}$ of urea	$-6.9 \text{ kJ mol}^{-1}$

- e. The student repeats the experiment and this time obtains a result for of urea that is 11 percent below the accepted value. Calculate the value of that the student obtained in this second trial.
- f. The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at  $5^\circ\text{C}$ . What effect, if any, would using the cold urea instead of urea at  $25^\circ\text{C}$  have on the experimentally obtained value of  $\Delta H_{\text{soln}}$ ? Justify your answer.

5. At  $25^\circ\text{C}$  the equilibrium constant,  $K_p$ , for the reaction shown is 0.281 atmosphere.  $\text{Br}_2(\text{l}) \leftrightarrow \text{Br}_2(\text{g})$

- What is the  $\Delta G^\circ_{298}$  for this reaction?
- b. It takes 193 joules to vaporize 1.00 gram of  $\text{Br}_2(\text{l})$  at  $25^\circ\text{C}$  and 1.00 atmosphere pressure. What are the values of  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$  for this reaction?
- c. Calculate the normal boiling point of bromine. Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  remain constant as the temperature is changed.



- d. What is the equilibrium vapor pressure of bromine at 25°C?
6. Propane, C<sub>3</sub>H<sub>8</sub>, is a hydrocarbon that is commonly used as fuel for cooking.
- Write a balanced equation for the complete combustion of propane gas, which yields CO<sub>2</sub>(g) and H<sub>2</sub>O(l).
  - Calculate the volume of air at 30°C and 1.00 atmosphere that is needed to burn completely 10.0 grams of propane. Assume that air is 21.0 percent O<sub>2</sub> by volume.
  - The heat of combustion of propane is -2,220.1 kJ/mol. Calculate the heat of formation,  $\Delta H_f^\circ$ , of propane given that  $\Delta H_f^\circ$  of H<sub>2</sub>O(l) = -285.3 kJ/mol and  $\Delta H_f^\circ$  of ClO<sub>2</sub>(g) = -393.5 kJ/mol.
  - Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kilograms of water (specific heat = 4.18 J/g°C), calculate the increase in temperature of the water.

☺ Extra Practice for the Extra Crazy Student ☺

1. The information given refers to the following reaction:  $\text{C}_2\text{H}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

Substance	$S^\circ$ (J/mol K)	$\Delta H_f^\circ$ (kJ/mol)
$\text{C}_2\text{H}_2(\text{g})$	200.9	226.7
$\text{H}_2(\text{g})$	130.7	0.00
$\text{C}_2\text{H}_6(\text{g})$	?	-84.7

Bond	Bond Energy (kJ/mol)
C-C	347
C=C	611
C-H	414
H-H	436

- If the value of the standard entropy change,  $\Delta S^\circ$ , for the reaction is -232.7 joules per mole Kelvin, calculate the standard molar entropy,  $S^\circ$ , of  $\text{C}_2\text{H}_6$  gas.
  - Calculate the value of the standard free-energy change,  $\Delta G^\circ$ , for the reaction. What does the sign of  $\Delta G^\circ$  indicate about the reaction above?
  - Calculate the value of the equilibrium constant,  $K$ , for the reaction at 298 K.
  - Calculate the value of the C [triple bond] C bond energy in  $\text{C}_2\text{H}_2$  in kilojoules per mole.
2. At 298 K, the standard enthalpy change,  $\Delta H^\circ$ , for the reaction represented below is -145 kilojoules.
- $$2 \text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \rightleftharpoons 3 \text{S}(\text{s}) + 2 \text{H}_2\text{O}(\text{g})$$
- Predict the sign of the standard entropy change,  $\Delta S^\circ$ , for the reaction. Explain the basis for your prediction.
  - At 298 K, the forward reaction (i.e., toward the right) is spontaneous. What change, if any, would occur in the value of  $\Delta G^\circ$  for this reaction as the temperature is increased? Explain your reasoning using thermodynamic principles.
  - What change, if any, would occur in the value of the equilibrium constant,  $K_{\text{eq}}$ , for the situation described in (b)? Explain your reasoning.
  - The absolute temperature at which the forward reaction becomes nonspontaneous can be predicted. Write the equation that is used to make the prediction. Why does this equation predict only an approximate value for the temperature?
3. The reaction represented below is spontaneous at 25°C. Assume that all reactants and products are in their standard states.
- $$\text{C}_4\text{H}_{10}(\text{g}) + 13 \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 10 \text{H}_2\text{O}(\text{l})$$
- Predict the sign of  $\Delta S^\circ$  for the reaction and justify your prediction.
  - What is the sign of  $\Delta G^\circ$  for the reaction? How would the sign and magnitude of  $\Delta G^\circ$  be affected by an increase in temperature to 50 °C? Explain your answer.
  - What must be the sign of  $\Delta H^\circ$  for the reaction at 25°C? How does the total bond energy of the reactants compare to that of the products?
  - When the reactants are placed together in a container, no change is observed even though the reaction is known to be spontaneous. Explain this observation.

## AP Chemistry: Chapter 18

### Electrochemistry

Whether we are referring to cell phones, calculators or cars, many things in our lives run off of batteries, so understanding the chemical reactions involved is important for all chemists. Electrochemistry is defined as the study of the interchange of chemical and electrical energy and involves the generation and use of electrical currents.

#### 18.1 Balancing Oxidation-Reduction Equations: A review

Electrochemistry involves the generation of an electric current due to an exchange of electrons between two substances.

- Oxidation-reduction reaction (redox)- involves the transfer of one or more electrons from one atom to another.
  - Oxidation can not occur without reduction!

Oxidation	Reduction
Loss of electrons	Gain of electrons
Increase in oxidation #	Decrease in oxidation number
Memory Tricks: OIL RIG (oxidation is loss of electrons, reduction is gain of electrons) or Leo the Lion Goes Ger! (lose electrons = oxidation, gain electrons = reduction)	
Reducing Agent- Substance which is oxidized and causes another substance to be reduced.	Oxidizing Agent- Substance which is reduced and causes another substance to be oxidized.

- Half-reaction- Equation written to show either the loss or the gain of electrons (shows number of electrons transferred)
  - Ex.  $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{e}^-$  &  $\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$

#### Balancing Oxidation-Reduction Equations: A Review

When balancing these reactions, use the half-reaction method that we practiced earlier in the year.

Common oxidizing agents	Products formed	Common reducing agents	Products formed
$\text{MnO}_4^-$ in acidic solution	$\text{Mn}^{2+}$	halide ions	free halogen
$\text{MnO}_2$ in acidic solution		free metals	metal ions
$\text{MnO}_4^-$ in neutral or basic solution	$\text{MnO}_2(\text{s})$	sulfite ions or $\text{SO}_2$	sulfate ions
$\text{Cr}_2\text{O}_7^{2-}$ in acidic solution	$\text{Cr}^{3+}$	nitrite ions	nitrate ions
$\text{HNO}_3$ , concentrated	$\text{NO}_2$	free halogens, dilute basic solution	hypohalite ions
$\text{HNO}_3$ , dilute	$\text{NO}$	free halogens, conc. basic solution	halate ions
$\text{H}_2\text{SO}_4$ , hot, concentrated	$\text{SO}_2$	metal-ous ions	metal-ic ions
$\text{Na}_2\text{O}_2$	$\text{NaOH}$	$\text{H}_2\text{O}_2$	$\text{O}_2$
$\text{HClO}_4$	$\text{Cl}^-$	$\text{C}_2\text{O}_4^{2-}$	$\text{CO}_2$
$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}$		
metal-ic ions	metal-ous ions		
free halogens	halide ions		

Practice:

- Potassium dichromate solution is added to an acidified solution of sodium sulfite.

Now You Try It!

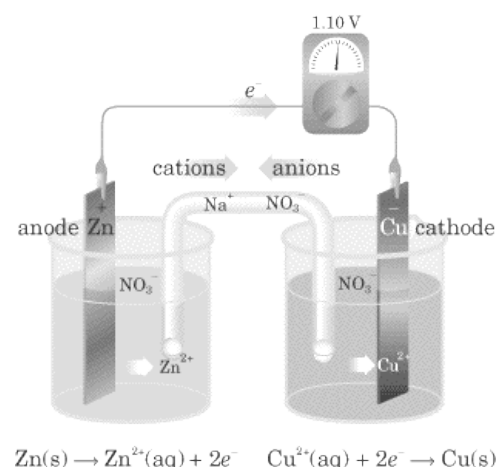
- Potassium permanganate is titrated with hydrobromic acid in a redox titration.

