Janine the Tutor's Guide for Introduction to Chemistry

Master Study Guide

- Comprehensive coverage of all material covered for the course
- Concise summary of everything you need to know
- Prepare for any upcoming midterm and final exam

Fundamentals of Chemistry

Importance of Chemistry

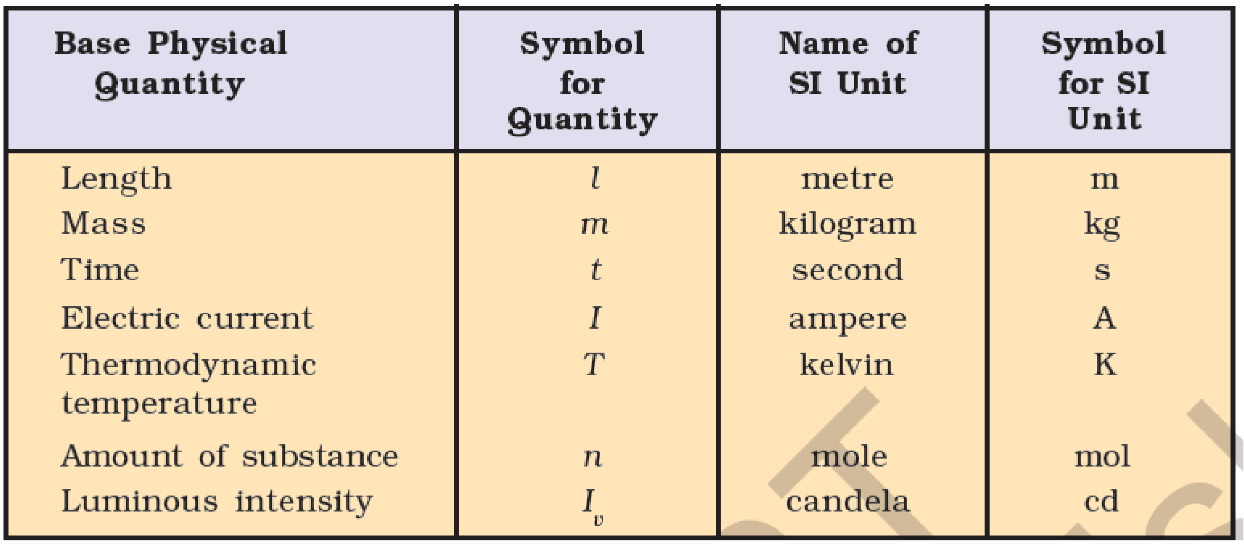
Science can be viewed as a continuing human effort to systematize knowledge for describing and understanding nature. For the sake of convenience science is sub-divided into various disciplines: chemistry, physics, biology, geology etc. Chemistry is the branch of science that studies the composition, properties and interaction of matter. Chemists are interested in knowing how chemical transformations occur. Chemistry plays a central role in science and is often intertwined with other branches of science like physics, biology, geology etc. Chemistry also plays an important role in daily life. Chemical industries manufacturing fertilizers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys and other inorganic and organic chemicals, including new materials, contribute in a big way to the national economy. Chemistry plays an important role in meeting human needs for food, health care products and other materials aimed at improving the quality of life. This is exemplified by the large scale production of a variety of fertilizers, improved varieties of pesticides and insecticides. Similarly many life saving drugs such as cisplatin and taxol, are effective in cancer therapy and AZT (Azidothymidine) used for helping AIDS victims, have been isolated from plant and animal sources or prepared by synthetic methods. With a better understanding of chemical principles it has now become possible to design and synthesize new materials having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres and large scale miniaturization of solid state devices. In recent years chemistry has tackled with a fair degree of success some of the pressing aspects of environmental degradation. Safer alternatives to environmentally hazardous refrigerants like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases like methane, carbon dioxide etc. Understanding of bio-chemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic materials are some of the intellectual challenges for the future generation of chemists.

Properties of Matter and their Measurement

Every substance has unique or characteristic properties. These properties can be classified into two categories – physical properties and chemical properties. Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. Some examples of physical properties are colour, odour, melting point, boiling point, density etc. The measurement or observation of chemical properties require a chemical change to occur. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc. Many properties of matter such as length, area, volume, etc., are quantitative in nature. Any quantitative observation or measurement is represented by a number followed by units in which it is measured. For example length of a room can be represented as 6 m;

here 6 is the number and m denotes *metre* – the unit in which the length is measured. Two different systems of measurement, i.e. the English System and the Metric System were being used in different parts of the world. The metric system which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. The need of a common standard system was being felt by the scientific community.

The International System of Units

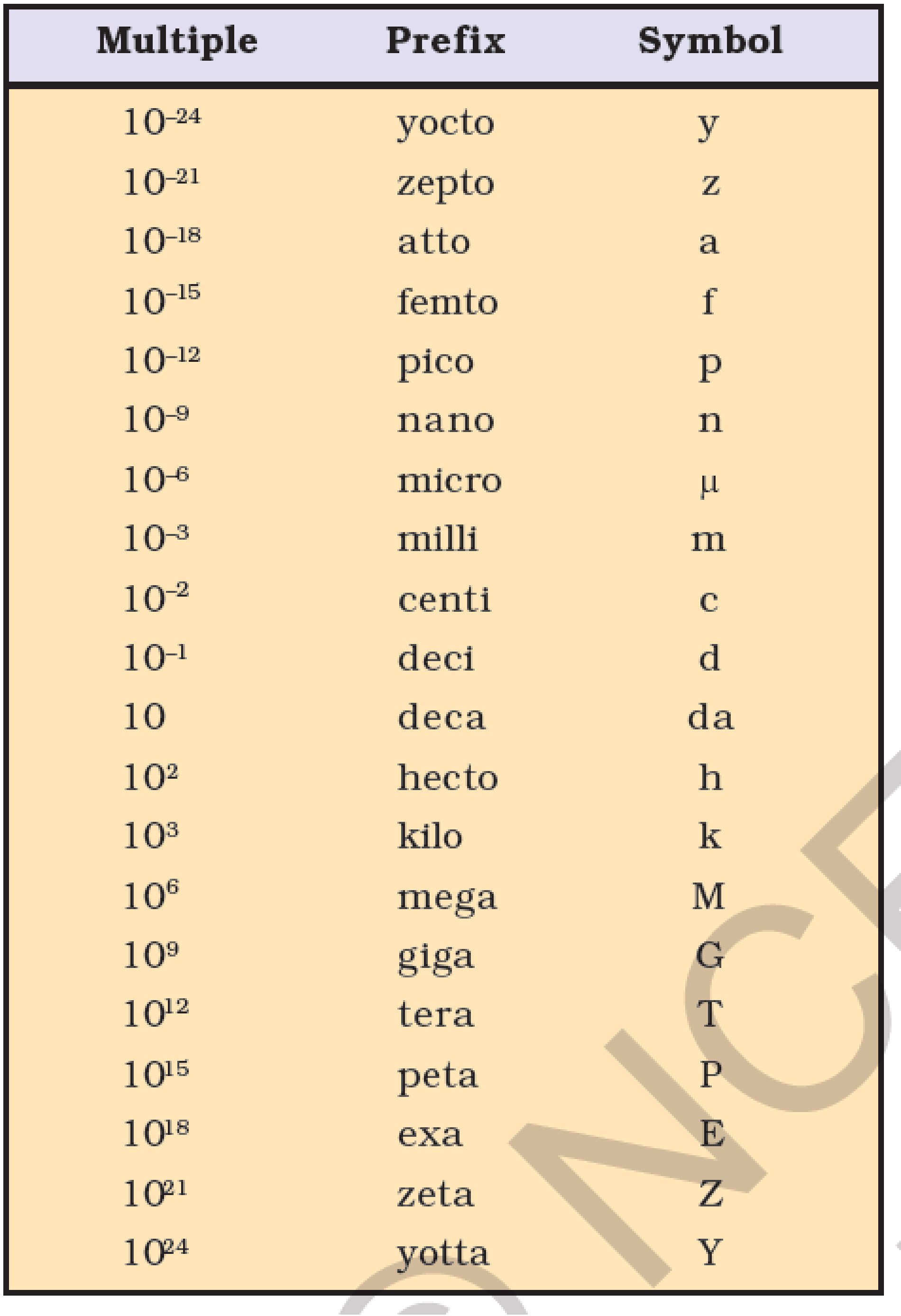


Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

Some basic concepts of Chemistry

Unit of length	**metre**	The *metre* is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.
Unit of mass	**kilogram**	The *kilogram* is the unit of mass; it is equal to the mass of the international prototype of the kilogram.
Unit of time	**second**	The *second* is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the caesium-133 atom.
Unit of electric current	**ampere**	The *ampere* is that constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per metre of length.
Unit of thermodynamic temperature	**kelvin**	The *kelvin*, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Unit of amount of substance	**mole**	1. The *mole* is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is "mol." 2. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	**candela**	The *candela* is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

Some basic concepts of Chemistry



Multiple	Prefix	Symbol
10^{-24}	yocto	y
10^{-21}	zepto	z
10^{-18}	atto	a
10^{-15}	femto	f
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	µ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
10	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zeta	Z
10^{24}	yotta	Y

Some basic concepts of Chemistry

Mass and Weight

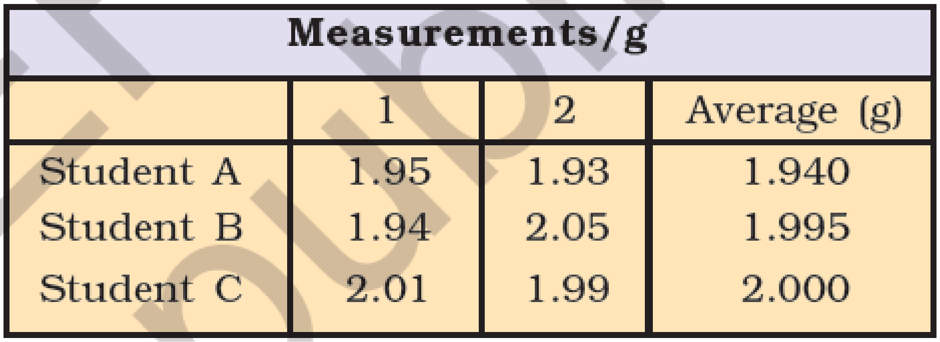
Mass of a substance is the amount of matter present in it while weight is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity.

Volume has the units of (length)3. So, in SI system, volume has units of m3. But again, in chemistry laboratories, smaller volumes are used. Hence, volume is often denoted in cm3 or dm3 units.

Density of a substance is its amount of mass per unit volume. So, SI units of density can be obtained as follows:
SI unit of density = SI unit of mass /SI unit of volume
= $kg / m^3 = kg\ m^{-3}$
This unit is quite large, and a chemist often expresses density in g cm–3, where mass is expressed in gram and volume is expressed in cm^3.

Significant Figures

Every experimental measurement has some amount of uncertainty associated with it. However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk
about the measurement.
Precision refers to the closeness of various measurements for the same quantity. However, accuracy is the agreement of a particular value to the true value of the result. For example, if the true value for a result is 2.00 g and a student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate. Another student repeats the experiment and obtains 1.94 g and 2.05 g as the results for two measurements. These observations are neither precise nor accurate. When a third student repeats these measurements and reports 2.01g and 1.99g as the result. These values are both precise and accurate.



Measurements/g			
	1	2	Average (g)
Student A	1.95	1.93	1.940
Student B	1.94	2.05	1.995
Student C	2.01	1.99	2.000

Some basic concepts of Chemistry

The uncertainty in the experimental and calculated values is indicated by mentioning the significant figures. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be +1 in the last digit.
Unless otherwise stated, an uncertainty of +1 in the last digit is always understood.

There are certain rules for determining the number of significant figures. These are stated below:
(1) All non-zero digits are significant. For example, in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.
(2) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.
(3) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.
(4) Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100. has three significant figures and 100.0 has four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×102 for one significant figure, 1.0×102 for two significant figures and 1.00×102 for three significant figures.
(5) Counting numbers of objects, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000

Empirical and Molecular Formula

An empirical formula represents the simplest whole number ratio of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound. If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following example illustrates this sequence.

Review Question
A compound contains 4.07 % hydrogen, 24.27 % carbon and 71.65 % chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas?

Solution: Step 1. Conversion of mass per cent to grams. Since we are having mass per cent, it is convenient to use 100 g of the compound as the starting material. Thus, in the 100 g sample of the above compound,
4.07g hydrogen is present, 24.27g carbon is present and 71.65 g chlorine is present.
Step 2. Convert into number moles of each element Divide the masses obtained above by respective atomic masses of various elements.
Moles of hydrogen = 4.07 g /1.008 g = 4.04
Moles of carbon = 24.27 g /12.01g = 2.021
Moles of chlorine = 71.65g /35.453 g = 2.021
Step 3. Divide the mole value obtained above by the smallest number Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl . In case the ratios are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient.

Step 4. Write empirical formula by mentioning the numbers after writing the symbols of respective elements.
CH2Cl is, thus, the empirical formula of the above compound.
Step 5. Writing molecular formula
(a) Determine empirical formula mass Add the atomic masses of various atoms present in the empirical formula. For CH2Cl, empirical formula mass is
$12.01 + 2 \times 1.008 + 35.453$
$= 49.48$ g
(b) Divide Molar mass by empirical
formula mass
Molar mass /Empirical formula mass = 98.96 g/ 49.48g = 2 = (*n*)
(c) Multiply empirical formula by *n* obtained above to get the molecular formula
Empirical formula = CH2Cl, *n* = 2. Hence molecular formula is $C_2H_4Cl_2$.

Limiting Reagent

Many a time, the reactions are carried out when the reactants are not present in the amounts as required by a balanced chemical reaction. In such situations, one reactant is in excess over the other. The reactant which is present in the lesser amount gets consumed after some time and after that no further reaction takes place whatever be the amount of the other reactant present. Hence, the reactant which gets consumed, limits the amount of product formed and is, therefore, called the limiting reagent.

Reactions in Solution

The concentration of a solution or the amount of substance present in its given volume can be expressed in any of the following ways.

Mass per cent or weight per cent

Molarity

Molality

Mass per cent = Mass of solute/ Mass of Solution x 100

Mole Fraction = No. of moles of A / No. of moles of solution

Molarity = No. of moles of solute / Volume of solution in litres

Molality = No. of moles of solute / Mass of solvent in kg

Oxidation State

An oxidation state is a number that is assigned to an element in a chemical combination. This number represents the number of electrons that an atom can gain, lose, or share when chemically bonding with an atom of another element. The terms "oxidation state" and "oxidation number" are often used interchangeably. The transfer of electrons is described by the oxidation state of the molecule. One might mistaken formal charge for oxidation state but they are different. Oxidation state is commonly used to determine the changes in redox reactions and is numerically similar to valence electrons, but different from formal charge. Formal charge determines the arrangement of atoms and the likelihood of the molecule existing.

Oxidation State Rules

To effectively assign oxidation states to a compound, the seven basic rules must be followed in order. Remember to use the rule that comes first if two rules conflict with each other. These rules hold true for most compounds..

- RULE 1: Any individual atom uncombined with other elements has the oxidation state of 0 (zero).

Ex.) The OS for Ag is 0. The oxidation state for O (oxygen) or O_2 is 0 as long as it is uncombined with any other element.

- RULE 2: The total sum of the oxidation state of all atoms in any given species is equal to the net charge on that species.

a.) In neutral species, the total sum of the oxidation state of all atoms is 0.

Ex.) The sum of OS for NaCl is 0 since the OS of Na = +1 and the OS of Cl = -1, therefore NaCl total OS = 0

b.) In ions, the total sum of the oxidation state is the charge of the ion.

Ex.) The OS of Ca^{2+} (Calcium) is = +2. The total sum of the OS of all atoms in CrO_4^{2-} (Chromate ion) is -2. The total sum of the oxidation states of all atoms in CH_3COO^- (Acetate ion) is -1.

- RULE 3: In a compound, the Oxidation state for Group 1(1A) metal is +1 and for Group 2(2A) metal, the oxidation state is +

Ex.) In NaCl, Na has the oxidation state of +1 since it is a Group 1 Alkali metal. Cl would have an oxidation number of -1 to make the sum of the oxidation states 0 (Rule 2). In $MgCl_2$, Mg has the oxidation state of +2, since it is a Group 2 Alkaline Earth metal. Cl would have an oxidation state of -1, and since there are 2 Cl atoms, the overall charge of the species would again be 0 (Rule 2).

- RULE 4: The oxidation state of FLOURINE is -1 in a compound.

Ex.) OS of F is -1 in HF, SF_6

- RULE 5: The oxidation state of HYDROGEN is +1 in a compound.

Ex.) OS of H is +1 in HI, CH_4, NH_4^+

- RULE 6: The oxidation state of OXYGEN is -2 in a compound.

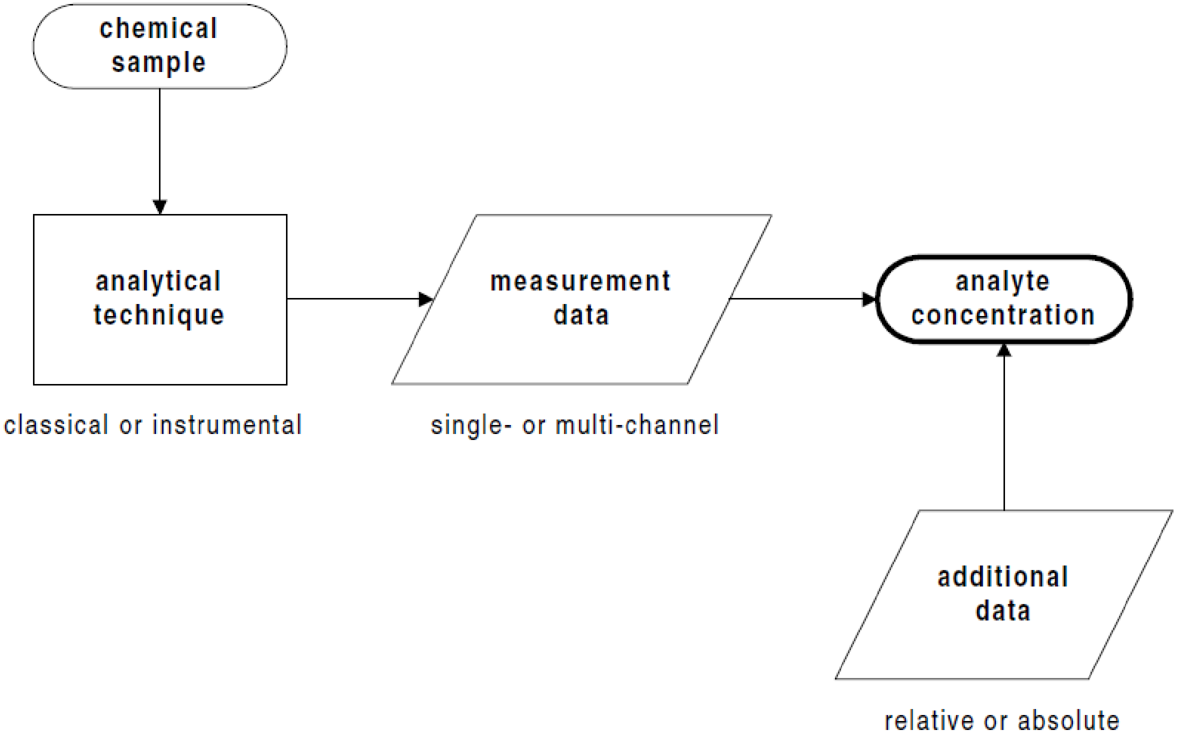
Ex.) OS of Oxyen is -2 in OH^-, H_2O, CO_3^{2-}

- RULE 7: In two-element compounds with metals, Group 15(3A) elements have the oxidation state of -3, Group 16(6A) elements have the oxidation state of -2, and Group 17(7A) elements have the oxidation state of -1.

Ex.) In $MgBr_2$, Br has the oxidation state of -1, since it is a Group 17 element. In Li_2S, S has the oxidation state of -2, since it is a Group 16.

Instrumental Method of Analysis

In quantitative chemical analysis, a sample is prepared and then analyzed to determine the concentration of one (or more) of its components. The following figure gives a general overview of this process.



Some basic concepts of Chemistry

There are a very large number of techniques used in chemical analysis. It can be very useful to classify the measurement process according to a variety of criteria:

- by the type of analytical technique – ***classical*** or ***instrumental*** techniques;
- by the nature of the measurement data generated – ***single-channel*** or ***multi-channel*** techniques;
- by the quantitation method (by which the analyte concentration is calculated) – ***relative*** or ***absolute*** techniques.

Classical *vs* Instrumental Techniques

In ***classical*** analysis, the signal depends on the chemical properties of the sample: a reagent reacts completely with the analyte, and the relationship between the measured signal and the analyte

concentration is determined by chemical stoichioimetry. In ***instrumental*** analysis, some physical property of the sample is measured, such as the electrical potential difference between two electrodes immersed in a solution of the sample, or the ability of the sample to absorb light. Classical methods are most useful for accurate and precise measurements of analyte concentrations at the 0.1% level or higher. On the other hand, some specialized instrumental techniques are capable of detecting individual atoms or molecules in a sample! Analysis at the
ppm (µg/mL) and even ppb (ng/mL) level is routine.
The advantages of instrumental methods over classical methods include:

1. The ability to perform *trace analysis*, as we have mentioned.
2. Generally, large numbers of samples may be analyzed very quickly.
3. Many instrumental methods can be automated.
4. Most instrumental methods are multi-channel techniques (we will discuss these shortly).
5. Less skill and training is usually required to perform instrumental analysis than classical analysis.

Because of these advantages, instrumental methods of analysis have revolutionized the field of analytical chemistry, as well as many other scientific fields. However, they have not entirely supplanted classical analytical methods, due to the fact that the latter are generally more accurate and precise, and more suitable for the analysis of the major constituents of a chemical sample. In addition, the cost of many analytical instruments can be quite high.

Questions

1. Calculate the molecular mass of glucose $C_6H_{12}O_6$?
Solution: Molecular mass of glucose (C6H12O6) = 6(12.011 u) + 12(1.008 u) + 6(16.00 u)
= (72.066 u) + (12.096 u) + (96.00 u)
= 180.162 u

2. 50.0 kg of N_2 (g) and 10.0 kg of H_2 (g) are mixed to produce NH_3 (g). Calculate the NH_3 (g) formed. Identify the limiting reagent in the production of NH_3 in this situation.

Solution: A balanced equation for the above reaction is written as follows :
Calculation of moles :
N_2 (g) + $3H_2$ (g) ⇌$2NH_3$ (g)
moles of N_2 = 50.0 kg N_2 × 1000 g N_2/ 1 kg N_2 x 1mol N_2/28.0 g N_2
= 17.86×10^2mol
moles of H_2 = 10.00 kg H_2 × 1000 g H_2/ 1 kg H_2 x 1mol H2/2.016g H_2
= 4.96×10^3 mol
According to the above equation, 1 mol N_2 (g) requires 3 mol H_2 (g), for the reaction.
Hence, for 17.86×10^2 mol of N_2, the moles of H_2 (g) required would be
17.86×10^2 mol N_2 × 3mol H_2 (g)/1molN_2 (g)
= 5.36×10^3 mol H_2

But we have only 4.96×10^3 mol H_2. Hence, dihydrogen is the limiting reagent in this case. So NH_3(g) would be formed only from that amount of available dihydrogen *i.e.,* 4.96×10^3 mol
Since 3 mol H_2(g) gives 2 mol NH_3(g) 4.96×10^3 mol H_2 (g) × 2molNH_3 (g)/ 3molH_2 (g)
= 3.30×10^3 mol NH_3 (g)
3.30×10^3 mol NH_3 (g) is obtained.
If they are to be converted to grams, it is done as follows:
1 mol NH_3 (g) = 17.0 g NH_3 (g)

3. A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute.
Solution: Mass percentage of A = Mass of A/ Mass of solution x 100
= 2g / 2g of A + 18 g of water = 20 %

4.Calculate the molarity of NaOH in the solution prepared by dissolving its 4g in enough water to form 250 ml of the solution?
Solution: Molarity = No. of moles of solute/ Volume of solution in litres
= 0.1 mol/ 0.250 L = 0.4 M
5. The density of 3M solution of NaCl is 1.25 g mL-1. Calculate molality of the solution?
Solution: Mass of NaCl in 1L solution = 3 x 58.5 = 175.5 g
Mass of 1L solution = 1000 x 1.25 = 1250 g
Mass of water in solution = 1250- 175.5 = 1074.5
Molality = No. of moles of solute/Mass of solvent in kg = 3 mol/1.0745 kg = 2.79 m

6. Find the oxidation state of C in $C_2H_3O_2^-$?
Solution: From Rule #2, we know that the sum of OS for this compound is -1
From Rule #5, we know that Hydrogen in a compound is +1. Since we have three Hydrogen, +1 x 3 = +3
From Rule #6, we know that Oxygen in a compound is -2. Since we have two oxygen, -2 x 2 = -4
With those information, set up an equation
2C+(+3)+(−4)=−1(2)(2)2C+(+3)+(−4)=−1

Rewrite as

2C+3−4=−1(3)(3)2C+3−4=−1

2C=0(4)(4)2C=0

C=0/2=0(5)(5)C=0/2=0

The oxidation state for C is 0.

7. Find the oxidation state of S in $S_2O_3^{2-}$?

Solution: From Rule #2, we know that the sum of OS for this compound is -2

From Rule #6, we know that Oxygen in a compound is -2. Since we have three oxygen, -2 x 3 = -6

With those information, set up an equation $2S + (-6) = -2$

Rewrite as

$2S-6=-2(6)(6)2S-6=-2$

$2S=4(7)(7)2S=4$

$S=4/2=2(8)(8)S=4/2=2$

The oxidation state for S is 2.

Advanced Questions

1.Calculate the molar mass of following?

a) CH_4 b) CO_2 c) H_2O

2.Determine the empirical formula of an oxide of iron which has 69.9% iron and 30.1% dioxygen by mass?

3.What is the concentration of sugar in $molL^{-1}$ if its 20 g is dissolved in enough water to make a final volume up to 2L?

4.If the density of methanol is 0.793 kg L^{-1}, what is its volume needed for making 2.5 L of its 0.25M solution?

5. Determine the oxidation states of the underlined elements in

1) $\underline{Cl}_2$ 2)$Na\underline{H}$ 3) $H_2\underline{C}O$ 4) $\underline{S}_2O_3{}^{2-}$ 5) $K\underline{Mn}O_4$.;6)$\underline{Fe}Cl_3$ 7)$\underline{N}_2$ 8)$H_2\underline{S}O_4$ 9)$H\underline{Cl}O_2$ 10)$Cu\underline{S}O_4$

The Scientific Method

The process of Science

Socrates (469 B.C. - 399 B.C.), Plato (427 B.C. - 347 B.C.), and Aristotle (384 B.C. - 322 B.C.) are among the most famous of the Greek philosophers. Plato was a student of Socrates, and Aristotle was a student of Plato. These three were probably the greatest thinkers of their time. Aristotle's views on physical science profoundly shaped medieval scholarship, and his influence extended into the Renaissance (14th century - 16th century). Aristotle's opinions were the authority on nature until well into the 1300s. Unfortunately, many of Aristotle's opinions were wrong. It is not intended here to denigrate Aristotle's intelligence; he was without doubt a brilliant man. It was simply that he was using a method for determining the nature of the
physical world that is inadequate for that task. The philosopher's method was logical thinking, not making observations on the natural world. This led to many errors in Aristotle's thinking on nature. Let's consider two of Aristotle's opinions as examples. In Aristotle's opinion, men were bigger and stronger than women; therefore, it was logical to him that men would have more teeth than women. Thus, Aristotle concluded it was a true fact that men had more teeth than women.

Apparently, it never entered his mind to actually look into the mouths of both genders and count their teeth. Had he done so, he would have found that men and women have exactly the same number of teeth.

Scientific Methods in Problem Solving

In the 16th and 17th centuries, innovative thinkers were developing a new way to discover the nature of the world around them. They were developing a method that relied upon making observations of phenomena and insisting that their explanations of the nature of the phenomena corresponded to the observations they made.

The **scientific method** is a method of investigation involving experimentation and observation to acquire new knowledge, solve problems, and answer questions. Scientists frequently list the scientific method as a series of steps. Other scientists oppose this listing of steps because not all steps occur in every case, and sometimes the steps are out of order. The scientific method is listed in a series of steps here because it makes it easier to study. You should remember that not all steps occur in every case, nor do they always occur in order.

Steps in Scientific Method

Step 1: Identify the problem or phenomenon that needs explaining. This is sometimes referred to as "defining the problem."
Step 2: Gather and organize data on the problem. This step is also known as "making observations."
Step 3: Suggest a possible solution or explanation. A suggested solution is called a **hypothesis**.
Step 4: Test the hypothesis by making new observations.

Step 5: If the new observations support the hypothesis, you accept the hypothesis for further testing. If the new observations do not agree with your hypothesis, add the new observations to your observation list and return to Step 3.

Introduction to Chemistry by Tracy Poulsen

Experimentation

Experimentation is the primary way through which science gathers evidence for ideas. It is more successful for us to cause something to happen at a time and place of our choosing. When we arrange for the phenomenon to occur at our convenience, we can have all our measuring instruments present and handy to help us make observations, and we can control other variables. Experimentation involves causing a phenomenon to occur when and where we want it and under the conditions we want. An **experiment** is a controlled method of testing an idea or to find patterns. When scientists conduct experiments, they are usually seeking new information or trying to verify someone else's data.

Experimentation involves changing and looking at many variables. The **independent variable** is the part of the experiment that is being changed or manipulated. There can only be one independent variable in any experiment. Consider, for example, that you were trying to determine the best fertilizer for your plants. It would be important for you to grow your plants with everything else about how they are grown being the same except for the fertilizer you were using. You would be changing the type of fertilizer you gave the plants and this would be the independent variable. If you also changed how much water the plants received, the type of plants you were growing, and some of the plants were grown inside and others outside, you could not determine whether or not it was actually the fertilizer that caused the plants to grow better or if it was something else you had changed. This is why it is important that there is only one independent variable.

The **dependent variable** is what is observed or measured as a result of what happened when the independent variable was changed. In the plant experiment described above, you might measure the height of the plant and record their appearance and color. These would be the dependent variables. The dependent variable is also sometimes called the resultant variable.

Controlled variables are conditions of the experiment that are kept the same for various trials of the experiment. Once again, if we were testing how fertilizer affected how well our plants grew, we would want everything else about how the plants are grown to be kept the same. We would need to use the same type of plant (maybe green beans), give them the same amount of water, plant them in the same location (all outside in the garden), give them all the same pesticide treatment, etc. These would be controlled variables.

Hypothesis, Law, & Theory

Hypothesis

One of the most common terms used in science classes is a “hypothesis”. The word can have many different definitions, depending on the context in which it is being used: “An educated guess” – because it provides a suggested solution based on the evidence. Note that it isn’t just a random guess. It has to be based on evidence to be a scientific hypothesis.
Prediction – if you have ever carried out a science experiment, you probably made this type of hypothesis, in which you predicted the outcome of your experiment.
Tentative or Proposed explanation – hypotheses can be suggestions about why something is observed, but in order for it to be scientific, we must be able to test the explanation to see if it works, if it is able to correctly predict what will happen in a situation, such as: if my hypothesis is correct, we should see ___ result when we perform ___ test. A hypothesis is very tentative; it can be easily changed.

Theories

“Some scientific explanations are so well established that no new evidence is likely to alter them. The explanation becomes a scientific theory. In everyday language a theory means a hunch or speculation. Not so in science. In science, the word **theory** refers to a comprehensive explanation of an important feature of nature supported by facts gathered over time. Theories also allow scientists to make predictions about as yet unobserved phenomena.”
“A scientific theory is a well-substantiated explanation of some aspect of the natural world, based on a body of facts that have been repeatedly confirmed through observation and experimentation. Such fact-supported theories are not "guesses" but reliable accounts of the real world. The theory of biological evolution is more than "just a theory." It is as factual an explanation of the universe as the atomic theory of matter (stating that everything is made of atoms) or the germ theory of disease (which states that many diseases are caused by germs). Our understanding of gravity is still a work in progress. But the phenomenon of gravity, like evolution, is an accepted fact. “
Note some key features of theories that are important to understand from this description:

- Theories are explanations of natural phenomenon. They aren’t predictions (although we may use theories to make predictions). They are explanations why we observe something.
- Theories aren’t likely to change. They have so much support and are able to explain satisfactorily so many observations, that they are not likely to change. Theories can, indeed, be facts. Theories can change, but it is a long and difficult process. In order for a theory to change, there must be many observations or evidence that the theory cannot explain.

- Theories are not guesses. The phrase “just a theory” has no room in science. To be a scientific theory carries a lot of weight; it is not just one person’s idea about something.

Laws

Scientific laws are similar to scientific theories in that they are principles that can be used to predict the behavior of the natural world. Both scientific laws and scientific theories are typically well-supported by observations and/or experimental evidence. Usually scientific laws refer to rules for how nature will behave under certain conditions, frequently written as an equation. Scientific theories are more overarching explanations of how nature works and why it exhibits certain characteristics. As a comparison, theories explain why we observe what we do and laws describe what happens.

For example, around the year 1800, Jacques Charles and other scientists were working with gases to, among other reasons, improve the design of the hot air balloon. These scientists found, after many, many tests, that certain patterns existed in the observations on gas behavior. If the temperature of the gas increased, the volume of the gas increased. This is known as a natural law. A law is a relationship that exists between variables in a group of data. Laws describe the patterns we see in large amounts of data, but do describe why the patterns exist.

A common misconception is that scientific theories are rudimentary ideas that will eventually graduate into scientific laws when enough data and evidence has been accumulated. A theory does not change into a scientific law with the accumulation of new or better evidence. Remember, theories are explanations and laws are patterns we see in large amounts of data, frequently written as an equation. A theory will always remain a theory; a law will always remain a law.

A **model** is a description, graphic, or 3-D representation of theory used to help enhance understanding. Scientists often use models when they need a way to communicate their understanding of what might be very small (such as an atom or molecule) or very large such as the universe). A model is any simulation, substitute, or stand-in for what you are actually studying. A good model contains the essential variables that you are concerned with in the real system, explains all the observations on the real system, and is as simple as possible. A model may be as uncomplicated as a sphere representing the earth or billiard balls representing gaseous molecules, or as complex as mathematical equations representing light.

Chemists rely on both careful observation and well-known physical laws. By putting observations and laws together, chemists develop models. Models are really just ways of predicting what will happen given a certain set of circumstances. Sometimes these models are mathematical, but other times, they are purely descriptive.

Reactions and Stoichiometry

Chemical reactions are classified into types to help us analyze them and also to help us predict what the products of the reaction will be. The five major types of chemical reactions are synthesis, decomposition, single replacement, double replacement, and combustion.

Synthesis Reaction

A synthesis reaction is one in which two or more reactants combine to make one type of product.

General equation: $A + B \rightarrow AB$

Synthesis reactions occur as a result of two or more simpler elements or molecules combining to form a more complex molecule. Look at the example below. Here two elements (hydrogen and oxygen) are combining to form one product (water).

Example: $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

We can always identify a synthesis reaction because there is only one product of the reaction.

Decomposition Reaction

When one type of reactant breaks down to form two or more products, we have a decomposition reaction. The best way to remember a decomposition reaction is that for all reactions of this type, there is only one reactant.

General Equation: $AB \rightarrow A + B$

Look at the example below for the decomposition of ammonium nitrate to dinitrogen oxide and water.

Example: $NH_4NO_3 \rightarrow N_2O + 2\ H_2O$

Notice the one reactant, NH4NO3, is on the left of the arrow and there is more than one on the right side of the arrow. This is the exact opposite of the synthesis reaction type.

When studying decomposition reactions, we can predict reactants in a similar manner as we did for synthesis reactions. Look at the formula for magnesium nitride, Mg_3N_2. What elements do you see in this formula? You see magnesium and nitrogen. Now we can write a decomposition reaction for magnesium nitride. Notice there is only one reactant.

$$Mg_3N_2 \rightarrow 3\ Mg + N_2$$

Single Replacement Reaction

A third type of reaction is the single replacement reaction. In single replacement reactions one element reacts with one compound to form products. The single element is said to replace an element in the compound when products form, hence the name single replacement. Metal elements will always replace other metals in ionic compounds or hydrogen in an acid. Nonmetal elements will always replace another nonmetal in an ionic compound.

General equation: $A + BC \rightarrow B + AC$

Consider the following examples.

$$Zn(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu(s)$$

element will always replace a metal in an ionic compound. Also, note that the charges of the ionic compounds must equal zero. To correctly predict the formula of the ionic product, you must know the charges of the ions you are combining.

$$Zn(s) + 2\ HBr(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

When a metal element is mixed with acid, the metal will replace the hydrogen in the acid and release hydrogen gas a product. Once again, note that the charges of the ionic compounds must equal zero. To correctly predict the formula of the ionic product, you must know the charges of the ions you are combining, in this case Zn2+ and Cl-.

$$Cl_2(g) + 2\ KI(aq) \rightarrow 2\ KCl(aq) + I_2(s)$$

When a nonmetal element is added to an ionic compound, the element will replace the nonmetal in the compound. Also, to correctly write the formulas of the products, you must first identify the charges of the ions that will be in the ionic compound.

Double Replacement Reaction

For double replacement reactions two ionic compound reactants will react by having the cations exchange places, forming two new ionic compounds. The key to this type of reaction, as far as identifying it over the other types, is that it has two compounds as reactants. This type of reaction is more common than any of the others and there are many different types of double replacement reactions. Precipitation and neutralization reactions are two of the most common double replacement reactions. **Precipitation reactions** are ones where two aqueous compound reactants combine to form products where one of the products is an insoluble solid. A **neutralization reaction** is one where the two reactant compounds are an acid and a base and the two products are a salt and water (i.e. acid + base salt + water).

General equation: $AB + CD \rightarrow AD + CB$

For example, when solutions of silver nitrate and sodium chloride are mixed, the following reaction occurs:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

This is an example of a precipitate reaction. Notice that two aqueous reactants form one solid, the precipitate, and another aqueous product.

An example of a neutralization reaction occurs when sodium hydroxide, a base, is mixed with sulfuric acid:

$$2\ NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

Combustion Reaction

In a combustion reaction oxygen reacts with another substance to produce carbon dioxide and water. This is what happens when fuel burns. In a particular branch of chemistry, known as organic chemistry, we study compounds known as hydrocarbons. A **hydrocarbon** is compound consisting of only hydrogen and carbon. Hydrocarbons represent the major components of all organic material including fuels. Combustion reactions usually have the same products, CO_2 and H_2O, and one of its reactants is always oxygen. In other words, the only part that changes from one combustion reaction to the next is the actual hydrocarbon that burns. The general equation is given below. Notice the oxygen, carbon dioxide, and water parts of the reaction are listed for you to show you how these reactants and products remain the same from combustion reaction to combustion reaction.

General equation: C_xH_y *(hydrocarbon)* + $O_2 \rightarrow CO_2 + H_2O$

Look at the reaction for the combustion of octane, C_8H_{18}, below. Octane has 8 carbon atoms hence the prefix "oct".

Example: $2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

This reaction is referred to as complete combustion. Complete combustion reactions occur when there is enough oxygen to burn the entire hydrocarbon. This is why there are only carbon dioxide and water as products.

Oxidation – Reduction (Redox) Reactions

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Rules for Assigning Oxidation State

The oxidation state (OS) of an element corresponds to the number of electrons, e^-, that an atom loses, gains, or appears to use when joining with other atoms in compounds. In determining the oxidation state of an atom, there are seven guidelines to follow:

1. The oxidation state of an individual atom is 0.
2. The total oxidation state of all atoms in: a *neutral species* is 0 and in an *ion* is equal to the ion charge.
3. Group 1 metals have an oxidation state of +1 and Group 2 an oxidation state of +2
4. The oxidation state of fluorine is -1 in compounds
5. Hydrogen generally has an oxidation state of +1 in compounds
6. Oxygen generally has an oxidation state of -2 in compounds
7. In binary metal compounds, Group 17 elements have an oxidation state of -1, Group 16 elements of -2, and Group 15 elements of -3.

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is called the **oxidizing agent**; by accepting electrons it causes the oxidation of another species. Conversely, the species that donates electrons is called the **reducing agent**; when the reaction occurs, it reduces the other species. In other words, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3.

$$Fe_2O_3(s)+2Al(s)\rightarrow Al_2O_3(s)+2Fe(l)$$

Stoichiometry and Balancing Reactions

Stoichiometry is a section of chemistry that involves using relationships between reactants and/or products in a chemical reaction to determine desired quantitative data. In Greek, *stoikhein* means element and *metron* means measure, so stoichiometry literally translated means the measure of elements. In order to use stoichiometry to run calculations about chemical reactions, it is important to first understand the relationships that exist between products and reactants and why they exist, which require understanding how to balanced reactions.

Balancing

In chemistry, chemical reactions are frequently written as an equation, using chemical symbols. The reactants are displayed on the left side of the equation and the products are shown on the right, with the separation of either a single or double arrow that signifies the direction of the reaction. The significance of single and double arrow is important when discussing solubility constants, but we will not go into detail about it in this module. To balance an equation, it is necessary that there are the same number of atoms on the left side of the equation as the right. One can do this by raising the coefficients.

Reactants to Products

A chemical equation is like a recipe for a reaction so it displays all the ingredients or terms of a chemical reaction. It includes the elements, molecules, or ions in the reactants and in the products as well as their states, and the proportion for how much of each particle is create relative to one another, through the stoichiometric coefficient. The following equation demonstrates the typical format of a chemical equation:

$$2Na(s)+2HCl(aq)\rightarrow 2NaCl(aq)+H2(g)$$

In the above equation, the elements present in the reaction are represented by their chemical symbols. Based on the Law of Conservation of Mass, which states that matter is neither created nor destroyed in a chemical reaction, every chemical reaction has the same elements in its reactants and products, though the elements they are paired up with often change in a reaction. In this reaction, sodium (Na), hydrogen (H), and chloride (Cl) are the elements present in both reactants, so based on the law of conservation of mass, they are also present on the product side of the equations. Displaying each element is important when using the chemical equation to convert between elements.

Stoichiometric Coefficients

In a balanced reaction, both sides of the equation have the same number of elements. The stoichiometric coefficient is the number written in front of atoms, ion and molecules in a chemical reaction to balance the number of each element on both the reactant and product sides of the equation. Though the stoichiometric coefficients can be fractions, whole numbers are frequently used and often preferred. This stoichiometric coefficient are useful since they establish the mole ratio between reactants and products. In the balanced equation:

$$2Na(s)+2HCl(aq)\rightarrow 2NaCl(aq)+H2(g)$$

we can determine that 2 moles of HCl will react with 2 moles of Na(s) to form 2 moles of NaCl (aq) and 1 mole of H_2(g). If we know how many moles of Na we start out with, we can use the ratio of 2 moles of NaCl to 2 moles of Na to determine how many moles of NaCl were produced or we can use the ration of 1 mole of H2 to 2 moles of Na to convert to NaCl. This is known as the coefficient factor. The balanced equation makes it possible to convert information about one reactant or product to quantitative data about another element. Understanding this is essential to solving stoichiometric problems.

The Mole and Avogadro's Constant

The number of moles in a system can be determined using the atomic mass of an element, which can be found on the periodic table. This mass is usually an **average** of the abundant forms of that element found on earth. An element's mass is listed as the average of all its isotopes on earth.

One mole of oxygen atoms contains 6.02214179×10^{23} oxygen atoms. Also, one mole of nitrogen atoms contains 6.02214179×10^{23} nitrogen atoms. The number 6.02214179×10^{23} is called *Avogadro's number* or *Avogadro's constant*, after the 19th century scientist Amedeo Avogadro.

Each carbon-12 atom weighs about 1.99265×10^{-23}g; therefore,

$(1.99265\times10^{-23}g)\times(6.02214179\times10^{23}atoms)=12g$ of carbon-12

Application of Mole

The mass of a mole of substance is called the **molar mass** of that substance. The molar mass is used to convert grams of a substance to moles and is used often in chemistry. The molar mass of an element is found on the periodic table, and it is the element's atomic weight in grams/mole (g/mol). If the mass of a substance is known, the number of moles in the substance can be calculated. Converting the mass, in grams, of a substance to moles requires a conversion factor of (one mole of substance/molar mass of substance).

The mole concept is also applicable to the composition of chemical compounds. For instance, consider methane, CH_4. This molecule and its molecular formula indicate that per mole of methane there is 1 mole of carbon and 4 moles of hydrogen. In this case, the mole is used as a common unit that can be applied to a ratio as shown below:

$$2 \text{ mol H} + 1 \text{ mol O} = 1 \text{ mol } H_2O$$

In this chemical reactions, the moles of H and O describe the number of atoms of each element that react to form 1 mol of H_2O.

To think about what a mole means, one should relate it to quantities such as dozen or pair. Just as a pair can mean two shoes, two books, two pencils, two people, or two of anything else, a mole means 6.02214179×10^{23} of anything. Using the following relation:

1 mole=6.02214179×10^{2} is analogous to saying: 1 Dozen=12 eggs

It is quite difficult to visualize a mole of something because Avogadro's constant is extremely large. For instance, consider the size of one single grain of wheat. If all the people who have existed in Earth's history did nothing but count individual wheat grains for their entire lives, the total number of wheat grains counted would still be much less than Avogadro's constant; the number of wheat grains produced throughout history does not even approach Avogadro's Number.

Review Question

How many moles of potassium (K) atoms are in 3.04 grams of pure potassium metal?

Solution: In this example, multiply the mass of K by the conversion factor (inverse molar mass of potassium):

$$1\text{mol K}/39.10\text{grams K}$$

39.10 grams is the molar mass of one mole of K; cancel out grams, leaving the moles of K:

$$3.04gK\ (1mol\ K/39.10gK)=0.0778\ mol\ K$$

Similarly, if the moles of a substance are known, the number grams in the substance can be determined. Converting moles of a substance to grams requires a conversion factor of *molar mass of substance/one mole of substance*. One simply needs to follow the same method but in the opposite direction.

Mole Ratios

A mole ratio is the relationship of the number of moles of the substances in a reaction. For instance, in the following reaction we read the coefficients as molecules (or formula units) and moles:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

2 moles of H_2 react with 1 mole of O_2 to produce 2 moles of H_2O. Or, an alternate method to represent this information is with mole ratios. The following mole ratios can be obtained from this reaction:

2 mol H_2/1 mol O_2 or 1 mol O_2/2 mol H_2 or 2 mol H_2O/2 mol H_2 or 2 mol H_2O/1 mol O_2

Using the coefficients of a balanced reaction, you can compare any two substances in the reaction you are interested in, whether they are reactants or products. The correct mole ratios of the reactants and products in a chemical equation are determined by the balanced equation. Therefore, the chemical equation MUST always be balanced before the mole ratios are used for calculations.

Questions

1. (a) Write the chemical equation for the synthesis reaction of silver bromide, AgBr.

(b) Predict the products for the following reaction: CO2*(g)* + H2O*(l)*

Solution: (a) $2\ Ag + Br_2 \rightarrow 2\ AgBr$

(b) $CO_2\ (g)\ + H_2O\ (l)\ \rightarrow H_2CO_3$

2. Write the chemical equation for the decomposition of:

(a) Al_2O_3

(b) Ag_2S

(c) MgO

Solution: (a) 2 Al2O3 → 4 Al + 3 O2

(b) Ag2S → 2 Ag + S

(c) 2 MgO → 2 Mg + O2

3. What would be the products of the reaction between solid aluminum and iron(III) oxide? The reactants are: Al + Fe2O3 →

Solution: In order to predict the products we need to know that aluminum will replace iron and form aluminum oxide (the metal will replace the metal ion in the compound). Aluminum has a charge of +3 and oxygen has a charge of -2. The compound formed between aluminum and oxygen, therefore, will be Al_2O_3. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products. The unbalanced equation will be:
$Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$
and the balanced equation will be:
$2\ Al + Fe_2O_3 \rightarrow Al_2O_3 + 2\ Fe$

4. (a) Write the chemical equation for the single replacement reaction between zinc solid and lead(II) nitrate solution to produce zinc nitrate solution and solid lead. (*Note: zinc forms ions with a +2 charge)
(b) Predict the products for the following reaction: $Fe + CuSO_4$ (in this reaction, assume iron forms ions with a +2 charge)
(c) Predict the products for the following reaction: $Al + CuCl_2$
(d) Complete the following reaction. Then balance the equation: $Al + HNO_3 \rightarrow$

Solution: (a) $Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2$
(b) $Fe + CuSO_4 \rightarrow Cu + FeSO_4$
(c) $2\ Al + 3\ CuCl_2 \rightarrow 3\ Cu + 2\ AlCl_3$
(d) $2\ Al + 6\ HNO_3 \rightarrow 2\ Al(NO_3)_3 + 3\ H_2$
5. A common laboratory experiment involves the reaction between lead(II) nitrate and sodium iodide, both colorless solutions. The reactants are given below. Predict the products.

$Pb(NO_3)_2(aq) + NaI(aq) \rightarrow$

Solution: We know that the cations exchange anions. We now have to look at the charges of each of the cations and anions to see what the products will be. In $Pb(NO_3)_2$, the nitrate, NO^{3-} has a charge of -1. This means the lead must be +2, Pb^{2+}. In the sodium iodide, we are combining Na+ and I-. Now we switch ions and write the correct subscripts so the total charge of each compound is zero. The Pb2+ will combine with the I- to form PbI_2. The Na+ will combine with the NO^{3-} to form $NaNO_3$. Only after we have the correct formulas can we worry about balancing the two sides of the reaction. The final balanced reaction will be:

$Pb(NO_3)_2(aq) + 2\ NaI(aq) \rightarrow PbI_2(s) + 2\ NaNO_3(aq)$

6. Write the balanced reaction for the complete combustion of propane, C_3H_8.

Solution: The reactants of all combustion reactions include the fuel (a compound with carbon and hydrogen) reacting with oxygen. The products are always carbon dioxide and water.

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$

7. Using the equations from the previous examples, determine what is oxidized in the following reaction.

$$\mathrm{Zn+2H+\rightarrow Zn2++H2}$$

Solution: The oxidation state of H changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the reducing agent.

8. What is reduced species in this reaction?

$$\mathrm{Zn+2H+\rightarrow Zn2++H2}$$

Solution: The oxidation state of H changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, H+ ion is reduced and acts as the oxidizing agent.

9. For each of the following equations, indicate the number of formula units or molecules, and the number of moles present in the balanced chemical equation.
(a) $2\ C_2H_6 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O$
(b) $KBrO_3 + 6\ KI + 5\ HBr \rightarrow 7\ KBr + 3\ I_2 + 3\ H_2O$

Solution: (a) Two molecules of C2H6 plus seven molecules of O_2 yields four molecules of CO_2 plus six molecules of H_2O. Two moles of C_2H_6 plus seven moles of O_2 yields four moles of CO_2 plus six moles of H_2O.
(b) Two formula units of $KBrO_3$ plus six formula units of KI plus six formula units of HBr yields seven formula units of KBr plus three molecules of I_2 and three molecules of H_2O. Two moles of $KBrO_3$ plus six moles of KI plus six moles of HBr yields seven moles of KBr plus three moles of I_2 and three moles of H_2O.

10. Lead (IV) hydroxide and sulfuric acid react as shown below. Balance the reaction.

$$\mathrm{Pb(OH)4+H2SO4\rightarrow Pb(SO4)2+H2O}$$

Solution: UNBALANCED

Element	Reactant (# of atoms)	Product (# of atoms)
Pb	1	1
O	8	9
H	6	2
S	1	2

The reaction is not balanced; the reaction has 16 reactant atoms and only 14 product atoms and does not obey the conservation of mass principle. Stoichiometric coefficients must be added to make the equation balanced. In this example, there are only one sulfur atom present on the reactant side, so a coefficient of 2 should be added in front of H2SO4 to have an equal number of sulfur on both sides of the equation. Since there are 12 oxygen on the reactant side and only 9 on the product side, a 4 coefficient should be added in front of H2O where there is a deficiency of oxygen. Count the number of elements now present on either side of the equation. Since the numbers are the same, the equation is now balanced.

$$Pb(OH)4+2H2SO4 \rightarrow Pb(SO4)2+4H2O$$

BALANCED

Element	Reactant (# of atoms)	Product (# of atoms)
Pb	1	1
O	12	12
H	8	8
S	2	2

11. How many grams are 10.78 moles of Calcium (Ca)?

Solution: Multiply moles of Ca by the conversion factor (molar mass of calcium) **40.08 g Ca/ 1 mol Ca,** which then allows the cancelation of moles, leaving grams of Ca.

10.78molCa(40.08gCa/1molCa)=432.1gCa

The total number of atoms in a substance can also be determined by using the relationship between grams, moles, and atoms. Then the number of moles of the substance must be converted to atoms. Converting moles of a substance to atoms requires a conversion factor of **Avogadro's constant ($6.02214179 \times 10^{23}$) / one mole of substance**. Verifying that the units cancel properly is a good way to make sure the correct method is used.

Advanced Questions

1. (a) Write a chemical equation for the double replacement reaction between calcium chloride solution and potassium hydroxide solution to produce potassium chloride solution and a precipitate of calcium hydroxide.

(b) Predict the products for the following reaction: $AgNO_3$*(aq)* + NaCl*(aq)* →

(c) Predict the products for the following reaction: $FeCl_3$*(aq)* + KOH*(aq)* →

2. Distinguish between synthesis and decomposition reactions?

3. When dodecane, $C_{10}H_{22}$, burns in excess oxygen, what will be the products?

4. Classify each type of reaction as synthesis, decomposition, single replacement, double replacement or combustion.

$Cu + O_2 \rightarrow CuO$

$H_2O \rightarrow H_2 + O_2$

$Fe + H_2O \rightarrow H_2 + Fe_2O_3$

$AsCl_3 + H_2S \rightarrow As_2S_3 + HCl$

$Fe_2O_3 + H_2 \rightarrow Fe + H_2O$

$CaCO_3 \rightarrow CaO + CO_2$

$H_2S + KOH \rightarrow HOH + K_2S$

$NaCl \rightarrow Na + Cl_2$

$Al + H_2SO_4 \rightarrow H_2 + Al2(SO_4)_3$

$CH_4 + O_2 \rightarrow CO_2 + H_2O$

5. If sulfuric acid is mixed with sodium cyanide, the deadly gas hydrogen cyanide is produced. How many moles of sulfuric acid would have been placed in the container to produce 12.5 g of hydrogen cyanide? The balanced reaction is:

$2\ NaCN + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCN$

6. How many atoms are in a 3.5 g sample of sodium (Na)?

7. How many moles are in 3.00 grams of potassium (K)?

8. Hydrochloric acid reacts with a solid chunk of aluminum to produce hydrogen gas and aluminum ions. Write the balanced chemical equation for this reaction?

9. Why are the following equations not considered balanced?

a. $H_2O(l) \rightarrow H_2(g) + O_2(g)$
b. $Zn(s) + Au+(aq) \rightarrow Zn2+(aq) + Ag(s)$

ATOMS, IONS and MOLECULES

The Structure of Atom

All matter in the universe is made from tiny building blocks called atoms. All modern scientists accept the concept the concept of atom, but when the concept of the atom was first proposed 2,500 years ago, ancient philosophers laughed at the idea. It has been difficult to convince people of the existence of things that are too small to see.

About 2,500 years ago, early Greek philosophers believed the entire universe was a single, huge entity. They believed that all objects, all matter and all substances were connected as a big single thing. One of the first person to propose "atoms" was a man known as Democritus. Democritus suggested that atomos, or atomon- tiny, indivisible, solid objects-, make up all the matter in the universe. He even extended his theory, suggesting that there were different varieties of atomos with different shapes, sizes, and masses. Greek philosophers dismissed Democritus theory entirely. Sadly, it took over two millennia before the theory of atoms was fully appreciated. Dalton used this idea to generate what is known Dalton's Atomic Theory.

Dalton's Atomic Theory

In the late 1700's Antoine Lavoisier, a French Scientist, experimented with the reactions of many metals. He found out that no matter what reaction he looked at, the mass of the starting materials was always equal to mass of the end materials. This is now called the law of conservation of mass. At the same time that scientists were finding this pattern out, a man named John Dalton was experimenting with several reactions in which the reactant elements formed more than one type of product.

Dalton's Atomic Theory states that:

a) Matter is made of tiny particles called atoms.
b) Atoms are indivisible. During a chemical reaction, atoms are rearranged, but they do not break apart, nor are they created or destroyed.
c) All atoms of a given element are identical in mass and other properties.
d) The atoms of different elements differ in mass and other properties
e) Atoms of one element can combine with atoms of another element to form 'compounds', new, complex particles. In a given compound, however, the different types of atoms are always present in the same relative numbers.

Rutherford's Atomic Model

The classic model of an atom was given by Ernest Rutherford called the Rutherford Atomic Model. In Rutherford's experiment, he bombarded high energy streams of α-particles on a thin gold foil of 100 nm thickness. The streams of α-particles were directed from a radioactive source. He conducted the experiment to study the deflection produced in the trajectory of α-particles after interaction with the thin sheet of gold. To study the deflection, he placed a screen made up of zinc sulfide around the gold foil. The observations made by Rutherford contradicted the plum pudding model given by J.J. Thomson.

Postulates of Rutherford atomic model based on observations and conclusions

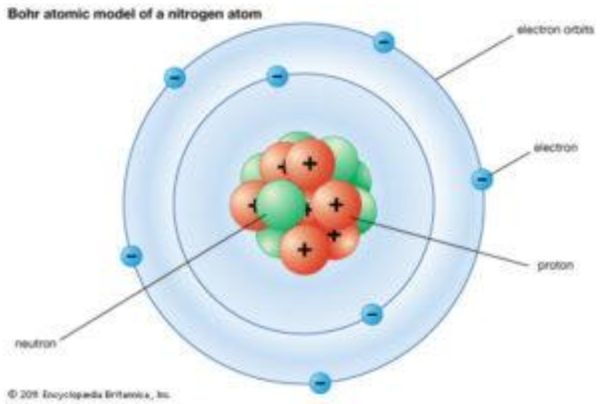
- An atom is composed of positively charged particles. Majority of the mass of an atom was concentrated in a very small region. This region of the atom was called as the **nucleus** of an atom. It was found out later that the very small and dense nucleus of an atom is composed of neutrons and protons.
- Atoms nucleus is surrounded by negatively charged particles called **electrons**. The electrons revolve around the nucleus in a fixed circular path at very high speed. These fixed circular paths were termed as **"orbits."**
- An atom has no net charge, or they are **electrically neutral** because electrons are negatively charged and the densely concentrated nucleus is positively charged. A strong electrostatic force of attractions holds together the nucleus and electrons.
- The size of the nucleus of an atom is very small in comparison to the total size of an atom.

Bohr's Atomic Model

The physicist Niels Bohr said, **"Anyone who is not shocked by quantum theory has not understood it."** He also said, **"We must be clear that when it comes to atoms, language can only be used as in poetry."** So what exactly is this Bohr atomic model?

Bohr atomic model and the models after that explain the properties of atomic electrons on the basis of certain allowed possible values. The model explained how an atom absorb or emit radiation when electrons on subatomic level jump between the allowed and stationary states.

According to Bohr Atomic model, a small positively charged nucleus is surrounded by revolving negatively charged electrons in fixed orbits. He concluded that electron will have more energy if it is located away from the nucleus whereas the electrons will have less energy if it located near the nucleus.



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Postulates of the Bohr Atomic Model

- Electrons revolve around the nucleus in a fixed circular path termed "orbits" or "shells" or "energy level."
- The orbits are termed as "stationary orbit."
- Every circular orbit will have a certain amount of fixed energy and these circular orbits were termed orbital shells. The electrons will not radiate energy as long as they continue to revolve around the nucleus in the fixed orbital shells.
- The different energy levels are denoted by integers such as n=1 or n=2 or n=3 and so on. These are called as quantum numbers. The range of quantum number may vary and begin from the lowest energy level (nucleus side n=1) to highest energy level.
- The different energy levels or orbits are represented in two ways such as 1, 2, 3, 4… or K, L, M, N.. shells. The lowest energy level of the electron is called the ground state.
- The change in energy occurs when the electrons jump from one energy level to other. In an atom, the electrons move from lower to higher energy level by acquiring the required energy. However, when an electron loses energy it moves from higher to lower energy level.

2 Subatomic Particles

2.1 Protons, Neutrons, and Electrons in Atoms

J.J Thomson discovered a negatively charged particle, called the electron. Rutherford proposed that these electrons orbit a positive nucleus. In subsequent experiments, he found that there is a smaller positively charged particle in the nucleus which is called a proton. There is a third subatomic particle, known as neutron. Ernest Rutherford proposed the existence of a neutral particle, with the approximate mass of a proton. James Chadwick proved that the nucleus of the atom contains this neutral particle.

Electrons, protons, and neutrons all have different size. Electrons have an extremely small mass, compared to either protons or neutrons. On the other hand, the masses of protons and neutrons are fairly similar, although technically, the mass of a neutron is slightly larger than the mass of a proton.

Subatomic Particles, Properties and Location

Particle	Relative mass (amu)	Electric Charge	Location
electron	1/1840	-1	Outside the nucleus
Proton	1	+1	Nucleus
neutron	1	0	Nucleus

Review Question

Label each of the following statements as true or false.

1) The nucleus of an atom contains all of the protons in the atom. 2) The nucleus of an atom contains all of the electrons in the atom. 3) Neutral atoms must contain the same number of neutrons as protons. 4) Neutral atoms must contain the same number of electrons as protons.

Solution: 1) True 2) False 3) False 4) True

Atomic and Mass number

An element's **atomic number** is equal to the number of protons in the nuclei of any of its atoms. The atomic number is a whole number usually written above the chemical symbol of each element. For example, hydrogen has an atomic number of 1, because every hydrogen atom has 1 proton. Similarly, the atomic number of helium is 2 because every helium atom has 2 protons.

The **mass number** of an atom is the total number of protons and neutrons in its nucleus. Most of the mass of an atom of an atom is concentrated in its nucleus and hence, mass of an atom depends on the number of protons and neutrons.

Review Question

1. What is the mass number of an atom of helium that contains 2 neutrons?

Solution: (number of protons) = 2 (Remember that an atom of helium always has 2 protons.) (number of neutrons) = 2 mass number = (number of protons) + (number of neutrons) mass number = 2 + 2 = 4

Isotopes

Unlike the number of protons, which is always the same in atoms of the same element, the number of neutrons can be different, even in atoms of the same element. Atoms of the same element, containing the same number of protons but different numbers of neutrons are known as isotopes. Since isotopes of any given element all contain the same number of protons, they have the same atomic number but different mass numbers.

Atomic Mass

The atomic mass of an element is the weighted average mass of the atoms in a naturally occurring sample of the element. Atomic mass is typically reported in atomic mass units.

Calculating Atomic Mass

We can calculate atomic mass by the following equation:

Atomic mass = (%)mass1 + (%) mass2 + …..

Review Question

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of 19.99 amu. Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of 20.99 amu. The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of 21.99 amu. What is the atomic mass of neon?

Solution: Neon has three isotopes.

We will use the equation: Atomic mass = (%1) (mass1) + (%2)(mass2) + …

Isotope 1: %1=0.9092 (write all percentages as decimals), mass1=19.99

Isotope 2: %2=0.003, mass2=20.99

Isotope 3: %3=0.0885, mass3=21.99

Substitute these into the equation, and we get:

Atomic mass = (0.9092) (19.99) + (0.003) (20.99) + (0.0885)(21.99) Atomic mass = 20.17 amu. The mass of an average neon atom is 20.17 amu

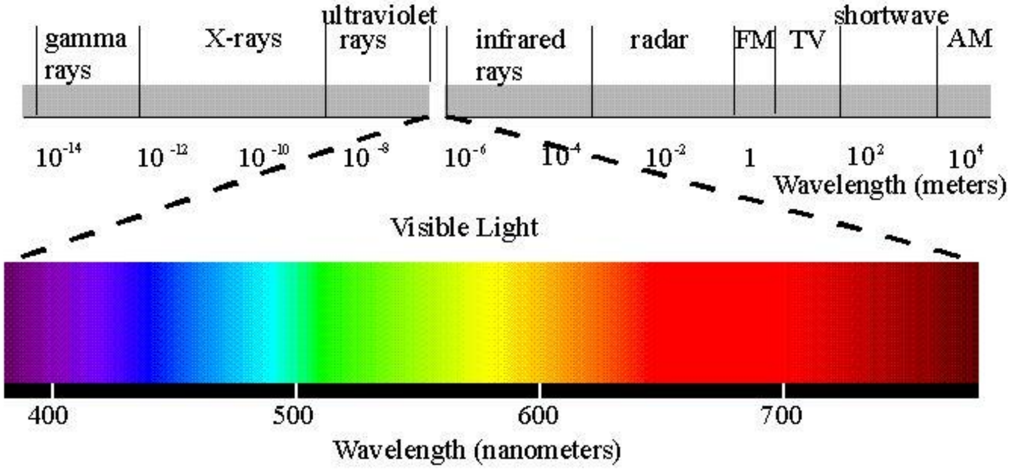
Nature of Light

Most of us are familiar with waves, whether they are waves of water in the ocean, waves made by wiggling the end of a rope, or waves made when a guitar string is plucked. Light, also called electromagnetic radiation, is a special type of energy that travels as a wave.

Before we talk about the different forms of light or electromagnetic radiation (EMR), it is important to understand some of the general characteristics that waves share. The high point of a wave is called the crest. The low point is called the trough. The distance from one point on a wave to the same point on the next wave is called the **wavelength** of the wave. You could determine the wavelength by measuring the distance from one trough to the next or from the top (crest) of one wave to the crest of the next wave. The symbol used for wavelength is the Greek letter lambda, λ.

Another important characteristic of waves is called **frequency**. The frequency of a wave is the number of waves that pass a given point each second. If we choose an exact position along the path of the wave and count how many waves pass the position each second, we would get a value for frequency. Frequency has the units of cycles/sec or waves/sec, but scientists usually just use units of 1/sec or Hertz (Hz).

All types of light (EMR) travels at the same speed, 3.00×10^8 m/s. Because of this, as the wavelength increases (the waves get longer), the frequency decreases (fewer waves pass). On the other hand, as the wavelength decreases (the waves get shorter), the frequency increases (more waves pass). Electromagnetic waves (light waves) have an extremely wide range of wavelengths, frequencies, and energies. The electromagnetic spectrum is the range of all possible frequencies of electromagnetic radiation. The highest energy form of electromagnetic waves is gamma rays and the lowest energy form (that we have named) is radio waves.



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Dual Nature of Light

Light has dual nature

a) Sometimes it behaves like a particle (called a photon), which explains how light travels in straight lines.

b) Sometimes it behaves like a wave, which explains how light bends (or diffracts) around an object.

de Broglie Relation

In 1924, Louis de Broglie presented his research thesis, in which he proposed electrons have properties of both waves and particles. The de Broglie equation is an equation to describe the wave properties of matter, specifically, the wave nature of the electron:

$\lambda = h/mv$,

where λ= wavelength, h is Planck's constant, m is the mass of the particle moving at a velocity v.

Heisenberg's Uncertainty Principle

Heisenberg's Uncertainty Principle states that there is inherent uncertainty in the act of measuring a variable of a particle. Commonly applied to the position and momentum of a particle, the principle states that the more precisely the position is known the more uncertain the momentum is and vice versa. This is contrary to classical Newtonian physics which holds all variables of particles to be measurable to an arbitrary uncertainty given good enough equipment. The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously.

More specifically, if one knows the precise momentum of the particle, it is impossible to know the precise position, and vice versa. This relationship also applies to energy and time, in that one cannot measure the precise energy of a system in a finite amount of time. Uncertainties in the products of "conjugate pairs" (momentum/position) and (energy/time) were defined by Heisenberg as having a minimum value corresponding to Planck's constant divided by $4\pi 4\pi$. More clearly:

$$\Delta p \Delta x \geq h/4\pi$$

$$\Delta t \Delta E \geq h/4\pi$$

Where Δ refers to the uncertainty in that variable and h is Planck's constant.

It is hard to imagine not being able to know exactly where a particle is at a given moment. It seems intuitive that if a particle exists in space, then we can point to where it is; however, the Heisenberg Uncertainty Principle clearly shows otherwise. This is because of the wave-like nature of a particle. A particle is spread out over space so that there simply is not a precise location that it occupies, but instead occupies a range of positions. Similarly, the momentum cannot be precisely known since a particle consists of a packet of waves, each of which have their own momentum so that at best it can be said that a particle has a range of momentum.

Elements

Elements are substances that cannot be separated into simpler substances. Salt is made up of the elements sodium and chloride. Water is made up of the elements hydrogen and oxygen. Chemists use symbols to represent elements. A symbol is a letter or picture used to represent something. Chemists use one or two letters to represent elements. The symbol for aluminum is Al. The symbol for oxygen is O.

The Organization of Elements

Mendeleev's Periodic Table

During the 1800s, when most of the elements were being discovered, many chemists tried to classify the elements according to their similarities. By 1869, a total of 63 elements had been discovered. As the number of known elements grew, scientists began to recognize patterns in the way chemicals reacted and began to devise ways to classify the elements. Dmitri Mendeleev, a Siberian-born Russian chemist, was the first scientist to make a periodic table much like the one we use today. Mendeleev's table listed the elements in order of increasing atomic mass. Then he placed elements underneath other elements with similar chemical behavior. For example, lithium is a shiny metal, soft enough to be cut with a spoon. It reacts readily with oxygen and reacts violently with water. When Mendeleev found an element, whose chemistry was very similar to a previous element, he placed it below the similar element.

How was Mendeleev able to make such accurate predictions? He understood the patterns that appeared between elements within a family, as well as patterns according to increasing mass, that he was able to fill in the missing pieces of the patterns. The ability to make accurate predictions is was put Mendeleev's table apart from other organization systems that were made at the same time and is what led to scientists accepting his table and periodic law.

The periodic table we use today is similar to the one developed by Mendeleev but is not the same. There are some important distinctions: Mendeleev's table did not include any of the noble gases, which were discovered later. These were added by Sir William Ramsay as Group 0, without any disturbance to the basic concept of the periodic table. As previously noted, Mendeleev organized elements in order of increasing atomic mass, with some problems in the order of masses. In 1914 Henry Moseley found a relationship between an element's X-ray wavelength and its atomic number, and therefore organized the table by nuclear charge (or atomic number) rather than atomic weight. Thus, Moseley placed argon (atomic number 18) before potassium (atomic number 19) based on their X-ray wavelengths, even though argon has a greater atomic weight (39.9) than potassium (39.1). The new order agrees with the chemical properties of these elements since argon is a noble gas and potassium an alkali metal.

Metals, Non- metals, and Metalloids

There is a progression from metals to non-metals across each row of elements in the periodic table. The diagonal line at the right side of the table separates the elements into two groups: the metals and the non-metals. The elements that are on the left of this line tend to be metals, while those to the right tend to be non-metals (except for hydrogen which is a nonmetal). The elements that are directly on the diagonal line are metalloids, with some exceptions.

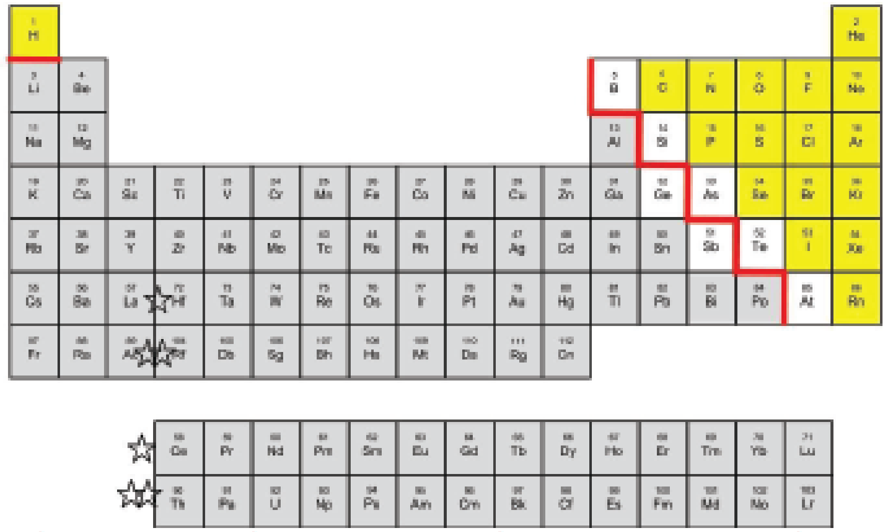
Aluminum touches the line but is considered a metal.

Metallic character generally increases from top to bottom down a group and right to left across a period, meaning that francium (Fr) has the most metallic character of all of the discovered elements.

The metalloids are most of the elements along the line drawn.

Most of the chemical elements are metals. Most metals have the common properties of being shiny, very dense, and having high melting points. Metals tend to be ductile (can be drawn out into thin wires) and malleable (can be hammered into thin sheets). Metals are good conductors of heat and electricity. All metals are solids at room temperature except for mercury. In chemical reactions, metals easily lose electrons to form positive ions. Examples of metals are silver, gold, and zinc. Nonmetals are generally brittle, dull, have low melting points, and they are generally poor conductors of head heat and electricity. In chemical reactions, they tend to gain electrons to form negative ions. Examples of non-metals are hydrogen, carbon, and nitrogen.

Metalloids have properties of both metals and nonmetals. Metalloids can be shiny or dull. Electricity and heat can travel through metalloids, although not as easily as they can through metals. They are also called semimetals. They are typically semi-conductors, which means that they are elements that conduct electricity better than insulators, but not as well as conductors. They are valuable in the computer chip industry. Examples of metalloids are silicon and boron.



The division of the periodic table into metals and non-metals. The metalloids are most of the elements along the line drawn. Additionally, the element hydrogen is a NONMETAL, even though it is on the left side of the periodic table.
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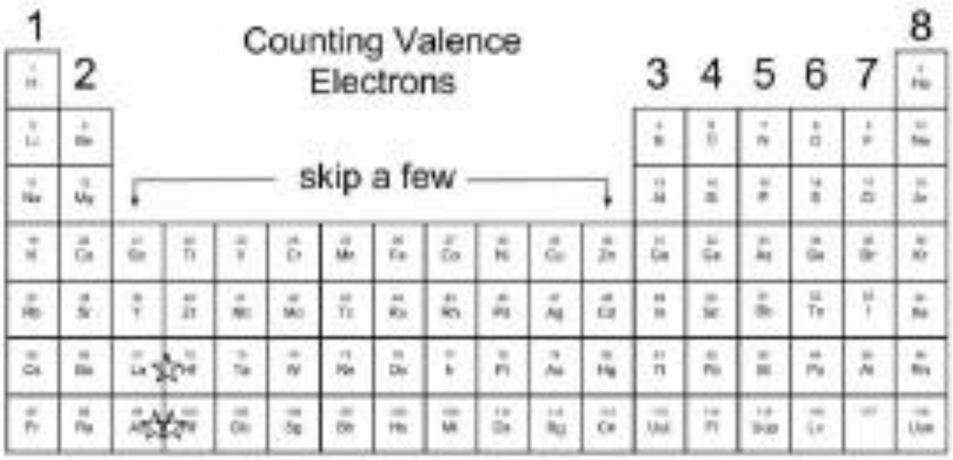
Valence Electrons

The electrons in the outermost shell are the valence electrons these are the electrons on an atom that can be gained or lost in a chemical reaction.

The number of valence electrons for an atom can be seen in the electron configuration. The electron configuration for magnesium is $1s^2\ 2s^2\ 2p^6\ 3s^2$. The outer energy level for this atom is n=3 and it has two electrons in this energy level. Therefore, magnesium has two valence electrons.

The electron configuration for sulfur is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$. The outer energy level in this atom is n=3 and it holds six electrons, so sulfur has six valence electrons.



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Families and Periods of the Periodic Table

The chemical behavior of atoms is controlled by their electron configuration. Since the families of elements were organized by their chemical behavior, it is predictable that the individual members of each chemical family will have similar electron configurations.

A **group** is a vertical column of the periodic table. All the 1A elements have one valence electron. This is what causes these elements to react in the same ways as the other members of the family. The elements in 1A are all very reactive and form compounds in the same ratios with similar properties with other elements. Group 1A is also known as the **alkali metals**.

Group 2A is also called the **alkaline earth metals**. Once again, because of their similarities in electron configurations, these elements have similar properties to each other.

Group 7A (or 17) elements are also called **halogens**. This group contains very reactive nonmetals elements.

The **noble gases** are in group 8A. These elements also have similar properties to each other, the most significant property being that they are extremely unreactive rarely forming compounds.

A **period** is a horizontal row of elements on the periodic table. For example, the elements sodium (Na) and magnesium (Mg) are both in period 3.

Periodic Trends

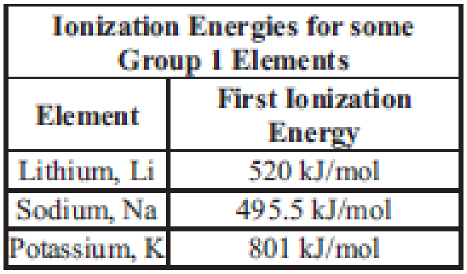
The periodic table is a powerful tool that provides a way for chemists to organize the chemical elements. The word “periodic” means happening or recurring at regular intervals. The periodic law states that the properties of the elements recur periodically as their atomic numbers increase. Because the physical and chemical properties of elements depend on their electron configurations, many of the physical and chemical properties of the elements tend to repeat in a pattern.

Trends in Atomic Radius

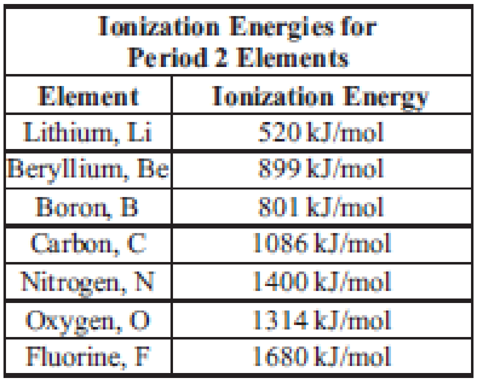
The trend within a group or family on the periodic table is that the atomic size increases with increased number of energy levels. The largest atom on the periodic table is all the way to the left and all the way to the bottom, francium, #87, and the smallest atom is all the way to the right and all the way to the top, helium, #2.

Periodic Trends in Ionization Energy

The ionization energy is the energy required to remove the most loosely held electron from a gaseous atom. The higher the value of the ionization energy, the harder it is to remove that electron.



Ionization Energies for some Group 1 Elements	
Element	First Ionization Energy
Lithium, Li	520 kJ/mol
Sodium, Na	495.5 kJ/mol
Potassium, K	801 kJ/mol



Ionization Energies for Period 2 Elements	
Element	Ionization Energy
Lithium, Li	520 kJ/mol
Beryllium, Be	899 kJ/mol
Boron, B	801 kJ/mol
Carbon, C	1086 kJ/mol
Nitrogen, N	1400 kJ/mol
Oxygen, O	1314 kJ/mol
Fluorine, F	1680 kJ/mol

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As we move across the period, the atoms become smaller which causes the nucleus to have greater attraction for the valence electrons. Therefore, as you move from left to right in a period on the periodic table, the ionization energy increases.

Review Question

Which of the following has a greater ionization energy? (a) As or Sb (b) Ca or K (c) Polonium or Sulfur

Solution: (a) As because it is above Sb in Group 15. (b) Ca because it is further to the right on the periodic table. (c) S because it is above Po in Group 16.

Periodic Trends in Electronegativity

Around 1935, the American chemist Linus Pauling developed a scale to describe the attraction an element has for electrons in a chemical bond. This is the **electronegativity**. The values of electronegativity are higher for elements that more strongly attract electrons.

On this Pauling scale fluorine, with an electronegativity of 4.0 is the most electronegative element, and cesium and francium, with electronegativities of 0.7, are the least electronegative.

a) The electronegativity of atoms increases as you move from left to right across a period in the periodic table. This is because as you go from left to right across a period, the atoms of each element have the same number of energy levels. However, the nucleus charge increases, so the attraction that the atoms have for the valence electrons increases.
b) The electronegativity of atoms decreases as you move from top to bottom down a group in the periodic table. This is because as you go from top to bottom down a group, the atoms of each element have an increasing number of energy levels.
c) Atoms with low ionization energies have low electronegativities because their nuclei do not have a strong attraction for electrons. Atoms with high ionization energies have high electronegativities because the nucleus has a strong attraction for electrons.

Compounds

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition (meaning it's the same everywhere) and properties that are constant throughout the sample (meaning there is only one set of properties such as melting point, color, boiling point, etc throughout the matter). Elements and compounds are both example of pure substances.

Mixtures are physical combinations of two or more elements and/or compounds. The term "physical combination" refers to mixing two different substances together where the substances do not chemically react. The physical appearance of the substances may change but the atoms and/or molecules in the substances do not change.

Chemical Formulas of Compounds

The formula for a compound uses the symbols to indicate the type of atoms involved and uses subscripts to indicate the number of each atom in the formula. For example, aluminum combines with oxygen to form the compound aluminum oxide. To form aluminum oxide requires two atoms of aluminum and three atoms of oxygen. Therefore, we write the formula for aluminum oxide as Al_2O_3. The symbol Al tells us that the compound contains aluminum, and the subscript 2 tells us that there are two atoms of aluminum in each molecule. The O tells us that the compound contains oxygen, and the subscript 3 tells us that there are three atoms of oxygen in each molecule.

Types of Compounds and Their Properties

There are three types of compounds: ionic, covalent and metallic.

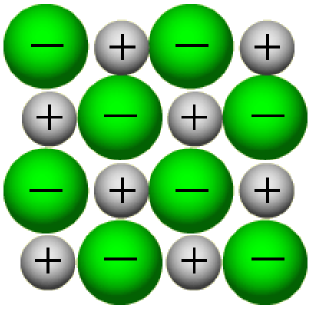
The Octet Rule

The octet rule is a chemical **rule** of thumb that reflects observation that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electron configuration as a noble gas.

When an atom gains electron, the atom will obtain a negative charge and is now called an **anion**. When an atom loses electrons, the atom will obtain a positive charge and is now called a **cation**. When anions and cations are bonded together, the bond is said to be **ionic**. Metal atoms will lose electrons to obtain an octet and nonmetals will gain electrons. Therefore, in an ionic bond metals are typically bonded to nonmetals. Some atoms can obtain an octet by sharing their valence electrons with another atom. This type of bonding is called a **covalent bond**. Only nonmetals can form covalent bonds with other nonmetals.