- A concentrated solution of sulfuric acid reacts with nickel.

## 18.2 Galvanic Cells

There are two types of chemical cells.

- Galvanic cell- chemical cell in which chemical energy is changed into electrical energy
  - Also called a voltaic cell
  - These reactions are spontaneous
- Electrolytic cell- chemical cell in which electrical energy is changed into chemical energy
  - These reactions are non-spontaneous
- In a galvanic or voltaic cell, the transfer of electrons can be used as an energy source if it is harnessed. One way that this may be done is by separating the two half-reactions and requiring the electron transfer to occur through a wire.
- The electron flow (electricity) can be used to do useful work.
- The solutions must also be connected in another way or the charge will become unbalanced and the electrical flow will stop. This connection is often by a salt bridge (tube filled with conducting solution) or porous disk. Ions flow from one compartment to the other to keep the net charge zero.
  - Anode- The electrode at which oxidation occurs. After a period of time, the anode may appear to become smaller as it falls into solution.
  - Cathode- Electrode at which reduction occurs. After a period of time, it may appear larger, due to ions from solution plating out on it.



An Ox and Red Cat    Oxidation occurs at the anode, Reduction occurs at the cathode.

FAT Cat    Electrons travel from anode to cathode (from reducing agent to oxidizing agent) in a galvanic cell.

Cell potential ( $\mathcal{E}_{\text{cell}}$ ) or electromotive force (emf):

- A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment. This “pull” is the emf or cell potential of the battery and is the driving force of the reaction.
- It is measured in volts: (1 joule of work per coulomb of charge transferred)  $1\text{V} = 1\text{J}/1\text{C}$
- Cells with positive  $E_{\text{cell}}$  values are always spontaneous.
- $\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{ox}} + \mathcal{E}^{\circ}_{\text{red}}$  (Standard cell potential is the sum of the standard oxidation potential for the oxidation half-reaction and the standard reduction potential for the reduction half-reaction.)
- $\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{ox}} + \mathcal{E}_{\text{red}}$  when the reaction is carried out under non-standard conditions
- Standard conditions are 1 atm,  $25^{\circ}\text{C}$ , and 1 M solutions
- *Note: The cell potential that you measure in an experiment will often be lower than what you expect. In the real world, the resistivity of the wire that carries the current can reduce the amount of electrons that “get through”, thus reducing the cell’s overall potential.*

### 18.3 Standard Reduction Potentials

The values for  $\mathcal{E}$  are usually written as reduction reactions (to change to oxidation, reverse reaction and change the sign of the potential) and can't be determined directly.

These values are determined by the use of a standard hydrogen electrode which is arbitrarily assigned a value of 0.00

- All other half reactions are expressed in reference to the standard hydrogen electrode
  - Standard hydrogen electrode- a platinum electrode in contact with 1M  $\text{H}^+$  and bathed by hydrogen gas at 1 atm  
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
  - $\mathcal{E}^\circ = 0.00 \text{ V}$

Standard Reduction Potentials in Aqueous Solution at 25°C			
Half Reaction	$E^\circ (V)$	Half Reaction	$E^\circ (V)$
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.28
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	1.50	$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}(\text{s})$	-0.34
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.07	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$2\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.92	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.85	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.18
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	0.79	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}(\text{s})$	-1.70
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-$	0.53	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.15	$\text{Sr}^{2+} + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	0.15	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{S}(\text{s}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}(\text{g})$	0.14	$\text{Rb}^+ + \text{e}^- \rightarrow \text{Rb}(\text{s})$	-2.92
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00	$\text{K}^+ + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13	$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}(\text{s})$	-2.92
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05

- Elements with very negative values (metals) are easily oxidized (thus the negative value for gaining electrons) while elements with very positive values (nonmetals) are more easily reduced (have higher electronegativity and thus easily gain electrons).
- The more positive the reduction potential, the more likely to gain electrons and act as an oxidizing agent.
- Substances with negative reduction potentials (and thus positive oxidation potentials) are more easily oxidized and act as reducing agents. The more negative the reduction potential, the stronger the reducing agent.
- When combining half reactions to obtain balanced redox reactions and calculating cell potential, you do not multiply the cell potential by an integer even if you multiply the half-reaction by an integer when writing the redox reaction. The cell potential is an intensive property and is not affected by how many times the reaction occurs.
  - If  $\mathcal{E}_{\text{cell}}$  is positive, the reaction is spontaneous.
  - If  $\mathcal{E}_{\text{cell}}$  is negative, the reaction is nonspontaneous.
  - Electrons will flow in the direction that will make the  $\mathcal{E}_{\text{cell}}$  positive.
  - Ex. A voltaic cell is made of chromium (III) and lead (II) metals in solutions of their own ions. Draw the cell below and label the anode, cathode and salt bridge. Indicate the direction of electron flow, calculate the cell potential and write the overall cell reaction. Indicate if this reaction is spontaneous or not.

*Note: When diagramming an electrochemical cell, the anode is traditionally drawn on the left and the cathode on the right.*

- A voltaic cell may be described in an abbreviated manner called line-notation. In this form the anode is on the left, followed by its aqueous solution. The right side consists of the aqueous solution for the cathode and finally the cathode. A single vertical line separates the electrodes from their solutions and a double vertical line between the anode solution and the cathode solution represents a salt bridge.

- Ex.  $\text{Mg}(s) | \text{Mg}^{2+}(aq) || \text{Al}^{3+}(aq) | \text{Al}(s)$
- This cell has solid magnesium as the anode immersed in a solution of magnesium ions. The cathode is solid aluminum immersed in a solution of aluminum ions.
- Ex. A galvanic cell is composed of solid zinc as the anode immersed in a solution of 1.0 M zinc ions and a cathode which is an inert platinum electrode immersed in a 1.0 M hydrogen ion solution with hydrogen gas bubbled in at 1 atm pressure. Write the line notation for this cell and the half reactions. Calculate the cell potential and indicate whether it is spontaneous or not.

### 18.4 Cell Potential, Electrical Work and Free Energy

- The greater the positive potential of a cell, the greater the spontaneity of the reaction.
- The difference in the potentials of the anode and cathode provide the thermodynamic driving force of the reaction. This force can accomplish work.
- Since  $\Delta G$ ,  $K$ , and  $\mathcal{E}^0$  are all measurements of the spontaneity of a reaction, we can write equations to interrelate them.

- $\text{Emf} (\mathcal{E}) = \text{work} (w)/\text{charge} (q)$  (measured in J/C)
- $w = \mathcal{E} q$  and  $q = n (\# \text{ mol}) \times F$  (faraday = 96,485 C/mol  $e^-$ )
- If  $\mathcal{E}^0$  is positive,  $\Delta G$  is negative (spontaneous) and work is flowing out of the system into the surroundings
- Don't forget, to find  $K$ :  $\Delta G = -RT \ln K$

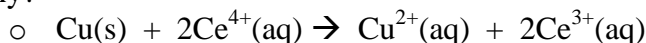
$$\Delta G^0 = -nF \mathcal{E}^0$$

$\Delta G^0$  is the standard free energy change (units are J)  
 $n$  is the number of moles of electrons transferred  
 $F$  is a Faraday (see above) 96,485 Coulombs/mol  $e^-$   
 $\mathcal{E}^0$  is standard cell potential (J/C)

### 18.5 Dependence of Cell Potential on Concentration

All of the calculations of cell potential we have done thus far have been for cells at standard conditions, or 1M solutions.

- Ask yourself, based on the reaction below, what would happen to the cell potential if the concentration of the cerium IV ion was doubled? Why?



- If cell concentrations are not standard (1 M) and 25<sup>0</sup>C, the cell potential is affected. This effect can be determined by using the Nernst equation.
  - This equation is derived from the equation used for free energy when pressures were not all 1 atm :  $\Delta G = \Delta G^0 + RT \ln Q$
  - The amount of electrical charge carried by 1 mol of electrons = 96,485 coulombs
  - Faraday- The amount of electricity that reduces one equivalent mass of a substance at the cathode and oxidizes one equivalent mass of a substance at the anode (equivalent mass is the mass of a species that will yield or consume one mole of electron).
  - Another form of the Nernst equation is only valid at 25<sup>0</sup>C :  $\mathcal{E} = \mathcal{E}^0 - (0.0592/n) \log Q$
  - The  $\mathcal{E}$  value calculated is the maximum potential at the very beginning of the reaction. As the reaction progresses,  $\mathcal{E}$  decreases until it reaches zero and the battery is at equilibrium (dead).
  - Ex. Calculate the emf of the Zn/Cu cell at 25<sup>0</sup>C under the following conditions:

Nernst equation:  $\mathcal{E} = \mathcal{E}^0 - (RT/nF) \ln Q$

$R = 8.3148 \text{ J/K mol}$

$T = \text{temp in Kelvin}$

$Q = \text{ratio of concentrations or pressures of products over reactants each raised to the power of their coefficients}$

$n = \text{number of moles of electrons transferred}$

$F = 96,500 \text{ Coulombs/mol}$

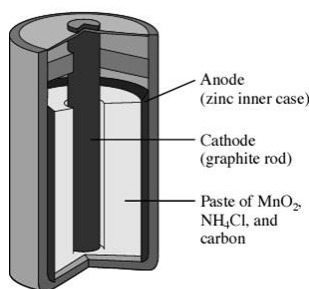
- $\text{Zn}(s) | \text{Zn}^{2+}(0.40 \text{ M}) || \text{Cu}^{2+}(0.020 \text{ M}) | \text{Cu}(s) \quad \mathcal{E}_{\text{cell}} = 1.10 \text{ V}$
- Therefore, the reaction is *more / less* (circle one) spontaneous when the ratio of concentration of products to concentration of reactants is greater than one. This could also be predicted using LeChatelier's principle.

Some electrodes are sensitive to the concentration of the solution into which they are placed. A pH meter behaves this way by being sensitive to hydrogen ions.

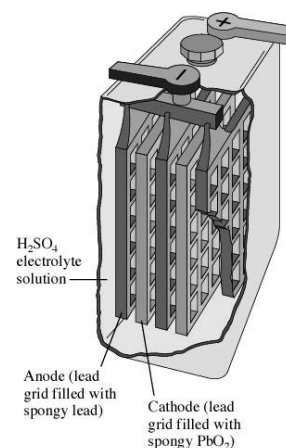
- Equilibrium constants can also be calculated using cell potentials. At equilibrium,  $\mathcal{E} = 0$  and  $Q = K$ .
  - $0 = \mathcal{E}^{\circ} - (0.0592/n) \log K$  (at 298 K) so  $\mathcal{E}^{\circ} = (0.0592/n) \log K$
  - Ex. Determine whether the following reaction is spontaneous and calculate its equilibrium constant at 25°C.
 
$$\text{Sn}(s) + \text{Ni}^{2+} \rightarrow \text{Sn}^{2+} + \text{Ni}(s)$$

## 18.6 Batteries

- A battery is a galvanic cell, or group of interconnected galvanic cells, whose potential energy can be used to do work.
- There are many types of galvanic cells that are used to power different types of equipment.
  - The common dry cell battery is one example of this. In the original acid version of the battery, the cathode is a graphite rod (inert) immersed in a paste of  $\text{MnO}_2$ ,  $\text{NH}_4\text{Cl}$  and carbon. The anode is the zinc case.



- The alkaline dry cell battery has the  $\text{NH}_4\text{Cl}$  replaced with  $\text{KOH}$  or  $\text{NaOH}$ . It lasts longer because the zinc corrodes more slowly under basic conditions.
- The lead storage battery (common car battery) consists of lead as the anode and lead coated with lead dioxide as the cathode. The electrolyte solution (battery acid) is sulfuric acid. The car's alternator recharges the battery by forcing current to flow in the opposite direction.



## 18.8 Electrolysis

A galvanic cell reaction proceeds in a spontaneous manner. When the desired chemical reaction is nonspontaneous, ( $\mathcal{E}_{\text{cell}}^{\circ}$  is negative) the reaction can proceed by the addition of electrons from an outside source. This results in the conversion of electrical energy into chemical energy.

- Examples are electrolysis of water,  $\text{NaCl}$  solution, and silver plating
- During this process, electrons are forced from the anode to the cathode when the cell voltage is exceeded. This causes the identity of the anode and cathode to reverse.
- The stoichiometry of these reactions is dictated by Faraday's Law which states that the amount of substance being oxidized or reduced at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.
- This stoichiometry can be determined with the following:
  - Time  $\rightarrow$  coulombs  $\rightarrow$  mol  $e^-$   $\rightarrow$  Faradays (mol/ $e^-$ )  $\rightarrow$  mol reactant  $\rightarrow$  grams reactant or
  - Grams reactant  $\rightarrow$  mol reactant  $\rightarrow$  Faradays (mol/ $e^-$ )  $\rightarrow$  mol  $e^-$   $\rightarrow$  coulombs  $\rightarrow$  Time
    - Coulomb = amp x s: amount of charge that passes a given point when 1 amp of electrical current flows for 1 second.
    - Ampere (amp): flow rate of 1 coulomb/s ( $i$  is used as symbol for current)
    - Joule (J): amount of energy absorbed or evolved when 1 coulomb of electrical charge moves

through a potential difference of 1 V ( $1\text{J} = 1\text{V}\cdot\text{C}$  and  $1\text{F} = 1\text{J}/\text{V}\cdot\text{mol}$ )

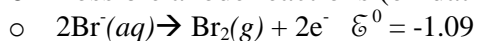
- Ex. How many grams of Cr can be plated out by passing 2.05 amps through acidic  $\text{CrO}_3$  for  $1.0 \times 10^4$  s?

- Ex. How many hours would it take to produce 25.0 g of Cr from a solution of  $\text{CrCl}_3$  by a current of 2.75A?

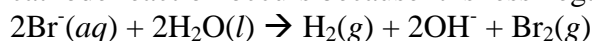
- When electrolysis is carried out in aqueous solutions, there is always the possibility that water will be oxidized and/or reduced instead of the solute. In order to predict the products produced when aqueous solutions are electrolyzed, you must determine the potentials of each possibility.

- Ex. The electrolysis of aqueous NaBr

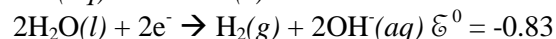
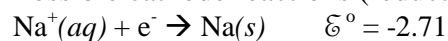
- Possible anode reactions (oxidation):



- The first anode reaction occurs because it is less negative (more spontaneous) and the second cathode reaction occurs because it is less negative (more spontaneous). The overall reaction is:

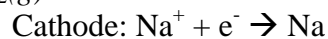


- Possible cathode reactions (reduction):

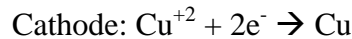
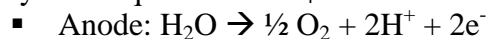


- This method of determining whether water is oxidized or reduced does not always work. In the electrolysis of salt water (brine), we would predict that water would be both oxidized and reduced. In fact, the chloride ions are oxidized instead of the water. This is due to some fairly complex factors. This phenomenon is called overpotential or overvoltage.