Properties of Ionic Compounds

When ionic compounds are formed in laboratory conditions, many cations and anions are formed at the same time. The positive and negative ions are not just attracted to a single oppositely charged ion. The ions arrange themselves into organized patterns where each ion is surrounded by several ions of the opposite charge. The organized patterns of positive and negative ions are called **lattice structures.** The image shows the solid structure of sodium chloride. Each sodium ion is touching six chloride ions – the four surrounding ones and one above and one below. Each chloride ion is touching six sodium ions in the same way



Positively charged Na ions and negatively charged Cl ions

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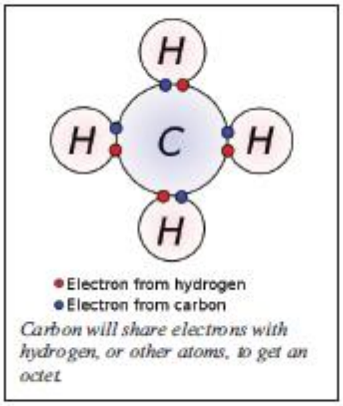
a) The electrostatic attraction between the oppositely charge ions is quite strong and therefore, ionic compounds have very high melting and boiling points.
b) Ionic substances generally dissolve readily in water.
c) The presence of the mobile ions in liquid or solution allow the solution to conduct electric current.

Properties of Covalent Compounds

The term covalent bond dates from 1939. The prefix co- means jointly; "valent" is referring to an atom's valence electrons. Thus, a "co-valent bond", essentially, means that the atoms share valence electrons.



Carbon will share electrons with hydrogen, or other atoms, to get an octet

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Covalent compounds have properties very different from ionic compounds.

a) Covalent compounds have low melting points, and many are liquids or gases at room temperature.
b) Whereas most ionic compounds are capable of dissolving in water, many covalent compounds do not
c) Also, unlike ionic compounds, when covalent compounds are dissolved in water, they are not conductors of electricity.

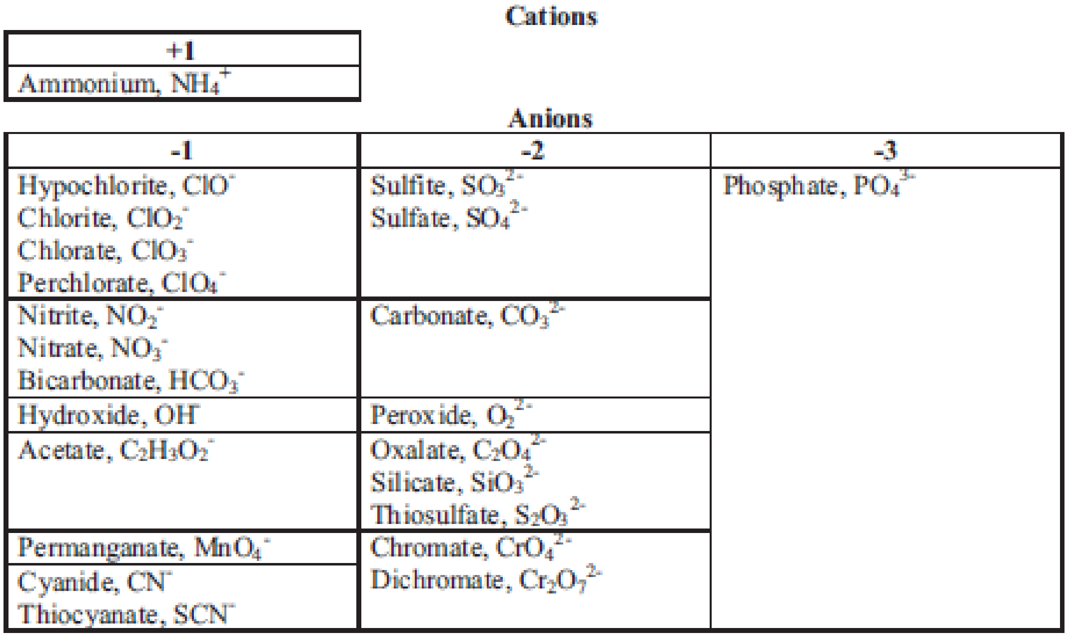
Properties of Metallic Compounds

There is a third type of bond that may be formed between two atoms. In metallic bonding, the electrons between neighboring metal atoms are delocalized, meaning that the electrons are not tied to one atoms specifically. The electrons, instead, are gathered in what we call an "electron sea". In an electron sea, the metal nuclei form the basis, and the electrons move around the nuclei.

Because of this unique type of bonding structure, metallic bonding accounts for many physical properties of metals, such as strength, malleability (or bendability), ductility, conductivity (allows heat and electricity to go through), and luster (shine).

Polyatomic Ions

There also exists a group of polyatomic ions, ions composed of a group of atoms that are covalently bonded and behave as if they were a single ion. Almost all the common polyatomic ions are negative ions.



Cations

+1
Ammonium, NH_4^+

Anions

-1	-2	-3
Hypochlorite, ClO^- Chlorite, ClO_2^- Chlorate, ClO_3^- Perchlorate, ClO_4^-	Sulfite, SO_3^{2-} Sulfate, SO_4^{2-}	Phosphate, PO_4^{3-}
Nitrite, NO_2^- Nitrate, NO_3^- Bicarbonate, HCO_3^-	Carbonate, CO_3^{2-}	
Hydroxide, OH^-	Peroxide, O_2^{2-}	
Acetate, $C_2H_3O_2^-$	Oxalate, $C_2O_4^{2-}$ Silicate, SiO_3^{2-} Thiosulfate, $S_2O_3^{2-}$	
Permanganate, MnO_4^-	Chromate, CrO_4^{2-} Dichromate, $Cr_2O_7^{2-}$	
Cyanide, CN^- Thiocyanate, SCN^-		

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Naming Inorganic Compounds

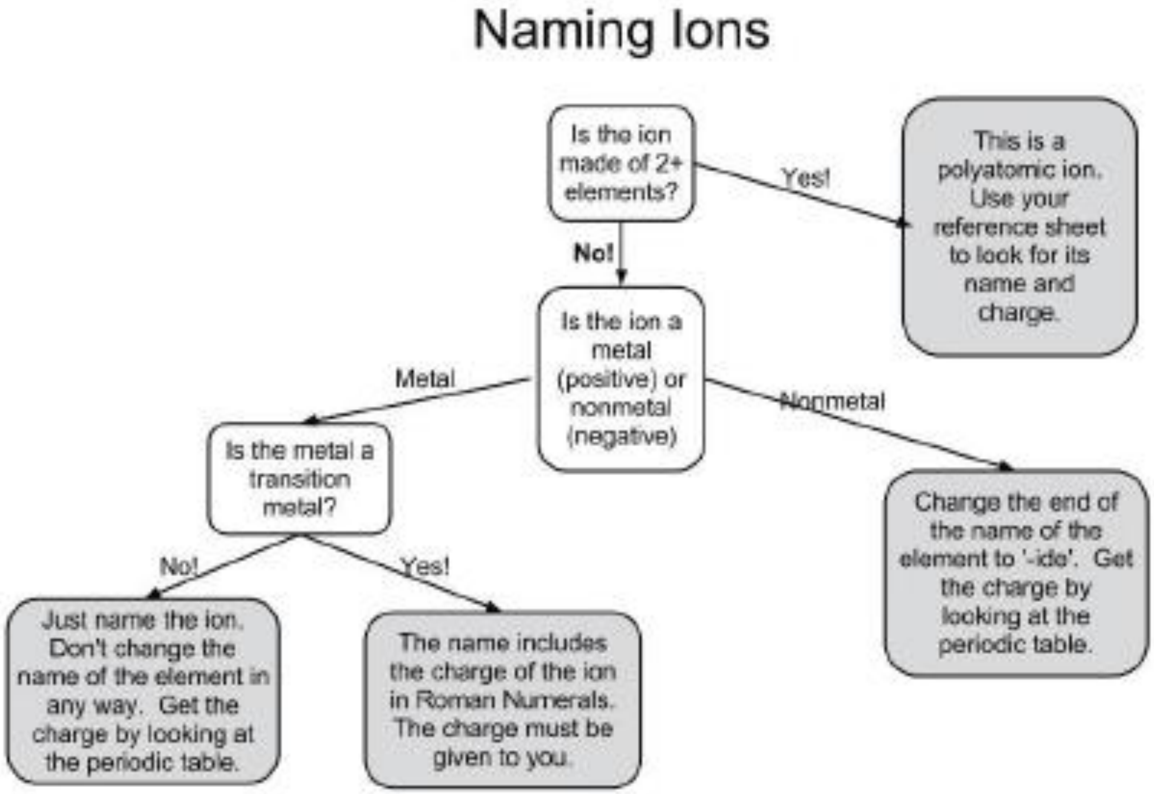
When a pair of elements form more than one type of covalent compound, Greek prefixes are used to indicate how many of each element are in a compound. The more electronegative element is written last and its ending is changed to -ide.

N_2O dinitrogen monoxide

NO nitrogen monoxide

N_2O_3 dinitrogen trioxide

N_2O_5 dinitrogen pentoxide



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Writing Ionic Formulas

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattices containing many ions each of the cation and anion. An ionic formula, like NaCl, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Sodium sulfide, another ionic compound, has the formula Na2S. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions.

To write the formula for an ionic compound:

1) Write the symbol and charge of the cation (first word)

a) If the element is in group 1, 2, Al with a consistent charge, you can get the charge using your periodic table.

b) If the metal is a transition metal with a variable charge, the charge will be given to you in Roman numerals.

2) Write the symbol and charge of the anion (second word).

a) Look at your polyatomic ion chart first. If your anion is a polyatomic ion, write the ion in parentheses.

b) If the anion is not on the polyatomic chart, it is a nonmetal anion from your periodic table. You can get its charge using your table.

3) Write the correct subscripts so that the total charge of the compound will be zero.

4) Write the final formula. Leave out all charges and all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses.

Nuclear Reactivity and Radioactivity

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ${}^{1}{}_{1}H$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$${}_{Z}{}^{A}X$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, ${}_{6}^{14}C$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^{6} meters, 30,000 times larger).

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

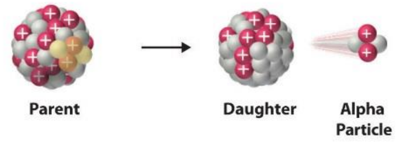
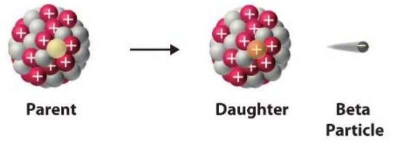
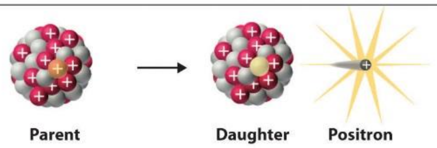
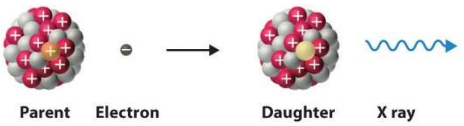
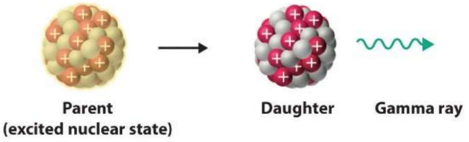
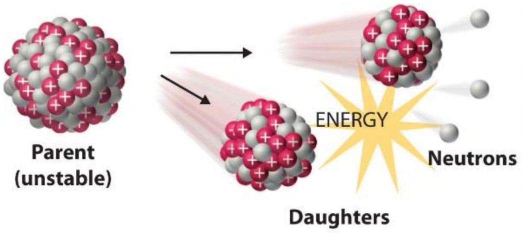
If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}_{8}^{17}O$ is a product of the nuclear reaction of ${}_{7}^{14}N$ and ${}_{2}^{4}He$ if we knew that a proton, ${}_{1}^{1}H$, was one of the two products.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed.

In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	${}^{4}_{2}\alpha$	${}^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}X' + {}^{4}_{2}\alpha$	
Beta decay	${}^{0}_{-1}\beta$	${}^{A}_{Z}X \longrightarrow {}_{Z+1}^{A}X' + {}^{0}_{-1}\beta$	
Positron emission	${}^{0}_{+1}\beta$	${}^{A}_{Z}X \longrightarrow {}_{Z-1}^{A}X' + {}^{0}_{+1}\beta$	
Electron capture	X rays	${}^{A}_{Z}X + {}^{0}_{-1}e \longrightarrow {}_{Z-1}^{A}X' + \text{X ray}$	
Gamma emission	${}^{0}_{0}\gamma$	${}^{A}_{Z}X^{*} \xrightarrow{\text{Relaxation}} {}^{A}_{Z}X' + {}^{0}_{0}\gamma$	
Spontaneous fission	Neutrons	${}^{A+B+C}_{Z+Y}X \longrightarrow {}^{A}_{Z}X' + {}^{B}_{Y}X' + C{}^{1}_{0}n$	

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Alpha Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$A_{Z}X \text{ parent} \rightarrow {}^{A-4}_{Z-2}X' \text{ daughter} + {}^{4}_{2}\alpha \text{ alpha particle}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$$^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus, the nuclear equation is balanced.

Beta β Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$^{1}_{0}\text{n} \rightarrow {}^{1}_{1}\text{p} + {}^{0}_{-1}\beta$$

The general reaction for beta decay is therefore

$$^{A}_{Z}\text{Xparent} \rightarrow {}^{A}_{Z+1}\text{X}'\text{daughter} + {}^{0}_{-1}\beta\text{beta}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus, beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron β+ Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$$^{1}_{1}\text{p}_{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta_{+}$$

The general reaction for positron emission is therefore

$${}^{A}_{Z}\mathrm{X}_{\text{parent}} \rightarrow {}^{A}_{Z-1}\mathrm{X}'_{\text{daughter}} + {}^{0}_{+1}\beta^{+}_{\text{positron}}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta^{+}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

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Gamma γ Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$${}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th}^{*} + 4/2\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$${}^{234}_{88}\mathrm{Th}^{*} \rightarrow {}^{234}_{88}\mathrm{Th} + {}^{0}_{0}\gamma$$

or more generally,

$${}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Questions

1. What is the mass number of an atom of helium that contains 2 neutrons?
   Solution: (number of protons) = 2

   (number of neutrons) = 2

   Mass number = (number of protons) + (number of neutrons)

   = 2+2 =4

2. How many protons, neutrons, and electrons are in an atom of $^{40}_{19}K$?

   Solution: The number of protons is equal to the atomic number which is 19. For all atoms with no charge, the number of electrons is equal to number of protons which is 19.

   Mass number = no. of protons + no. of neutrons
   No. of neutrons = 40- 19 = 21.

3. How many protons, electrons, and neutrons in an atom of Zinc-65?
   Solution: Atomic Number = No. of Protons = 30
   For all atoms with no charge, no. of electrons = no. of protons = 30
   No. of neutrons = 65-30 = 35

4. What is the atomic number and the mass number of an isotope of lithium containing 3 neutrons. A lithium atom contains 3 protons in its nucleus. What is the atomic number and the mass number of an isotope of lithium containing 4 neutrons. A lithium atom contains 3 protons in its nucleus?
   Solution: Atomic number = (no. of protons) = 3
   (no. of neutrons) = 3
   Mass number = (no. of protons) + (no. of neutrons) = 3+3 = 6
   Atomic number = (no. of protons) = 3
   (no. of neutrons) = 4
   Mass number = (no. of protons) + (no. of neutrons) = 4+3 = 7

5. Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are B-10, which is the isotope of boron with 5 neutrons and a mass of 10 amu. The other 80% of the atoms are B-11, which is the isotope of boron with 6 neutrons and a mass of 11 amu. What is the atomic mass of boron?
   Solution: Boron has two isotopes.

   Atomic mass = (%)mass1 + (%) mass2 + …..

   Isotope1 = 0.20; Isotope2 = 0.80

Atomic mass = 0.20 x 10 + 0.80 x 11 = 10.8 amu.

6. State the de Broglie equation and define all the symbols?
   Solution: The de Broglie equation is an equation to describe the wave properties of matter, specifically, the wave nature of the electron:
   $\lambda = h/mv$,
   where λ= wavelength, h is Planck's constant, m is the mass of the particle moving at a velocity v.

7. What is the wavelength of an electron moving at 5.31×10^{6} m/sec?

   Given: mass of electron=9.11×10^{-31} kg h = 6.626×10^{-34} J·s
   Solution: de Broglie's equation is $\lambda = h/mv$,

   $\lambda = 6.626 \times 10^{-34}$ J.s/9.11×10^{-31} kg x 5.31×10^{6} m/sec

   $\lambda = 1.37 \times 10^{-10}$ m = 1.37 Å

8. Calculate the speed v of a neutron having a de Broglie wavelength of 2.6×10^{-10}m? The mass of a neutron is 1.7×10^{-27}kg.
   Solution: $2.6 \times 10^{-10} = 6.63 \times 10^{-34}/m \times v$
   $v = 6.63 \times 10^{-34}/1.7 \times 10^{-27} \times 2.6 \times 10^{-10} = 1.5 \times 10^{3}$ ms-1

9. The uncertainty in the momentum Δp of a football thrown by Tom Brady during the super bowl traveling at 40m/s is 1×10^{-6} 1 of its momentum. What is its uncertainty in position Δx? Mass=0.40kg
   Solution: p = mv = (0.40kg) x (40 m/s) = 16 kgm/s
   $\Delta p = p(1 \times 10^{-6}) = 16$ kgm/s $(1 \times 10^{-6}) = 16 \times 10^{-6}$ kgm/s
   $\Delta p \Delta x \geq h/4\pi$
   $\Delta x \geq h/4\pi \, \Delta p$
   $\geq 6.626 \times 10^{-34}$ Js/ 4π (16×10^{-6} kgm/s)
   $\geq 3.3 \times 10^{-30}$ m
10. What general organization did Mendeleev use when he constructed his table?
    Solution: Mendeleev organized his table according to chemical behavior. Mendeleev's table listed the elements in order of increasing atomic mass. Then he placed elements underneath other elements with similar chemical behavior.
11. What discovery did Henry Moseley make that changed how we currently recognize the order of the elements on the periodic table?
    Solution: As previously noted, Mendeleev organized elements in order of increasing atomic mass, with some problems in the order of masses. In 1914 Henry Moseley found a relationship between an element's X-ray wavelength and its atomic number, and therefore organized the table by nuclear charge (or atomic number) rather than atomic weight. Thus, Moseley placed argon (atomic number 18) before potassium (atomic number 19) based on their X-ray

wavelengths, despite the fact that argon has a greater atomic weight (39.9) than potassium (39.1). The new order agrees with the chemical properties of these elements since argon is a noble gas and potassium an alkali metal

12. Label each of the following elements as a metal, nonmetal, or metalloid?
    Carbon, Bromine, Oxygen, Plutonium, Potassium, Helium
    Solution: Carbon- nonmetal, Bromine-nonmetal, Oxygen-nonmetal, Plutonium-metal, Potassium-metal
13. The elements mercury and bromine are both liquids at room temperature, but mercury is considered a metal and bromine is considered a non-metal. How can that be? What properties do metals and nonmetals have?
    Solution: Metals are elements that tend to lose electrons and non-metals tend to gain electrons. Bromine gains one electron to form the Br- ion. The metallic property of elements decreases going from left to right on the Periodic Table, with non-metals like bromine being on the right.
    Metals are good conductors of heat and electricity. All metals are solids at room temperature except for mercury. In chemical reactions, metals easily lose electrons to form positive ions.
    Nonmetals are generally brittle, dull, have low melting points, and they are generally poor conductors of head heat and electricity. In chemical reactions, they tend to gain electrons to form negative ions.
    Metalloids have properties of both metals and nonmetals. Metalloids can be shiny or dull. Electricity and heat can travel through metalloids, although not as easily as they can through metals. They are also called semimetals. They are typically semi-conductors.

14. How many valence electrons are present in the following electron configuration: 1s2 2s2 2p6 3s2 3p3 ?
    Solution: No. of valence electrons = 3
15. How many valence electrons are present in the following electron configuration: 1s2 2s2 2p6 3s2 3p6 4s2 3d104p1 ?
    Solution: No. of valence electrons = 1
16. Which of the following elements is in the same family as fluorine? a) silicon b) antimony c) iodine d) arsenic e) None of these.
    Solution: Iodine
17. Elements in a ______________ have similar chemical properties. a) period b) family c) both A and B d) neither A nor B
    Solution Family
18. Which of the following elements would you expect to be most similar to carbon? a) Nitrogen b) Boron c) Silicon
    Solution: Silicon
19. Define electronegativity?
    Solution: Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is most commonly used.

20. Define ionization energy.
    Solution: The ionization energy is qualitatively defined as the minimum amount of energy required to remove the most loosely bound electron, the valence electron, of an isolated gaseous atom to form a cation.
21. Which of the following has a greater radius? (a) As or Sb (b) Ca or K (c) Polonium or Sulfur
    Solution: (a) Sb because it is below As in Group 15. (b) K because it is further to the left on the periodic table. (c) Polonium because it is below Sulfur in Group 16.
22. What does the octet rule state?
    Solution: The **octet rule** is a chemical **rule** of thumb that reflects observation that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electron configuration as a noble gas.
23. Write the formula for aluminum chloride?
    Solution: Cation, aluminum: Al^{3+} (you can find this charge using your periodic table) Anion, chloride: Cl^- (chloride is chlorine as an ion, get its charge from your periodic table) To balance the charges you need $Al_1 \cdot^{(+3)}$ and $Cl_3 \cdot^{(-1)}$ .Giving: The final formula is: $AlCl_3$.
24. What is the name of Na_2O?
    Solution: Split up the formula: Na2 | O
    Name the cation: Na is a group 1 metal with a consistent charge. It does not need Roman numerals. Its name is "sodium"
    Name the anion: O is not polyatomic. When oxygen atoms get a -2 charge, the name changes to end in –ide, so the anion is "oxide" Final answer: sodium oxide
25. Write the name of PbS_2?
    Solution: Split up the formula: Pb | S2
    Name the cation: Pb is a post-transition metal with a variable charge. It needs Roman numerals. To find the charge, consider the charge of the other ion and the number of both ions. The copper must have a charge of +4 to balance out the negatives: $1\cdot(+4)$ to cancel out $2\cdot(-2)$. Its name is "lead (IV)"
    Name the anion: S is not polyatomic. When sulfur atoms get a -2 charge, the name changes to end in –ide, so the anion is "sulfide". Final answer: Lead (IV) sulfide.
26. Write the formula for calcium nitrate?
    Solution: Cation, calcium: Ca^{2+} (you can find this charge using your periodic table)
    Anion, nitrate: $(NO_3)^-$ (this is a polyatomic ion) To balance the charges you need $1\cdot(+2)$ and $2\cdot(-1)$. Giving: The final formula is: $Ca(NO_3)_2$
27. Write a balanced nuclear equation to describe each reaction.

a. the beta decay of ${}^{35}_{16}S$
b. the decay of ${}^{201}_{80}Hg$by electron capture
c. the decay of ${}^{30}_{15}P$ by positron emission

1. Solution: a) We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}X$.

$${}^{35}_{16}S \rightarrow {}^{A}_{Z}X + {}^{0}_{-1}\beta$$

Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$${}^{35}_{16}S \rightarrow {}^{35}_{17}Cl + {}^{0}_{-1}\beta$$

b) We know the identities of both reactants: ${}^{201}_{80}Hg$ and an inner electron, ${}^{0}_{-1}e$. The reaction is as follows:

$${}^{201}_{80}Hg + {}^{0}_{-1}e \rightarrow {}^{A}_{Z}X$$

Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$${}^{201}_{80}Hg + {}^{0}_{-1}e \rightarrow {}^{201}_{79}Au$$

c)As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$${}^{30}_{15}P \rightarrow {}^{A}_{Z}X + {}^{0}_{+1}\beta$$

The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$${}^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{+1}\beta$$

Advanced Questions

1. Copper has two naturally occurring isotopes. 69.15% of copper atoms are Cu-63 and have a mass of 62.93amu. The other 30.85% of copper atoms are Cu-65and have a mass of 64.93amu. What is the atomic mass of copper?
2. Copper has two naturally occurring isotopes. 69.15% of copper atoms are Cu-63 and have a mass of 62.93amu. The other 30.85% of copper atoms are Cu-65and have a mass of 64.93amu. What is the atomic mass of copper?
3. According to Bohr's theory, how can an electron gain or lose energy?
4. Which of the following would have the largest ionization energy? a) Na b) Al c) H d) He
5. Which of the following would have the smallest ionization energy? a) K b) P c) S d) Ca
6. For each pair of elements, choose the element that has the lower electronegativity. 13) Li or N 14) Cl or Na 15) Na or K 16) Mg or F
7. Name the following ions. Cu^{2+}, Co^{2+}, Co^{3+}, Fe^{3+}, NO_3^{-}, OH-, $CO_3^{\ 2-}$

8. What are polyatomic ions?

9. Write the formulas from the names of the following compounds.
Magnesium sulfide, Potassium Carbonate, Aluminum Bromide, Aluminum sulfide, Iron(III) Chloride, Lead(II) Nitrate

10. Write a balanced nuclear equation to describe each reaction.

a. ${}^{11}_{6}C$ by positron emission

b. the beta decay of molybdenum-99

c. the emission of an α particle followed by gamma emission from ${}^{185}_{74}W$

Solutions

Solutions are homogeneous mixtures. The major component is called **solvent**, and the minor components are called **solute**. If both components in a solution are 50%, the term solute can be assigned to either component. When gas or solid material dissolves in a liquid, the gas or solid material is called the solute. When two liquids dissolve in each other, the major component is called the **solvent** and the minor component is called the **solute**.

Solubility

The maximum amount of a substance dissolved in a given volume of solvent is called **solubility**.

A solution that has reached the maximum solubility is called a **saturated solution**. Often, another phase such as gas, liquid, or solid of the solute is present and in contact within the solution. In general, there is no net change in the amount of solute dissolved, but the system is by no means static. In fact, the solute is constantly being dissolved and deposited at an equal rate. Such a phenomenon is called **equilibrium**.

In case another phase is not present, a solution may be **unsaturated or supersaturated**. Yes, due to what can be attributed to a kinetic factor, a solution may stay supersaturated for a long time. When promoted by a seed, a solution may start to precipitate quickly. Sodium acetate has a very high solubility at say 270 K. In fact, it can dissolve in the water of crystallization similar to melting. When cooled, such a solution stays in a **meta-stable state**. When a *seeding* crystal is present or started due to the surface of another medium, the entire solution will solidify. During the crystallization process, heat is evolved, and the solution becomes warm. Thus, such a solution, when properly packaged, has been used as hand warmer packs for skiers.

Solubility Rules

When a substance is mixed with a solvent, there are several possible results. The determining factor for the result is the solubility of the substance, which is defined as the maximum possible concentration of the solute. The solubility rules help determine which substances are soluble, and to what extent.

Depending on the solubility of a solute, there are three possible results: 1) if the solution has less solute than the maximum amount that it is able to dissolve (its solubility), it is a dilute solution; 2) if the amount of solute is exactly the same amount as its solubility, it is saturated; 3) if there is more solute than is able to be dissolved, the excess solute separates from the solution. If this separation process includes crystallization, it forms a precipitate. Precipitation lowers the concentration of the solute to the saturation in order to increase the stability of the solution.

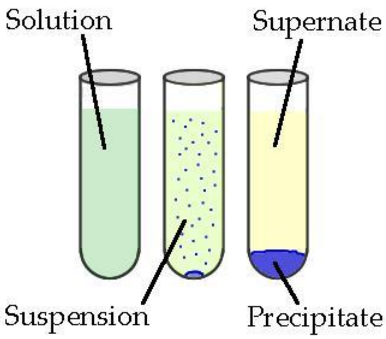
The following are the solubility rules for common ionic solids.

1. Salts containing Group I elements (Li^+, Na^+, K^+, Cs^+, Rb^+) are soluble . There are few exceptions to this rule. Salts containing the ammonium ion (NH_4^+) are also soluble.
2. Salts containing nitrate ion (NO_3^-) are generally soluble.
3. Salts containing Cl^-, Br^-, or I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)^{2+}$. Thus, AgCl, $PbBr_2$, and Hg_2Cl_2 are insoluble.
4. Most silver salts are insoluble. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually all others are insoluble.
5. Most sulfate salts are soluble. Important exceptions to this rule include $CaSO_4$, $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.
6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.
7. Most sulfides of transition metals are highly insoluble, including CdS, FeS, ZnS, and Ag_2S. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
8. Carbonates are frequently insoluble. Group II carbonates ($CaCO_3$, $SrCO_3$, and $BaCO_3$) are insoluble, as are $FeCO_3$ and $PbCO_3$.
9. Chromates are frequently insoluble. Examples include $PbCrO_4$ and $BaCrO_4$.
10. Phosphates such as $Ca_3(PO_4)_2$ and Ag_3PO_4 are frequently insoluble.
11. Fluorides such as BaF_2, MgF_2, and PbF_2 are frequently insoluble.

Precipitation Reaction

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution and allows industries to form chemicals by extracting components from these reactions.

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.



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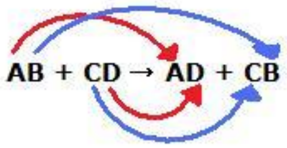
The use of solubility rules requires an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as "switching partners"; that is, the two reactants each "lose" their partner and form a bond with a different partner:



Introduction to Chemistry by Tracy Poulsen

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

$$CdSO_4(aq)+K_2S(aq)\rightarrow CdS(s)+K_2SO_4(aq)$$

Both reactants are aqueous, and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Electrolytes

Substances that give ions when dissolved in water are called **electrolytes**. They can be divided into acids, bases, and salts, because they all give ions when dissolved in water. These solutions conduct electricity due to the mobility of the positive and negative ions, which are called **cations** and **anions** respectively. **Strong electrolytes** completely ionize when dissolved, and no neutral molecules are formed in solution.

For example, NaCl, HNO_3, $HClO_3$, $CaCl_2$ etc. are strong electrolytes. An ionization can be represented by

$$NaCl(s)\rightarrow Na+(aq)+Cl-(aq)$$

Since NaCl is an **ionic solid** (s), which consists of cations Na+ and anions Cl−, no molecules of NaCl are present in NaCl solid or NaCl solution. The ionization is said to be complete. The solute is one hundred percent (100%) ionized. Some other ionic solids are $CaCl_2$, NH_4Cl, KBr, $CuSO_4$, $NaCH_3COO$ (sodiumacetate), $CaCO_3$, and $NaHCO_3$(baking soda).

Small fractions of **weak electrolytes'** molecules ionize when dissolve in water. Some neutral molecules are present in their solutions. For example, NH4OH (ammonia), H2CO3H(carbonic acid), CH_3COOH (acetic acid), and most organic acids and bases are weak electrolytes. The following ionization is not complete,

$$H_2CO_3(aq) \rightleftharpoons H+(aq)+HCO^{-3}$$

In a solution, H_2CO_3 molecules are present. The fraction (often expressed as a %) that undergoes ionization depends on the concentration of the solution.

On the other hand, ionization can be viewed as an equilibrium established for the above reaction, for which the **equilibrium constant** is defined as

$$K=[H+][HCO^{-3}]/[H_2CO_3]$$

where we use [ ] to mean the concentration of the species in the [ ]. For carbonic acid, $K = 4.2x10^{-7}$.

The ionization or **autoionization** of pure water can be represented by the ionization equation

$$H_2O \rightleftharpoons H++OH-$$

and the equilibrium constant is

$$K=[H+][OH-]/[H_2O]$$

For pure water, $[H_2O]$is a constant (1000/18 = 55.6 M), and we often use the **ion product**, K_w, for water,

$$Kw=K[H_2O]/[H+][OH-]$$

The constant K_w depends on temperature. At 298 K, $K_w = 1x10^{-14}$. If there is no solute in water, the solution has equal concentrations of [H+]and [OH−].

$$[H+] =[OH-]=1\times10^{-7}$$

and

$$pH=-\log[H+]=7$$

Note that only at 298 K is the pH of water = 7. At higher temperatures, the pH is slightly less than 7, and at lower temperatures, the pH is greater than 7.

Questions

1. Is milk a solution or a mixture?

Solution: Milk may appear to be a homogeneous mixture to the unaided eye, but the tiny oil and protein droplets in the system make milk appear as white. Actually, milk is a **colloid.**

2. Red brass consists of 90% copper and 10% zinc, whereas bronze consists of 90% copper and 10% tin. What is or are the solvent(s) in these alloys?

Solution: Copper

3. Is $FeCO_3$ soluble?

Solution: According to Rule #5, carbonates tend to be insoluble. Therefore, *$FeCO_3$ is likely to form a precipitate.*

4. Does ClO_4^- tend to form a precipitate?

Solution: This is perchlorate, which according to Rule #2 is likely to be soluble. Therefore, *it will not form a precipitate.*

5. Which of these substances is likely to form a precipitate?

a) $CaSO_4$ b) table salt c) AgBr

Solution: a) $CaSO_4$, although sulfates tend to be soluble, Rule #5 indicates that calcium sulfate is an important exception to this rule.

For b), Rule #1 indicates that table salt (NaCl) is soluble because it is a salt of an alkali metal.

c) is an example of two rules contradicting each other. Rule #4 states that bromides are usually soluble, but Rule #3 states that salts of silver are insoluble. Because Rule #3 precedes Rule #4, the compound is insoluble and will form a precipitate.

6. Complete the double replacement reaction and then reduce it to the net ionic equation.

$$CoCl_2(aq)+Na_2SO_4(aq)\rightarrow$$

Solution: The predicted products of this reaction are $CoSO^4$ and NaCl. From the solubility rules, $CoSO^4$ is soluble because rule 4 states that sulfates ($SO2^{-4}$) are soluble. Similarly, we find that NaCl is soluble based on rules 1 and 3. After balancing, the resulting equation is as follows:

$$CoCl_2(aq)+Na_2SO_4(aq)\rightarrow CoSO_4(aq)+2NaCl(aq)$$

Separate the species into their ionic forms, as they would exist in an aqueous solution. Balance the charge and the atoms. Cancel out all spectator ions (those that appear as ions on both sides of the equation.):

$\cancel{\text{Co}}^{2-}$ (*aq*) + $\cancel{\text{2Cl}}^{-}$(*aq*) + $\cancel{\text{2Na}}^{+}$ (*aq*) + $\cancel{\text{SO}_4}^{2-}$(*aq*) → $\cancel{\text{Co}}^{2-}$ (*aq*) + $\cancel{\text{SO}_4}^{2-}$(*aq*) + $\cancel{\text{2Na}}^{+}$ (*aq*) + $\cancel{\text{2Cl}}^{-}$(*aq*)

No precipitation reaction

This particular example is important because all of the reactants and the products are aqueous, meaning they cancel out of the net ionic equation. There is no solid precipitate formed; therefore, no precipitation reaction occurs.

Advanced Questions

1. The solubility of salt is 35.7 g per 100 mL of water at 298 K. What is the percentage of salt in a saturated solution?

2. Which of the following are solid solutions?

a. ice from salt water at 272 K
b. solid from copper and zinc melt
c. solid calcium carbonate from reaction of carbon dioxide and calcium oxide
d. ice crystals from cold and moist air
e. 18 K gold

3. Predict if a precipitate will form as a result of this reaction:

$$2NaOH + K_2CrO_4 \rightarrow KOH + Na_2CrO_4$$

4. Predict whether a precipitate will form as a result of this reaction:

$$2AgNO_3 + Na_2S \rightarrow Ag_2S + 2NaNO_3$$

5. Write the net ionic equation for the potentially double displacement reactions. Make sure to include the states of matter and balance the equations.

a) $Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow$
b) $Al_2(SO_4)_3(aq) + BaCl_2(aq) \rightarrow Al_2(SO_4)_3(aq) + BaCl_2(aq) \rightarrow$
c) $HI(aq) + Zn(NO_3)_2(aq) \rightarrow HI(aq) + Zn(NO_3)_2(aq) \rightarrow$
d) $CaCl_2(aq) + Na_3PO_4(aq) \rightarrow CaCl_2(aq) + Na_3PO_4(aq) \rightarrow$
e) $Pb(NO_3)_2(aq) + K_2SO_4(aq) \rightarrow$

Gases

1.Gases and Kinetic Theory

The Kinetic Molecular Theory allows us to explain the existence of the three phases of matter: solid, liquid, and gas. In addition, it helps explain the physical characteristics of each phase and how phases change from one to another. The Kinetic Molecular Theory is essential for the explanations of gas pressure, compressibility, diffusion, and mixing. Our explanations for reaction rates and equilibrium also rest on the concepts of the Kinetic Molecular Theory. Gases are tremendously compressible, can exert massive pressures, expand nearly instantaneously into a vacuum, and fill every container they are placed in regardless of size. All of these properties of gases are due to their molecular arrangement.

1.1 Volume of Gases

In dealing with gases, we lose the meaning of the word “full.” A glass of water may be 1/4 full or 1/2 full or full, but a container containing a gaseous substance is always full. The same amount of gas will fill a quart jar, or a gallon jug, a barrel, or a house. The gas molecules separate farther from each other and spread out uniformly until they fill whatever container they are in. Gases can be compressed to small fractions of their original volume and expand to fill virtually any volume. If gas molecules are pushed together to the point that they touch, the substance would then be in the liquid form. One method of converting a gas to a liquid is to cool it and another method is to compress it. The two most common ways of expressing volume are using mL and L. You will need to be able to convert between these two units. The relationship is as follows: 1000 mL = 1 L

1.2 Pressure of Gases

The constant random motion of the gas molecules causes them to collide with each other and with the walls of their container. These collisions of gas molecules with their surroundings exert a pressure on the surroundings. Pressure is defined as the force exerted divided by the area over which the force is exerted.

There are three two units of pressure commonly used in chemistry. Pressure is commonly measured on a device called a monometer, similar to the barometer which a meteorologist uses. Pressures in monometers are typically recorded in units of millimeters of mercury, abbreviated mmHg.

chemistry has many different units for measuring and expressing gas pressure Because instruments for measuring pressure often contain a column of mercury, the most commonly used units for pressure are based on the height of the mercury column that the gas can support. The original unit in chemistry for gas pressure was mmHg (millimeters of mercury). Standard atmospheric pressure at sea level is 760. mmHg. This unit is something of a problem because while it is a pressure unit, it looks a lot like a length unit. Students, in particular, occasionally leave off the Hg and then it definitely appears to be a length unit. To eliminate this problem, the unit was given another name. It Barometer 224 was called the torr in honor of Torricelli. 760 torr is exactly the same as 760 mmHg. For certain work, it became convenient to express gas pressure in terms of multiples of normal atmospheric pressure at sea level and so the unit atmosphere (atm) was introduced. The conversion you need to know between various pressure units are: 1.00 atm = 760. mmHg = 760. Torr

Review Question

1. Convert 425 mmHg to atm?

Solution: The conversion factor is 760. mmHg = 1.00 atm

425 mmHg x 1 atm/760 mmHg = 0.559 atm

1.3 Gas Temperature and Kinetic Energy

Kinetic energy is the energy of motion and therefore, all moving objects have kinetic energy. The mathematical formula for calculating the kinetic energy of an object is KE=1/2 mv^2, where m is the mass and v is the velocity of the object or particle. This physics formula applies to all objects in exactly the same way whether we are talking about the moon moving in its orbit, a baseball flying toward home plate, or a gas molecule banging around in a bottle. All of these objects have kinetic energy and their kinetic energies can all be calculated with the same formula.

When you measure the temperature of a group of molecules, what you are actually measuring is their average kinetic energy. They are the same thing but expressed in different units. The formula for this relationship is KEave=3/2RT where R is the gas constant and T is the absolute temperature, measured in Kelvin. When a substance is heated, the average kinetic energy of the molecules is increased. Since the mass of the molecules cannot be increased by heating, it is clear that the velocity of the molecules is increasing.

Remember, the motion of molecules is related to their temperature. If you think of the average kinetic energy of a group of molecules and temperature measured in degrees Kelvin, the relationship is a direct proportion. That means that if the temperature, in Kelvin, is doubled the kinetic energy of the particles is also doubled. It is absolutely vital that you keep in mind that the mathematical relationship between the temperature and the average kinetic energy of molecules only exists when the temperature is expressed in the Kelvin scale. In order for the direct proportion to exist, the molecules must have zero kinetic energy when the temperature is zero. The temperature at which molecular motion stops is 0 K (-273 ˚C). It is surely apparent to you that molecules do NOT have zero kinetic energy at 0 ˚C. Balloons and automobile tires do not go flat when the outside temperature reaches 0 ˚C. If temperature is measured in Kelvin degrees, then the average kinetic energy of a substance at 100 K is exactly double the average kinetic energy of a substance at 50 K

Kelvin temperature: The absolute temperature scale where 0 K is the theoretical absence of all thermal energy (no molecular motion).

Kinetic energy: Kinetic energy is the energy a body possesses due to its motion, KE=1/2mv^2.

2.Gas Laws

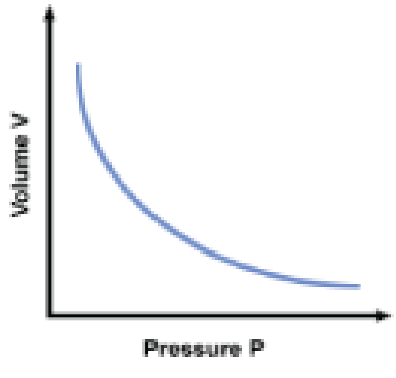
Gases are often characterized by their volume, temperature, and pressure. These characteristics, however, are not independent of each other. Gas pressure is dependent on the force exerted by the molecular collisions and the area over which the force is exerted. The force exerted by the molecular collisions is dependent on the absolute temperature and so forth. The relationships between these characteristics can be determined both experimentally and logically from their mathematical definitions. The gas laws are mathematical relationships that exist for gases between the volume, pressure, temperature, and quantity of gas present. They were determined experimentally over a period of 100 years. They are logically derivable from our present-day definitions of pressure, volume, and temperature.

2.1 Boyles' Law: Pressure vs Volume

The relationship between the pressure and volume of a gas was first determined experimentally by an Irish chemist named Robert Boyle (1627-1691). The relationship between the pressure and volume of a gas is commonly referred to as Boyle's Law.