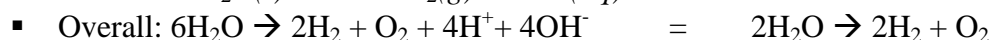
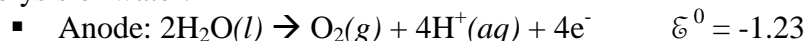
- The electrolysis of molten NaCl:  $\text{NaCl}(l) \rightarrow \text{Na}(l) + \frac{1}{2}\text{Cl}_2(g)$



- The electrolysis of aqueous  $\text{CuSO}_4$ :



- The electrolysis of water:





## AP Chemistry: Electrochemistry Worksheet #1

1. 
$$\text{Sn} + 2\text{Ag}^+ \rightarrow \text{Sn}^{2+} + 2\text{Ag}$$
- Calculate the standard voltage of a cell involving the system above.
  - What is the equilibrium constant for the system above?
  - Calculate the voltage at 25°C of a cell involving the system above when the concentration of  $\text{Ag}^+$  is 0.0010 molar and that of  $\text{Sn}^{2+}$  is 0.20 molar.
2. A steady current of 1.00 ampere is passed through an electrolytic cell containing a 1 molar solution of  $\text{AgNO}_3$  and having a silver anode and a platinum cathode until 1.54 grams of silver is deposited.
- How long does the current flow to obtain this deposit?
  - What weight of chromium would be deposited in a second cell containing 1 molar chromium (III) nitrate and having a chromium anode and a platinum cathode by the same current in the same time as was used in the silver cell?
  - If both electrodes were platinum in this second cell, what volume of  $\text{O}_2$  gas measured at standard temperature and pressure would be released at the anode while the chromium is being deposited at the cathode? The current and the time are the same as in (b).
3. 
$$\text{Zn} + \text{Cu}^{2+} (1\text{M}) \rightarrow \text{Zn}^{2+}(1\text{M}) + \text{Cu}$$
- Calculate the value of  $\Delta G^\circ$  for the standard cell reaction shown above.
  - One half cell of an electrochemical cell is made by placing a strip of pure zinc in 500 milliliters of 0.10 molar  $\text{ZnCl}_2$  solution. The other half cell is made by placing a strip of pure copper in 500 milliliters of 0.010 molar  $\text{Cu}(\text{NO}_3)_2$  solution. Calculate the initial voltage of this cell when the two half cells are joined by a wire.

- c. Calculate the final concentration of copper ion,  $\text{Cu}^{2+}$ , in the cell described in part (b) if the cell were allowed to produce an average current of 1.0 ampere for 3 minutes 13 seconds.
4. 
$$\text{Ti}^{3+} + \text{HOBr} \leftrightarrow \text{TiO}^{2+} + \text{Br}^- \text{ (acid solution)}$$
- a. Write the correctly balanced half-reactions and net ionic equation for the skeletal equation shown above.
- b. Identify the oxidizing agent and the reducing agent in this reaction.
- c. A galvanic cell is constructed that utilizes the reaction above. The concentration of each species is 0.10 molar. Compare the cell voltage that will be observed with the standard cell potential. Explain your reasoning.
- d. Give one example of a property of this reaction, other than the cell voltage, that can be calculated from the standard cell potential,  $\mathcal{E}^\circ$ . State the relationship between  $\mathcal{E}^\circ$  and the property you have specified.
5. Titanium can be reduced in an acid solution from  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  with zinc metal.
- a. Write a balanced equation for the reaction of  $\text{TiO}^{2+}$  with zinc in acid solution.
- b. What mass of zinc metal is required for the reduction of a 50.00 milliliter sample of a 0.115 molar solution of  $\text{TiO}^{2+}$ ?
- c. Alternatively, the reduction of  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  can be carried out electrochemically. What is the minimum time, in seconds, required to reduce another 50.000 milliliter sample of the 0.115 molar  $\text{TiO}^{2+}$  solution with a direct current of 1.06 amperes?
- d. The standard reduction potential,  $\mathcal{E}^\circ$ , for  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  is +0.060 volt. The standard reduction potential,  $\mathcal{E}^\circ$ , For  $\text{Zn}^{2+}$  to  $\text{Zn(s)}$  is -0.763 volt. Calculate the standard cell potential,  $\mathcal{E}^\circ$ , and the standard free energy change,  $\Delta G^\circ$ , for the reaction described in part (a).

6. A dilute solution of sodium sulfate,  $\text{Na}_2\text{SO}_4$ , was electrolyzed using inert platinum electrodes. In a separate experiment, a concentrated solution of sodium chloride,  $\text{NaCl}$ , was electrolyzed also using inert platinum electrodes. In each experiment, gas formation was observed at both electrodes.
- Explain why metallic sodium is not formed in either experiment.
  - Write balanced equations for the half-reactions that occur at the electrodes during electrolysis of the dilute sodium sulfate solution. Clearly indicate which half-reaction occurs at each electrode.
  - Write balanced equations for the half-reactions that occur at the electrodes during electrolysis of the concentrated sodium chloride solution. Clearly indicate which half-reaction occurs at each electrode.
  - Select two of the gases obtained in these experiments, and for each gas, indicate one experimental procedure that can be used to identify it.
7. 300.0 milliliters of a solution of 0.200 molar  $\text{AgNO}_3$  is mixed with 100.0 milliliters of a 0.0500 molar  $\text{CaCl}_2$  solution.
- What is the concentration of silver ion after the reaction has gone to completion?
  - Write the net cell reaction for a cell formed by placing a silver electrode in the solution remaining from the reaction above and connecting it to a standard hydrogen electrode.
  - Calculate the voltage of a cell of this type in which the concentration of silver ion is  $4 \times 10^{-2}$  M.
  - Calculate the value of the standard free energy change  $\Delta G^\circ$  for the following half reaction:

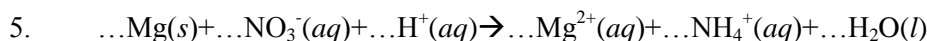
## Chapter 17 Practice Test

The spontaneous reaction that occurs when the cell above operates is:  $2\text{Ag}^+ + \text{Cd}(s) \rightarrow 2\text{Ag}(s) + \text{Cd}^{2+}$

- (A) Voltage increases  
 (B) Voltage decreases but remains above zero.  
 (C) Voltage becomes zero and remains at zero.  
 (D) No change in voltage occurs.  
 (E) Direction of voltage change cannot be predicted without additional information.

Which of the above occurs for each of the following circumstances?

- A 50-milliliter sample of a 2-molar  $\text{Cd}(\text{NO}_3)_2$  solution is added to the left beaker.
- The silver electrode is made larger.
- The salt bridge is replaced by a platinum wire.
- Current is allowed to flow for 5 minutes.



When the skeleton equation above is balanced and all coefficients reduced to their lowest whole-number terms, what is the coefficient for  $\text{H}^+$ ?

- (A) 4                      (B) 6                      (C) 8                      (D) 9                      (E) 10

6. If 0.060 faraday is passed through an electrolytic cell containing a solution of  $\text{In}^{3+}$  ions, the maximum number of moles of In that could be deposited at the cathode is

- (A) 0.010 mole (B) 0.020 mole (C) 0.030 mole (D) 0.060 mole (E) 0.18 mole

7. Which of the following species CANNOT function as an oxidizing agent?

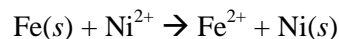
- (A)  $\text{Cr}_2\text{O}_7^{2-}$                       (B)  $\text{MnO}_4^-$                       (C)  $\text{NO}_3^-$                       (D) S                      (E) I



The standard reduction potentials for two half reactions are given above. The Nernst equation for a galvanic cell at  $25^\circ\text{C}$  in which  $\text{Fe}(s)$  reduced  $\text{Ni}^{2+}$  is the following.

$$E = E^\circ - \frac{0.059}{2} \log[\text{Fe}^{2+}]/[\text{Ni}^{2+}]$$

What is the equilibrium constant for the reaction shown?



- (A)  $1.9 \times 10^{-23}$                       (B)  $7.6 \times 10^{-8}$                       (C)  $3.6 \times 10^{+3}$                       (D)  $1.3 \times 10^{+7}$                       (E)  $5.2 \times 10^{+22}$

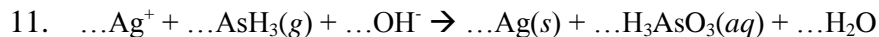
9. If a copper sample containing some zinc impurity is to be purified by electrolysis, the anode and the cathode must be which of the following?

- | <i>Anode</i>             | <i>Cathode</i>       |
|--------------------------|----------------------|
| (A) Pure copper          | Pure zinc            |
| (B) Pure zinc            | Pure copper          |
| (C) Pure copper          | Impure copper sample |
| (D) Impure copper sample | Pure copper          |
| (E) Impure copper sample | Pure zinc            |



Which species acts as an oxidizing agent in the reaction represented above?

- (A)  $\text{H}_2\text{O}$                       (B)  $\text{ClO}_4^-$                       (C)  $\text{ClO}_2^-$                       (D)  $\text{MnO}_2$                       (E)  $\text{MnO}_4^-$



When the equation above is balanced with lowest whole-number coefficients, the coefficient for  $\text{OH}^-$  is

- (A) 2                      (B) 4                      (C) 5                      (D) 6                      (E) 7

12. When an aqueous solution of NaOH is added to an aqueous solution of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , the dichromate ion is converted to  
 (A)  $\text{CrO}_4^{2-}$  (B)  $\text{CrO}_2^-$  (C)  $\text{Cr}^{3+}$  (D)  $\text{Cr}_2\text{O}_3(s)$  (E)  $\text{Cr}(\text{OH})_3(s)$
13.  $\text{Zn}(s) + \text{Cu}^{2+} \leftrightarrow \text{Zn}^{2+} + \text{Cu}(s)$   
 An electrolytic cell based on the reaction represented above was constructed from zinc and copper half-cells. The observed voltage was found to be 1.00 volt instead of the standard cell potential,  $E^\circ$ , of 1.10 volts. Which of the following could correctly account for this observation?  
 (A) The copper electrode was larger than the zinc electrode  
 (B) The  $\text{Zn}^{2+}$  electrolyte as  $\text{Zn}(\text{NO}_3)_2$ , while the  $\text{Cu}^{2+}$  electrolyte was  $\text{CuSO}_4$ .  
 (C) The  $\text{Zn}^{2+}$  solution was more concentrated than the  $\text{Cu}^{2+}$  solution.  
 (D) The solutions in the half-cells had different volumes.  
 (E) The salt bridge contained KCl as the electrolyte.
14.  $\dots\text{Fe}(\text{OH})_2 + \dots\text{O}_2 + \dots\text{H}_2\text{O} \rightarrow \dots\text{Fe}(\text{OH})_3$   
 If 1 mole of  $\text{O}_2$  oxidizes  $\text{Fe}(\text{OH})_2$  according to the reaction represented above, how many moles of  $\text{Fe}(\text{OH})_3$  can be formed?  
 (A) 2 (B) 3 (C) 4 (D) 5 (E) 6
15. A direct-current power supply of low voltage (less than 10 volts) has lost the markings that indicate which output terminal is positive and which is negative. A chemist suggests that the power supply terminals be connected to a pair of platinum electrodes that dip into 0.1-molar KI solution. Which of the following correctly identifies the polarities of the power supply terminals?  
 (A) A gas will be evolved only at the positive electrode.  
 (B) A gas will be evolved only at the negative electrode.  
 (C) A brown color will appear in the solution near the negative electrode.  
 (D) A metal will be deposited on the positive electrode.  
 (E) None of the methods above will identify the polarities of the power supply terminals.

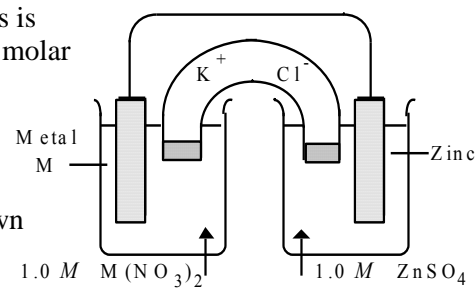
## Free Response

16. The electrolysis of an aqueous solution of potassium iodide, KI, results in the formation of hydrogen gas at the cathode and iodine at the anode. A sample of 80.0 mL of a 0.150 M solution of KI was electrolyzed for 3.00 minutes, using a constant current. At the end of this time, the  $\text{I}_2$  produced was titrated against a 0.225 M solution of sodium thiosulfate, which reacts with iodine according to the equation below. The end point of the titration was reached when 37.3 mL of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution had been added.
- $$\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}$$
- a. How many moles of  $\text{I}_2$  was produced during the electrolysis?
- b. The hydrogen gas produced at the cathode during the electrolysis was collected over water at  $25^\circ\text{C}$  at a total pressure of 752 millimeters of mercury. Determine the volume of hydrogen collected. (The vapor pressure of water at  $25^\circ\text{C}$  is 24 millimeters of mercury.)
- c. Write the equation for the half-reaction that occurs at the anode during the electrolysis.
- d. Calculate the current used during the electrolysis.
17. Explain each of the following.
- a. When an aqueous solution of NaCl is electrolyzed,  $\text{Cl}_2(g)$  is produced at the anode, but no Na(s) is produced at the cathode.

- b. The mass of Fe(s) produced when 1 faraday is used to reduce a solution of FeSO<sub>4</sub> is 1.5 times the mass of Fe(s) produced when 1 faraday is used to reduce a solution of FeCl<sub>3</sub>.
- c.  $\text{Zn} + \text{Pb}^{2+} (1\text{-molar}) \rightarrow \text{Zn}^{2+} (1\text{-molar}) + \text{Pb}$       The cell that utilizes the reaction above has a higher potential when [Zn<sup>2+</sup>] is decreased and [Pb<sup>2+</sup>] is held constant, but a lower potential when [Pb<sup>2+</sup>] is decreased and [Zn<sup>2+</sup>] is held constant.
- d. The cell that utilizes the reaction given in (c) has the same cell potential as another cell in which [Zn<sup>2+</sup>] and [Pb<sup>2+</sup>] are each 0.1-molar.

18. An unknown metal M forms a soluble compound, M(NO<sub>3</sub>)<sub>2</sub>.

- a. A solution of M(NO<sub>3</sub>)<sub>2</sub> is electrolyzed. When a constant current of 2.50 amperes is applied for 35.0 minutes, 3.06 grams of the metal M is deposited. Calculate the molar mass of M and identify the metal.



- b. The metal identified in (a) is used with zinc to construct a galvanic cell, as shown below. Write the net ionic equation for the cell reaction and calculate the cell potential,  $E^\circ$ .
- c. Calculate the value of the standard free energy change,  $\Delta G^\circ$ , at 25°C for the reaction in (b).
- d. Calculate the potential,  $E$ , for the cell shown in (b) if the initial concentration of ZnSO<sub>4</sub> is 0.10-molar, but the concentration of the M(NO<sub>3</sub>)<sub>2</sub> solution remains unchanged.

19. In an electrolytic cell, a current of 0.250 ampere is passed through a solution of a chloride of iron, producing Fe(s) and Cl<sub>2</sub>(g).

- a. Write the equation for the reaction that occurs at the anode.
- b. When the cell operates for 2.00 hours, 0.521 gram of iron is deposited at one electrode. Determine the formula of the chloride of iron in the original solution.
- c. Write the balanced equation for the overall reaction that occurs in the cell.
- d. How many liters of Cl<sub>2</sub>(g), measured at 25 °C and 750 mmHg, are produced when the cell operates as described in part (b)?
- e. Calculate the current that would produce chlorine gas at a rate of 3.00 grams per hour.

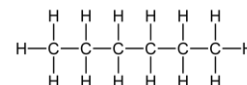
## AP Chemistry Chapter 22: Organic and Biological Molecules

Group 4A elements, most especially carbon and silicon, form the basis of most natural substances. Silicon generally forms chains and ring structures with oxygen, which allows it to make up most of Earth's rocks, sand and soil. Carbon, on the other hand, also forms chains and rings, but generally with itself and many other nonmetals. Because of this, carbon is the basic structural unit for many biomolecules, or life molecules.

### 22.1 Alkanes: Saturated Hydrocarbons

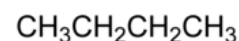
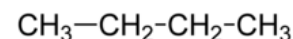
Organic chemistry is the chemistry of carbon compounds; the chemistry of life molecules.

- Several million carbon compounds are currently known, with more being discovered each day. The reason for this is that carbon can form four covalent bonds with other atoms.
- Carbon can form single, double, and triple bonds.
- Hydrocarbon- a compound containing only hydrogen and carbon Ex.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ 
  - Saturated hydrocarbon- a hydrocarbon with no double or triple bonds
    - It is saturated with hydrogen!
  - Unsaturated hydrocarbon- a hydrocarbon that contains double and/or triple bonds
    - It is not "saturated" with hydrogen



#### Alkanes

- The simplest type of hydrocarbon is called an alkane.
  - Alkanes are composed on carbon atoms single bonded to other carbon atoms or other nonmetals.
  - General formula:  $\text{C}_n\text{H}_{2n+2}$
  - Alkane names end in -ane
  - Alkanes can be written as structural formulas or as condensed formulas
  - Alkane melting and boiling points increase with the number of carbons

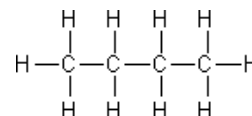


Question: Why would the melting and boiling points of alkanes increase as the number of carbon atoms increase?