You may have noticed that when you try to squeeze a balloon, the resistance to squeezing is greater as the balloon becomes smaller. That is, the pressure inside the balloon becomes greater when the volume is reduced.

In the picture on the right, the volume of the gas is 4.0 L and the pressure exerted by the gas is 2.0 atm. If the piston is pushed down to decrease the volume of the gas to 2.0 L, the pressure of the gas is found to increase to 4.0 atm. The piston can be moved up and down to positions for several different volumes and the pressure of the gas read at each of the volumes. We might note from casual observation of the data that doubling volume is associated with the pressure being reduced to half and if we move the piston to cause the pressure to double, the volume is halved. The data show that the relationship is an inverse relationship, meaning that as volume increases the pressure decreases. The opposite is also true.



The relationship between volume and pressure is an inverse relationship.

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Boyle's Law can be summarized in the following equation:

$$P_1V_1 = P_2V_2$$

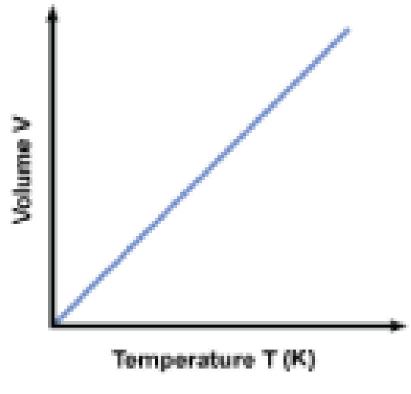
Where: P_1=the initial pressure V_1=the initial volume P_2=the final pressure V_2=the final volume. For this equation, the units used for pressure are unimportant, as long as both pressures have the same unit (either mmHg or atm) and each volume has the same unit (either mL or L).

2.2 Charles's Law: Temperature and Volume

The relationship between the volume and temperature of a gas was investigated by a French physicist, Jacques Charles (1746-1823). (As a piece of trivia, Charles was also the first person to fill a large balloon with hydrogen gas and take a solo balloon flight.) The relationship between the volume and temperature of a gas is often referred to as Charles's Law.

This relationship is a direction relationship. If the temperature, in Kelvin, doubles, so does the volume. This relationship would also be expected when we recognize that we are increasing the total force of molecular collisions with the walls by raising the temperature and the only way to keep the pressure from increasing is to increase the area over which that larger force is exerted. This mathematical relationship is known as a direct proportionality. When one variable is increased, the other variable also increases by exactly the same factor. An equation to show how these values are related is given by:

$$V_1/V_2 = T_1/T_2$$



Volume and temperature (in K) are directly related.

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This relationship is ONLY true if the temperature is measured in Kelvin. However, the units of volume are irrelevant, as long as the two volumes are measured in the same units.

2.3 Gay-Lussac's Law: Temperature and Pressure

The relationship between temperature and pressure was investigated by the French chemist, Joseph Gay-Lussac (1778-1850).

After a series of temperatures and pressures have been measured, a data table like the others can be produced. Temperature and pressure are also directly related, meaning that if the temperature, in Kelvin, doubles, so does the pressure. This relationship is also logical since by increasing temperature, we are increasing the force of molecular collision and keeping the area over which, the force is exerted constant requires that the pressure increases.

$$\mathbf{P_1/P_2 = T_1/T_2}$$

2.4 Standard Temperature and Pressure

Chemists have found it useful to have a standard temperature and pressure with which to express gas volume. The standard conditions of temperature and pressure (STP) were chosen to be 0 C (273 K) and 1.00 atm (760 mmHg).

2.5 The Combined Gas Law

Boyle's Law shows how the volume of a gas changes when its pressure is changed (temperature held constant) and Charles's Law shows how the volume of a gas changes when the temperature is changed (pressure held constant). Is there a formula we can use to calculate the change in volume of a gas if both pressure and temperature change? The answer is "yes", we can use a formula that combines Boyle's Law and Charles's Law. This equation is most commonly written in the from shown below and is known as the Combined Gas Law.

$$\mathbf{P_1V_1/T_1 = P_2V_2/T_2}$$

Another interesting point about the combined gas law is that all the other gas laws (Charles', Gay-Lussac's, and Boyle's) can be derived from this equation. To do this, you simply cancel out the variable that was held constant in the reaction. For example, temperature is constant in Boyle's Law. If you cancel the temperature's out of Boyle's Law, you get:

$$\mathbf{P_1V_1 = P_2V_2}$$

Review Question

A sample of gas has a volume of 400. liters when its temperature is 20. C and its pressure is 300. mmHg. What volume will the gas occupy at STP?

Solution: Step 1: Identify the given information & check units. Temperature must be in Kelvin. Volume units must match, and pressure units must match. P_1=300 mmHg V_1=400 L ,T_1=293 K (remember, ALL temperatures must be in Kelvin) P_2=760 mmHg (standard pressure) V_2=?

T_2=273 K Step 2: Solve the combined gas law for the unknown variable.

$$\mathbf{P_1V_1/T_1 = P_2V_2/T_2}$$

(300 mmHg) (400L)/293 K = (760 mmHg) V_2/273 K

V_2=147 L

2.6 Avogadro's Law

Avogadro's Law was known as Avogadro's hypothesis for the first century of its existence. Since Avogadro's hypothesis can now be demonstrated mathematically, it was decided that it should be called a law instead of a hypothesis. Avogadro's Law postulates that equal volumes of gas under the same conditions of temperature and pressure contain the same number of molecules.

It means that all gases under the same conditions behave the same way: all of these equations work equally well for carbon dioxide, helium, or a mixture of gases. Furthermore, we will be able to use this relationship again when we deal with balanced reactions. The volume of two gases at the same temperature and pressure are directly related to the number of molecules (or moles) of the gases involved in a chemical reaction.

2.7 Daltons Law of Partial Pressure

Dalton's Law of Partial Pressure states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressure of individual gases. The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of each individual gas, also known as Dalton' Law of Partial Pressures.

$$\mathbf{P_{total} = P_1+P_2+P_3+\ldots..P_n}$$

Boyle's law and the Ideal Gas Law tell us the total pressure of a mixture depends on the number of moles of gas, and not the kinds of molecules; Dalton's Law allows us to calculate the total pressure in a system from each gas individual contribution.

Review Question

A 2.0 L container is pressurized with 0.25 atm of oxygen gas and 0.60 atm of nitrogen gas. What is the total pressure inside the container?

Solution: Ptotal = $P_{O2} + P_{N2}$ = 0.25+ 0.60 atm = 0.85 atm

2.8 Ideal Gas Law

The individual gas laws and the combined gas law all require that the quantity of gas remain constant. The Universal Gas Law (also sometimes called the Ideal Gas Law) allows us to make calculations on different quantities of gas as well.

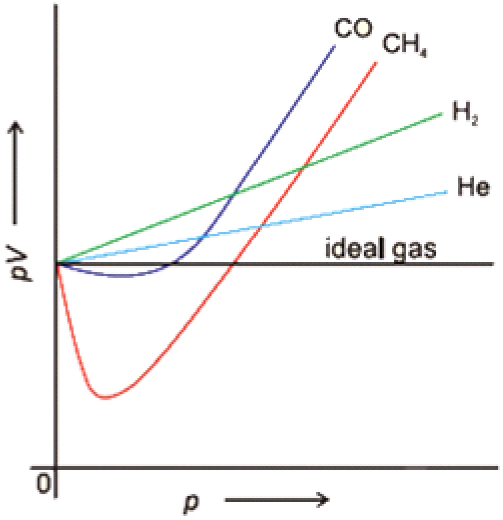
We have considered four laws that describe the behavior of gases: Boyle's Law, Charles's Law, Avogadro's Law, and Gay-Lussac's Law. These three relationships, which show how the volume of a gas depends on pressure, temperature, and the number of moles of gas, can be combined to form the ideal gas law:

$$PV = nRT$$

Where each variable and its units are: P=pressure (atm) V=volume (L) n=number of moles of gas (mol) T=temperature (K) R=ideal gas constant = 0.0821 atmL/molK

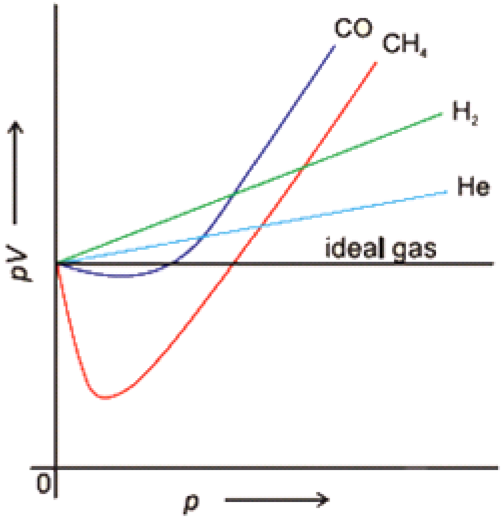
3. Deviations from Ideal Gas Law

To understand the deviations from ideal behavior, let us first see how the real gases show deviations from Boyle's law. According to Boyle's law, PV = constant, at constant temperature. Hence, at constant temperature, plot of PV vs. P has to be a straight line which is parallel to x-axis. However, the real gases do not show such a behavior as shown below.



Oxtoby, Gillis and Campion. Principles of Modern Chemistry. 6th Edition. California: Thomson Brooks/Cole. 2008.

From the plots, we observe that for gases like H_2 and He, PV increases continuously with increase of pressure whereas for gases like CO, CH_4 etc. PV first decreases with increase of pressure and reaches a minimum value and then increases continuously with increase of pressure. Similarly, if we plot experimental values of pressure versus volume at constant temperature (that is, for real gas) and theoretically calculated values from Boyle's law (that is, for ideal gas) the two curves do not coincide as shown below.



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From above graphs, we observe that at higher pressure, volume which is observed is higher than that of calculated volume. At lower pressures, the observed and the calculated volumes approach each other.

Alternatively, upto what extent a real gas deviates from ideal behaviour can be studied using the terms of a quantity 'Z' which is known as the **compressibility factor**, and defined as:

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

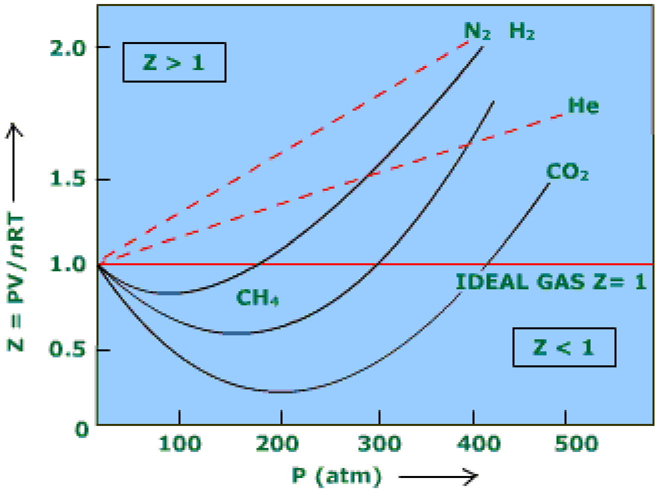
(i) For an ideal gas, as PV = nRT, Z = 1

(ii) For a real gas, as PV ≠ nRT, Z ≠ 1.

Hence, two cases arise:
(a) When Z < 1, (**For Example:** for CH_4, CO_2 etc.) The gas is said to show negative deviation. Therefore, gas will show more compression than expected from ideal behavior. This is caused by predominance of attractive forces among the molecules of these gases.
(b) When Z > 1, the gas is said to show positive deviation. This implies that the gas will show less

compression than expected from ideal behavior. This is caused by the predominance of the strong repulsive forces among the molecules. Greater the departure in the value of Z from unity, greater are the deviations from ideal behavior.

At the same temperature and pressure, the extent of deviation depends upon the nature of the gas, as shown in figure no. 3 Thus, at intermediate pressures, CO_2 shows much larger negative deviation than H_2 or N_2.



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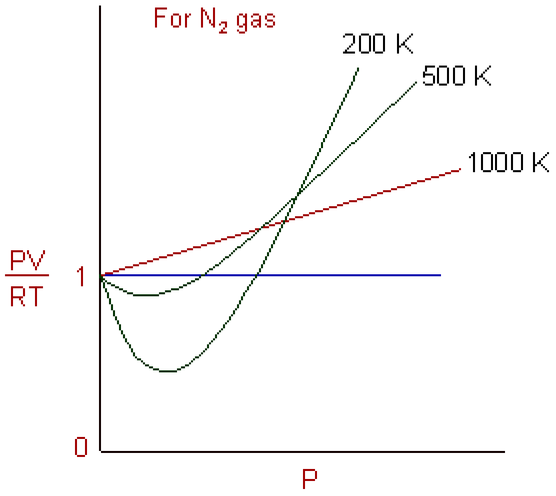
For the same gas, at a particular pressure, the extent of deviation depends upon temperature, as shown.



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Plots in above figure show that as the temperature increases, the minimum in the curve shifts upwards. Ultimately, a temperature is reached at which the value of Z remains close to 1 over an appreciable range of pressure. **For Example**, in case of N2, at 323 K, the value of Z remains close to 1 upto nearly 100 atmospheres.

The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.
Further, from the plots shown in figure no. 3 and 4, it may be seen that at ordinary pressures (1-10 atm), Z is very near to 1, that is, the deviations from ideal behaviour are so small that the ideal gas laws can be applied.

Significance of Compressibility Factor

The significance of compressibility factor can be further understood from the following derivation:

$$Z = \frac{PV_{real}}{nRT} \quad \text{... (equation no. 1)}$$

If the gas shows ideal behavior,

$$\frac{PV_{ideal}}{nRT} \text{ that is, } V_{ideal} = \frac{nRT}{P} \qquad \text{... (equation no. 2)}$$

Substituting this value of nRT/P in eqn. (1), we get

$$Z = \frac{V_{real}}{V_{ideal}}$$

Thus, compressibility factor is defined as the ratio of the actual molar volume of the gas (**For Example:** experimentally observed value) to the calculated molar volume (considering it as an ideal gas) at the same temperature and pressure.

3.1 Causes of deviation from Ideal Behavior

As stated above, the real gases obey ideal gas equation (PV = nRT) only if the pressure is low the temperature is high. However, if the pressure is high or the temperature is low, the real gases show marked deviations from ideal behavior. The reasons for such a behavior shown by the real gases have been found to be as follows:

The derivation of the gas laws (and hence of the ideal gas equation) is based upon the Kinetic Theory of Gases which in turn is based upon certain assumptions. Thus, there must be something wrong with certain assumptions. A careful study shows that at high pressure or low temperature, two assumptions of Kinetic Theory of Gases are fails:

- When compared to the total volume of the gas, the volume occupied by the gas molecules is negligible.
- The forces of attraction or repulsion between the gas molecules are negligible.

The above two assumptions are true only if the pressure is low or the temperature is high so that the distance between the molecules is large. However, if the pressure is high or the temperature is low, the gas molecules come close together. Hence, under these conditions:

- The forces of attraction or repulsion between the molecules.
- The volume occupied by the gas may be so small that the volume occupied by the molecules may not be negligible.

3.2 Van der Waals Equation

To explain the behavior of real gases, J.D. van der Waals, in 1873, modified the ideal gas equation applying appropriate corrections so as to take into account

- The volume of the gas molecules
- The forces of attraction between the gas molecules

He put forward the modified equation, known after him as van der Waals equation. The equation is

For 1 mole of the gas,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

For n moles of the gas,

$$\left(P\ +\frac{an^2}{V^2}\right)(V-nb)=nRT$$

Where ‘a’ and ‘b’ van der Waals constant. There values depend upon nature of gas.

3.2.1 Significance of Van der Waals Constant

- **Van der Waals constant ‘a’:** Its value is a measure of the magnitude of the attractive forces among the molecules of the gas. There would be large intermolecular forces of attraction if the value ‘a’, is large.
- **Van der Waals constant ‘b’:** Its value is a measure of the effective size of the gas molecules. Its value is equal to four times the actual volume of the gas molecules. It is called **Excluded Volume** or **Co-volume**.

- **Units of ‘a’:** As $p = am^2/V^2$, therefore $a = (p \times V^2) / n^2 = \text{atm } L^2 \text{ mol}^{-2}$ or $\text{bar dm}^6 \text{ mol}^{-2}$
- **Units of ‘b’:** As volume correction $v = n\,b$, therefore $b = v/n = \text{Lmol}^{-1}$ or $\text{dm}^3\text{mol}^{-1}$

Behavior of Real Gases

- **At Very Low Pressures**, V is very large. Hence, the correction term a/V^2 is so small that it can be neglected, Similarly, the correction term ‘b’ can also be neglected in comparison to V. Thus, van der Waals equation reduces to the form PV = RT. This explains why at very low pressures; the real gases behave like ideal gases.
- **At Moderate Pressures**, V decreases. Hence, a/V^2 increases and cannot be neglected. However, is still large enough in comparison to ‘b’ so that ‘b’ can be neglected. Thus, van der Waals equation becomes

$$\left(P + \frac{a}{V^2}\right)V = RT \ \text{ or } \ RV + \frac{a}{V} = RT \ \text{ or } PV = \ RT - \frac{a}{V}$$

$$\text{OR} \quad \frac{PV}{RT} = 1 - \frac{q}{RTV}$$

$$\text{OR} \quad Z = 1 - \frac{a}{RTV}$$

Thus, compressibility factor is less than 1. So, at when at constant temperature, pressure is increased, V decreases so that the factor a/RTV increases. This explains why initially a dip in the plot of Z versus P is observed.

- **At High Pressures**, V is so small that ‘b’ cannot be neglected in comparison to V. The factor a/V^2 is no doubt large but as P is very high, a/V^2 can be neglected in comparison to P. Thus, van der Waals equation reduces to the form:

$$P\,(V-b)=RT\ \text{ or } PV=RT+Pb$$

$$\text{OR}\qquad \frac{PV}{RT}=1+\frac{Pb}{RT}$$

$$\text{OR}\qquad Z=1+\frac{Pb}{RT}$$

Thus, compressibility factor is greater than 1. As P is increased (at constant T), the factor Pb/RT increases. This explains why after minima in the curves, the compressibility factor increases continuously with pressure.

- **At High Temperatures:** V is very large (at a given pressure) so that both the correction factors (a/V^2 and b) become negligible as in case (i). Hence, at high temperature, real gases behave like ideal gas.

4.Kinetic Molecular Theory of Gases

To better understand the molecular origins of the ideal gas law, the basics of the Kinetic Molecular Theory of Gases (KMT) should be understood. This model is used to describe the behavior of gases. More specifically, it is used to explain macroscopic properties of a gas, such as pressure and temperature, in terms of its microscopic components, such as atoms. Like the ideal gas law, this theory was developed in reference to ideal gases, although it can be applied reasonably well to real gases.

In order to apply the kinetic model of gases, five assumptions are made:

1. Gases are made up of particles with no defined volume but with a defined mass. In other words, their volume is miniscule compared to the distance between themselves and other molecules.
2. Gas particles undergo no intermolecular attractions or repulsions. This assumption implies that the particles possess no potential energy and thus their total energy is simply equal to their kinetic energies.
3. Gas particles are in continuous, random motion.
4. Collisions between gas particles are completely elastic. In other words, there is no net loss or gain of kinetic energy when particles collide.
5. The average kinetic energy is the same for all gases at a given temperature, regardless of the identity of the gas. Furthermore, this kinetic energy is proportional to the absolute temperature of the gas.

4.1 Temperature and KMT

The last assumption can be written in equation form as:

$$KE=1/2mv^2=3/2k_BT$$

where

- k_B is Boltzmann's constant ($k_B = 1.381\times10^{-23}$ m^2 kg s^{-2} K^{-1}) and
- T is the absolution temperature (in Kelvin)

This equation says that the speed of gas particles is related to their absolute temperature. In other words, as their temperature increases, their speed increases, and finally their total energy increases as well. However, it is impossible to define the speed of any *one* gas particle. As such, the speeds of gases are defined in terms of their root-mean-square speed.

4.2 Pressure and KMT

The macroscopic phenomena of pressure can be explained in terms of the kinetic molecular theory of gases. Assume the case in which a gas molecule (represented by a sphere) is in a box, length *L (*Figure 1). Through using the assumptions laid out above, and considering the sphere is only moving in the x-direction, we can examine the instance of the sphere colliding elastically with one of the walls of the box.

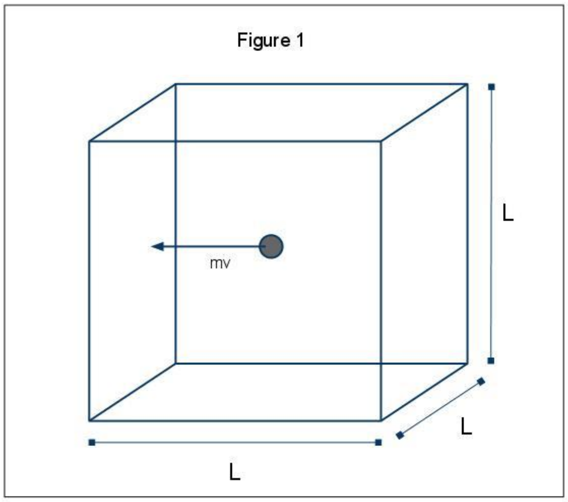


Figure 1 Oxtoby, Gillis and Campion. Principles of Modern Chemistry. 6th Edition. California: Thomson Brooks/Cole. 2008.

The momentum of this collision is given by $p=mv$, in this case $p=mv_x$, since we are only considering the x dimension. The total momentum change for this collision is then given by

$$mv_x-m(-v_x)=2mv_x$$

Given that the amount of time it takes between collisions of the molecule with the wall is L/v_x we can give the frequency of collisions of the molecule against a given wall of the box per unit time as $v_x/2L$. One can now solve for the change in momentum per unit of time:

$$(2mv_x)(v_x/2L)=mv^2_x/L$$

Solving for momentum per unit of time gives the force exerted by an object ($F=ma=p/time$). With the expression that $F=mv_x^2/L$ one can now solve for the pressure exerted by the molecular collision, where area is given as the area of one wall of the box, $A=L^2$:

$$P=F/A$$

$$P=mv^2_x/[L(L2)$$

The expression can now be written in terms of the pressure associated with collisions from N number of molecules:

$$P=Nmv^2_x/V$$

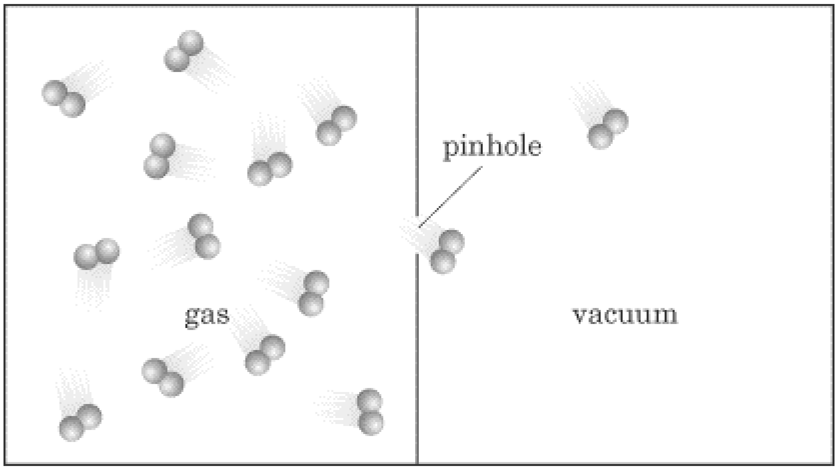
This expression can now be adjusted to account for movement in the x, y and z directions by using mean-square velocity for three dimensions and a large value of N. The expression now is written as:

$$P=Nmv^2/3V$$

This expression now gives pressure, a macroscopic quality, in terms of atomic motion. The significance of the above relationship is that pressure is proportional to the mean-square velocity of molecules in a given container. Therefore, as molecular velocity increases so does the pressure exerted on the container.

5.Graham's Law of Diffusion and Effusion

- Graham's law states that the rates of effusion of two gases are inversely proportional to the square roots of their molar masses at the same temperature and pressure:
- $$\frac{Rate\ of\ effusion\ of\ gas\ 1}{Rate\ of\ effusion\ of\ gas\ 2} = \sqrt{\frac{FW_2}{FW_1}}$$
- **Effusion** is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber, as shown in the figure below.

- 

- The **rate of effusion** measures the **speed** at which the gas travels through the tiny hole into a vacuum. Another term to remember for the test is diffusion. **Diffusion** is the term used to describe the spread of a gas throughout a space or throughout a second substance.

Questions

1. If molecules of H_2, O_2, and N_2 are all placed in the same container at the same temperature, which molecules will have the greatest velocity?

   Solution: Because they are at the same temperature, they will have the same energy. However, lighter particles must move faster to have the same kinetic energy. We must, therefore, look at their masses. Use your periodic table:

   Mass of H_2 = 2(1.008 g/mol) = 2.016 g/mol

   Mass of O_2 = 2(16.00 g/mol) = 32.00 g/mol

   Mass of N_2 = 2(14.01 g/mol) = 28.02 g/mol

   Because H_2 is the lightest, it must have the greatest velocity to have the same energy (the same temperature) as the other gases.

2. A sample of gas occupies 1.00 under standard conditions. What temperature would be required for this sample of gas to occupy 1.50 L and exert a pressure of 2.00 atm?

Solution: Step 1: Identify the given information & check units. Temperature must be in Kelvin. Volume units must match, and pressure units must match.

P_1=1.00 atm (standard pressure)

V_1=1.00 L

T_1=273 K (standard temperature, remember, ALL temperatures must be in Kelvin)

P_2=2.00 atm

V_2=1.50 L T_2=?

Step 2: Solve the combined gas law for the unknown variable.

(1.00 atm)(1.00 L)/273 K = (2.00 atm)(1.50 L)/T_2

T_2=819 K

3. 8.278 x 10^{-4} mol of an unidentified gaseous substance effuses through a tiny hole in 86.9 s Under identical conditions, 1.740 x 10^{-4} mol of argon gas takes 81.3 s to effuse.

a) What is the molar mass of the unidentified substance (in g/mol)?

b)What is the molecular formula of the substance?

c) Under identical conditions, how many moles of ethene (C_2H_4) gas would effuse in 91.0 s?

Solution: Calculate the rates of effusion:

unknown ⇒ 8.278 x 10^{-4} mol / 86.9 s = 9.525892 x 10^{-6} mol/s

argon ⇒ 1.740 x 10^{-4} / 81.3 s = 2.140221 x 10^{-6} mol/s

The above is a rate, a number of moles of gas effuse through a pinhole in a unit amount of time.

b) Use Graham's Law:

$r_1 / r_2 = MM_2 / MM_1$

Assign the unknown molar mass to be MM_2. I will cancel the exponent on the rates, since they are both 10^{-6}.

2.140221 / 9.525892 = MM_2 / 39.948

Solve:

0.05047844 = MM_2 / 39.948

MM_2 = 2.0165 g/mol (the answer to part a)

The gas is hydrogen, H_2 (the answer to part b; no other gas weighs 2).

c) The solution to part c:

the molecular weight of ethene is 28.0536 g/mol

let us use the data from argon

let the rate for ethene be r_1

$r_1 / r_2 = MM_2 / MM_1$

$x / 2.140221 \times 10^{-6} = 39.948 / 28.0536$

$x / 2.140221 \times 10^{-6} = 1.19331$

$x = 2.55395 \times 10^{-6}$ mol/s

2.55395×10^{-6} mol/s times 91.0 s = 2.324×10^{-4} mol

4. A sample of gas has a volume of 500.mL under a pressure of 500.mmHg. What will be the new volume of the gas if the pressure is reduced to 300.mmHg at constant temperature?

Solution: Step 1: Identify the given information & check units. Temperature must be in Kelvin. Volume units must match, and pressure units must match.

P_1=500. mmHg

V_1=500. mL

P_2=300. mmHg

V_2=?

Temperature is constant, so it cancels out of the combined gas law.

Step 2: Solve the combined gas law for the unknown variable. (Or, recognize this is Boyle's Law and start with that equation.)

$P_1V_1=P_2V_2$

(500 mmHg)(500 mL)=(300 mg Hg)V_2

V_2 = 833 mL

5. A sample of nitrogen gas, N2, has a volume of 5.56 L at 0 C and 1.50 atm pressure. How many moles of nitrogen are present in this sample?

Solution: Step 1: Identify the given information & check units. Temperature must be in Kelvin. Volume and pressure units must match R.

P=1.50 atm V=5.56 L n=? T=273 K (must be in K)

Step 2: Solve the ideal gas law for the unknown variable.

PV = nRT

(1.50atm)(5.56L) = n(0.0821 atm.L/mol.K)(273 K)

n = 0.372 mol

6. 2.00 mol of methane gas, CH_4, are placed in a rigid 500. mL container and heated to 100. C. What pressure will be exerted by the methane?

Solution: P = ?

V= 500 mL = 0.500 L

n = 2.00 mol

T = 100 °C = 373 K

PV = nRT

P(0.500L) = (2.00 mol)(0.0821 atm.L/mol. K)(373K)

P = 122 atm

7. Which of the following is not an assumption of the kinetic theory of gases?
   a) Collisions between gas particles are elastic
   b) The kinetic energy of gas particles are different for all gases at a certain temperature
   c) Gas particles do not experience attractions/repulsions to other particles
   d) The volumes of the particles of a gas are negligible
   e) Gas particles are in random, continuous motion

Solution: The answer is (a).

8. Why does a higher temperature result in a faster reaction?

Solution: It increases the number of effective molecular collisions.

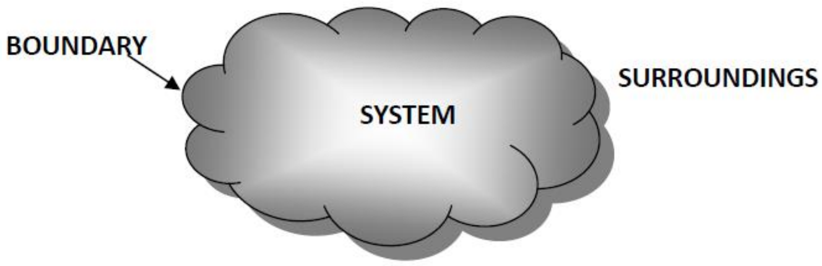
Advanced Questions

1. What is the density (in g/L) of a gas with a molar mass of 60 g/mol at 0.75 atm and 27 °C?
2. A mixture of helium and neon gases is held in a container at 1.2 atmospheres. If the mixture contains twice as many helium atoms as neon atoms, what is the partial pressure of helium?
3. 4 moles of nitrogen gas are confined to a 6.0 L vessel at 177 °C and 12.0 atm. If the vessel is allowed to expand isothermally to 36.0 L, what would be the final pressure?
4. A 9.0 L volume of chlorine gas is heated from 27 °C to 127 °C at constant pressure. What is the final volume?
5. The temperature of a sample of an ideal gas in a sealed 5.0 L container is raised from 27 °C to 77 °C. If the initial pressure of the gas was 3.0 atm, what is the final pressure?
6. A 9.0 L volume of chlorine gas is heated from 27 °C to 127 °C at constant pressure. What is the final volume?
7. It takes 354 seconds for 1.00 mL of Xe to effuse through a small hole. Under the same conditions, how long will it take for 1.00 mL of nitrogen to effuse?
8. It takes 354 seconds for 1.00 mL of Xe to effuse through a small hole. Under the same conditions, how long will it take for 1.00 mL of nitrogen to effuse?
9. The reaction $A+B \rightarrow C$ obeys the rate law $r=-k[A]^{1/2}[B]^{2/3}$.What are the units of the rate constant, k?

Thermodynamics

Closed and Open System

A system is defined as a quantity of matter or a region in space chosen for study. The mass or region outside the system is called the surroundings.



Basic Concepts of Thermodynamics by M.Bahrami

Boundary: the real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.

Closed system or control mass: consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.

Basic Concepts of Thermodynamics by M.Bahrami

Open system or control volume: is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.

Basic Concepts of Thermodynamics by M.Bahrami

Isolated system: A closed system that does not communicate with the surroundings by any means.
Rigid system: A closed system that communicates with the surroundings by heat only.

Basic Concepts of Thermodynamics by M.Bahrami

Adiabatic system: A closed or open system that does not exchange energy with the surroundings by heat.

Properties of a System

Any characteristic of a system is called a *property*. In classical thermodynamics, the substance is assumed to be a *continuum*, homogenous matter with no microscopic holes. This assumption holds as long as the volumes, and length scales are large with respect to the intermolecular spacing.

Intensive properties: are those that are independent of the size (mass) of a system, such as temperature, pressure, and density. They are not additive.

Extensive properties: values that are dependent on size of the system such as mass, volume, and total energy U. They are additive.

Thermodynamic Process

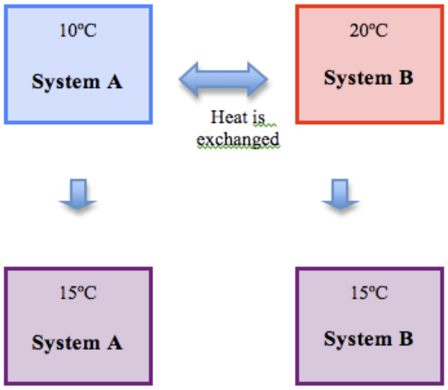
A system undergoes a thermodynamic process when there is some sort of energetic change within the system, generally associated with changes in pressure, volume, internal energy (i.e. temperature), or any sort of heat transfer.

There are several specific types of thermodynamic processes that have special properties:

- Adiabatic process - a process with no heat transfer into or out of the system.
- Isochoric process - a process with no change in volume, in which case the system does no work.
- Isobaric process - a process with no change in pressure.
- Isothermal process - a process with no change in temperature.

Laws of Thermodynamics

- *Zeroeth Law of Thermodynamics* - The Zeroth Law of Thermodynamics states that if two systems are in thermodynamic equilibrium with a third system, the two original systems are in thermal equilibrium with each other. Basically, if system A is in thermal equilibrium with system C and system B is also in thermal equilibrium with system C, system A and system B are in thermal equilibrium with each other.



Physical Chemistry by Atkins &Paula

- *First Law of Thermodynamics* - The change in the energy of a system is the amount of energy added to the system minus the energy spent doing work.

- *Second Law of Thermodynamics* - It is impossible for a process to have as its sole result the transfer of heat from a cooler body to a hotter one.
- *Third Law of Thermodynamics* - It is impossible to reduce any system to absolute zero in a finite series of operations. This means that a perfectly efficient heat engine cannot be created.

Calorimetry

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction.

Heat Capacity

The heat capacity, C, of an object is the ratio of change in heat (energy change, ΔQ, where the Greek symbol Delta, Δ, denotes a change in the quantity) to change in temperature (ΔT).

$C = \Delta Q / \Delta T$

The heat capacity of a substance indicates the ease with which a substance heats up. A good thermal conductor would have a low heat capacity, indicating that a small amount of energy causes a large temperature change. A good thermal insulator would have a large heat capacity, indicating that much energy transfer is needed for a temperature change.

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the *same* sign. If (Δ*T)* and (*q)* are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (Cp) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of Cp are thus J/(mol•°C).

Internal Energy and Enthalpy

The internal energy is the grand total energy of the system with a value that depends on the temperature and, in general, the pressure. It is an extensive property.
A change in internal energy is written

$$\Delta U = w + q$$

where *w* is the energy transferred to the system by doing work and *q* the energy transferred to it by heating.
The internal energy is an accounting device, like a country's gold reserves for monitoring transactions with the outside world (the surroundings) using either currency (heat or work).

In general, when a change takes place in a system open to the atmosphere, the volume of the system changes. For example, the thermal decomposition of 1.0 mol $CaCO_3$(s) at 1 bar results in an increase in volume of 89 L at 800°C on account of the carbon dioxide gas produced. To create this large volume for the carbon dioxide to occupy, the surrounding atmosphere must be pushed back. That is, the system must perform expansion work. Therefore, although a certain quantity of heat may be supplied to bring about the endothermic decomposition, the increase in internal energy of the system is not equal to the energy supplied as heat because some energy has been used to do work of expansion.

The **enthalpy**, *H*, of a system is defined as

$$H = U + pV$$

A change in enthalpy (the only quantity we can measure in practice) arises from a change in the internal energy and a change in the product pV:

$$\Delta H = \Delta U + \Delta(pV)$$

where $\Delta(pV) = p_f V_f - p_i V_i$.

If the change takes place at constant pressure p, the second term on the right simplifies to

$$\Delta(pV) = \Delta pV_f - \Delta pV_i = \Delta p(V_f - V_i) = p\Delta V$$

and we can write

$$\textit{At constant pressure: } \Delta H = \Delta U + p\Delta V$$

Order, Disorder, and Entropy

We now have a better understanding of the energy due to microscopic motion of molecules. This motion is called internal energy. However, there are still features of such motion that our discussions thus far have not considered. For example, it is our common experience that hot objects and cold objects sitting in a room will eventually come to a common temperature, that water runs downhill, not uphill, that electric batteries wear out and do not recharge themselves, and that dye dropped into water spreads throughout the water but does not separate from the water once it has mixed with it. None of these everyday occurrences violates the first law of thermodynamics, but neither does the first law explain them. It is obvious that in our consideration of energy on a microscopic level, we have missed something. To see what we have missed, it is necessary to introduce the concept of order and disorder and a method physicist have devised for measuring order and disorder – a concept called entropy.

Entropy

Once set up, the checkerboard stays set up until we decide to change it, a situation which we can refer to as static disorder. As we have found, most physical systems change with time, a situation we can refer to as dynamic disorder. Because a system changes with time, the large ratio of the number of disordered situations relative to an ordered situation can be used to predict how the system will change with time. Based on the number of disordered situations compared to the number of ordered situations, it is extremely unlikely that a system will go by itself from a disordered to an ordered condition. If the system is ordered, it is likely to become disordered. It is useful to define a quantity S called entropy, which is a measure of the degree of disorder in a system. The entropy of a system increases as the disorder of the system increases. We now focus on the molecular motion of a system, which gives rise to the internal energy of this system. Adding heat to this system increases the disorder because the heat increases the randomness of the molecular motion. So, the entropy of the system increases. The effect of adding heat to a system increases the molecular motion, and this results in more disorder of the system. The effect of adding heat to a cold system, one that has small molecular motion, produces more disorder than would happen if one added the same amount of heat to the system if it were at a higher temperature. Why? It is because the hot system already has more molecular motion than the cold system, so the percentage change in motion is not as great.

If the change in entropy only comes about because the internal energy of the system changes, the result is called a reversible process. In this case, the change in entropy ΔS is given by following equation

Change in entropy = change in the heat of the system/temperature

$$\Delta S = \Delta Q/T$$

where ΔS = change in entropy of a reversible process (joules/Kelvin or calories/Kelvin)

ΔQ = change in the heat of the system (joules or calories)

T = temperature (Kelvin)

Equilibrium and the Second Law of Thermodynamics

As mentioned above, an increase in entropy is associated with an increase in randomness in the system. Thermal energy consists of the random motion of the molecules of which matter is composed. Recall that the random motion of molecules in solids is less vigorous than in liquids; the motion of molecules in liquids is in turn less vigorous than in gases. When thermal energy is added to solid ice, it melts from ice at zero degrees Celsius into liquid water that is also at zero degrees Celsius. When the liquid water is further heated it can evaporate, becoming a gas, water vapor. The more thermal energy a molecule has, the faster it moves and the more disordered the motion of a collection of such molecules becomes. In other words, as the thermal energy of the system of molecules increases (solid to liquid to gas), there is a progression from less disordered to more disordered behavior, that is, from a lower entropy state to a higher entropy state. Recall that the random motion of gas molecules is an example of dynamic disorder. Dynamic arrangements depend on time, but static arrangements do not. We are now in a position to summarize this discussion into a law that applies to situations for which, although the first law of thermodynamics is valid, the first law gives an incomplete observation of what is happening. This law is known as the second law of thermodynamics and can be stated in many forms (which may or may not appear at first glance to be equivalent).

One form, suggested by the very large number of disordered arrangements is: The entropy of a physical system left to itself will increase or, if the system is already at its maximum entropy, the entropy will remain the same.

Gibbs Free Energy

The great American theoretician J.W. Gibbs (1839–1903), who laid the foundations of chemical thermodynamics toward the end of the nineteenth century, discovered how to combine the two calculations into one.
The total entropy change that accompanies a process is

$$\Delta S_{\text{total}} = \Delta S + \Delta S_{\text{sur}}$$

where ΔS is the entropy change for the system; for a spontaneous change, $\Delta S\text{total} > 0$.
If the process occurs at constant pressure and temperature, we can use the following equation.

At constant temperature and pressure: $\boldsymbol{\Delta S\text{total} = \Delta S \_ \Delta H/T}$

The great advantage of this formula is that it expresses the total entropy change of the system and its surroundings in terms of properties of the system alone. The only restriction is to changes at constant pressure and temperature.
Now we take a very important step. First, we introduce the **Gibbs energy**, G, which is defined as

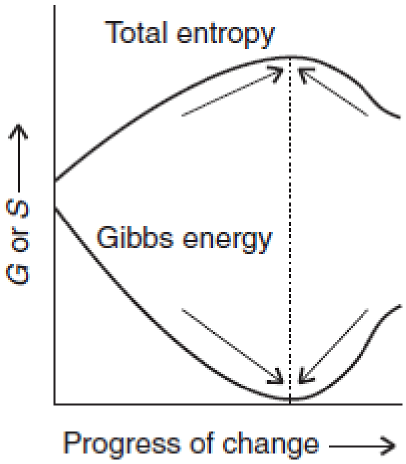
$$G= \Delta H - T\Delta S$$

Because H, T, and S are state functions, G is a state function too. A change in Gibbs energy, ΔG, at constant temperature arises from changes in enthalpy and entropy and is

At constant temperature: $\boldsymbol{\Delta G= \Delta H - T\Delta S}$

By comparing the above equations,

At constant temperature and pressure: $\boldsymbol{\Delta G= - T\Delta S_{\text{total}}}$



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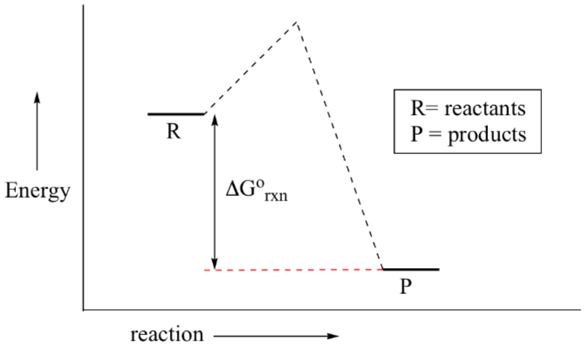
Spontaneity and Gibbs Free Energy

The difference in sign between ΔG and ΔS_{total} implies that the condition for a process being spontaneous changes from $\Delta S\text{total} > 0$ in terms of the total entropy (which is universally true) to $\Delta G < 0$ in terms of the Gibbs energy (for processes occurring at constant temperature and pressure). That is, *in a spontaneous change at constant temperature and pressure, the Gibbs energy decreases.*
It may seem more natural to think of a system as falling to a lower value of some property. However, it must never be forgotten that to say that a system tends to fall toward lower Gibbs energy is only a modified way of saying that a system and its surroundings jointly tend toward a greater total entropy. The *only* criterion of spontaneous change is the total entropy of the system and its surroundings; the

Gibbs energy merely contrives a way of expressing that total change in terms of the properties of the system alone and is valid only for processes that occur at constant temperature and pressure.

Reaction Energy Diagrams

You may recall from general chemistry that it is often convenient to describe chemical reactions with energy diagrams. In an energy diagram, the vertical axis represents the overall energy of the reactants, while the horizontal axis is the 'reaction coordinate', tracing from left to right the progress of the reaction from starting compounds to final products. The energy diagram for a typical one-step reaction might look like this:



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Despite its apparent simplicity, this energy diagram conveys some very important ideas about the thermodynamics and kinetics of the reaction. Recall that when we talk about the **thermodynamics** of a reaction, we are concerned with the difference in energy between reactants and products, and whether a reaction is 'downhill' (exergonic, energy releasing) or 'uphill (endergonic, energy absorbing). When we talk about **kinetics**, on the other hand, we are concerned with the *rate* of the reaction, regardless of whether it is uphill or downhill thermodynamically.

First, let's review what this energy diagram tells us about the thermodynamics of the reaction illustrated by the energy diagram above. The energy level of the products is *lower* than that of the reactants. This tells us that the change in standard Gibbs Free Energy for the reaction (ΔG°_{rnx}) is negative. In other words, the reaction is exergonic, or 'downhill'. Recall that the ΔG°_{rnx} term encapsulates both ΔH°_{rnx}, the change in enthalpy (heat) and ΔS°_{rnx} , the change in entropy (disorder):

$$\mathbf{\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}}$$

where T is the absolute temperature in Kelvin.

For chemical processes where the entropy change is small (~0), the enthalpy change is essentially the same as the change in Gibbs Free Energy. Energy diagrams for these processes will often plot the enthalpy (H) instead of Free Energy for simplicity.

The standard Gibbs Free Energy change for a reaction can be related to the reaction's equilibrium constant by a simple equation:

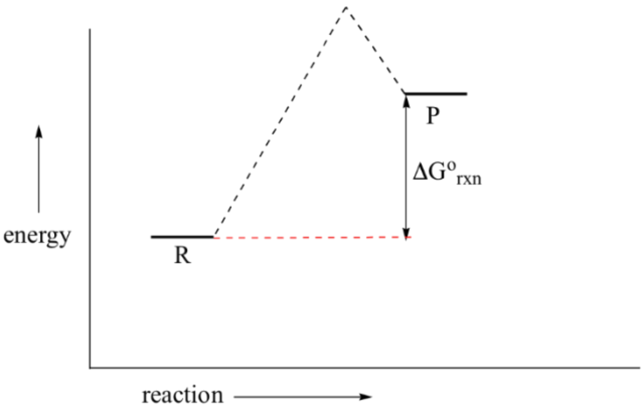
$$\Delta G^{\circ} = -RT\ln Keq$$

where:

- K_{eq} = [product] / [reactant] at equilibrium
- $R = 8.314\ J\times K^{-1}\times mol^{-1}$ *or* $1.987\ cal\times K^{-1}\times mol^{-1}$
- T = temperature in Kelvin (K)

If you do the math, you see that a negative value for ΔG°_{rnx} (an exergonic reaction) corresponds - as it should by intuition - to K_{eq} being greater than 1, an equilibrium constant which favors product formation.

In a hypothetical endergonic (energy-absorbing) reaction the products would have a higher energy than reactants and thus ΔG°_{rnx} would be positive and K_{eq} would be less than 1, favoring reactants.



Physical Chemistry by Atkins &Paula

Thermochemistry

The heat that flows across the boundaries of a system undergoing a change is a fundamental property that characterizes the process. It is easily measured, and if the process is a chemical reaction carried out at constant pressure, it can also be predicted from the difference between the enthalpies of the products and reactants. The quantitative study and measurement of heat and enthalpy changes is known as ***thermochemistry***.

In order to define the thermochemical properties of a process, it is first necessary to write a thermochemical equation. To take a very simple example, here is the complete thermochemical equation for the vaporization of water at its normal boiling point:

$$H_2O(l,\ 373\ K,\ 1\ atm) \rightarrow H_2O(g,\ 373\ K,\ 1\ atm) \qquad \Delta H = 40.7\ kJ\ mol^{-1}$$

The quantity 40.7 is known as enthalpy of vaporization.

Hess's Law

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

Enthalpies of Formation

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔHf) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The corresponding relationship is

$$\text{elements} \rightarrow \text{compound} \quad \Delta Hrxn = \Delta Hf$$

For example, consider the combustion of carbon:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta Hrxn = \Delta Hf[CO_2(g)]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta Hf > 0$ if heat is absorbed.

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

The standard enthalpy of formation of any element in its standard state is zero by definition.

Questions

1. Which type of thermodynamic is an ocean, an aquarium, a pizza delivery bag and a greenhouse?

Solution: Ocean: Open system, aquarium: Closed system, a pizza delivery bag: isolated, Greenhouse: Closed.

2. A closed system contains 2g of ice. Another 2g of ice are added to the system. What is the final mass of the system?

Solution: The final mass will be 2g. Remember, a closed system does not allow for mass exchange.

3. An isolated system has an initial temperature of 30ºC. It is then placed on top of a Bunsen burner for an hour. What is the final temperature?

Solution: The final temperature will be 30ºC. Remember, an isolated system does not allow energy transfer.

4. 1 kg of water at 10º C is added to 10 kg of water at 50º C. What is the temperature of the water when it reaches thermal equilibrium?

Solution: 46.36º C

5. A gas in a system has constant pressure. The surroundings around the system lose 62 J of heat and does 474 J of work onto the system. What is the internal energy of the system?

Solution: To find internal energy, ΔU, we must consider the relationship between the system and the surroundings. Since the First Law of Thermodynamics states that energy is not created nor destroyed we know that anything lost by the surroundings is gained by the system. The surrounding area loses heat and does work onto the system. Therefore, q and w are positive in the equation $\Delta U=q+w$ because the system gains heat and gets work done on itself.

$\Delta U=q+w = 62\ J + 474\ J = 536\ J$

6. A system has constant volume ($\Delta V=0$) and the heat around the system increases by 45 J.

a. What is the sign for heat (q) for the system?
b. What is ΔU equal to?
c. What is the value of internal energy of the system in Joules?

Solution: Since the system has constant volume ($\Delta V=0$) the term $-P\Delta V=0$ and work is equal to zero. Thus, in the equation $\Delta U=q+w$ $w=0$ and $\Delta U=q$. The internal energy is equal to the heat of the system. The surrounding heat increases, so the heat of the system decreases because heat is not created nor destroyed. Therefore, heat is taken away from the system making it exothermic and negative. The value of Internal Energy will be the negative value of the heat absorbed by the surroundings.

a. negative ($q<0$)
b. $\Delta U=q + (-P\Delta V) = q+ 0 = q$
c. $\Delta U = -45J$

7. $2H_{2(g)}+O_{2(g)}\rightarrow 2H_2O_{(g)}$

The enthalpy, ΔH, for this reaction is -241.82 kJ, and the entropy, ΔS, of this reaction is -233.7 J/K. If the temperature is at 25° C, calculate the standard free energy change, ΔG?

Solution: The first step is to convert the temperature to Kelvin, so add 273.15 to 25 and the temperature is at 298.15 K. Next plug ΔH, ΔS, and the temperature into the $\Delta G=\Delta H-T\Delta S$.

$$\Delta G= -241.8\ kJ + (298.15\ K)\ (-233.7\ J/K)$$

$$= -241.8\ kJ + -69.68\ kJ \text{ (Don't forget to convert Joules to Kilojoules)}$$

$$= -311.5\ kJ$$

8. Here is a little more complex reaction:

$2ZnO_{(s)}+2C_{(g)}\rightarrow 2Zn_{(s)}+2CO_{(g)}$

If this reaction occurs at room temperature (25° C) and the enthalpy, ΔH, and standard free energy, ΔG, is given at -957.8 kJ and -935.3 kJ, respectively. Calculate entropy?

Solution: $-935.3\ kJ = -957.8\ kJ + (298.15\ K)\ (\Delta S\Delta S)$

22.47 kJ = (298.15 K) (ΔS) (Add -957.8 kJ to both sides)

0.07538 kJ/K = ΔS (Divide by 298.15 K to both sides)

Multiply the entropy by 1000 to convert the answer to Joules, and the new answer is 75.38 J/K.

9. Predict the entropy changes of the converse of SO2 to SO3: $2\ SO_2\ (g) + O_2\ (g) \rightarrow 2\ SO_3\ (g)$
Solution: Entropy decreases.
10. The specific heat capacity of water is 4.18 joules per gram per degree Celsius. How many joules of heat must be added to one gram of water to increase its temperature by 10 degrees Celsius?

Solution: amount of heat= (mass of substance) x (specific heat capacity) x (change of temperature)

amount of heat=(1gram) (4.18 joules)/ (grams °C) (10°C)

amount of heat=41.8 joules

Advanced Questions

1. What do the first and second laws of thermodynamics have to do with systems?

2. For the following dissociation reaction

$O_2(g) \rightarrow 2O(g)$

under what temperature conditions will it occur spontaneously?

3. The following reaction

$$CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$$

occurs spontaneously under what temperature conditions? The enthalpy of the reaction is -40 kJ.

4. In a calorimeter there is only water at room temperature (25°C). About 1.6 grams of ice are added to the system, and the temperature decreases to 1.2°C. The specific heat of water is 4.186 J/(g °C). What is the quantity of heat of calorimeter and the reaction?

5. From the following data,

$$CH_4+2O_2 \rightarrow CO_2+2H_2O \quad \Delta H^\circ=-890 kJ/mol$$

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta H^\circ=44 kJ/mol \text{ at } 298K$$

Calculate the enthalpy of the reaction

$$CH_4+2O_2(g) \rightarrow CO_2(g)+2H_2O(g) \quad \Delta H^\circ=?$$

Chemical Bonding and Molecular Geometry

Chemical Bond

Chemical bond refers to the forces holding atoms together to form molecules and solids. This force is of electric nature, and the attraction between electrons of one atom to the nucleus of another atom contribute to what is known as **chemical bonds**. Although electrons of one atom repel electrons of another, but the repulsion is relatively small. So is the repulsion between atomic nuclei.

Past on Chemical Bond Concepts

Various concepts or theories have been proposed to explain the formation of compounds. In particular, chemical bonds were proposed to explain why and how one element reacted with another element.

In 1852, E. Frankland proposed the concept of **valence**. He suggested that each element formed compounds with definite amounts of other elements due to a valence connection. Each element has a definite number of valance.

Five years later, F.A. Kekule and others proposed a valence of 4 for carbon. Lines were used to represent valance, and this helped the development of organic chemistry. The structure of benzene was often quoted as an achievement in this development. More than 10 years later, J.H. van't Hoff and le Bel proposed the **tetrahedral arrangement for the four valences around the carbon**. These theories helped chemists to describe many organic compounds. In the meantime, **chemical bonds** were taught to be electric nature. Since electrons have not been discovered as the negative charge carriers, they were thought to be involved in chemical bonds.

Following the discoveries of electrons by J.J. Thomson and R. A. Millikan, G.N. Lewis proposed to use dots to represent **valence electrons**. His dots made the valence electrons visible to chemists, and he has been credited as the originator of modern bonding theory. He published a book, in 1923, called ***Valence and the Structure of Atoms and Molecules.***

X-ray diffractions by crystal allow us to calculate details of bond length and bond angles. Using computers, we are able to generate images of molecules from the data provided by X-ray diffraction studies. These data prompted Linus Pauling to look at ***The Nature of Chemical Bond***, a book that introduced many new concepts such as the **resonance, electronegativity, ionic bond**, and **covalent bond.**

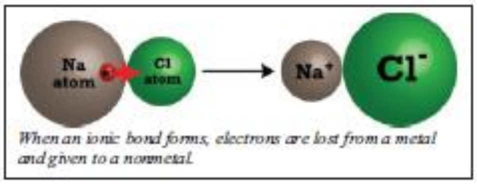
In England, N.V. Sidgwick and H.E. Powell paid their attention to the lone pairs in a molecule. They developed the valence bond theory, the VSEPR (Valence Shell Electron Pair Repulsion)theory.

Types of Bonds

Ionic Bond

Molecular collisions between atoms that tend to lose electrons (metals) and atoms that tend to gain electrons (non-metals) are sometime sufficient to remove electrons from the metal atom and add them to the non-metal atom. This transference of electrons from metals to non-metals forms positive and negative ions, which in turn, attract each other due to opposite charges. The compounds formed by this electrostatic attraction are said to be ionically bonded.

The process of transferring an electron from a sodium atom to a chlorine atom as shown the diagram produces oppositely charged ions which then stick together because of electrostatic attraction. Electrostatic attraction is the attraction between opposite charges. The electrostatic attraction between oppositely charged ions is called an ionic bond. These ions are chemically more stable than the atoms were.



When an ionic bond forms, electrons are lost from a metal and given to a nonmetal.

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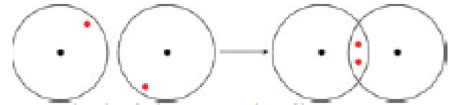
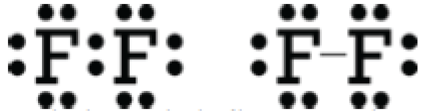
If we had been using sodium and sulfur atoms for the transfer discussion, the process would be only slightly different. Sodium atoms have a single electron in their outermost energy level and therefore, can lose only one electron. Sulfur atoms, however, require two electrons to complete their outer energy level. In such a case, two sodium atoms would be required to collide with one sulfur atom. Each sodium atom would contribute one electron for a total of two electrons and the sulfur atom would take on both electrons. The two Na atoms would become Na+ ions and the sulfur atom would become a S2- ion. Electrostatic attractions would cause all three ions to stick together. The cation forming elements, metals, lose all valence electrons so the electron configuration for the ions formed will have the eight electrons of the previous noble gas. (Those whose electron dot formula matches helium, of course, will have only two.) The anion forming elements, nonmetals, will gain enough electrons so the electron dot formulas of their ions will match those of the following noble gas. In all cases, for the "A" groups elements, the ions will have eight electrons in their electron dot formula. The **octet rule** is an expression of this end result of eight electrons in the outer most energy level. An atom becomes an ion when it gains or loses electrons. The ions that are formed when an atom loses electrons are positively charged because they have more protons in the nucleus than electrons in the electron cloud. Positively charged ions are called **cations.** The ions that are formed when an atom gains electron is negatively charged because they have more electrons in the electron cloud than protons in the nucleus. Negatively charged ions are called **anions.**

Covalent Bond

In covalent bonding, the atoms acquire a stable octet of electrons by sharing electrons. The covalent bonding process produces molecular substances as opposed to the lattice structures of ionic bonding. There are far more covalently bonded substances than ionic substances.



In a covalent bond, electrons are shared by atoms in overlapping orbitals.



We can also show a covalent bond between atoms with an electron dot formula where the shared pair of electrons are the bonding electrons or with the bond represented by a dash.

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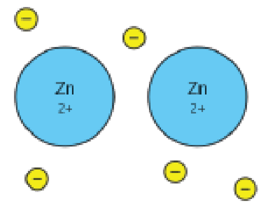
The diatomic hydrogen molecule, H_2, is one of the many molecules that are covalently bonded. Each hydrogen atom has a *1s* electron cloud containing one electron. These *1s* electron clouds overlap and produce a common volume which the two electrons occupy.

Metallic Bond

There is a third type of bond that may be formed between two atoms. In **metallic bonding,** the electrons between neighboring metal atoms are delocalized, meaning that the electrons are not tied to one atoms specifically. The electrons, instead, are gathered in what we call an "electron sea". In an electron sea, the metal nuclei form the basis, and the electrons move around the nuclei. Because of this unique type of bonding structure, metallic bonding accounts for many physical properties of metals, such as strength, malleability (or bendability), ductility, conductivity (allows heat and electricity to go through), and luster(shine).



Metallic Bonding has delocalized electrons, in which the electrons are free to move throughout the metal.

Octet Rule

Recall that the noble gas elements are the least reactive of all the elements on the periodic table – they almost never form any type of compound. Their electron configuration is the most stable of all of the elements, having their *s* and *p* sublevels filled. The noble gases have what is frequently referred to as an "octet", meaning they have eight valence electrons. The other elements are typically more stable if they have an octet, too. Other atoms will gain electrons, lose electrons, or share electrons in order to obtain an octet. The way in which an atom gets an octet determines the type of bond formed. When an atom gains electron, the atom will obtain a negative charge and is now called an **anion**. When an atom loses electrons, the atom will obtain a positive charge and is now called a **cation**. This may feel backwards but remember that electrons themselves have a negative charge. When anions and cations are bonded together, the bond is said to be ionic. Metal atoms will lose electrons to obtain an octet and nonmetals will gain electrons. Therefore, in an ionic bond metals are typically bonded to nonmetals.

Some atoms are capable of obtaining an octet by sharing their valence electrons with another atom. This type of bonding is called a **covalent bond**. Only nonmetals are capable of forming covalent bonds with other nonmetals.

Lattice Energy

The force of attraction between oppositely charged particles is directly proportional to the product of the charges on the two objects (q_1 and q_2) and inversely proportional to the square of the distance between the objects (r^2).

$$F = \frac{q_1 \text{ x } q_2}{r^2}$$

The strength of the bond between the ions of opposite charge in an ionic compound therefore depends on the charges on the ions and the distance between the centers of the ions when they pack to form a crystal.

An estimate of the strength of the bonds in an ionic compound can be obtained by measuring the **lattice energy** of the compound, which is the energy given off when oppositely charged ions in the gas phase come together to form a solid.

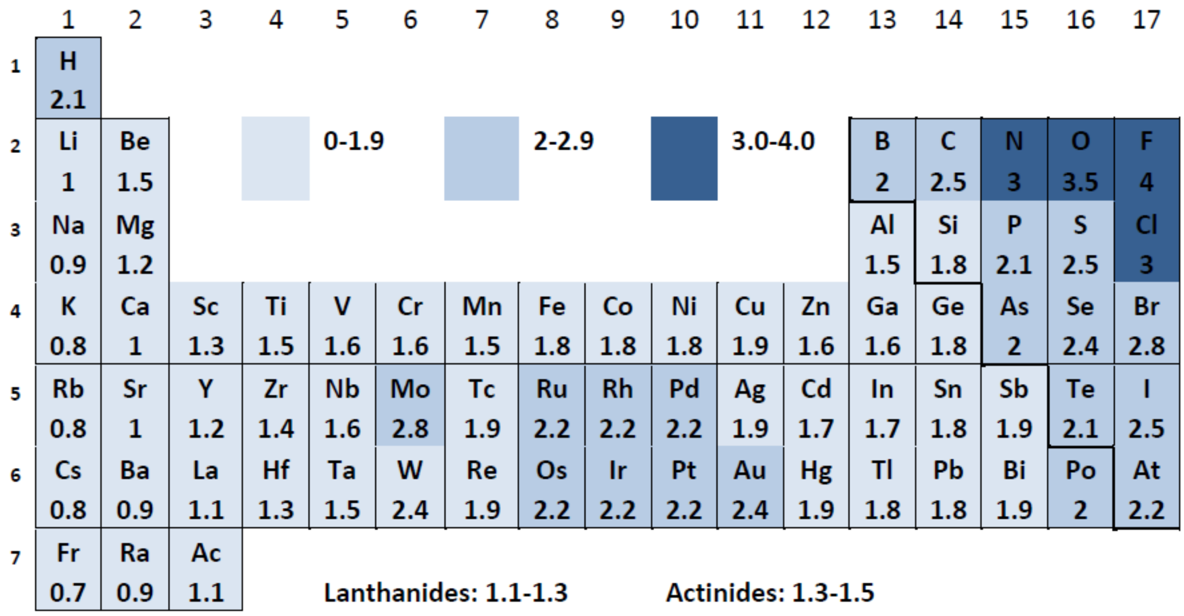
Bond Polarity

Polar and Non-Polar Bonds

In homonuclear diatomic molecules such as H2 or Cl2 electrons are **shared equally** between equal atoms. The result is that the electron distribution in such molecules is symmetrical with the center of the molecule intercepting a mirror plane that is perpendicular to the inter-nuclear axis (perpendicular to the bond). There is an equal amount of chare (electron charge density) distributed on either side of this mirror plane (on either side of the molecule) resulting in a **non-polar covalent bond**.

In heteronuclear molecules such as HCl or HBr the electrons are not shared equally resulting in a polar bond. Recall from earlier that each atom is characterized by an atomic property we called electron affinity, which was the energy change that occurred when an isolated gaseous atom gained an electron. In general atoms with a greater electron affinity attract the shared electron pair more strongly. In molecules, however we do not have isolated gas phase atoms and it is therefore not appropriate to refer to electron affinity. **A measure that describes the ability of an atom in a molecule to attract shared electrons to itself is known as electronegativity.** A widely used scale is the Pauling electronegativity scale.

From the table below, you can see that electronegativity correlates extremely well with electron affinity. It generally decreases from the top to the bottom in a group and increases from the left to the right within a period making fluorine the most electronegative atom.



□ 0-1.9   ▨ 2-2.9   ■ 3.0-4.0

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	H 2.1																
2	Li 1	Be 1.5											B 2	C 2.5	N 3	O 3.5	F 4
3	Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3
4	K 0.8	Ca 1	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2	Se 2.4	Br 2.8
5	Rb 0.8	Sr 1	Y 1.2	Zr 1.4	Nb 1.6	Mo 2.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
6	Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2	At 2.2
7	Fr 0.7	Ra 0.9	Ac 1.1														

Lanthanides: 1.1-1.3   Actinides: 1.3-1.5

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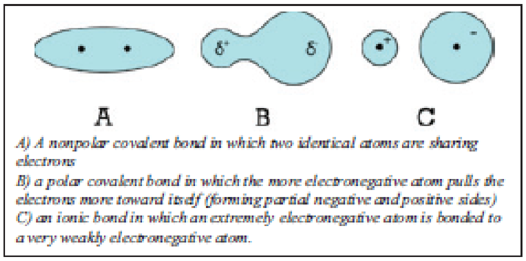
Nonpolar covalent bonds (e.g. H_2) and ionic bonds (e.g. NaCl) represent extremes of types of chemical bonds. Polar covalent bonds have both, covalent and ionic character.

The greater the difference in electronegativity between two atoms that are chemically bound the more polar is the bond and the closer it will be to an ionic bond.



A) A nonpolar covalent bond in which two identical atoms are sharing electrons
B) a polar covalent bond in which the more electronegative atom pulls the electrons more toward itself (forming partial negative and positive sides)
C) an ionic bond in which an extremely electronegative atom is bonded to a very weakly electronegative atom.

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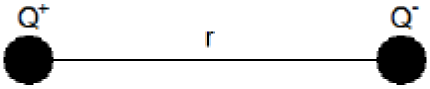
Dipole Moment

We can actually measure how polar a bond is.
When two atoms share electrons unequally a **bond dipole** results. Two equal but opposite charges **Q** that are separated by a distance **r** produce a dipole moment μ which is calculated: $\mu = Q \times r$



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The dipole moment can be measured by introducing molecules between the plates of a capacitor. Without an electric field the molecules orient randomly. When an electric field is applied the polar molecules will align in the field so that the positive ends of the molecules point to the negative plate and vice versa. This weakens the applied electric field and the greater the dipole moment in the molecules the greater the effect.
The unit of the dipole moment is the Debye (D). 1D = 3.34 ×10-30 coulomb × meter (Cm).

Compound	Bond Length (pm)	Δ Electronegativity	Dipole Moment (D)
HF	92	1.9	1.82
HCl	127	0.9	1.08
HBr	141	0.7	0.82
HI	161	0.4	0.44

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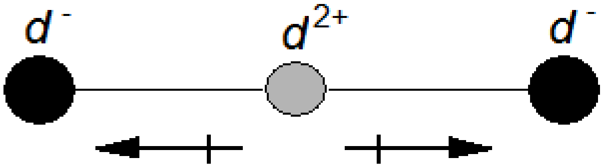
Positive or negative fractional charges also known as partial charges arising from the unequal sharing of bonding electron pairs are indicated as **δ+** and **δ-** above the atom which gives rise to the partial charge.

Polar Molecules

Polarity is of immense importance. It affects a wide range of chemical and physical properties including reactivity, states of matter, vapour pressure, surface tension, solubility, cohesion, viscosity, capillary forces, melting point depression, osmosis and many more.
In diatomic molecules the case is trivial. There is only one bond and thus if the bond is polar the molecule **will be** polar.
In tri or polyatomic molecules, the decision if a molecule is polar or not, does not solely rest on the presence of polar bonds within the molecule but critically depends on the orientation of these polar bonds with respect to each other.
Carbon dioxide for example contains two C=O double bonds which are clearly polar. The shared electron pairs are attracted to the electronegative oxygens more so then to the less electronegative carbon. If one measures the dipole moment of CO_2 one finds though that the molecule is non-polar with a dipole moment of exactly 0 Debye. How can this be? The answer lies in the shape of the molecule. CO_2 is a linear molecule. The two polar C=O bonds are aligned much like two equal teams in a *tug o war.*



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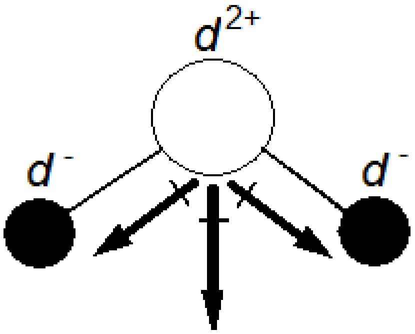
Sulfur dioxide on the other hand is a polar molecule. The molecule is bent with an OSO bond angle of approximately 120°. This means the individual bond dipoles in SO_2 do not cancel as in CO_2 but add up to give resultant dipole moment (**bold** vertical arrow).



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HOW TO DETERMINE MOLECULAR POLARITY (EXCLUDING DIRECTION OF DIPOLE MOMENT

- Molecules that are not totally symmetrical are polar molecules. In a polar molecule, electron density accumulates toward one side of the molecule giving that side a slight negative charge δ-, and the other side a slight positive charge of equal value δ+. Polar molecules are said to possess a dipole moment which means that it has 2 poles (+ and -). A polar molecule is a **dipole**.
- Polarity is due to the polarity of the bonds and the lone pairs on the central atom. One lone pair on the central atom makes the molecule polar. This only works for one lone pair, not 2, 3, 4, etc. If more than one lone pair, determine the polarity from the bonded atoms.

To determine if a molecule is polar (has a dipole moment):

1. Draw an acceptable Lewis dot structure,
2. Predict the electron-pair geometry
3. Determine whether the molecule is totally symmetrical.
4. An analogy for polarity is to imagine that an object is being pulled in directions determined by the electronegativities of the atoms. If the forces are equal, the object will not move (nonpolar).

Criteria for polarity:

- If a molecule is diatomic (2 atoms) and the atoms are different, it is polar.
- A molecule having just one lone pair of electrons is polar.
- If all of the terminal atoms are the same and there are no lone pairs of electrons around the central atom, the molecule is totally symmetrical and nonpolar.
- If the molecule is not symmetrical, it is polar. The terminal atoms are different, and the dipole moments do not cancel each other out. (Pulling moves the object).

Hydrogen Bonding

When a hydrogen atom is bonded to a very electronegative atom, including fluorine, oxygen, or nitrogen, a very polar bond is formed. The electronegative atom obtains a negative partial charge and the hydrogen obtains a positive partial charge. These partial charges are similar to what happens in every polar molecule. However, because of the big difference in electronegativities between these two atoms and the amount of positive charge exposed by the hydrogen, the dipole is much more dramatic. These molecules will be attracted to other molecules which also have partial charges. This attraction for other molecules which also have a hydrogen bonded to a fluorine, nitrogen, or oxygen atom is called a **hydrogen bond**.

Hydrogen Bonds in Water

The most important, most common, and perhaps simplest example of a hydrogen bond is found between water molecules. This interaction between neighboring water molecules is responsible for many of the important properties of water.

Hydrogen bonding strongly affects the crystal structure of ice, helping to create an open hexagonal lattice. The density of ice is less than water at the same temperature; thus, the solid phase of water floats on the liquid, unlike most other substances in which the solid form would sink in the liquid form.

Water also has a high boiling point (100°C) compared to the other compounds of similar size without hydrogen bonds. Because of the difficulty of breaking these bonds, water has a very high boiling point, melting point, and viscosity compared to otherwise similar liquids not conjoined by hydrogen bonds. Water is unique because its oxygen atom has two lone pairs and two hydrogen atoms, meaning that the total number of bonds of a water molecule is up to four. For example, hydrogen fluoride——which has three lone pairs on the F atom but only one H atom——can form only two bonds; (ammonia has the opposite problem: three hydrogen atoms but only one lone pair).H-F...H-F...H-F.

Lewis Structure

The **Lewis structure** of a molecule show how the valence electrons are arranged among the atoms of the molecule. These representations are named after G. N. Lewis. The rules for writing Lewis structures are based on observations of thousands of molecules. From experiment, chemists have learned that when a stable compound forms, the atoms usually have a noble gas electron configuration or eight valence electrons. Hydrogen forms stable molecules when it shares two electrons (sometimes called the duet rule). Other atoms involved in covalent bonding typically obey the octet rule. (Note: Of course, there will be exceptions.)

To draw a Lewis structure:

1. Determine the number of valence electrons that will be drawn in the Lewis structure.

a. Use your periodic table to determine the number of valence electrons in each atom. Add these to get the total electrons in the structure.

b. If you are drawing the structure for a polyatomic ion, you must add or subtract any electrons gained or lost. If an ion has a negative charge, electrons were gained. If the ion has a positive charge, electrons were lost.

2. Draw a skeleton

a. Typically, the first element listed in the formula goes in the center, which the remaining atoms surrounding.

b. Draw bonds to each of the surrounding atoms. Each bond is two valence electrons.

3. Use the remaining electrons to give each atom an octet (except hydrogen which only gets a duet)

a. Place electrons left over after forming the bonds in the skeleton in unshared pairs around the atoms to give each an octet. *Remember, any bonds they have formed already count as two valence electrons each.

b. If you run out of electrons, and there are still atoms without an octet, move some of the electrons that are not being shared to form double, sometimes triple bonds.

Review Question

Draw a Lewis Structure for H_2O?
Solution: *1) add up all available valence electrons:* each H atom has 1, each oxygen atom has 6, so 2(1)+6=8
2) Draw a skeleton. Although the first atom written typically goes in the middle, hydrogen can't, so O gets the middle spot. We need to draw bonds connecting atoms in the skeleton. We get,

$$H-O-H$$

3) Use the remaining electrons to give each atom (except hydrogen) an octet. If we look at our skeleton, we drew two bonds, which uses 4 of our 8 available electrons. We are left with four more. Each H atom already has two valence electrons and O currently has 4 (each bond counts as two for each atom that it connects). We will give the remaining four electrons to O, in pairs. We get:

$$H{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{:}H \quad \text{or} \quad H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H$$

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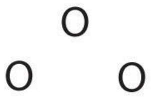
Resonance Structure

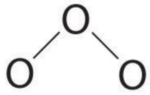
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds.
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

Ozone

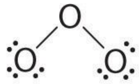
We know that ozone has a V-shaped structure, so one O atom is central:



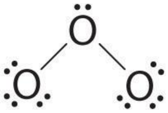
Each O atom has 6 valence electrons, for a total of 18 valence electrons.
Assigning one bonding pair of electrons to each oxygen–oxygen bond gives with 14 electrons left over.



If we place three lone pairs of electrons on each terminal oxygen, we obtain and have 2 electrons left over.



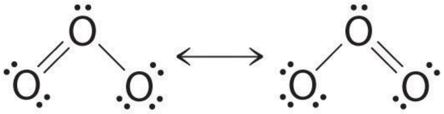
At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either

Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



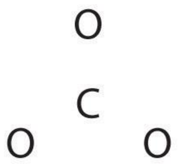
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

Review Question

Draw the resonance structure for carbonate ion?

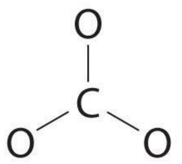
Solution:

Because carbon is the least electronegative element, we place it in the central position:

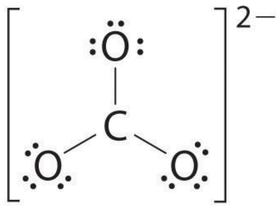


Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

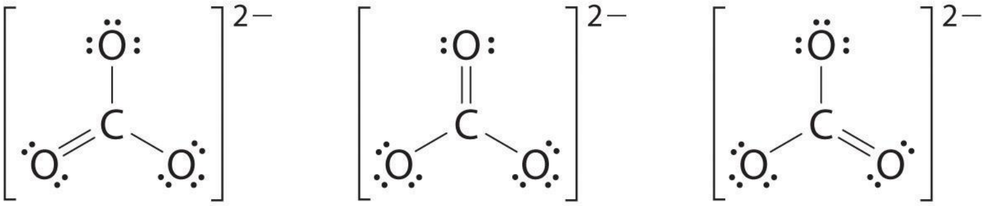


We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

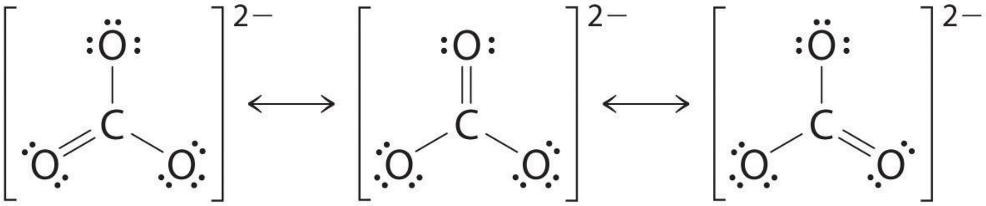


No electrons are left for the central atom.

At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

Bond Order and Bond Length

Bond order is the number of c;hemical bonds between a pair of atoms and indicates the stability of a bond. For example, in diatomic nitrogen, N≡N, the bond order is 3; in acetylene, H−C≡C−H, the carbon-carbon bond order is also 3, and the C−H bond order is 1. Bond order and bond length indicate the type and strength of covalent bonds between atoms. Bond order and length are inversely proportional to each other: when bond order is increased, bond length is decreased.

How to determine bond order

1. Draw the Lewis structure.
2. Determine the type of bonds between the two atoms.

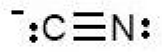
- 0: No bond
- 1: Single bond
- 2: double bond
- 3: triple bond

If the bond order is zero, the molecule cannot form. The higher bond orders indicate greater stability for the new molecule. In molecules that have resonance bonding, the bond order does not need to be an integer.

Review Question

Determine the bond order for cyanide, CN^-?

Solution: Draw the Lewis structure.

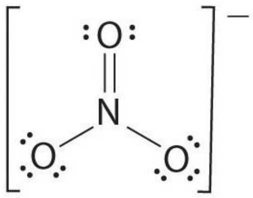


Determine the type of bond between the two atoms.

Because there are 3 dashes, the bond is a triple bond. A triple bond corresponds to a bond order of 3.

Determine the bond order for nitrate, NO_3^-?

Solution: Draw the Lewis structure.



The total number of bonds is 4.

The number of bond groups between individual atoms is 3.

Divide the number of bonds between individual atoms by the total number of bonds.

4/3 = 1.33

The bond order is 1.33

Bond length is defined as the distance between the centers of two covalently bonded atoms. The length of the bond is determined by the number of bonded electrons (the bond order). The higher the bond order, the stronger the pull between the two atoms and the shorter the bond length. Generally, the length of the bond between two atoms is approximately the sum of the covalent radii of the two atoms. Bond length is reported in picometers. Therefore, bond length increases in the following order: triple bond < double bond < single bond.

To find the bond length, follow these steps:

1. Draw the Lewis structure.
2. Look up the chart below for the radii for the corresponding bond.
3. Find the sum of the two radii.

Table for Covalent Radii

Atomic Number	Element	Covalent radii			
		Single Bonds [1]	Single Bonds [2]	Double Bonds [2]	Triple Bonds [2]
1	H	31	32		
2	He	28	46		
3	Li	128	133	124	
4	Be	96	102	90	85
5	B	84	85	78	73
6	C	76	75	67	60
7	N	71	71	60	54
8	O	66	63	57	53
9	F	57	64	59	53
10	Ne	58	67	96	

Atomic Number	Element	Covalent radii			
11	Na	166	155	160	
12	Mg	141	139	132	127
13	Al	121	126	113	111
14	Si	111	116	107	102
15	P	107	111	102	94
16	S	105	103	94	95
17	Cl	102	99	95	93
18	Ar	106	96	107	96
19	K	203	196	193	
20	Ca	176	171	147	133
21	Sc	170	148	116	114
22	Ti	160	136	117	108
23	v	153	134	112	106
24	Cr	139	122	111	103
25	Mn	150	119	105	103

Atomic Number	Element	Covalent radii			
26	Fe	142	116	109	102
27	Co	138	111	103	96
28	Ni	124	110	101	101
29	Cu	132	112	115	120
30	Zn	122	118	120	
31	Ga	122	124	117	121
32	Ge	120	121	111	114
33	As	119	121	114	106
34	Se	120	116	107	107
35	Br	120	114	109	110
36	Kr	116	117	121	108
37	Rb	220	210	202	
38	Sr	195	185	157	139
39	Y	190	163	130	124
40	Zr	175	154	127	121

Atomic Number	Element	Covalent radii			
41	Nb	164	147	125	116
42	Mo	154	138	121	113
43	Tc	147	128	120	110
44	Ru	146	125	114	103
45	Rh	142	125	110	106
46	Pd	139	120	117	112
47	Ag	145	128	139	137
48	Cd	144	136	144	
49	In	142	142	136	146
50	Sn	139	140	130	132
51	Sb	139	140	133	127
52	Te	138	136	128	121
53	I	139	133	129	125
54	Xe	140	131	135	122
55	Cs	244	232	209	

Atomic Number	Element	Covalent radii			
56	Ba	215	196	161	149
57	La	207	180	139	139
58	Ce	204	163	137	131
59	Pr	203	176	138	128
60	Nd	201	174	137	
61	Pm	199	173	135	
62	Sm	198	172	134	
63	Eu	198	168	134	
64	Gd	196	169	135	132
65	Tb	194	168	135	
66	Dy	192	167	133	
67	Ho	192	166	133	
68	Er	189	165	133	
69	Tm	190	164	131	
70	Yb	187	170	129	

Atomic Number	Element	Covalent radii			
71	Lu	187	162	131	131
72	Hf	175	152	128	122
73	Ta	170	146	126	119
74	W	162	137	120	115
75	Re	151	131	119	110
76	Os	144	129	116	109
77	Ir	141	122	115	107
78	Pt	136	123	112	110
79	Au	136	124	121	123
80	Hg	132	133	142	
81	Tl	145	144	142	150
82	Pb	146	144	135	137
83	Bi	148	151	141	135
84	Po	140	145	135	129
85	At	150	147	138	138

Atomic Number	Element	Covalent radii			
86	Rn	150	142	145	133
87	Fr	260	223	218	
88	Ra	221	201	173	159
89	Ac	215	186	153	140
90	Th	206	175	143	136
91	Pa	200	169	138	129
92	U	196	170	134	118
93	Np	190	171	136	116
94	Pu	187	172	135	
95	Am	180	166	135	
96	Cm	169	166	136	
97	Bk		168	139	
98	Cf		168	140	
99	Es		165	140	
100	Fm		167		

Atomic Number	**Element**	**Covalent radii**			
101	Md		173	139	
102	No		176	159	
103	Lr		161	141	
104	Rf		157	140	131
105	Db		149	136	126
106	Sg		143	128	121
107	Bh		141	128	119
108	Hs		134	125	118
109	Mt		129	125	113
110	Ds		128	116	112
111	Rg		121	116	118
112	Cn		122	137	130
113	Uut		136		
114	Uuq		143		
115	Uup		162		

Atomic Number	Element	Covalent radii
116	Uuh	175
117	Uus	165
118	Uuo	157

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Review Question

Determine the carbon-to-chlorine bond length in CCl_4.