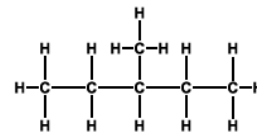
Name	Formula	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Number of Structural Isomers
Methane	$\text{CH}_4$	16	-182	-162	1
Ethane	$\text{C}_2\text{H}_6$	30	-183	-89	1
Propane	$\text{C}_3\text{H}_8$	44	-187	-42	1
Butane	$\text{C}_4\text{H}_{10}$	58	-138	0	2
Pentane	$\text{C}_5\text{H}_{12}$	72	-130	36	3
Hexane	$\text{C}_6\text{H}_{14}$	86	-95	68	5
Heptane	$\text{C}_7\text{H}_{16}$	100	-91	98	9
Octane	$\text{C}_8\text{H}_{18}$	114	-57	126	18
Nonane	$\text{C}_9\text{H}_{20}$	128	-54	151	35
Decane	$\text{C}_{10}\text{H}_{22}$	142	-30	174	75

Alkanes with four or more carbons may form isomers, or molecules that have the same atoms bonded in different ways.

- Straight-chained hydrocarbon- alkane in which carbon forms long "strings" or chains
  - Ex.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
  - $\text{C}_6\text{H}_{14}$



- Branched hydrocarbon- alkane in which carbon chains may be attached to the main chain

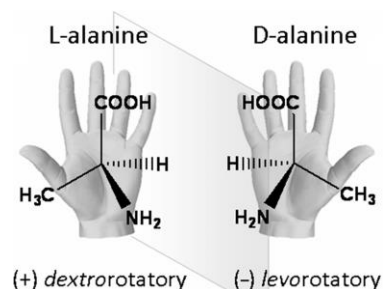


Practice: Draw all of the structural isomers of hexane,  $\text{C}_6\text{H}_{14}$ , in the space below.

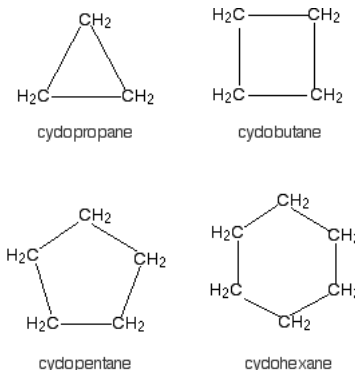
- Alkanes may also form stereoisomers. Stereoisomers include cis-trans isomers (discussed later) and optical isomers.

- Optical isomers, or enantiomers, are named due to their ability, in crystal form, to rotate plane-polarized light.

- Those that rotated the light to the right were called dextrorotatory, or right-hand isomers.
- Those that rotated the light to the left were called levorotatory, or left-handed isomers.
- These two types of crystals were found to be mirror images of one another; this is described with the word “chiral”.
- Chiral molecules exhibit different chemical affects when used in biological systems. Just as you shake hands with the right hand of someone if you are using your right hand, a biomolecule may only bind with one version of a chiral molecule and not another.

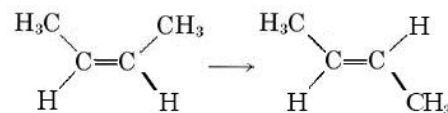


- Hydrocarbon derivative- a compound with some hydrogen atoms replaced by other elements (O, N, F, Cl, Br, I) Ex.  $\text{CH}_3\text{Br}$
- Cyclic Alkanes – alkanes in which the carbon atoms have formed rings
  - The general formula for a cyclic alkane is  $\text{C}_n\text{H}_{2n}$
  - The simplest cyclic alkane is  $\text{C}_3\text{H}_6$ , or cyclopropane
- Alkyl Groups – If one alkane is attached as a side chain on a longer-chain hydrocarbon, it is called an alkyl group. Alkyl groups have the same name as the alkane, but the –ane ending is changed to –yl.
  - Ex. Methane  $\rightarrow$  methyl
  - $\text{CH}_4 \rightarrow -\text{CH}_3$



## 22.2 Alkenes and Alkynes

- Alkenes- unsaturated hydrocarbons that contain at least one double bond
  - General formula:  $\text{C}_n\text{H}_{2n}$
  - The carbon atoms of alkenes are held in place around the double bond by sigma as well as pi bonds. Since this involves the overlap of p orbitals, the carbons around the double bond are fixed in place and unable to rotate like an alkane.
  - This leads to a specific type of stereoisomer called cis-trans isomerism.
  - Cis means “same side” and trans means “opposite side”
- Practice: Draw both cis-trans isomers of pentane,  $\text{C}_5\text{H}_{10}$ , in which the double bond is on carbon 2.





- Alkynes- unsaturated hydrocarbons that contain at least one triple bond
  - General formula:  $C_nH_{2n-2}$
  - The carbon atoms around the triple bond exhibit sp hybridization, giving them a linear structure.
- Both alkanes and alkynes can also form ring structures, which we will discuss later.

### Nomenclature

- The naming system for organic molecules is slightly different than the naming conventions for other chemical compounds.
- IUPAC (International Union of Pure and Applied Chemistry)- determines the naming system for hydrocarbons
- Rules for Naming Alkanes, Alkenes and Alkynes:
  - Name the longest carbon chain in the structure. If the chain is cyclic, include the prefix cyclo.
  - Name, in alphabetical order, the kinds of groups which are attached to the chain you named in step 1. Use the appropriate prefix, such as di-, tri-, tetra-, etc., to indicate how many of each group are present.
  - Number the carbon atoms in the longest chain consecutively from the end of the chain which allows the attached groups to have the lowest numbers possible. Assign to each group you named in step 2 the number(s) indicating its position(s) on the main chain.
  - If the compound contains double or triple bonds, name the longest carbon chain containing the carbon-carbon double or triple bond. The name of the longest chain ends in -ene for an alkene; in -yne for an alkyne. The position of the double or triple bond in the carbon chain is indicated by a number before the name of the chain.
  - When assigning numbers to atoms in the chain, start numbering from the end of the chain closest to the double or triple bond.

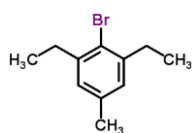
### Practice Naming These Compounds

$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\    \\  \text{CH}_2 \\    \\  \text{CH}_3  \end{array}  $	$  \begin{array}{c}  \text{Cl} \\    \\  \text{CH}_3 - \text{C} - \text{CH}_2\text{CH}_3 \\    \\  \text{Cl}  \end{array}  $	$  \begin{array}{c}  \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH}_2  \end{array}  $	$  \begin{array}{c}  \text{CH}_2 - \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH} - \text{CH}_3  \end{array}  $
$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\    \\  \text{CH}_2 \\    \\  \text{CH}_2 \\    \\  \text{CH}_3  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_3 - \text{CH} = \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{CH}_3\text{CH}_2\text{CH}_2\text{CH} - \text{CH} - \text{C} - \text{CH}_2 \\    \quad   \quad   \quad   \\  \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{CH}_2 \\    \quad   \quad   \\  \text{CH}_2 \quad \text{CH}_3 \quad \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 \quad \text{CH}_3 \\    \quad   \\  \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\    \quad   \quad   \\  \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \\    \quad   \quad   \\  \text{CH}_3\text{CH}_2\text{CH} - \text{CH} - \text{CH} - \text{CH}_2 \\    \\  \text{CH}_2 \\    \\  \text{CH}_2 \\    \\  \text{CH}_3  \end{array}  $
$  \begin{array}{c}  \text{CH}_3 \quad \text{CH}_3 \\  \diagdown \quad / \\  \text{C} \\  / \quad \backslash \\  \text{H}_2\text{C} \quad \text{CH}_3 \\    \quad   \\  \text{H}_2\text{C} - \text{CH}_2 \quad \text{H}  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 \quad \text{CH}_3 \\    \quad   \\  \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $		

		Draw: 3-ethyl-2-hexene	Draw: 4-bromo-2,2-dichloro-3,5-diethyl-6-fluorooctane
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### 22.3 Aromatic Hydrocarbons

- Aromatic hydrocarbons- unsaturated compounds that contain a hydrocarbon ring
  - Sometimes called arenes



- Benzene,  $C_6H_6$ , is an arene.
- Benzene is a flat molecule with resonance.
- Shorthand ways to draw benzene:
- A benzene ring used as a substituent on a hydrocarbon chain is called a phenyl group.
- Ex.