Solution: Using the above table, a C single bond has a length of 75 picometers and that a Cl single bond has a length of 99 picometers. When added together, the bond length of a C-Cl bond is approximately 174 picometers.

Bond Energy

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.*

When a chemical reaction occurs, molecular bonds are broken, and other bonds are formed to make different molecules. For example, the bonds of two water molecules are broken to form hydrogen and oxygen.

$$2H2O \rightarrow 2H2+O2$$

Energy is always required to break a bond, which is known as bond energy or bond dissociation energy.

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. We can calculate a more general bond energy by finding the average of the bond energies of a specific bond in different molecules to get the average bond energy.

Average Bond Energies in kj/mol

Single Bonds				Multiple Bonds	
N—H	391	**I—I**	149	**C = C**	614
N—N	160	**I—Cl**	208	**C ≡ C**	839
N—F	272	**I—Br**	175	**O = O**	495
N—Cl	200			**C = O***	745
N—Br	243	**S—H**	347	**C ≡ O**	1072
N—O	201	**S—F**	327	**N = O**	607
O—H	467	**S—Cl**	253	**N = N**	418
O—O	146	**S—Br**	218	**N ≡ N**	941
O—F	190	**S—S**	266	**C ≡ N**	891
O—Cl	203			**C = N**	615
O—I	234	**Si—Si**	340		
		Si—H	393		

Single Bonds				Multiple Bonds	
F—F	154	**Si—C**	360		
F—Cl	253	**Si—O**	452		
F—Br	237				
Cl—Cl	239				
Cl—Br	218				
Br—Br	193				

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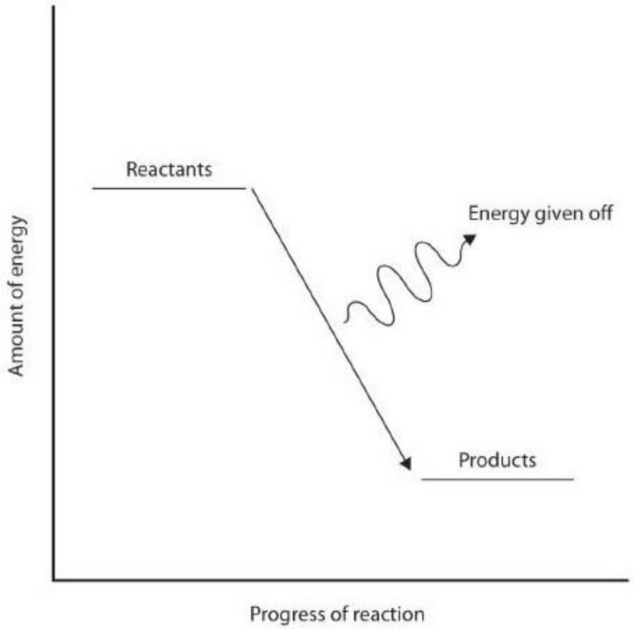
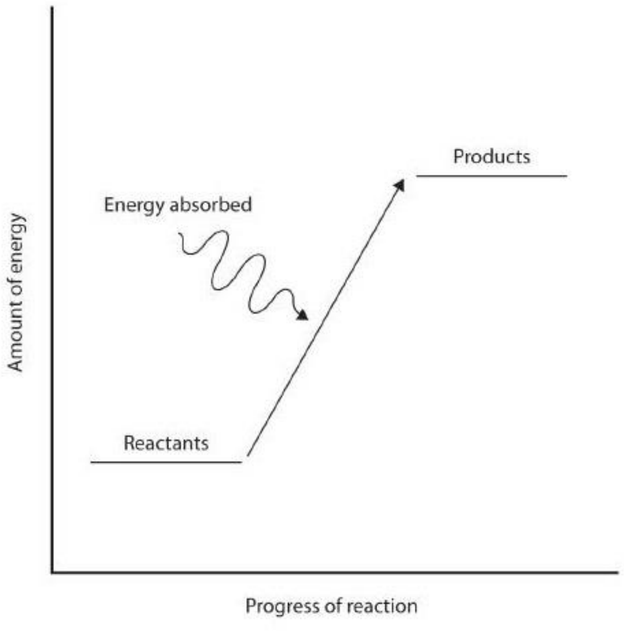
When a bond is strong, there is a higher bond energy because it takes more energy to break a strong bond. This correlates with bond order and bond length. When the Bond order is higher, bond length is shorter, and the shorter the bond length means a greater the Bond Energy because of increased electric attraction. In general, **the shorter the bond length, the greater the bond energy.**

Bond Breakage and Formation

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*.



Exothermic Reactions. For an exothermic chemical reaction, energy is given off as reactants are converted to products



Endothermic Reactions. For an endothermic chemical reaction, energy is absorbed as reactants are converted to products.

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Review Question

Is each chemical reaction exothermic or endothermic?

a. $2H_2(g)+O_2(g) \rightarrow 2H_2O(\ell)+135$ kcal
b. $N_2(g)+O_2(g)+45$ kcal$\rightarrow 2NO(g)$

Solution: No calculates are required to address this question. Just look at where the "heat" is in the chemical reaction.

a. Because energy is released; this reaction is exothermic.
b. Because energy is absorbed; this reaction is endothermic.

Valene Bond Theory

Valence bond theory states that overlap between two atomic orbitals forms a covalent bond between two atoms.

- Valence bond and molecular orbital theories are used to explain chemical bonding.
- Two atoms that have unpaired electrons in their orbitals can overlap to give rise to a chemical bond.
- A sigma bond (σ) forms when two atomic orbitals overlap between the nuclei of two atoms (also known as the internuclear axis).
- Pi bonds (π) occur when two atomic orbitals overlap outside of the space between the nuclei (outside of the internuclear axis).
- The strongest bonds form with maximum overlap between orbitals.
- **covalent bond**: a chemical bond that is formed from the sharing of two electrons between two atoms.
- **internuclear axis**: The space between the nuclei of two atoms bonded to each other.
- **atomic orbitals**: the physical region or space where an electron may be present or found, with a probability calculated from the precise mathematical form of the orbital.
- **valence bond theory**: a covalent bond forms between the two atoms by the overlap of half-filled valence atomic orbitals from each atom.

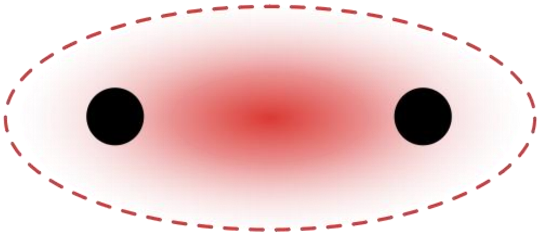
According to VB theory, a covalent bond forms from the physical overlap of half-filled valence orbitals in two atoms.

Mechanism of Bonding in VB Theory

The VB theory describes the formation of covalent bonds from the overlap of atomic orbitals on two different atoms. Because of the overlap, it is highly probable that a pair of electrons are found in the physical region or space where the orbitals overlap.

Sigma (σ) and Pi (π) Bonds

There are two types of overlapping orbitals: sigma (σ) and pi (π). Both bonds are formed from the overlap of two orbitals, one on each atom. σ bonds occur when orbitals overlap between the nuclei of two atoms, also known as the internuclear axis.



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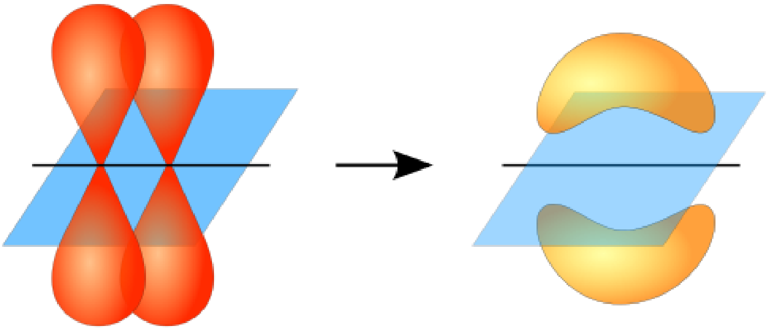
σ **Bond Formation**: *Atomic orbitals from two atoms overlap in the region between the nuclei (internuclear axis). Therefore, the resulting electron density of the shared electrons lies in the red region shown in the image*

π bonds occur when two (unhybridized) p-orbitals overlap. The p-orbitals, in one π bond, are located above and below the nuclei of the atoms. By occupying the region of space that is above, below, and on the sides of an atom's nuclei, two π bonds can form.



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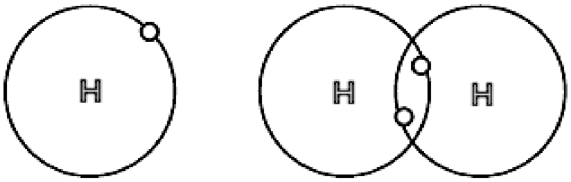
Both types of overlapping orbitals can be related to bond order. Single bonds have one sigma bond. Double bonds consist of one σ and one π bond, while triple bonds contain one σ and two π bonds.

An important aspect of the VB theory is the condition of maximum overlap which leads to the formation of the strongest possible bonds. This theory is used to explain the covalent bond formation in many molecules. In the F_2 molecule, the F–F σ covalent bond is formed by the overlap of p_z orbitals of the two F atoms, each containing an unpaired electron. Since the nature of the overlapping orbitals is different in H_2 and F_2 molecules, bond strength and bond lengths differ between H_2 and F_2 molecules.

In an HF molecule, the covalent σ bond forms from the overlap of the 1s orbital of H and the $2p_z$ orbital of F, each containing an unpaired electron. Mutual sharing of electrons between H and F results in a covalent bond in HF.



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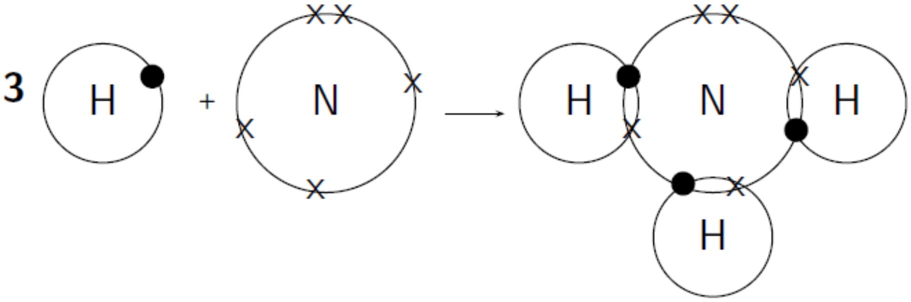
Covalent bond between hydrogen atoms*: Each hydrogen atom has one electron. To complete their valence shells, they bond and share one electron with each other. This allows electrons to move about both atoms and gives both atoms access to two electrons; they become a stable* H_2 *molecule joined by a single covalent bond.*



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Covalent bonding in a molecule of ammonia*: Each hydrogen atom needs one more electron to complete its valence energy shell. The nitrogen atom needs three more electrons to complete its valence energy shell. Therefore, three pairs of electrons must be shared between the four atoms involved. The nitrogen atom will share three of its electrons so that each of the hydrogen atoms now has a complete valence shell. Each of the hydrogen atoms will share its electron with the nitrogen atom to complete its valence shell.*

Hybridization

Hybridization is the idea that atomic orbitals fuse to form newly hybridized orbitals, which in turn, influences molecular geometry and bonding properties. Hybridization is also an expansion of the valence bond theory. In order to, explore this idea further, we will utilize three types of hydrocarbon compounds to illustrate sp^3, sp^2, and sp hybridization.

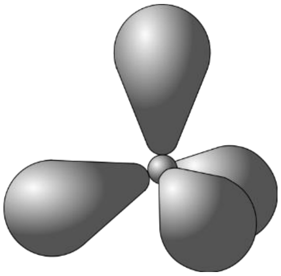
sp^3 Hybridization

sp^3 hybrid orbitals form when a single s and three p orbitals hybridize.

- The bonds in a methane (CH_4) molecule are formed by four separate but equivalent orbitals; a single 2s and three 2p orbitals of the carbon hybridize into four sp^3 orbitals.
- In the ammonia molecule (NH_3), 2s and 2p orbitals create four sp^3 hybrid orbitals, one of which is occupied by a lone pair of electrons.
- In a water molecule, two sp^3 hybrid orbitals are occupied by the two lone pairs on the oxygen atom, while the other two bonds with hydrogen.
- **tetravalent**: having a valence of 4

In a tetravalent molecule, four outer atoms are bonded to a central atom. Perhaps the most common and important example of this bond type is methane, CH_4. In the ground state of the free carbon atom, there are two unpaired electrons in separate 2p orbitals. To form four bonds, the atom must have four unpaired electrons; this requires that carbon's valence 2s and 2p orbitals each contain an electron for bonding.

The single 2s orbital is spherical, different from the dumbbell-shaped 2p orbitals. This would indicate that one of the four bonds differ from the other three, but scientific tests have proven that all four bonds have equal length and energy; this is due to the hybridization of carbon's 2s and 2p valence orbitals.



The methane molecule has four equal bonds

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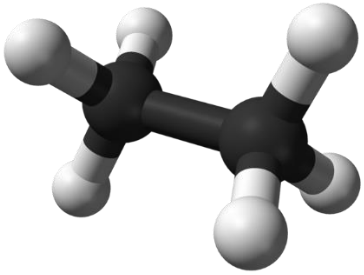
In hybridization, carbon's 2s and three 2p orbitals combine into four identical orbitals, now called sp^3 hybrids.

The bonds between carbon and hydrogen can form the backbone of very complicated and extensive chain hydrocarbon molecules. The simplest of these is ethane (C_2H_6), in which an sp^3 orbital on each of the two carbon atoms joins (overlaps) to form a carbon-carbon bond; then, the remaining carbon sp^3 orbital overlaps with six hydrogen 1s orbitals to form the ethane molecule.



***Ethane**: Ethane can form by replacing one of the hydrogen atoms in CH_4 with another sp^3 hybridized carbon fragment.*

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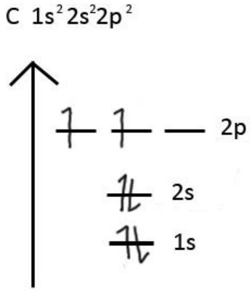
If lone electron pairs are present on the central atom, that can occupy one or more of the sp^3 orbitals. For example, in the ammonia molecule, the fourth of the sp^3 hybrid orbitals on the nitrogen contains the two-remaining outer-shell electrons, which form a non-bonding lone pair.

In the water molecule, the oxygen atom can form four sp^3 orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. The observed H-O-H bond angle in water (104.5°) is less than the tetrahedral angle (109.5°); one explanation for this is that the non-bonding electrons tend to remain closer to the central atom and thus exert greater repulsion on the other orbitals, pushing the two bonding orbitals closer together.

Methane

First and foremost, it is important to note that carbon has the electron configuration of $1s^2\ 2s^2\ 2p^2$. This means that carbon would have 2 unpaired electrons in its p orbitals. Theoretically, this means that carbon will only form 2 bonds, but that is definitely not the case.



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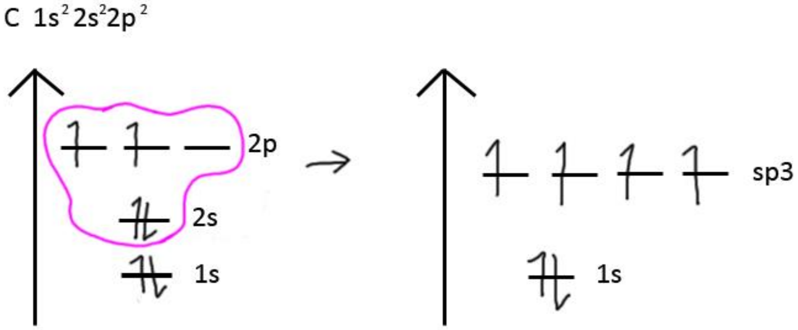
As seen in methane (CH_4), carbon can form 4 bonds. The rationale behind this phenomenon is hybridization. Supporting evidence shows that 1 s and 3 p orbitals are being combined to form hybrid orbitals, allowing polyatomic molecule to have 25% s character and 75% p character. Thus, we call methane a sp3-hybridized molecule.



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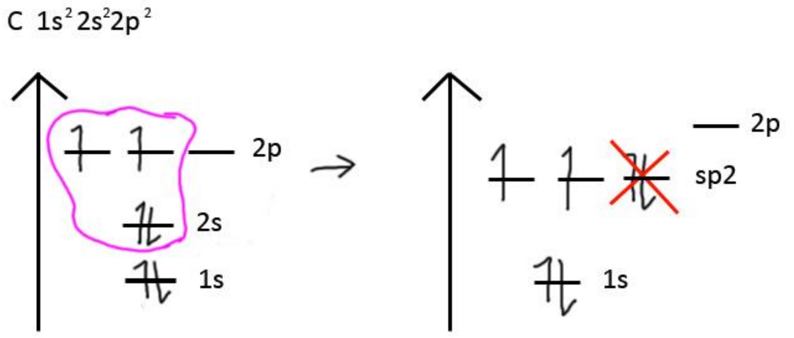
sp^2 Hybridization

- sp^2 hybridization occurs between one s-orbital and two p-orbitals. For boron to bond with three fluoride atoms in boron trifluoride (BF_3), the atomic s- and p- orbitals in boron's outer shell mix to form three equivalent sp^2 hybrid orbitals.
- In an ethene molecule, a double bond between carbons forms with one sigma and one pi bond.
- The sigma bond in the C=C for ethene forms between two sp^2 hybrid orbitals of two carbon atoms, and a pi bond for between two p orbitals.
- **sp^2 hybridization**: the 2s orbital mixes with only two of the three available 2p orbitals
- **hybridization**: mixing atomic orbitals into new hybrid orbitals, suitable for pairing electrons to form chemical bonds in valence bond theory

Ethene

Ethene (C_2H_4) has a double bond between the carbons. In this case, carbon will sp^2 hybridize; in sp^2 hybridization, the 2s orbital mixes with only two of the three available 2p orbitals, forming a total of three sp hybrid orbitals with one p-orbital remaining. The three hybridized orbitals explain the three sigma bonds that each carbon forms.



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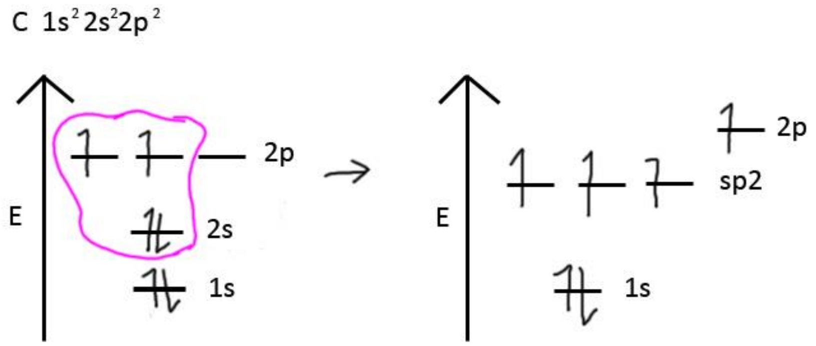
This time, the energy diagram setup is different because only 2 p orbitals are being mixed. While creating your energy diagram, however, be sure that you do not make the mistake as shown above. By placing two electrons in the same orbital, you have broken Hund's rule, which states that all orbitals among the same energy levels have to be filled with at least one electron before being paired up again. The 2p orbital here is considered low enough energy to be classified within the same energy level as the sp^2 orbitals. The figure below portrays the correct way to distribute your electrons.



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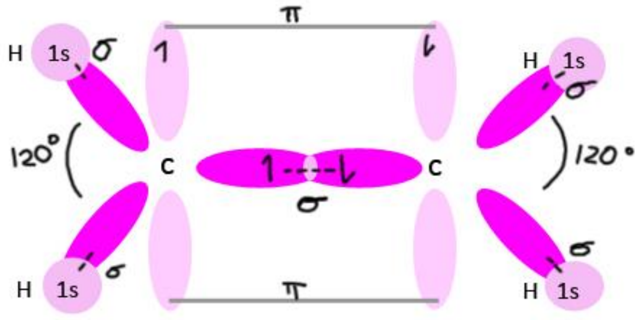
Notice how that lone electron in the 2p orbital is separate from the electrons in the sp^2 orbitals. This is what influence ethylene's shape. The lone electron from each carbon will remain in its respective p orbital and form a pi bond with the other p orbital electron. Thus, ethylene is a planar molecule, with orbitals spaced 120 °angles apart.



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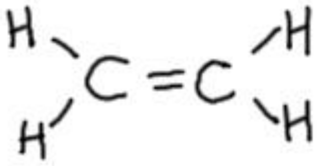
Nonetheless, the figure above accurately depicts the ethylene Lewis structure:



The double bond in the Lewis structure is indicative of one sigma bond and one pi bond.

sp Hybridization

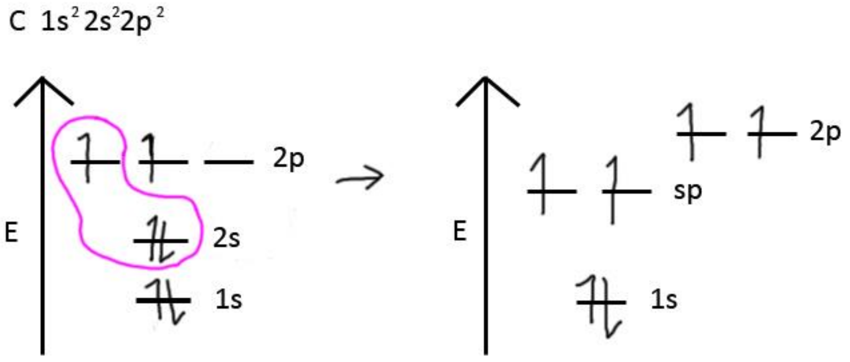
sp hybrid orbitals form from one s-orbital and one p-orbital.

- In *sp* hybridization, the s orbital overlaps with only one p orbital.
- Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization.
- *sp* orbitals are oriented at 180 degrees to each other.
- **hybrid orbital**: formed by combining multiple atomic orbitals on the same atom
- **sp hybrid**: an orbital formed between one s-orbital and one p-orbital

In *sp* hybridization, the s orbital overlaps with only one p orbital. Atoms that exhibit *sp* hybridization have *sp* orbitals that are linearly oriented; two *sp* orbitals will be at 180 degrees to each other.

Acetylene

Supporting evidence shows that acetylene is an sp molecule. This means that 1 s orbital is being mixed with 1 p orbital. Thus, the energy diagram setup would look like this:



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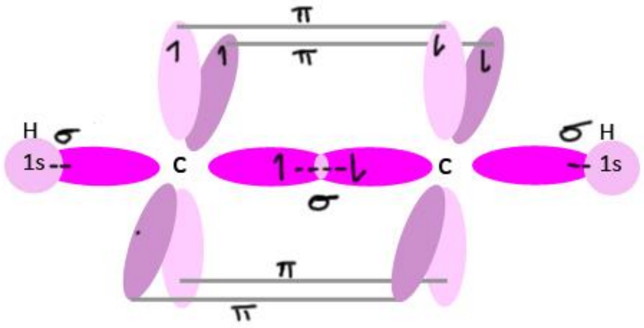
As previously discussed, the lone electrons in the 2p orbitals are not part of the sp orbitals. Instead, each electron is in its respective p orbital, and will bond with its respective p orbital of the other carbon. This in itself will create a sigma bond and two pi bonds, leading to the formation of a linear molecule!



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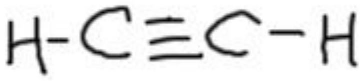
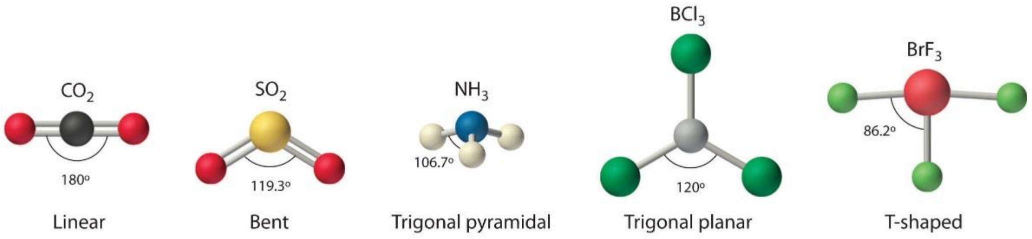
Thus, in a Lewis structure, acetylene is comprised of 2 triple-bond carbons:  As you can see, the bond angle is 180 degrees, indicative of a linear molecule. This information is consistent with what was explained earlier.

VSEPR Model

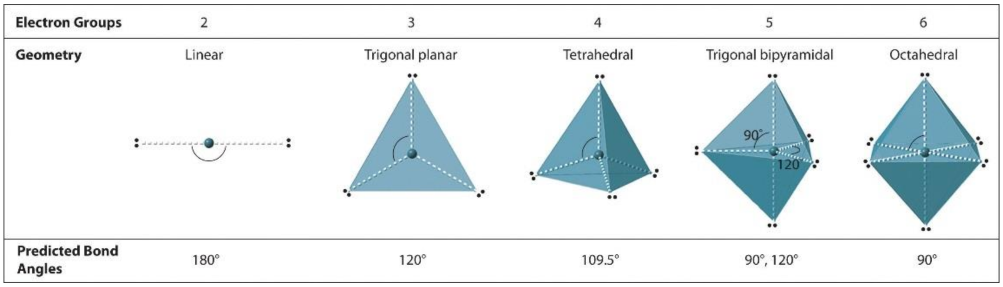
The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.



Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms

> *Petrucci, Ralph H., Harwood, William S., Herring, F. G., and Madura Jeffrey D. General Chemistry: Principles & Modern Applications*

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions.



Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions.

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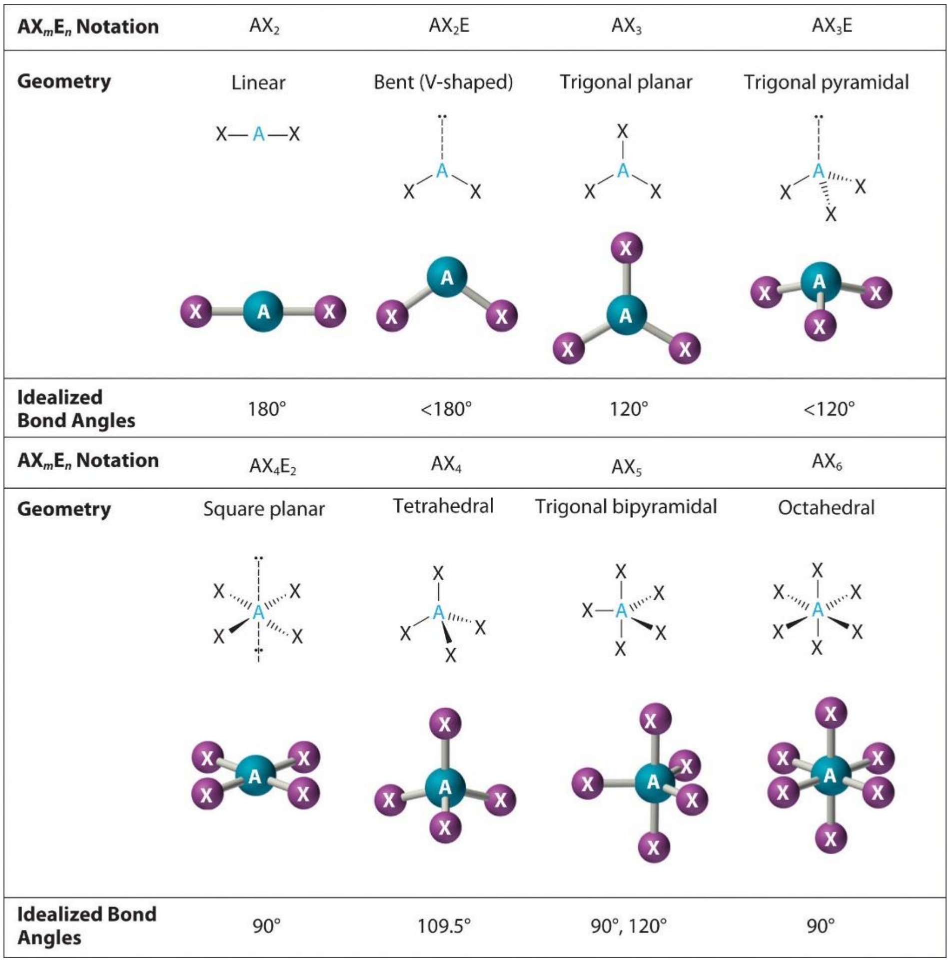
In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion. This procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.



AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
Idealized Bond Angles	180°	<180°	120°	<120°
AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.

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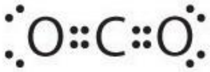
Two Electron Groups

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

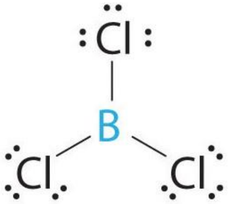
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear

Three Electron Groups

AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

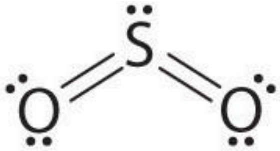
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart.

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From above figure, we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*.

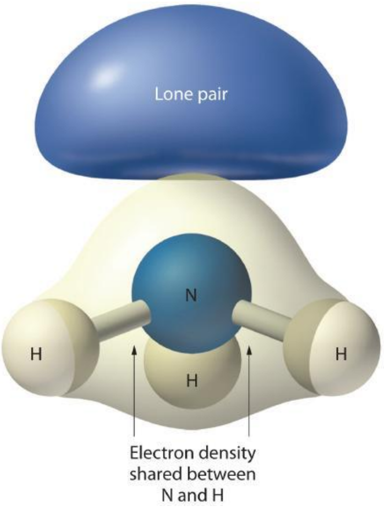
AX_2E: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair. Thus, bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.



The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

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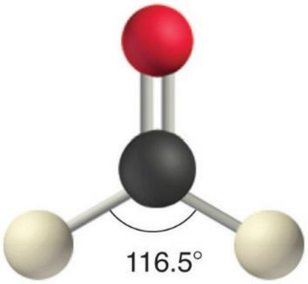
4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus, with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex. The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



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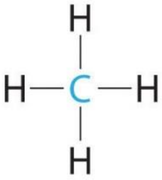
Four Electron Groups

AX_4: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

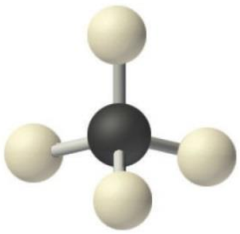


Lewis structure

2. There are four electron groups around the central atom. Repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral*.



Molecular geometry
(tetrahedral)

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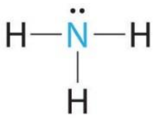
AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing. However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions

AX_2E_2: H_2O

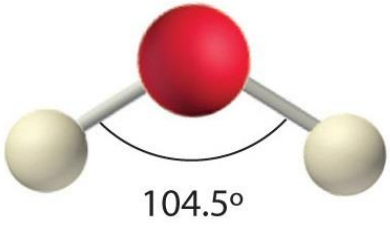
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

$H-\underset{\cdot\cdot}{\ddot{O}}-H$

2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 9.2.29.2.2.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



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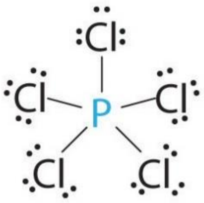
Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5: PCl_5

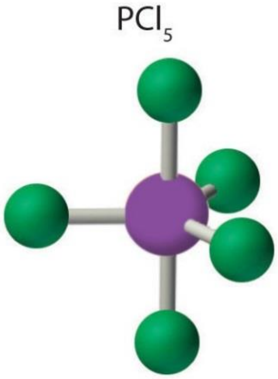
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base .

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



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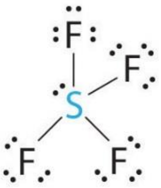
AX_4E: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

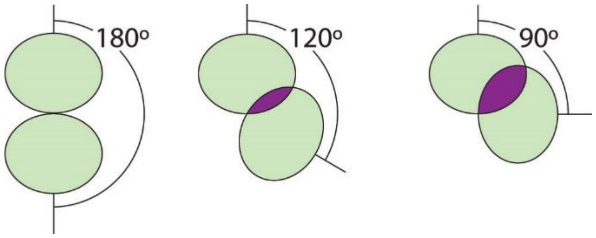


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

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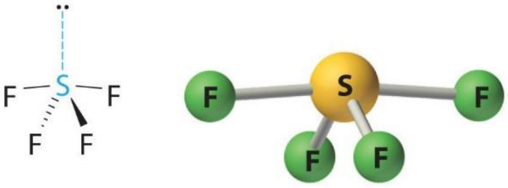
At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

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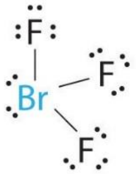
AX_3E_2: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

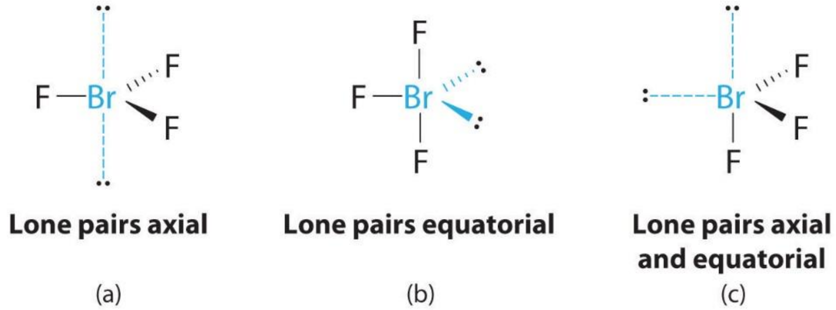


Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

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Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions.

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

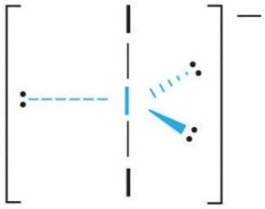
AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is

2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in

a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



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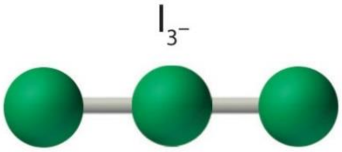
The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.



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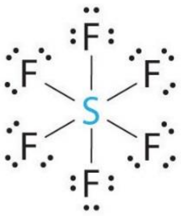
Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices.

AX_6: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



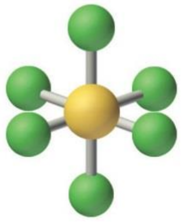
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from that the geometry that minimizes repulsions is *octahedral.*

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

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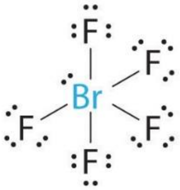
AX_5E: BrF_5

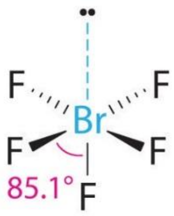
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



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3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.

Molecular geometry
(square pyramidal)

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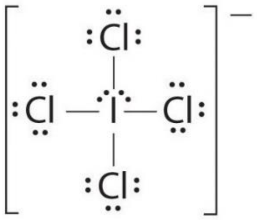
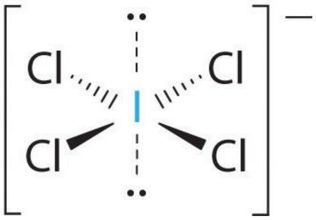
AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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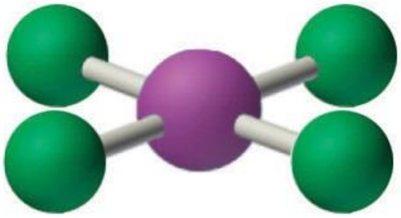
3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



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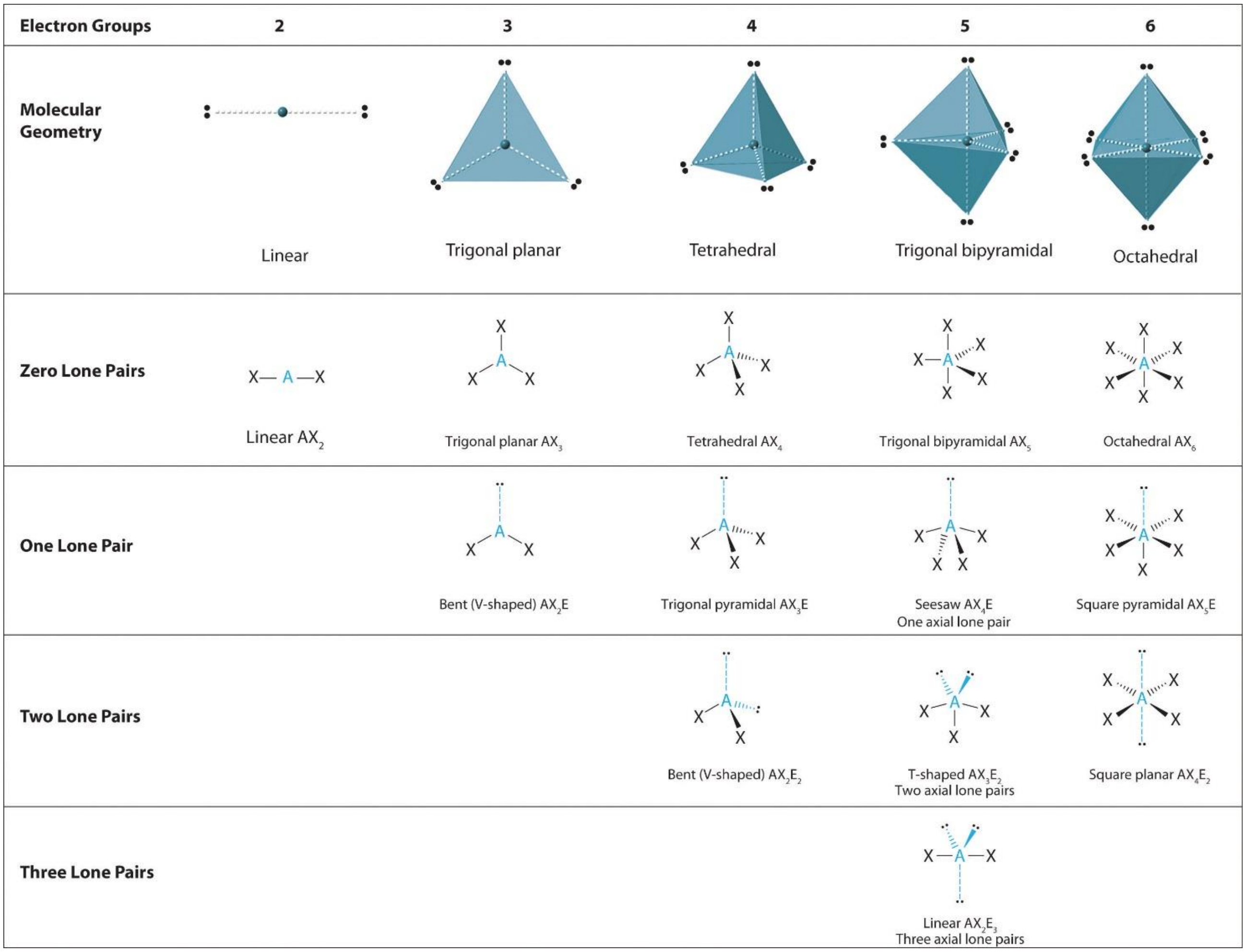
The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized below:



Electron Groups	2	3	4	5	6
Molecular Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Zero Lone Pairs	Linear AX_2	Trigonal planar AX_3	Tetrahedral AX_4	Trigonal bipyramidal AX_5	Octahedral AX_6
One Lone Pair		Bent (V-shaped) AX_2E	Trigonal pyramidal AX_3E	Seesaw AX_4E One axial lone pair	Square pyramidal AX_5E
Two Lone Pairs			Bent (V-shaped) AX_2E_2	T-shaped AX_3E_2 Two axial lone pairs	Square planar AX_4E_2
Three Lone Pairs				Linear AX_2E_3 Three axial lone pairs	

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Intramolecular Force

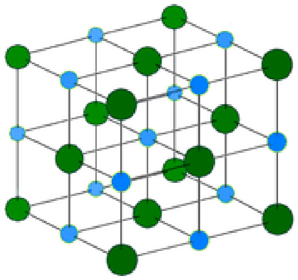
An intramolecular force is any force that binds together the atoms making up a molecule. Chemical bonds are considered to be intramolecular forces.

Types of Solids

There are four types of solids. Ionic, metallic, covalent and molecular.

Ionic crystals

The ionic crystal structure consists of alternating positively-charged cations and negatively-charged anions. The ions may either be monatomic or polyatomic. Generally, ionic crystals form from a combination of Group 1 or 2 metals and Group 16 or 17 nonmetals or nonmetallic polyatomic ions. Ionic crystals are hard and brittle and have high melting points. Ionic compounds do not conduct electricity as solids but do conduct when molten or in aqueous solution.



NaCl *crystal.*

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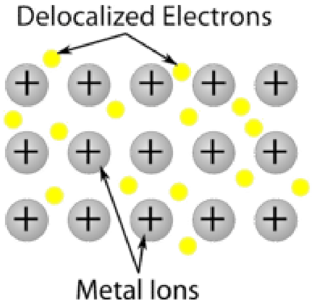
Metallic crystal

Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons. These electrons, also referred to as delocalized electrons, do not belong to any one atom, but are capable of moving through the entire crystal. As a result, metals are good conductors of electricity.



Metallic crystal lattice with free electrons able to move among positive metal atoms.