### Reactions of Hydrocarbons

No matter what type, all pure hydrocarbons are nonpolar due to a lack of free electrons in the structure. This means that they are not attracted to water. They tend to be relatively stable in the saturated form, but addition of energy to the system, like a spark or excess heat, as well as varying the molecule to make it unsaturated, can lead to greater reactivity in hydrocarbons.

- Hydrocarbons react in four distinct ways: Combustion, substitution, addition and dehydrogenation.
- Reactions of alkanes
  - Combustion
    - Ex. Butane burns.
  - Substitution – occurs primarily when a halogen replaces a hydrogen on a carbon chain
    - Ex.
  - Dehydrogenation – occurs when hydrogen atoms are removed from a carbon chain, forcing two carbons atoms to form a double bond or ring.
    - Ex.
- Reactions of alkenes and alkynes
  - Addition – occurs when atoms are added to the carbons of a double bond, breaking the double bond and saturating the molecule.
    - Ex. Halogenation or hydrogenation
- Reactions of aromatic hydrocarbons
  - Primarily undergo substitution reactions in which a hydrogen is replaced with another atom.
    - Ex.

Class	Functional Group	General Formula*	Example
Halohydrocarbons	$-X$ (F, Cl, Br, I)	$R-X$	$CH_3I$ Iodomethane (methyl iodide)
Alcohols	$-OH$	$R-OH$	$CH_3OH$ Methanol (methyl alcohol)
Ethers	$-O-$	$R-O-R'$	$CH_3OCH_3$ Dimethyl ether
Aldehydes	$\begin{array}{c} O \\    \\ -C-H \end{array}$	$\begin{array}{c} O \\    \\ R-C-H \end{array}$	$CH_2O$ Methanal (formaldehyde)
Ketones	$\begin{array}{c} O \\    \\ -C- \end{array}$	$\begin{array}{c} O \\    \\ R-C-R' \end{array}$	$CH_3COCH_3$ Propanone (dimethyl ketone or acetone)
Carboxylic acids	$\begin{array}{c} O \\    \\ -C-OH \end{array}$	$\begin{array}{c} O \\    \\ R-C-OH \end{array}$	$CH_3COOH$ Ethanoic acid (acetic acid)
Esters	$\begin{array}{c} O \\    \\ -C-O- \end{array}$	$\begin{array}{c} O \\    \\ R-C-O-R' \end{array}$	$CH_3COOCH_2CH_3$ Ethyl acetate
Amines	$-NH_2$	$R-NH_2$	$CH_3NH_2$ Aminomethane (methylamine)

\*R and R' represent hydrocarbon fragments.

### 22.5 Hydrocarbon Derivatives

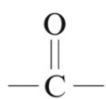
- The vast majority of organic molecules contain elements in addition to carbon and hydrogen.

- Functional Group- a group of atoms or groups of atoms bound to an organic molecule. It is a chemically reactive part of an organic molecule
- You need to learn these!

### Alcohols

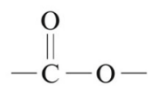
- Contain a hydroxyl group; -OH
- Named by replacing the hydrocarbon name ending with -ol.
- Question: Alcohols have much higher boiling points than their hydrocarbon counterparts. Explain.
- Alcohols can be described as primary secondary and tertiary. Draw one of each below.

### Aldehydes and Ketones



- Contain a carboxyl group;  $-\text{C}(=\text{O})-$
- Aldehydes are named by adding the suffix -al to the hydrocarbon name, while ketones are named by adding -one.
- In an aldehyde, the carboxyl group is located at the end of a hydrocarbon chain, while in ketones, it is located in the middle of the chain.
- They are often created by the oxidation of an alcohol. Primary alcohols yield aldehydes and secondary yield ketones.

### Carboxylic Acids and Esters



- Contain a carboxyl group;  $-\text{C}(=\text{O})-\text{O}-$
- In a carboxylic acid, the carboxyl group is bound to the end of a hydrocarbon chain and is named by adding -oic acid to the name.
- In esters, the carboxyl group is found in the middle of the chain and is named according to how many carbons are on each side of the carboxyl group.
- Esters are formed when an alcohol reacts with carboxylic acid, releasing water. This process is called esterification.

### Amines

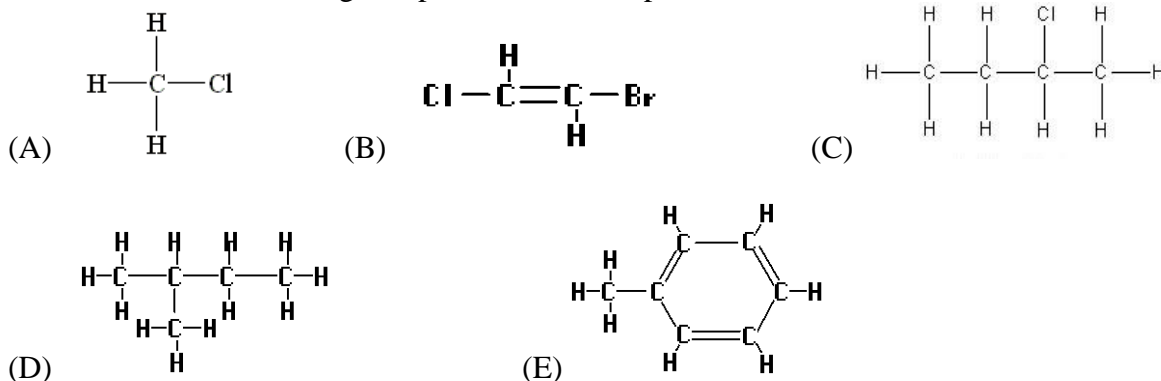
- Derivatives of ammonia and have an amine group; -NH<sub>2</sub>
- Amines are named by adding the suffix -amine to the hydrocarbon name, or by adding the prefix amino- if the group is included with another functional group.

### Ethers

- These molecules contain a lone oxygen with hydrocarbon chains bonded to both ends.
- Each hydrocarbon chain is named, followed with -ether.

## AP Chemistry: Organic Chemistry Worksheet #1

1. Which of the following compounds exhibits optical isomerism?



2. The structural isomers  $C_2H_5OH$  and  $CH_3OCH_3$  would be expected to have the same values for which of the following? (Assume ideal behavior.)

- |   |                          |
|---|--------------------------|
| a. Gaseous densities at the same temperature and pressure | c. Boiling points        |
| b. Vapor pressures at the same temperature                | d. Melting points        |
|   | e. Heats of vaporization |

3.  $CH_3CH_2OH$  boils at  $78^\circ C$  and  $CH_3OCH_3$  boils at  $-24^\circ C$ , although both compounds have the same composition. This difference in boiling points may be attributed to a difference in

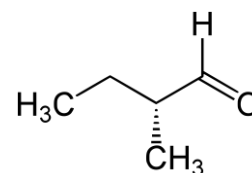
- |                   |                     |                       |
|-------------------|---------------------|-----------------------|
| a. molecular mass | c. specific heat    | e. heat of combustion |
| b. density        | d. hydrogen bonding |                       |

4. Which of the following pairs of compounds are isomers?

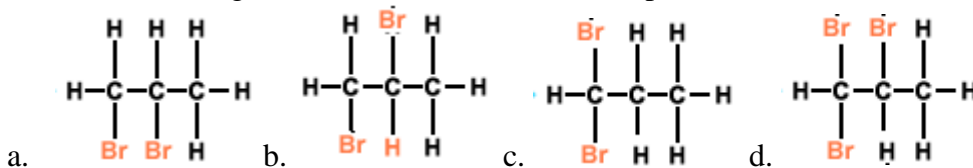
- |  |                         |
|--|-------------------------|
| a. Butane and isopentane                 | d. methanol and ethanol |
| b. 2-methyl pentane and 2-methyl pentene | e. methane and ethyne   |
| c. dimethyl ketone and dimethyl ether    |                         |

5. The organic compound shown to the right is an example of:

- |                    |                |             |
|--------------------|----------------|-------------|
| a. an organic acid | c. an ether    | e. a ketone |
| b. an alcohol      | d. an aldehyde |             |



6. Which of the following structural formulas does not represent an isomer of 1,3 dibromopropane?



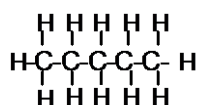
Answer each of the following using appropriate chemical principles.