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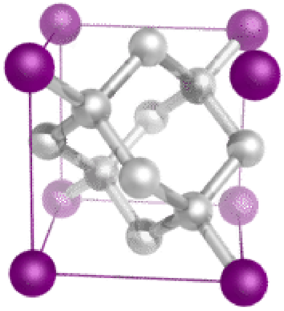
Covalent crystals

A covalent network crystal consists of atoms at the lattice points of the crystal, with each atom being covalently bonded to its nearest neighbor atoms. The covalently bonded network is three-dimensional and contains a very large number of atoms. Network solids include diamond, quartz, many metalloids, and oxides of transition metals and metalloids. Network solids are hard and brittle, with extremely high melting and boiling points. Being composed of atoms rather than ions, they do not conduct electricity in any state.



Diamond is a network solid and consists of carbon atoms covalently bonded to one another in a repeating three-dimensional pattern. Each carbon atom makes for single covalent bonds in a tetrahedral geometry.

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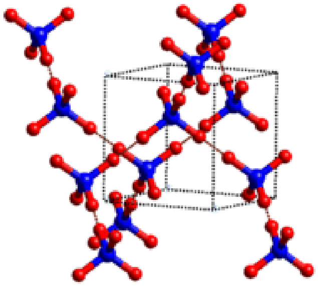
Molecular crystals

Molecular crystals typically consist of molecules at the lattice points of the crystal, held together by relatively weak intermolecular forces. The intermolecular forces may be dispersion forces in the case of nonpolar crystals, or dipole-dipole forces in the case of polar crystals. Some molecular crystals, such as ice, have molecules held together by hydrogen bonds. When one of the noble gases is cooled and solidified, the lattice points are individual atoms rather than molecules. In all cases, the intermolecular forces holding the particles together are far weaker than either ionic or covalent bonds. As a result, the melting and boiling points of molecular crystals are much lower. Lacking ions or free electrons, molecular crystals are poor electrical conductors.



Ice crystal structure

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Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

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Questions

1. Draw a Lewis structure for CO_2?

Solution: *add up all available valence electrons:*

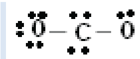
1(4) + 2(6) = 16

2) Draw a skeleton.

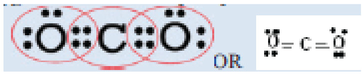
Carbon goes in the middle with the two oxygen atoms bonded to it:

3) Use the remaining electrons to give each atom (except hydrogen) an octet.

In this case, we have already used up four electrons to draw the two bonds in the skeleton, leaving 12 left. This is not enough to give everybody an octet. Our picture may look something like this with 16 electrons:



We have used up the 16 electrons, but neither O has an octet. The rules state that if you run out of electrons and still don't have octets, then you must use some of the unshared pairs of electrons as double or triple bonds instead. Move the electrons that are just on the carbon atom to share with the oxygen atom until everybody has an octet. We get:



Check:

Is the total number of valence electrons correct? Yes. Our final picture has 16 valence e-.

Does each atom have the appropriate duet or octet of electrons? Yes

2.Label each of the following as polar or non-polar?

a) Water b) Methanol c) Hydrogen cyanide d) Oxygen e) Propane

Solution: a) Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.

b) Methanol is polar. This is not a symmetric molecule. The –OH side is different from the other 3 –H sides.

c) Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.

d) Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.

e) Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

3. Label each of the following as polar or nonpolar and indicate which have hydrogen bonding.

a) Water b) ammonia c) methane d) acetone

Solution: a) This molecule is polar (the unshared pairs of electrons make a polar asymmetric shape), and hydrogen bonding (hydrogen is bonded to N, O, or F).

b) This molecule is polar (the unshared pairs of electrons make a polar asymmetric shape), and hydrogen bonding (hydrogen is bonded to N, O, or F).

c) This molecule is nonpolar (the molecule is symmetric with H's bonded to all four sides of the central atom) and does not have hydrogen bonding (hydrogen is not bonded to N, O, or F).

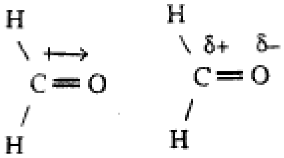
d) This molecule is polar (the O is not the same as the CH3 bonded to the central atom)

4. Predict whether the following molecules are polar or non-polar?

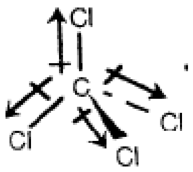
a) CO_2 b) CH_2O c) CCl_4 d) CCl_2F_2

Solution: a) In CO_2 , the two bond dipoles cancel. So, it's a non-polar molecule.

b)

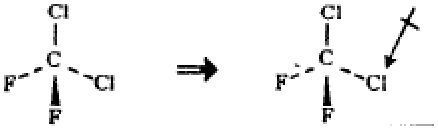


It's a polar molecule.



c)

All the bond dipoles cancel each other. Hence, it is a non-polar molecule.



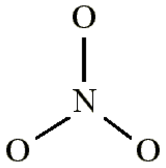
d)

It has a net dipole moment. Hence, it is polar.

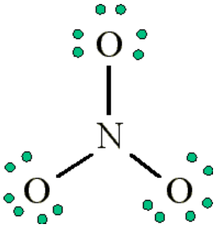
5. Draw the resonance structure for nitrate ion?

Solution: Valence electrons = 24

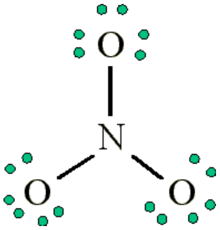
Bond connectivity



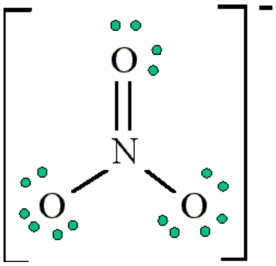
Add octet electrons to the atoms bonded to the center atom:



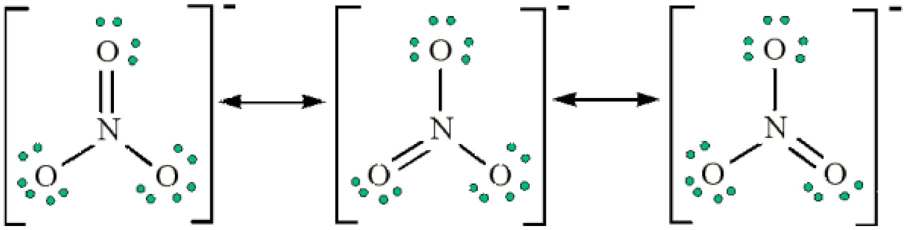
Place any leftover electrons (24-24 = **0**) on the center atom:



Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:

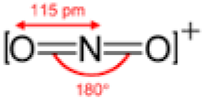


Are there possible resonance structures? YES



6.Determine the bond order for nitronium ion: NO_2^+?

Solution:



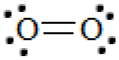
The total number of bonds is 4.

The number of bond groups between atoms is 2.

The bond order is 4/2 = 2.

7.What is the bond order of O_2?

Solution: The Lewis structure for O_2 is:



There is a double bond between the two oxygen atoms; therefore, the bond order of the molecule is 2.

7.What is the carbon-nitrogen bond length in HCN?

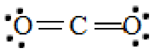
Solution: To find the carbon-nitrogen bond length in HCN, draw the Lewis structure of HCN.

$$H-C\equiv N\!:$$

The bond between carbon and nitrogen is a triple bond, and a triple bond between carbon and nitrogen has a bond length of approximately 60 + 54 =114 pm.

8.Is the carbon-to-oxygen bond length greater in CO_2 or CO?

Solution: From the Lewis structures for CO_2 and CO, there is a double bond between the carbon and oxygen in CO_2 and a triple bond between the carbon and oxygen in CO.

Referring to the table above, a double bond between carbon and oxygen has a bond length of approximately 67 + 57 = 124 pm and a triple bond between carbon and oxygen has a bond length of approximately 60 + 53 =113 pm. Therefore, the bond length is greater in CO_2.

Another method makes use of the fact that the more electron bonds between the atoms, the tighter the electrons are pulling the atoms together. Therefore, the bond length is greater in CO_2.

9. If the bond energy for H-Cl is 431 kJ/mol. What is the overall bond energy of 2 moles of HCl?

Solution: Simply multiply the average bond energy of H-Cl by 2. This leaves you with 862 kJ/mol.

10. What is the enthalpy change for this reaction and is it endothermic or exothermic?

$$H_2(g)+I_2(g)\rightarrow 2HI(g)$$

Solution: The sum of enthalpies on the reaction side is:

436 kJ/mole + 151 kJ/mole = 587 kJ/mol.

This is how much energy is needed to break the bonds on the reactant side. Then we look at the bond formation which is on the product side:

- 2 mol H-I bonds: 297 kJ/mol

The sum of enthalpies on the product side is:

$$2 \times 297 \text{ kJ/mol} = 594 \text{ kJ/mol}$$

This is how much energy is released when the bonds on the product side are formed. The net change of the reaction is therefore

$$587-594= -7 \text{ kJ/mol.}$$

Since this is negative, the reaction is *exothermic.*

11. When an atom is described as sp hybridized, its electron group geometry is?

Solution: Linear

12. When an atom is described as being ssss3 hybridized, its electron group geometry is?

Solution: Tetrahedral

13. What do you expect the bond angles to be in the NH_4^+ ion?

Solution: All bond angles are 109.5°, the ideal value for symmetric tetrahedral structure.

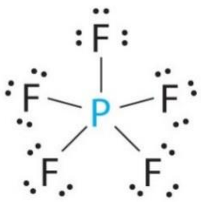
14. What is the shape of the molecule SF_6?

Solution: The shape is octahedral.

15. Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)

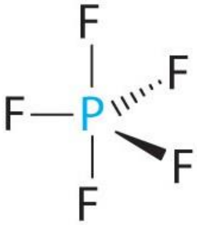
Solution: The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



16. Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Solution: **Germanium** lies in the p block just under Si, along the diagonal line of semi metallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus, Ge is probably a **covalent solid.**

RbI contains a metal from group 1 and a nonmetal from group 17, so it is **an ionic solid** containing Rb^+ and I^- ions.

The compound **$C_6(CH_3)_6$** is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form **a molecular solid** with no covalent bonds between them.

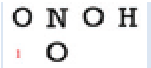
Zn is a d-block element, so it is **a metallic solid.**

Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is

$C_6(CH_3)_6 < Zn \sim RbI < Ge$.

Advanced Questions

1. Draw a Lewis structure for nitric acid, HNO3. The skeleton is given below:



2. For each of the following, determine the orientation of dipole moment (if any)

a) HI b) N_2 c) CCl_2F_2

3. What does it mean a molecule to be "polar?

4. Define hydrogen bonding?

5.Draw the resonance structure for benzene?

6.What is the bond order of NO_3^-?

7.What is the nitrogen-fluoride bond length in NF_3?

8. Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$2H_2O(g)\rightarrow 2H_2+O_2(g)$$

Is the reaction written above exothermic or endothermic? Explain.

9. Use the valence bond model to show the bonding in the following molecules; BeH_2, BH_3, CCl_4, PCl_5, SF_6?

10. Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

11. Classify CO_2, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

1.Organic Chemistry

Organic chemistry is the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds, which include not only hydrocarbons but also compounds with any number of other elements, including hydrogen (most compounds contain at least one carbon–hydrogen bond), nitrogen, oxygen, halogens, phosphorus, silicon, and sulfur. This branch of chemistry was originally limited to compounds produced by living organisms but has been broadened to include human-made substances such as plastics. The range of application of organic compounds is enormous and also includes, but is not limited to, pharmaceuticals, petrochemicals, food, explosives, paints, and cosmetics.

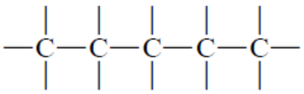
Organic chemistry is a highly creative science in which chemists create new molecules and explore the properties of existing compounds. It is the most popular field of study for ACS chemists and Ph.D. chemists. Organic compounds are all around us. They are central to the economic growth of the United States in the rubber, plastics, fuel, pharmaceutical, cosmetics, detergent, coatings, dyestuff, and agrichemical industries, to name a few. The very foundations of biochemistry, biotechnology, and medicine are built on organic compounds and their role in life processes. Many modern, high-tech materials are at least partially composed of organic compounds. Organic chemists spend much of their time creating new compounds and developing better ways of synthesizing previously known compounds.

Organic compounds, in general, differ greatly from inorganic compounds in seven respects:

1. Organic compounds are usually combustible.
2. Organic compounds, in general, have lower melting and boiling points.
3. Organic compounds are usually less soluble in water.
4. Several organic compounds may exist for a given formula. This is known as isomerism.
5. Reactions of organic compounds are usually molecular rather than ionic. As a result, they are often quite slow.
6. The molecular weights of organic compounds may be very high, often well over 1000.
7. Most organic compounds can serve as a source of food for bacteria.

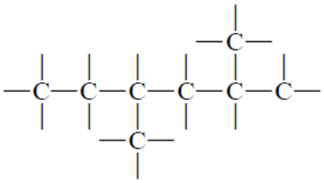
1.1 The Carbon Atom

A question commonly asked is: How is it possible to have so many compounds of carbon? There are two reasons. In the first place, carbon normally has four covalent bonds (four electrons to share). This factor alone allows many possibilities, but the most important reason is concerned with the ability of carbon atoms to link together by covalent bonding in a wide variety of ways. They may be in a continuous open chain,

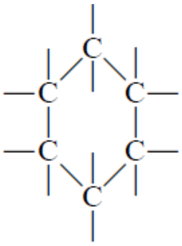


$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

Or chain with branches



Or in a ring



Review Question

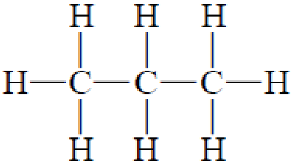
1.Why is it possible to have so many compounds of carbon?

Solution: Carbon normally has four covalent bonds (four electrons to share). This factor alone allows many possibilities, but the most important reason is concerned with the ability of carbon atoms to link together by covalent bonding in a wide variety of ways

2.Aliphatic Compounds

2.1Hydrocarbons

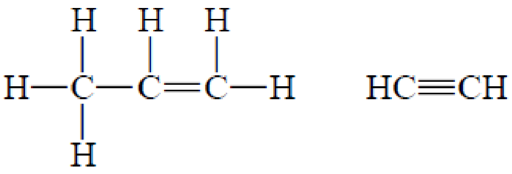
The hydrocarbons are compounds of carbon and hydrogen. There are two types, saturated and unsaturated. Saturated hydrocarbons are those in which adjacent carbon atoms are joined by a single covalent bond and all other bonds are satisfied by hydrogen.



$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & \\ & & H & & H & & H & \end{array}$$

A saturated compound

Unsaturated hydrocarbons have at least two carbon atoms that are joined by more than one covalent bond and all remaining bonds are satisfied by hydrogen.



Unsaturated compounds

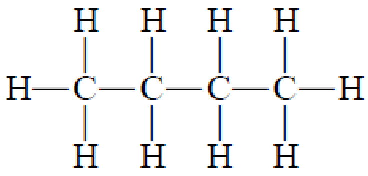
Review Question

1.Define hydrocarbons?

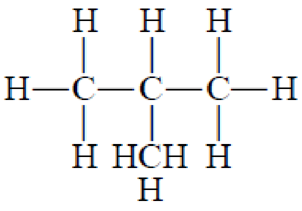
Solution: The hydrocarbons are compounds of carbon and hydrogen.

2.2Alkanes

The principal source of alkanes is petroleum. *Methane* (CH_4) is the simplest hydrocarbon. It is a gas of considerable importance to environmental engineers and scientists since it is a major end product of the anaerobic treatment process as applied to sewage sludge and other organic waste materials. It is a component of marsh gas and of natural gas and, in a mixture with air containing from 5 to 15 percent methane, it is highly explosive. This property allows its use as fuel for gas engines. Methane is commonly called "firedamp" by miners and makes their work particularly hazardous. Methane is also considered to be an important greenhouse gas; its concentration in the stratosphere affects the earth's heat balance, and thus temperature.
Ethane (CH_3-CH_3) is the second member of the series.
Propane (CH_3-CH_2-CH_3) is the third member of the series.
Butane (C_4H_{10}) is the fourth member of the series and is of interest because it occurs in two isomeric forms:

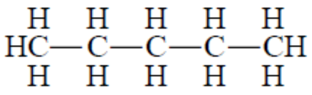


n-Butane

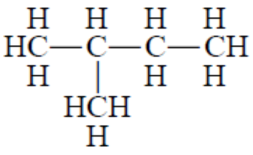


Isobutane

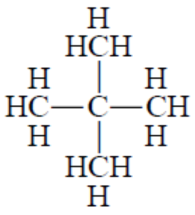
Pentane (C_5H_{12}) is the fifth member of the series and exists in three isomeric forms:



n-Pentane
bp, 36.2°C



Isopentane
bp, 28°C



Neopentane
bp, 9.5°C

As the number of carbon atoms increases in the molecule, the number of possible isomers increases accordingly. There are five possible isomers of *hexane* (C_6H_{14}) and 75 possible isomers of *decane* ($C_{10}H_{22}$).

2.2.1Physical Properties

The saturated hydrocarbons are colorless, practically odorless, and quite insoluble in water, particularly those with five or more carbon atoms. They dissolve readily in many organic solvents. At room temperature all members through C5 are gases, those from C6 to C17 are liquids, and those above C17 are solids. Solubility in water in general decreases with increasing size.

Physical constants of some alkanes

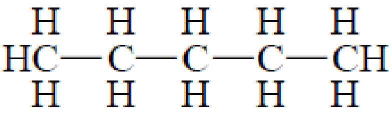
Name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°*	Calcd. no. of isomers
Methane	CH_4	−182.4	−161.5	$0.423^{-162°}$	1
Ethane	C_2H_6	−182.8	−88.6	$0.545^{-89°}$	1
Propane	C_3H_8	−187.6	−42.1	$0.493^{25°}$	1
Butane	C_4H_{10}	−138.2	−0.5	$0.573^{25°}$	2
Pentane	C_5H_{12}	−129.7	36.0	0.626	3
Hexane	C_6H_{14}	−95.3	68.7	0.655	5
Heptane	C_7H_{16}	−90.6	98.5	0.684	9
Octane	C_8H_{18}	−56.8	125.6	$0.699^{25°}$	18
Nonane	C_9H_{20}	−53.5	150.8	0.718	35
Decane	$C_{10}H_{22}$	−29.7	174.1	0.730	75

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

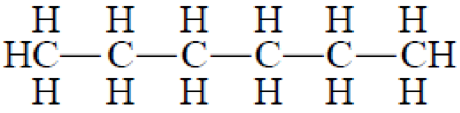
Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

2.2.2Nomenclature

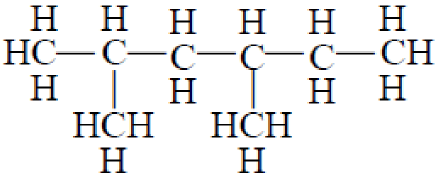
The alkanes are characterized by names ending in *-ane*. The straight-chain compounds are termed *normal* compounds. The branched-chain compounds and the derivatives of both straight- and branched-chain compounds are difficult to name with any degree of specificity. The IUPAC system, as proposed by the International Union of Pure and Applied Chemistry, is commonly used. In this system the compounds are named in terms of the longest continuous chain of carbon atoms in the molecule. A few examples will illustrate the method.


$\underset{H}{\overset{H}{HC}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{CH}}$

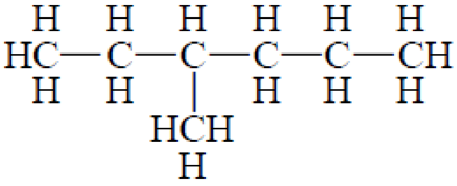
n-Pentane


$\underset{H}{\overset{H}{HC}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{CH}}$

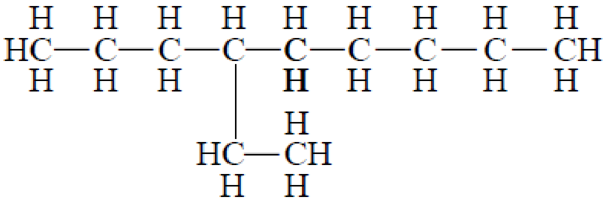
n-Hexane



2.4-Dimethylhexane
(an isomer of octane)



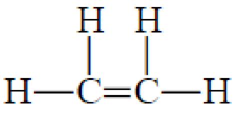
3-Methylhexane
(an isomer of heptane)



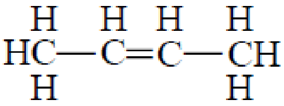
4-Ethylnonane
(an isomer of undecane)

2.3Alkenes

The alkenes all contain one double bond between two adjacent carbon atoms, and their names all end in *-ylene* (older nomenclature) or *-ene*. The alkenes are also called *olefins*. Alkenes, particularly ethene, propene, and butene are formed in great quantities during the cracking or pyrolysis of petroleum.


$H-\overset{H}{C}=\overset{H}{C}-H$

Ethylene
or
ethene


$\underset{H}{\overset{H}{HC}}-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{CH}}$

Butylene
or
2-butene

2.3.1Physical Properties

IUPAC name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°C/4°C*	Calcd. no. of isomers
Ethene	$CH_2{=}CH_2$	−169	−103.7	$0.568^{-104°}$	1
Propene	$CH_2{=}CHCH_3$	−185.2	−47.6	$0.505^{25°}$	1
1-Butene	$CH_2{=}CHCH_2CH_3$	−185.3	−6.2	$0.588^{25°}$	3
1-Pentene	$CH_2{=}CH(CH_2)_2CH_3$	−165.2	29.9	0.640	5
1-Hexene	$CH_2{=}CH(CH_2)_3CH_3$	−139.7	63.4	0.673	13
1-Heptene	$CH_2{=}CH(CH_2)_4CH_3$	−119.7	93.6	0.697	27
1-Octene	$CH_2{=}CH(CH_2)_5CH_3$	−101.7	121.2	0.715	66
1-Nonene	$CH_2{=}CH(CH_2)_6CH_3$	−81.3	149.9	$0.725^{25°}$	153
1-Decene	$CH_2{=}CH(CH_2)_7CH_3$	−66.3	170.5	0.741	377

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

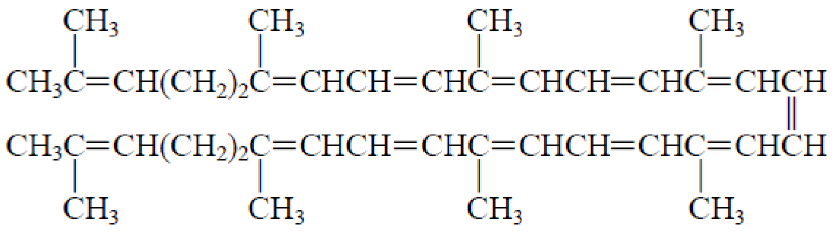
Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

2.3.2Nomenclature

When aliphatic compounds contain two double bonds in the molecule, they are called alkadienes, sometimes dienes for short. The compound 1,3-butadiene is an important example:

$$CH_2{=}CHCH{=}CH_2$$

Some organic compounds contain more than two double bonds per molecule. The red coloring matter of tomatoes, lycopene, and the yellow coloring matter of carrots are examples.



$$\begin{array}{r} CH_3\overset{CH_3}{\overset{|}{C}}{=}CH(CH_2)_2\overset{CH_3}{\overset{|}{C}}{=}CHCH{=}CH\overset{CH_3}{\overset{|}{C}}{=}CHCH{=}CH\overset{CH_3}{\overset{|}{C}}{=}CHCH \\ \| \quad \\ CH_3\underset{CH_3}{\underset{|}{C}}{=}CH(CH_2)_2\underset{CH_3}{\underset{|}{C}}{=}CHCH{=}CH\underset{CH_3}{\underset{|}{C}}{=}CHCH{=}CH\underset{CH_3}{\underset{|}{C}}{=}CHCH \end{array}$$

Lycopene ($C_{40}H_{56}$)

2.4Alkynes

The alkynes have a triple bond between adjacent carbon atoms. These compounds are found to some extent in industrial wastes from certain industries, particularly those from the manufacture of some types of synthetic rubber.

$$H{-}C{\equiv}C{-}H$$

3.Alcohols

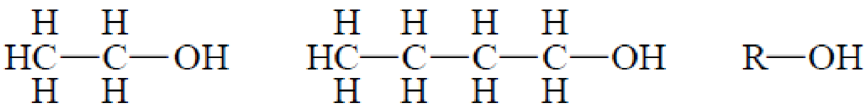
Alcohols are considered the primary oxidation product of hydrocarbons.

$$\underset{\text{Methane}}{CH_4} + \tfrac{1}{2}O_2 \rightarrow \underset{\text{Methyl alcohol or methanol}}{CH_3OH}$$

$$\underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3} + \tfrac{1}{2}O_2 \rightarrow \underset{n\text{-Propyl alcohol or propanol}}{CH_3{-}CH_2{-}CH_2OH}$$

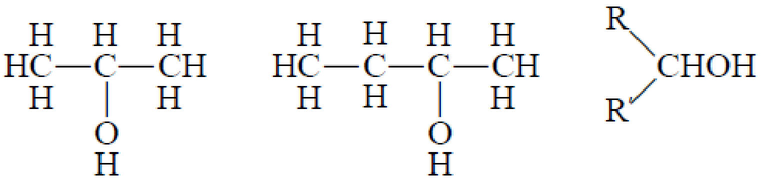
They cannot be prepared in this manner, however, because the reaction cannot be stopped with alcohols as the end product. Nevertheless, the reaction illustrates an initial step in biological degradation of hydrocarbons under aerobic conditions. Alcohols may be considered as *hydroxy alkyl* compounds. For convenience, the alkyl group in alcohols and other organic compounds is often represented by R-, and the general formula for alcohols is R-OH. The OH group does not easily ionize; consequently, alcohols are neutral in reaction. The chemistry of alcohols is related entirely to the OH group.

Alcohols are classified into three groups: primary, secondary, and tertiary, depending upon where the OH group is attached to the molecule. If the OH group is on a terminal (primary) carbon atom, it is a *primary* alcohol.



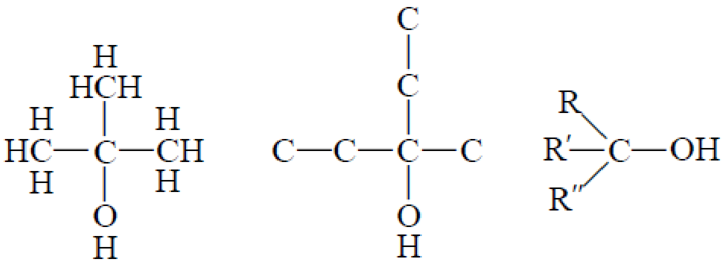
Primary alcohols

If the OH group is attached to a carbon atom that is joined to two other carbon atoms, it is a *secondary* alcohol, and the carbon atom to which it is attached is a *secondary carbon atom.*



Secondary alcohols

If the OH group is attached to a carbon atom that is joined to three other carbon atoms, it is a *tertiary* alcohol, and the carbon atom to which it is attached is a *tertiary carbon atom.*



Tertiary alcohols

The chemistry of the primary, secondary, and tertiary alcohols differs considerably (e.g., bacterial oxidation of tertiary alcohols is much more difficult than of primary alcohols). Therefore, it is important to know how to differentiate among them.

The alcohols of greatest commercial importance are methyl, ethyl, isopropyl, and *n*-butyl.

Methanol (also called methyl alcohol) is used to a considerable extent for synthesis of organic compounds. It has been used as an antifreeze for automobiles. It is prepared mainly by synthesis from natural gas and steam as follows:

$$CH_4 + H_2O \xrightarrow[\text{catalyst}]{\Delta\ \text{pressure}} CH_3OH + H_2$$

but may be manufactured from carbon monoxide and hydrogen.

Ethanol (ethyl alcohol) is used for the synthesis of organic compounds, the production of beverages, and the manufacture of medicines. Alcohol intended for beverages is often manufactured by the fermentation of starch derived from a variety of materials, such as corn, wheat, rye, rice, and potatoes. The reactions involved are as follows:

$$\text{Starch} + \text{water} \xrightarrow[\text{of malt}]{\text{enzyme}} \text{maltose}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{of yeast}]{\text{enzyme}} 2\ \text{glucose}$$

Fermentation of the glucose yields carbon dioxide and alcohol.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{fermentation}} 2CO_2 + 2C_2H_5OH$$

Isopropanol (isopropyl alcohol) **($CH_3CHOHCH_3$)** is widely used in organic synthesis, and considerable amounts are sold as “dry gas” to prevent separation of water in the fuel tanks of automobiles. It is prepared by hydration of propylene derived from the cracking of petroleum.

Normal butanol (*n*-butyl alcohol) **($CH_3CH_2CH_2CH_2OH$)** is used to prepare butyl acetate, an excellent solvent. It is often referred to as “synthetic banana oil” because of its odor which resembles natural banana oil, amyl acetate. Normal butanol is prepared from cornstarch by a fermentation process utilizing a particular microorganism, *Clostridium acetobutylicum.*

3.1Physical Properties

The short-chain alcohols are completely soluble in water due in part to the increased polarity caused by the hydroxyl group. As with alkanes and alkenes, as alcohol molecular size increases, melting and boiling points increase while water solubility decreases. The miscibility of C1–C3 alcohols makes them useful as co-solvents for remediation of contaminated subsurface environments. Alcohols with more than 12 carbon atoms are colorless waxy solids and very poorly soluble in water.

Name of radical	IUPAC name of alcohol	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°[*]	Calcd. no. of isomers
Methyl	Methanol	CH_3OH	−97.6	64.6	0.791	1
Ethyl	Ethanol	C_2H_5OH	−114.1	78.2	0.789	1
Propyl	1-Propanol	C_3H_7OH	−126.1	97.2	0.800^{25°	2
Butyl	1-Butanol	C_4H_9OH	−89.8	117.7	0.810	4
Pentyl	1-Pentanol	$C_5H_{11}OH$	−78.9	137.9	0.814	8
Hexyl	1-Hexanol	$C_6H_{13}OH$	−44.6	157.6	0.814	17
Heptyl	1-Heptanol	$C_7H_{15}OH$	−34	176.4	0.822	39
Octyl	1-Octanol	$C_8H_{17}OH$	−15.5	195.1	0.826^{25°	89
Nonyl	1-Nonanol	$C_9H_{19}OH$	−5	213.3	0.827	211[†]
Decyl	1-Decanol	$C_{10}H_{21}OH$	6.9	231.1	0.830	507

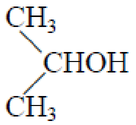
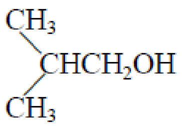
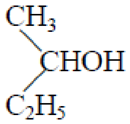
[*] Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

[†] These numbers are for all the isomers of a given carbon content.

Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

3.2Nomenclature

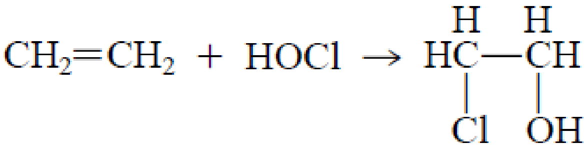
The alcohols of commercial significance are usually called by their common names. The IUPAC system must be employed, however, to differentiate among isomers and to name the higher members, such as hexadecanol. In this terminology, the names of all alcohols end in *-ol.*

Formula	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
C_2H_5OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	1-Propanol
 $\begin{matrix}CH_3\\ \quad CHOH\\ CH_3\end{matrix}$	Isopropyl alcohol	2-Propanol
$CH_3CH_2CH_2CH_2OH$	*n*-Butyl alcohol	1-Butanol
 $\begin{matrix}CH_3\\ \quad CHCH_2OH\\ CH_3\end{matrix}$	Isobutyl alcohol	2-Methyl-1-propanol
 $\begin{matrix}CH_3\\ \quad CHOH\\ C_2H_5\end{matrix}$	*sec*-Butyl alcohol	2-Butanol
$(CH_3)_3COH$	*tert*-Butyl alcohol	2-Methyl-2-propanol

Basic Concepts of Organic Chemistry by Sawyer

3.3Polyhydroxy Alcohol

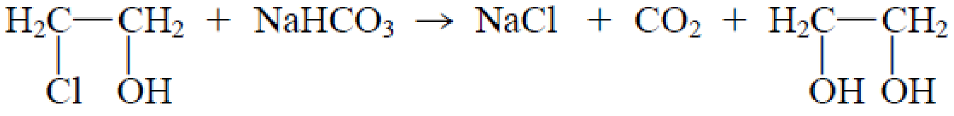
Those alcohols having two hydroxyl groups per molecule are known as *glycols*. The principal glycol of commercial significance is *ethylene glycol* (1,2-ethanediol), which is prepared from ethene. Ethene adds hypochlorous acid to form ethylene chlorohydrin.



$$CH_2{=}CH_2 + HOCl \rightarrow \underset{Cl}{\overset{H}{HC}}-\underset{OH}{\overset{H}{CH}}$$

Ethylene chlorohydrin

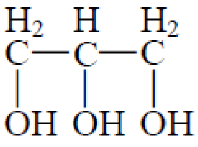
and treatment of the chlorohydrin with sodium bicarbonate produces ethylene glycol.



$$\underset{Cl}{H_2C}-\underset{OH}{CH_2} + NaHCO_3 \rightarrow NaCl + CO_2 + \underset{OH}{H_2C}-\underset{OH}{CH_2}$$

Ethylene glycol

It is used extensively as a nonevaporative, radiator antifreeze compound. *Glycerol* or glycerin is a trihydroxy alcohol (1,2,3-trihydroxypropane).



$$\underset{OH}{\overset{H_2}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H_2}{C}}$$

Glycerol

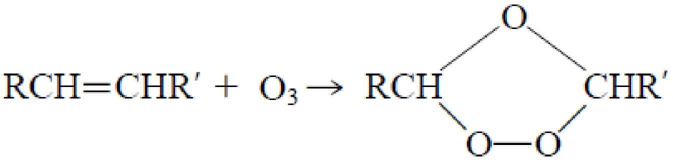
Glycerol is used in a wide variety of commercial products: foods, cosmetics, medicines, tobaccos, and so on. It is used for the manufacture of nitroglycerin, an important component of dynamite.

4.Aldehydes and Ketones

Aldehydes are the oxidation products of primary alcohols (ROH). *Ketones* are the oxidation products of secondary alcohols.

All aldehydes have the characteristic *carbonyl* group, O=C-H. The general structural formula for an aldehyde is R-CHO, where R represents any alkyl group: CH_3-, C_2H_5-and so on.

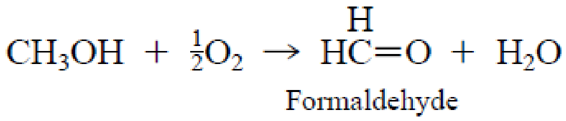
Aldehydes can also be formed from unsaturated hydrocarbons by ozonation. The hydrocarbons are first converted to an ozonide by ozone.



An ozonide

Although a wide variety of aldehydes can be formed from primary alcohols, only a few are of commercial importance. Aldehydes can also be produced by reduction of carboxylic acids.

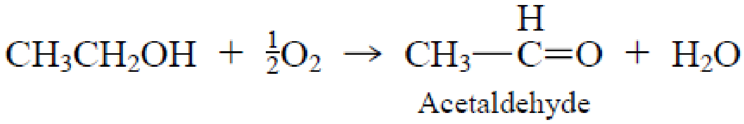
Formaldehyde Formaldehyde is formed by the oxidation of methanol.



$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow \underset{\text{Formaldehyde}}{\overset{\text{H}}{\text{H}C}=O} + H_2O$$

It is used extensively in organic synthesis. It is very toxic to microorganisms, and, because of this property, it is used in embalming fluids and fluids used for the preservation of biological specimens. Industrial wastes containing formaldehyde were considered at one time to be too toxic for treatment by biological methods.

Acetaldehyde Acetaldehyde is formed by the oxidation of ethanol.



$$CH_3CH_2OH + \tfrac{1}{2}O_2 \rightarrow \underset{\text{Acetaldehyde}}{CH_3{-}\overset{\text{H}}{C}=O} + H_2O$$

It is used extensively in organic synthesis. A major industrial use involves its condensation with formaldehyde to produce pentaerythritol [C(CH2OH)4], an important intermediate for the production of a wide variety of products, including aldehyde resin paints. Development of a biological treatment process for the formaldehyde bearing industrial wastes from the manufacture of pentaerythritol led to the concept of toxicity threshold mentioned earlier.

Common name	IUPAC name	Formula
Formaldehyde	Methanal	$HCHO$
Acetaldehyde	Ethanal	CH_3CHO
Propionaldehyde	*n*-Propanal	C_2H_5CHO
Butyraldehyde	*n*-Butanal	C_3H_7CHO
Valeraldehyde	*n*-Pentanal	C_4H_9CHO
Caproaldehyde	*n*-Hexanal	$C_5H_{11}CHO$
Heptaldehyde	*n*-Heptanal	$C_6H_{13}CHO$
Acrolein		$CH_2{=}CHCHO$
Citral		$C_9H_{15}CHO$
Citronellal		$C_9H_{17}CHO$

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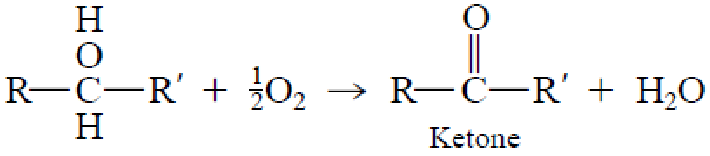
5.Ketones

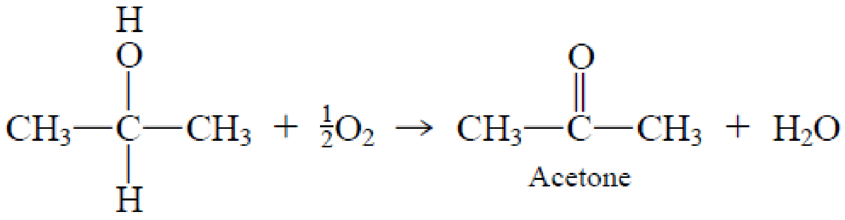
Ketones are prepared by the oxidation of secondary alcohols.



$$\mathrm{R{-}\overset{\overset{H}{O}}{\underset{H}{C}}{-}R' + \tfrac{1}{2}O_2 \rightarrow \underset{Ketone}{R{-}\overset{\overset{O}{\|}}{C}{-}R'} + H_2O}$$

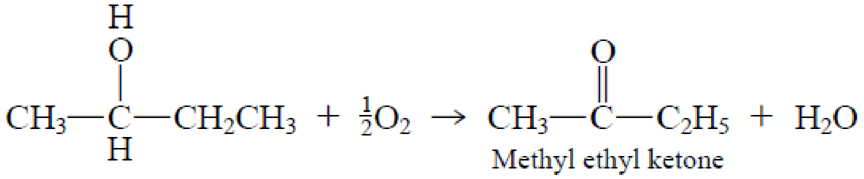
Ketones have two alkyl groups attached to the carbonyl group, -C=O while aldehydes have one R group and a hydrogen atom. The R groups in ketones may be the same or different.

Acetone Acetone (dimethyl ketone) is the simplest ketone and is produced by the oxidation of isopropyl alcohol (2-propanol).



$$\mathrm{CH_3{-}\overset{\overset{H}{\overset{O}{|}}}{\underset{\underset{H}{|}}{C}}{-}CH_3 + \tfrac{1}{2}O_2 \rightarrow \underset{Acetone}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + H_2O}$$

Methyl ethyl ketone Methyl ethyl ketone is prepared by the oxidation of 2-butanol.



$$\mathrm{CH_3{-}\overset{\overset{H}{\overset{O}{|}}}{\underset{H}{C}}{-}CH_2CH_3 + \tfrac{1}{2}O_2 \rightarrow \underset{Methyl\ ethyl\ ketone}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}C_2H_5} + H_2O}$$

Ketones are used as solvents in industry and for the synthesis of a wide variety of products.

Common name	**IUPAC name**
Acetone	Propanone
Methyl ethyl ketone	Butanone
Diethyl ketone	3-Pentanone
Methyl propyl ketone	2-Pentanone
Methyl isopropyl ketone	3-Methyl-2-butanone
n-Butyl methyl ketone	2-Hexanone
Ethyl propyl ketone	3-Hexanone
Dipropyl ketone	4-Heptanone
Dibutyl ketone	5-Nonanone

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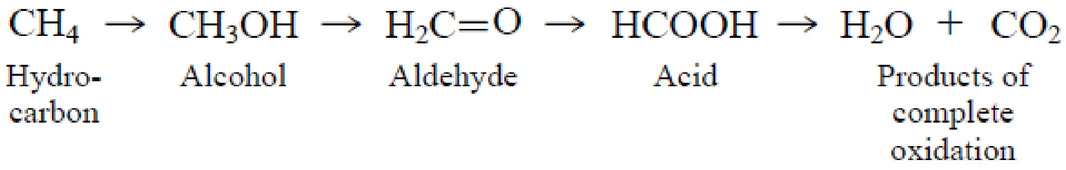
6.Acids

Acids represent the highest oxidation state that an organic compound can attain. Further oxidation results in the formation of carbon dioxide and water, which are classed as inorganic compounds, and the organic compound is considered completely destroyed.



Organic acids typically contain the group. This is called the *carboxyl* group and is commonly written OH-C=O. Acids with one carboxyl group are known as *monocarboxylic* acids, and those with more than one is *polycarboxylic* acids. In addition, derivatives of phenol can act as acids. The acids may be saturated or unsaturated. Some contain hydroxy groups within the molecule.

6.1Saturated Monocarboxylic Acids

A wide variety of saturated monocarboxylic acids occur in nature as constituents of fats, oils, and waxes. Unsaturated acids are also found in these materials, and, as a result, both types are commonly known as *fatty* acids. The majority of the fatty acids derived from natural products have an even number of carbon atoms and usually
have a straight-chain or normal structure.