7. Dimethyl ether,  $H_3C-O-CH_3$ , is not very soluble in water. Draw a structural isomer of dimethyl ether that is much more soluble in water and explain the basis of its increased water solubility.

8. Consider the hydrocarbon pentane,  $C_5H_{12}$  (molar mass 72.15 g).

- a. Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.

- b. What volume of dry carbon dioxide, measured at 25°C and 785 mm Hg, will result from the complete combustion of 2.50 g of pentane?
- c. The complete combustion of 5.00 g of pentane releases 243 kJ of heat. On the basis of this information, calculate the value of  $\Delta H$  for the complete combustion of one mole of pentane.
- d. Under identical conditions, a sample of an unknown gas effuses into a vacuum at twice the rate that a sample of pentane gas effuses. Calculate the molar mass of the unknown gas.
- e. The structural formula of one isomer of pentane is shown below. Draw the structural formulas for the other two isomers of pentane. Be sure to include all atoms of hydrogen and carbon in your structures.



9. Using the information in the table, answer the following questions about organic compounds.

- a. For propanone,
- Draw the complete structural formula (showing all atoms and bonds);
  - Predict the approximate carbon-to-carbon bond angle.

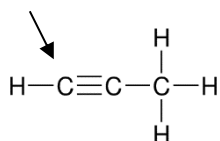
Compound Name	Compound Formula	$\Delta H^\circ \text{vap}$ (kJ mol <sup>-1</sup> )
Propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	19.0
Propanone	CH <sub>3</sub> COCH <sub>3</sub>	32.0
1-propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	47.3

- b. For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization,  $\Delta H^\circ \text{vap}$ .
- Propane and propanone
  - Propanone and 1-propanol

c. Draw the complete structural formula for an isomer of the molecule you drew in, part (a) (i).

d. Given the structural formula for propyne below,

- indicate the hybridization of the carbon atom indicated by the arrow in the structure;

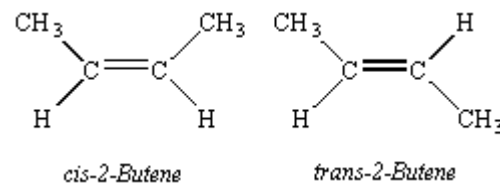


- indicate the total number of sigma ( $\sigma$ ) bonds and the total number of pi ( $\pi$ ) bonds in the molecule

## Organic Practice Test Questions

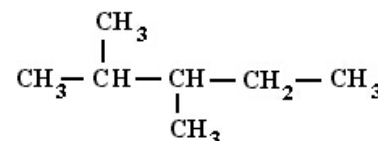
1. The molecules cis-2-butene and trans-2-butene are examples of:

- A. structural isomers
- B. geometric isomers
- C. optical isomers
- D. magnetic isomers
- E. allotropes

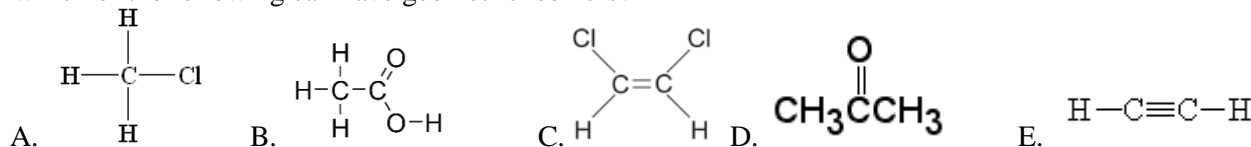


2. What is the correct name for this substance?

- A. n-heptane
- B. 2,3-dimethylpentane
- C. 1,1,2-trimethylbutane
- D. 2-ethyl-3-methylbutane
- E. 3,4-dimethylpentane

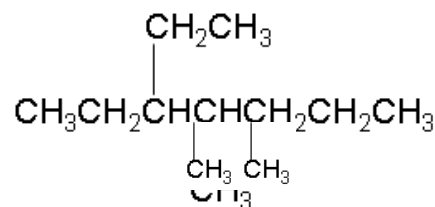


3. Which of the following can have geometric isomers?



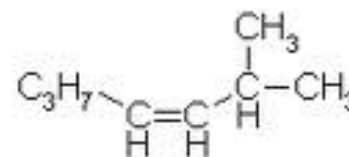
4. Select the correct name for the following compound.

- A. 1,1,2-triethyl-2-methylbutane
- B. 1,1-diethyl-2,3-dimethylpentane
- C. 2,4-diethyl-3-methylhexane
- D. 3-ethyl-4,5-dimethylheptane



5. Select the correct name for the following compound.

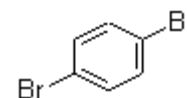
- A. cis-2-methyl-4-heptene
- B. trans-2-methyl-4-heptene
- C. cis-2-methyl-3-heptene
- D. trans-2-methyl-3-heptene



6. Select the correct name for the following compound.

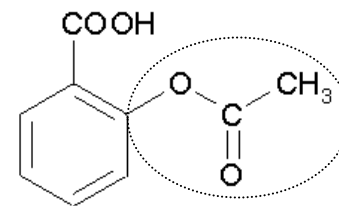
- A. ortho-dibromobenzene
- B. meta-dibromobenzene

- C. para-dibromobenzene
- D. 1,4-dibromocyclohexene



7. Aspirin is an effective and widely used pain reliever. Identify the functional group circled.

- A. aldehyde
- B. ketone
- C. ester
- D. carboxylic acid



*Short Answer*

8. What types of isomerism are possible among the molecules that can be obtained by substituting a chlorine atom and a bromine atom for two of the hydrogen atoms in each of the following? Show structures to illustrate each of the types of isomerism you name for each of these compounds.
- (a) Ethane,  $C_2H_6$   
 (b) Ethene,  $C_2H_4$
9. Write structural formulas for two stable isomers X and Y that have the molecular formula  $C_2H_4O_2$ . Select a physical property and a chemical property that would distinguish between the two isomers in the laboratory.
10. Dimethyl ether,  $H_3C-O-CH_3$ , is not very soluble in water. Draw a structural isomer of dimethyl ether that is much more soluble in water and explain the basis of its increased water solubility.
11. Consider the hydrocarbon pentane,  $C_5H_{12}$  (molar mass 72.15 g).
- Write the balanced equation for the combustion of pentane to yield carbon dioxide and water.
  - What volume of dry carbon dioxide, measured at  $25^\circ C$  and 785 mm Hg, will result from the complete combustion of 2.50 g of pentane?
  - The complete combustion of 5.00 g of pentane releases 243 kJ of heat. On the basis of this information, calculate the value of  $\Delta H$  for the complete combustion of one mole of pentane.
  - Under identical conditions, a sample of an unknown gas effuses into a vacuum at twice the rate that a sample of pentane gas effuses. Calculate the molar mass of the unknown gas.
12. Using the information in the table shown, answer the following questions about organic compounds.
- (a) For propanone,
- draw the complete structural formula (showing all atoms and bonds);
  - predict the approximate carbon-to-carbon-to-carbon bond angle.

Compound Name	Compound Formula	$\Delta H^{\text{vap}}$ (kJ mol <sup>-1</sup> )
Propane	$CH_3CH_2CH_3$	19.0
Propanone	$CH_3COCH_3$	32.0
1-propanol	$CH_3CH_2CH_2OH$	47.3

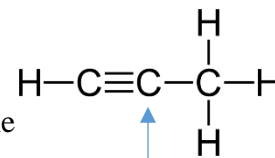
(b) For each pair of compounds below, explain why they do not have the same value for their standard heat of vaporization,  $\Delta H^\circ_{\text{vap}}$ . (You must include specific information about both compounds in each pair.)

(i) Propane and propanone

(ii) Propanone and 1-propanol

(c) Draw the complete structural formula for an isomer of the molecule you drew in, part (a) (i).

(d) Given the structural formula for propyne below,



(i) indicate the hybridization of the carbon atom indicated by the arrow in the structure above;

(ii) indicate the total number of sigma ( $\sigma$ ) bonds and the total number of pi ( $\pi$ ) bonds in the molecule