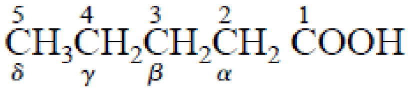
6.2Physical Properties The first nine members, C1 to C9, are liquids. All the others are greasy solids. Formic, acetic, and propionic acid have sharp penetrating odors; the remaining liquid acids have disgusting odors, particularly butyric and valeric. Butyric acid gives rancid butter its characteristic odor. Industrial wastes from the dairy industry must be treated with considerable care to prevent formation of butyric acid and consequent odor problems. The "volatile acids" (C1 to C5) are quite soluble in water.

Common name	IUPAC name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°*	pKa at 25°
Formic	Methanoic	$HCOOH$	8.3	101	1.220	3.75
Acetic	Ethanoic	CH_3COOH	16.6	117.9	$1.045^{25°}$	4.756
Propionic	Propanoic	C_2H_5COOH	−20.7	141.1	0.993	4.87
Butyric	Butanoic	C_3H_7COOH	−5.7	163.7	0.958	4.83
Valeric	Pentanoic	C_4H_9COOH	−34	186.1	0.939	$4.83^{20°}$
Caproic	Hexanoic	$C_5H_{11}COOH$	−3	205.2	0.927	4.85
Enanthic	Heptanoic	$C_6H_{13}COOH$	−7.5	222.2	0.918	4.89
Caprylic	Octanoic	$C_7H_{15}COOH$	16.3	239	0.911	4.89
Pelargonic	Nonanoic	$C_8H_{17}COOH$	12.3	254.5	0.905	4.96
Capric	Decanoic	$C_9H_{19}COOH$	31.9	268.7	$0.886^{40°}$	
Palmitic	Hexadecanoic	$C_{15}H_{31}COOH$	63.1	351.5	$0.853^{62°}$	
Stearic	Octadecanoic	$C_{17}H_{35}COOH$	68.8	232	0.941	

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.
Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

6.3Nomenclature

The common names are usually used for most of the acids, except for those with 7, 8, 9, and 10 carbon atoms. In naming derivatives of acids, the IUPAC system is frequently abandoned for a system using Greek letters to identify the carbon atoms. In this system the carboxyl group is the reference point, and carbon atoms are numbered from it as follows:



$$\overset{5}{\underset{\delta}{C}}H_3\overset{4}{\underset{\gamma}{C}}H_2\overset{3}{\underset{\beta}{C}}H_2\overset{2}{\underset{\alpha}{C}}H_2\ \overset{1}{C}OOH$$

The carbon atom next to the carboxyl group is *alpha,* the next *beta,* then *gamma, delta,* and so on. The terminal carbon atom is also referred to as being in the *omega* position.

6.4Unsaturated Monocarboxylic Acids

The principal unsaturated monocarboxylic acids are as follows:

Acrylic Acid (CH2¨CHCOOH) Acrylic acid is used extensively because of its ability to polymerize, a characteristic of many compounds with unsaturated linkages. Derivatives of the acid are used to form colorless plastics such as Lucite and Plexiglas.

Oleic Acid [$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$]

Linoleic Acid [$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$]

Linolenic Acid [$CH_3(CH_2CH{=}CH)_3CH_2(CH_2)_6COOH$]

Oleic, linoleic, and linolenic acids are normal constituents of the glycerides of most fats and oils. A glyceride is the ester formed by combining glycerol with these acids. Oleic acid is considered to be an essential acid in the diet of humans and animals. Linoleic and linolenic acids as glycerides are important constituents of linseed and other drying oils. Their value for this purpose is dependent upon the multiple double bonds that they possess.

6.5Polycarboxylic Acids

The most important of the polycarboxylic acids are those that have two carboxyl groups, one on each end of a normal chain of carbon atoms.

Name	Formula
Oxalic	$(COOH)_2$
Malonic	$CH_2(COOH)_2$
Succinic	$(CH_2)_2(COOH)_2$
Glutaric	$(CH_2)_3(COOH)_2$
Adipic	$(CH_2)_4(COOH)_2$
Pimelic	$(CH_2)_5(COOH)_2$
Suberic	$(CH_2)_6(COOH)_2$

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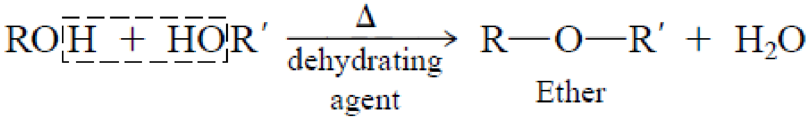
Adipic acid is of some interest because it is used in the manufacture of nylon fiber and may be expected to occur in the industrial wastes of that industry.

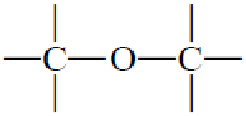
7.Ethers

Ethers are formed by treatment of alcohols with strong dehydrating agents. In the reaction, one molecule of water is removed from two molecules of alcohol.



$$\text{RO}\boxed{\text{H} + \text{HO}}\text{R}' \xrightarrow[\text{dehydrating agent}]{\Delta} \underbrace{\text{R—O—R}'}_{\text{Ether}} + H_2O$$

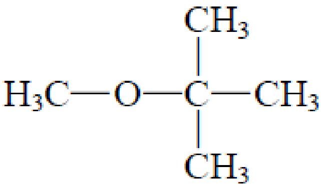
The two fragments of the alcohol join to form an ether. The alkyl groups are joined through an oxygen atom; thus, a carbon-to-oxygen-to-carbon bond is established.



$$-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$$

Ethers are used widely as solvents. The low-molecular-weight ethers are highly flammable. When left exposed to air, they are prone to form peroxides that are extremely explosive, particularly when recovery by distillation is practiced and the distillation is allowed to go to dryness. Diethyl ether has been used widely as an anesthetic. Ethers are generally resistant to biological oxidation. Fortunately, most are relatively insoluble in water and can be separated from industrial wastes by flotation or decantation procedures.

An important ether is methyl *tert*-butyl ether (MTBE).



$$H_3C-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

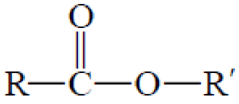
MTBE was first used in the late 1970s as an octane enhancer when lead additives to gasoline were being phased out. More recently it has been added to gasoline as a fuel oxygenate to help reduce carbon monoxide emissions from gasoline combustion. MTBE is very soluble in water, volatile, not strongly absorbed to particulate matter, and relatively nonbiodegradable. Thus, upon release to the environment, it is very mobile. Through leaking storage tanks, pipelines, and other uncontrolled releases to the environment, MTBE has been found in a large number of surface waters and groundwaters. Although the health effects associated with MTBE exposure are not yet completely known, action levels as low as 20 *u*g/L have been set due to taste and odor considerations. Because of these problems, there is a proposed ban on the use of MTBE as a fuel additive. Ethanol is an alternative for MTBE as a fuel additive.

8.Esters

Esters are compounds formed by the reaction of acids and alcohols, similar to the reactions of acids and bases to form salts in inorganic chemistry. The reaction between low-molecular-weight organic acids and alcohols is never complete. Hydrolysis occurs and a reversible reaction results. The reaction may be represented by the general equation

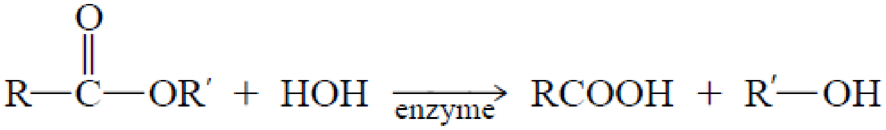
$$\mathrm{RCO{—}\boxed{OH\ +\ H}{—}OR_1} \leftrightharpoons \mathrm{H_2O} + \mathrm{RCOOR_1}$$

The general formula of an ester is



$$\mathrm{R{—}\overset{\overset{\displaystyle O}{\|}}{C}{—}O{—}R'}$$

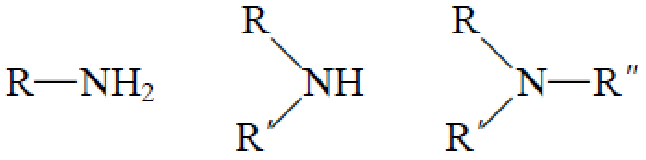
A wide variety of esters are used in chemical manufacturing. Most esters have highly pleasing odors. Butyl acetate smells like banana oil (amyl acetate) and is used for solvent purposes. Many esters are used in flavoring extracts and perfumes. Esters have been used to some extent as immiscible solvents in the separation and purification of antibiotics. Considerable quantities often reach the sewer system and become an industrial waste problem. Enzymes liberated by many microorganisms hydrolyze esters to yield the corresponding acid and alcohol.



$$\mathrm{R{—}\overset{\overset{\displaystyle O}{\|}}{C}{—}OR'} + \mathrm{HOH} \xrightarrow[\text{enzyme}]{} \mathrm{RCOOH} + \mathrm{R'{—}OH}$$

9.Amines

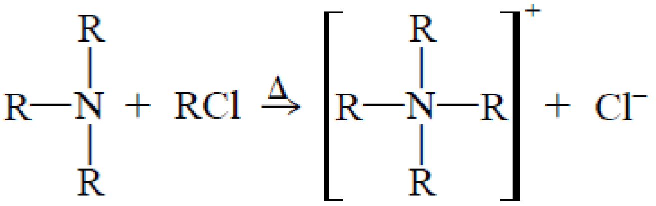
The amines are alkyl derivatives of ammonia. They are of three types: primary, secondary, and tertiary.



Primary *Secondary* *Tertiary*

In *primary amines,* one hydrogen atom of ammonia is replaced by an alkyl group such as CH_3-, C_2H_5-, and so on. In *secondary amines,* two hydrogen atoms of ammonia are replaced by alkyl groups, and in *tertiary amines,* all three hydrogens are replaced. The amines, like ammonia, are all basic in reaction. The basicity increases from primary to tertiary. The amines are found in certain industrial wastes, particularly those from the fish and beet-sugar industries. It is well known that deamination reactions (removal of ammonia) are easily accomplished with primary amines, and somewhat less easily with secondary amines.

Tertiary amines combine with alkyl halides to form *quaternary ammonium salts* as follows:

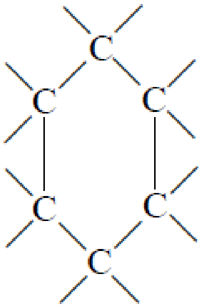


$$\mathrm{R}-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{N}}} + \mathrm{RCl} \xrightarrow{\Delta} \left[\mathrm{R}-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{N}}}-\mathrm{R}\right]^{+} + \mathrm{Cl}^{-}$$

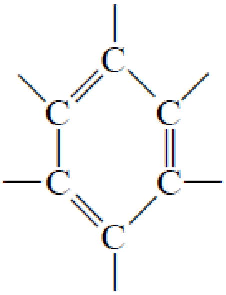
The compounds formed are actually chloride salts and ionize to form a quaternary ammonium ion and a chloride ion. The quaternary ammonium salts have bactericidal properties that can be enhanced by the proper choice of the R groups. They are therefore of interest to public health professionals, who find them useful as disinfecting agents in food- and beverage-dispensing establishments. They are also used as disinfectants in the laundering of babies' diapers to control infections of bacteria responsible for the rapid hydrolysis of urea. Solutions of the quaternary ammonium salts are sold for disinfecting purposes under a variety of trade names.

10.Aromatic Compounds

The *aromatic* organic compounds are all ring compounds or have cyclic groups of aromatic nature in their structure. The carbon atoms in these ring compounds have only one covalent bond, in contrast to those in aliphatic compounds with two.

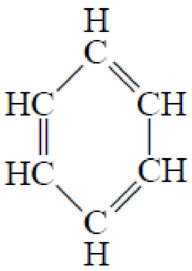


Aliphatic ring

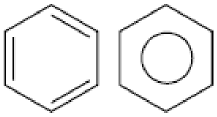


Aromatic ring

The simplest aromatic ring is made up of six carbon atoms and is known as the benzene ring. *Benzene* (C6H6) is known as the *parent compound* of the aromatic series. Hydrocarbons based on the benzene ring as a structural unit are also called *arenes*. The benzene ring is usually represented by the Kekule formula.



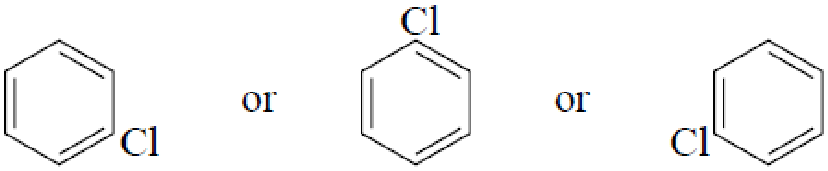
Kekule
benzene formula



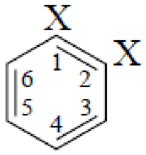
Simplified
formulas

This formula shows double bonds between alternate carbon atoms in the ring. The double bonds, however, are not like those in the aliphatic series. For example, halogens will not add to such bonds. For purposes of simplicity, most chemists represent the benzene ring as one of the simplified formulas shown.

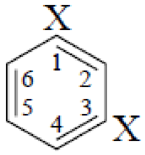
10.1Nomenclature
It is important to note that carbon atoms are not shown in the simplified benzene formula. Also, each carbon atom in a ring is like all others, and therefore, when substitution occurs on one carbon atom, the same compound is formed as though substitution had occurred on any of the other five carbon atoms. Thus, for monochlorobenzene (C_6H_5Cl) there is only one compound, no matter how the structural formula is written.



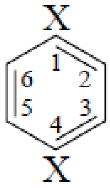
When substitution occurs on two or more carbon atoms of a benzene ring, it becomes necessary to establish some system of nomenclature. Two systems are used.



1,2- or *ortho*
placement

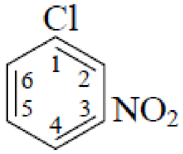


1,3- or *meta*
placement

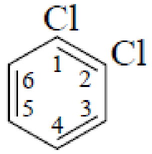


1,4- or *para*
placement

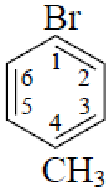
Di-substituted compounds, such as dichlorobenzene, are commonly referred to as *ortho, meta,* or *para,* depending on the point of substitution. If substitution is on adjacent carbon atoms, the term ortho is used; if on carbon atoms once removed, the term meta is used; and if on carbon atoms opposite each other, the term para is used. Tri- and other poly-substituted compounds must be named by another system. In this system, the carbon atoms of the benzene ring are numbered in a clockwise manner. Examples are



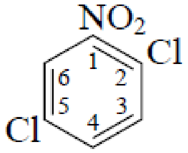
m-Chloronitrobenzene



o-Dichlorobenzene



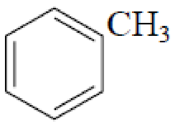
p-Bromotoluene



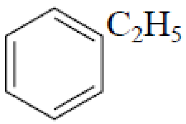
2,5-Dichloro-1-nitrobenzene

10.2Benzene Series

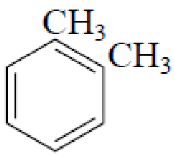
The benzene series of homologous compounds is made up of alkyl substitution products of benzene. They are found along with benzene in coal tar and in many crude petroleums. *Toluene,* or methylbenzene, is the simplest alkyl derivative of benzene. *Xylene* is a dimethyl derivative of benzene.



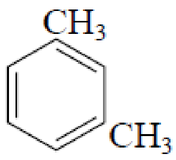
Toluene



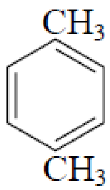
Ethylbenzene



o-Xylene



m-Xylene



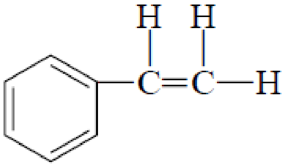
p-Xylene

It exists in three isomeric forms: ortho-xylene, meta-xylene, and para-xylene. All are isomeric with ethylbenzene in that they have the same general formula, C_8H_{10}. Together with benzene, these compounds are commonly referred to as the BTEX group. The benzene-series hydrocarbons are used extensively as solvents and in chemical synthesis, and are common constituents of petroleum products (e.g., gasoline). Although they are relatively insoluble in water, wastewaters and leachates containing 10 to as high as 1000 mg/L for the BTEXs have been observed. These compounds are frequently detected in groundwaters, with a major source being leaking underground gasoline storage tanks. The benzene-series compounds have been implicated in several human health effects, most notably cancer. Benzene is known to cause leukemia. The current drinking water MCLs are 5 *u*g/L for benzene, 700 ug/L for ethylbenzene, 1 mg/L for toluene, and 10 mg/L for the sum total of the xylenes.

Name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°
Benzene	C_6H_6	5.5	80.0	0.877
Toluene	$C_6H_5CH_3$	−94.9	110.6	0.867
o-Xylene	$C_6H_4(CH_3)_2$	−25.2	144.5	0.880^{10°
m-Xylene		−47.8	139.1	0.864
p-Xylene		13.2	138.3	0.861
Ethylbenzene	$C_6H_5C_2H_5$	−94.9	136.1	0.867

Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

Styrene (phenyl ethene), a benzene derivative, is an environmentally significant compound. It is used as a monomer in the production of a wide variety of polystyrene products (e.g., plastics, synthetic rubber). A drinking water MCL of 100 *u*g/L has been set for styrene.



Styrene

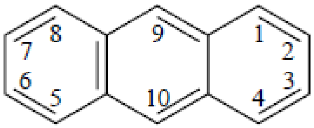
10.3Polyring Hydrocarbons

A wide variety of polycyclic aromatic hydrocarbons (PAHs) are known. A few examples will illustrate the possibilities.

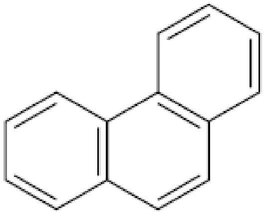
Naphthalene ($C_{10}H_8$) *Naphthalene* is a white crystalline compound derived from coal tar and was formerly used to produce mothballs.

It has been displaced largely from this market by paradichlorobenzene. A new system of nomenclature is applied to this type of compound. Carbon atoms adjacent to those shared in common by the two rings are known as _-carbon atoms and the others are known as _-carbon atoms. The carbon atoms shared by the two rings do not have hydrogen attached to them and so are given no designation.

Anthracene ($C_{14}H_{10}$) and Phenanthrene ($C_{14}H_{10}$) *Anthracene* and *phenanthrene* are isomers.

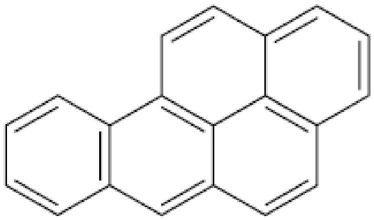


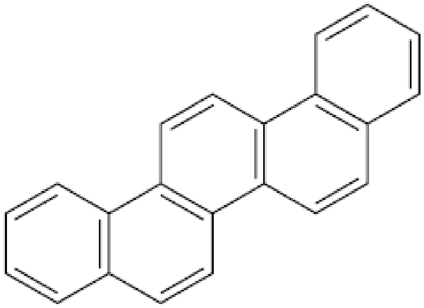
Anthracene



Phenanthrene

Their formulas illustrate the possible ways in which polycyclic aromatic hydrocarbons may occur. Many other more complex compounds, such as *benzo(a)pyrene* and *picene,* are known. Benzo(a)pyrene is a potent carcinogen.

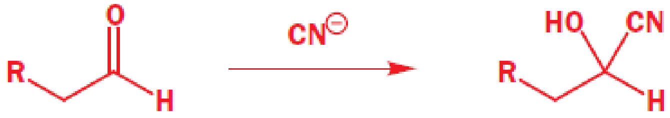

Benzo(a)pyrene


Picene

It should be remembered that hydrogen atoms occur on all carbon atoms of these compounds that are not common to two rings. Naphthalene and anthracene are widely used in the manufacture of dyestuffs. The phenanthrene nucleus is found in important alkaloids, such as morphine, vitamin D, sex hormones, and other compounds of great biological significance.

11.Chirality and Stereochemistry

Some compounds can exist as a pair of mirror-image forms. Let us take the example of a reaction.



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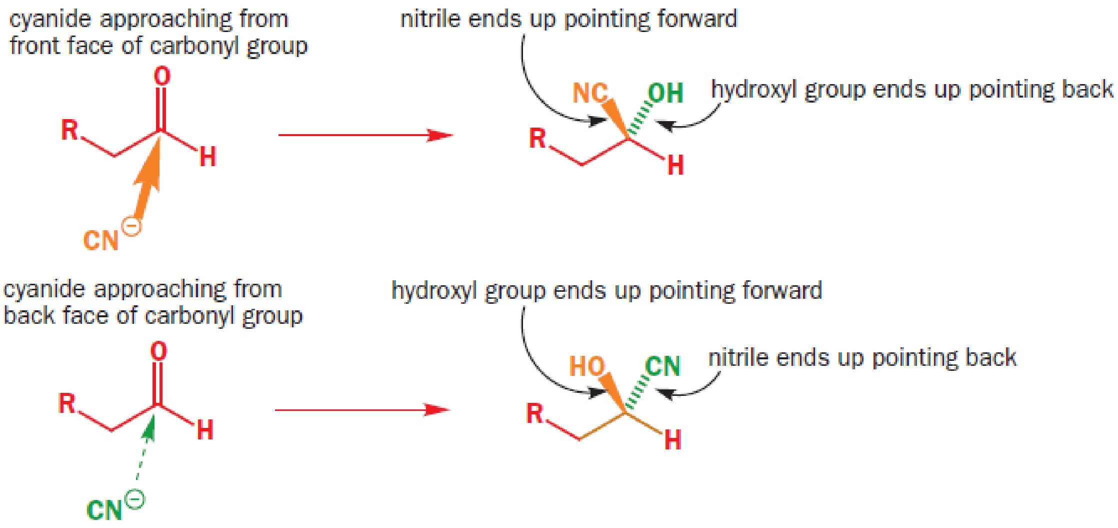
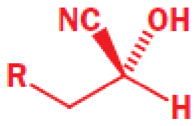
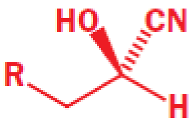
How many products are formed in this reaction? Well, the straightforward answer is one—there's only one aldehyde, only one cyanide ion, and only one reasonable way in which they can react. But this analysis is not *quite* correct. One point that we ignored when we first talked about this reaction, because it was irrelevant at that time, is that the carbonyl group of the aldehyde has two faces. The cyanide ion could attack either from the front face or the back face, giving, in each case, a distinct product.





A



B

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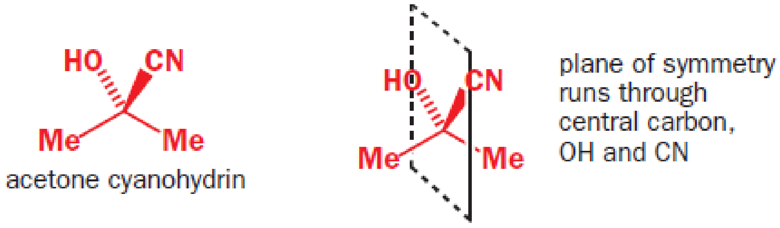
The structures are non-superimposable—so they are not identical. In fact, they are **mirror images** of each other: if we reflected one of the structures, A, in a mirror, we would get a structure that *is* identical with B.

We call two structures that are not identical but are mirror images of each other (like these two) **enantiomers**. Structures that are not superimposable on their mirror image, and can therefore exist as two enantiomers, are called **chiral**.

Chiral molecules have no plane of symmetry

What is the essential difference between these two compounds that means one is superimposable on its mirror image and one is not? The answer is symmetry. Acetone cyanohydrin has a plane of symmetry running through the molecule. This plane cuts the central carbon and the OH and CN groups in half and has one methyl group on each side.



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Any structure that has no plane of symmetry can exist as two mirror-image forms (*enantiomers*)

Any structure with a plane of symmetry cannot exist as two enantiomers

Some examples

Gloves , hands, and socks

Most gloves exist in pairs of nonidentical mirror-image forms: only a left glove fits a left hand and only a right glove fits a right hand. This property of gloves and of the hands inside them gives us the word 'chiral'—*cheir* is Greek for 'hand'. Hands and gloves are chiral; they have no plane of symmetry, and a left glove is not superimposable on its mirror image (a right glove). Feet are chiral too, as are shoes. But socks (usually!) are not. Though we all sometimes have problems finding two socks of a matching colour, once you've found them, you never have to worry about which sock goes on which foot, because socks are achiral. A pair of socks is manufactured as two identical objects, each of which has a mirror plane.

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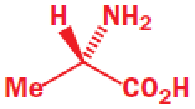
If a molecule contains one carbon atom carrying four different groups it will not have a plane of symmetry and must therefore be chiral. A carbon atom carrying four different groups is a stereogenic or chiral centre.

A racemic mixture is a mixture of two enantiomers in equal proportions. This principle is very important. Never forget that, if the starting materials of a reaction are achiral, and the products are chiral, they will be formed as a racemic mixture of two enantiomers.

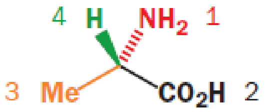
***R* and *S* can be used to describe the configuration of a chiral center**

Before going on to talk about single enantiomers of chiral molecules in more detail, we need to explain how chemists explain which enantiomer they're talking about. We can, of course, just draw a diagram, showing which groups go into the plane of the paper and which groups come out of the plane of the paper. This is best for complicated molecules. Alternatively, we can use the following set of rules to assign a letter, *R* or *S*, to describe the configuration of groups at a chiral center in the molecule.

Here again is the enantiomer of alanine you get if you extract alanine from living things.
1 Assign a priority number to each substituent at the chiral center. Atoms with higher atomic numbers get higher priority.
Alanine’s chiral center carries one N atom (atomic number 7), two C atoms (atomic number 6), and one H atom (atomic number 1). So, we assign priority 1 to the NH_2 group, because N has the highest atomic number. Priorities 2 and 3 will be assigned to the CO_2H and the CH_3 groups, and priority 4 to the hydrogen atom; but we need a way of deciding which of CO_2H and CH_3 takes priority over the other. If two (or more) of the atoms attached to the chiral center are identical, then we assign priorities to these two by assessing the atoms attached to those atoms. In this case, one of the carbon atoms carries oxygen atoms (atomic number 8), and one carries only hydrogen atoms (atomic number 1). So CO_2H is higher priority that CH_3; in other words, CO_2H gets priority 2 and CH_3 priority 3.



natural alanine



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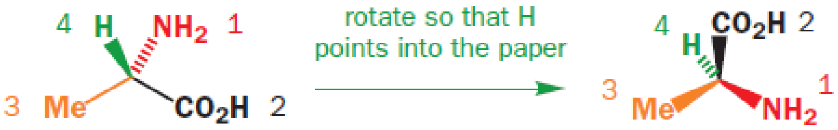
2 Arrange the molecule so that the lowest priority substituent is pointing away from you.
In our example, naturally extracted alanine, H is priority 4, so we need to look at the molecule with the H atom pointing into the paper, like this.



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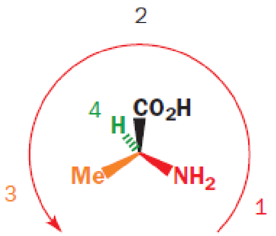
3 Mentally move from substituent priority 1 to 2 to 3. If you are moving in a clockwise manner, assign the label *R* to the chiral center; if you are moving in an anticlockwise manner, assign the label *S* to the chiral center.
A good way of visualizing this is to imagine turning a steering wheel in the direction of the numbering. If you are turning your car to the right, you have *R*; if you are turning to the left you have *S*. For our molecule of natural alanine, if we move from NH_2 (1) to CO_2H (2) to CH_3 (3) we’re going anticlockwise (turning to the left), so we call this enantiomer (*S*)-alanine.



(*S*)-alanine

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12.Spectroscopy

Spectroscopy is an important tool to distinguish between functional groups.

Spectroscopy: a technique to obtain structural information by studying how molecules interact with appropriate energy probes

Energy sources utilized in modern organic structure determination:

energy (eV)	source	wavelength (λ)	effect	information obtained
$\approx 10^4$	X-rays	≈ 1 Å	diffraction	atomic coordinates
10-70	electron bombardment	-----	fragmentation	mass of molecule & of its fragments
6.5-3.5 3.1-1.5	UV light VIS light	190-350 nm 400-800 nm	electronic transitions	nature of the π systems present in the molecule
0.5-0.04	IR light	2.5-30.0 μm	vibrational transitions	functional groups present in the molecule
10^{-6}-10^{-7}	radiowaves	0.5-15 m	nuclear transitions	chemical environment of H and C atoms

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12.1Infrared (IR) Spectroscopy

Infrared (IR) spectroscopy: a technique that derives information about functional groups present in a molecule on the basis of how the molecule reacts to energy absorption in the infrared range

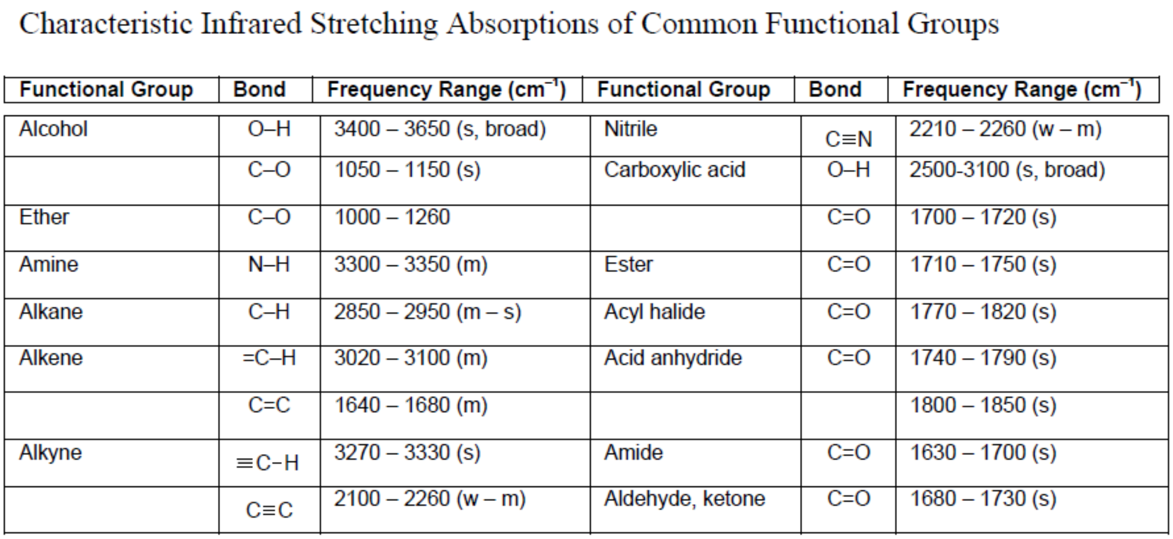
Wavelength of IR light of interest in structural organic chemistry: $2.5 < \lambda < 20\ \mu$ ($1\ \mu = 10^{-6}$ m)

Frequency of above IR radiation: $120 \geq \nu \geq 15$ GHz (1 GHz = 1012 Hz)

Spectrometer: the instrument required for the conduct of a spectroscopic experiment

Principle: given the way IR spectrometers are built, it is most convenient to express the energy of IR radiation in terms of its frequency. However, expressing frequencies is GHz is impractical because of the large numbers involved

Principle: absorption of IR light causes a molecule to undergo bond stretching and bond bending vibrations. We are only interested in **stretching vibrations** observed between 4000 and 1600 cm–1 Wavenumber (ν): a quantity measured in cm–1, and linearly related to frequency, that expresses the number of ondulations of the EM field in 1 cm of propagation.



Characteristic Infrared Stretching Absorptions of Common Functional Groups

Functional Group	Bond	Frequency Range (cm^{-1})	Functional Group	Bond	Frequency Range (cm^{-1})
Alcohol	O–H	3400 – 3650 (s, broad)	Nitrile	C≡N	2210 – 2260 (w – m)
	C–O	1050 – 1150 (s)	Carboxylic acid	O–H	2500-3100 (s, broad)
Ether	C–O	1000 – 1260		C=O	1700 – 1720 (s)
Amine	N–H	3300 – 3350 (m)	Ester	C=O	1710 – 1750 (s)
Alkane	C–H	2850 – 2950 (m – s)	Acyl halide	C=O	1770 – 1820 (s)
Alkene	=C–H	3020 – 3100 (m)	Acid anhydride	C=O	1740 – 1790 (s)
	C=C	1640 – 1680 (m)			1800 – 1850 (s)
Alkyne	≡C–H	3270 – 3330 (s)	Amide	C=O	1630 – 1700 (s)
	C≡C	2100 – 2260 (w – m)	Aldehyde, ketone	C=O	1680 – 1730 (s)

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12.2Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy

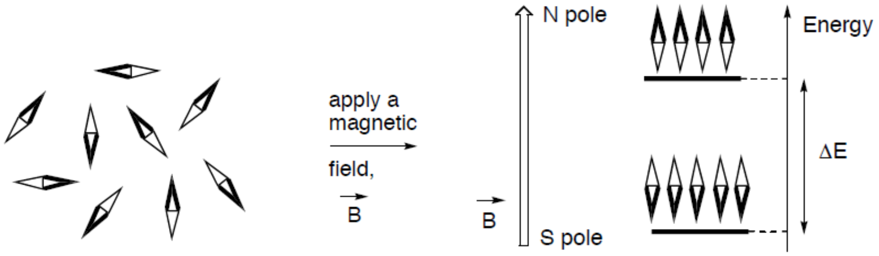
Nuclear Magnetic Resonance (NMR) spectroscopy: a technique that derives structural information on the basis of how a molecule reacts to energy absorption in the radiowave range.

Absorption of radiowaves induces transitions of magnetic nuclei such as 1H (= a proton: the nucleus of H atoms) and ^{13}C (the nucleus of a less common, non-radioactive, isotope of carbon that constitutes about 1% of total carbon), which reveal a great deal about the chemical surroundings of the corresponding atoms

NMR spectroscopy as one of the most powerful tools available for organic structural studies. The basis of NMR: quantum behavior of magnetic nuclei, such as ^{1}H and ^{13}C, in a magnetic field

- certain nuclei, such as 1H and 13C, have a permanent magnetic dipole, i.e., they behave like tiny "compass needles"
- if one takes a population of compass needles and places them in a magnetic field (e.g., the magnetic field of the Earth), the needles all orient themselves in such a way that their own magnetic field opposes the external one: their S pole would point to the magnetic N pole, and their N pole would point to the magnetic S pole. This corresponds to an energetically favorable situation
- Atomic nuclei, however, are subatomic particles, and as such they are subject to the laws of quantum mechanics. Quantum theory teaches that if a population of magnetic nuclei (1H, 13C, ...) is

placed in a magnetic field (e.g., inside a powerful magnet), they may orient themselves in such a way that their magnetic field either *opposes* the external one (= more energetically favorable situation), or *reinforces* it (less energetically favorable situation)! Moreover, only a very small excess population (of the order of parts per million) will position itself in the more energetically favorable state:



A population of magnetic nuclei (1H, 13C, ...) in the absence of a strong external field. The magnetic moments are oriented at random.

In the presence of magnetic field B, the nuclei populate two energy states that differ by ΔE

• Subjecting the population of magnetic nuclei thus distributed between the two energy states to an external source of energy exactly equal to ΔE will induce transitions of nuclei between the two states. Some nuclei will jump from the lower state to the higher one; some will decay from the higher state to the lower one.

• The energy corresponding to ΔE is readily available in the form of radio-waves. Modern NMR spectrometers employ radiofrequencies of the order of 100-900 MHz.

• Nuclei jumping from the lower to the higher state will absorb an energy equal to ΔE; those decaying from the higher to the lower state will emit an energy equal to ΔE.

Different protons in an organic molecule are embedded in regions of the molecule possessing distinct electronic densities; i.e., they find themselves in distinct chemical environments that shield them to a greater or lesser extent from B_0

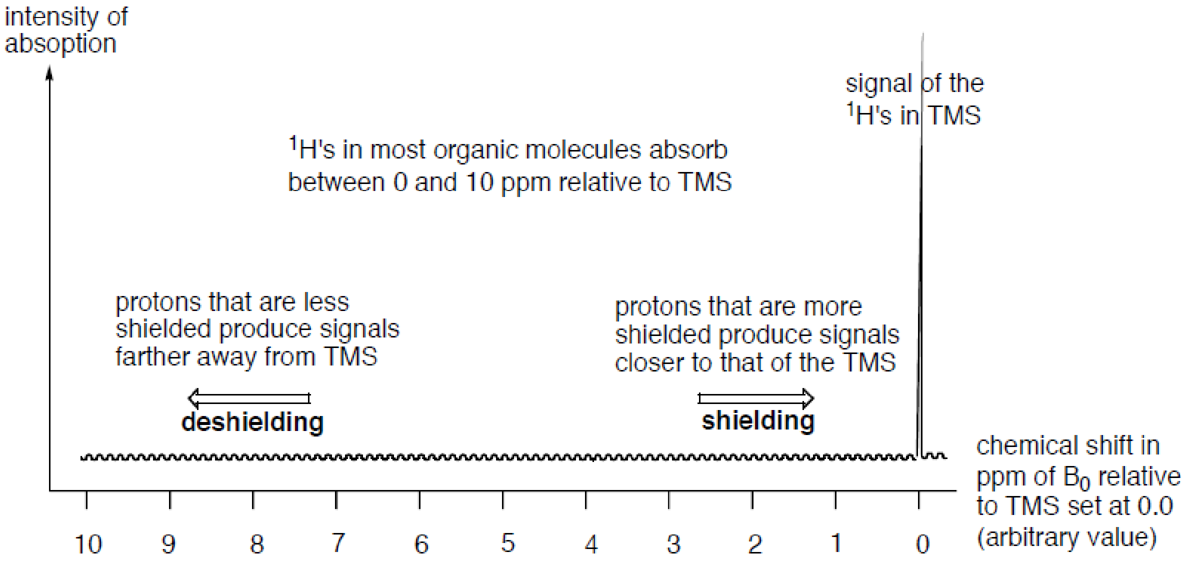
Each proton in a given chemical environment will absorb at a specific frequency, giving rise to a characteristic absorption signal.

Two or more protons in a molecule that happen to be in the same chemical environment, and that Therefore, will absorb at the same frequency, are said to be **chemically equivalent**.

Principle: each group of chemically equivalent protons within a molecule will produce its own characteristic absorption signal
The difference between the external field B0 and the effective field B_{eff} felt by a proton embedded in a molecule is called the **chemical shift**

Chemical shifts are very small: of the order of parts per million (ppm) of the external field. However, chemical shifts can be determined with great precision by measuring the frequency of the radio waves absorbed by the nuclei undergoing the above transitions.

Reference compound in NMR spectroscopy: tetramethylsilane [(CH3)4Si, "TMS"]
The ^{1}H NMR chart:



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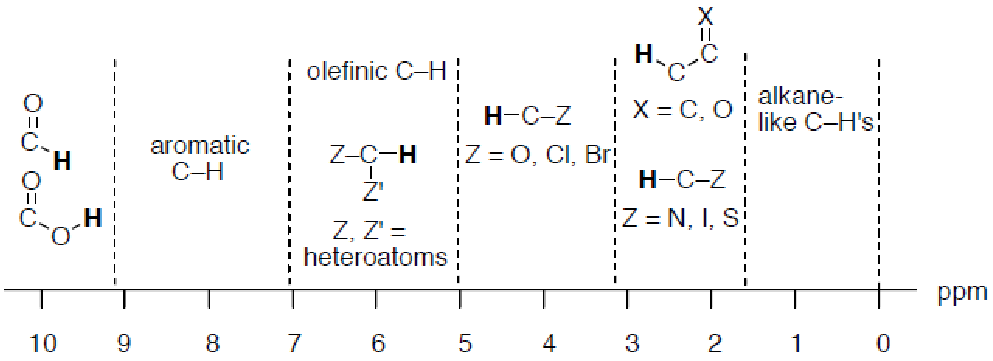
Typical proton chemical shifts:



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Characteristic Proton (^1H) NMR Chemical Shifts

Type of Hydrogen	Structure	Chemical Shift δ (ppm)	Type of Hydrogen	Structure	Chemical Shift δ (ppm)
Reference	$(CH_3)_4Si$	0.00	Amines	$>N-\overset{\vert}{\underset{\vert}{C}}-H$	2.3 – 3.0
Alkane, primary	$-CH_3$	0.7 – 1.3	Alcohol, ether	$-O-\overset{\vert}{\underset{\vert}{C}}-H$	3.3 – 4.0
Alkane, secondary	$-CH_2-$	1.2 – 1.4	Ester	$-\overset{O}{\overset{\Vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-H$	3.7 – 4.2
Alkane, tertiary	$-\overset{\vert}{\underset{\vert}{C}}-H$	1.4 – 1.7	Olefinic	$C=C-H$	5.0 – 6.5
Allylic, primary	$C=C-CH_3$	1.6 – 1.9	Aromatic	Ar–H	6.5 – 8.0
Methyl carbonyl	$-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.1 – 2.4	Aldehyde	$-\overset{O}{\overset{\Vert}{C}}-H$	9.7 – 10.0
Aromatic methyl	$Ar-CH_3$	2.5 – 2.7	Amine	$-NH_2$	1 – 5, variable
Alkyne	$\equiv C-H$	2.5 – 2.7	Alcohol	–OH	1 – 5, variable
Alkyl halide (X = Cl, Br, I)	$-\overset{H}{\underset{\vert}{C}}-X$	2.5 – 4.0	Carboxylic acid	–COOH	11.0 – 12.0

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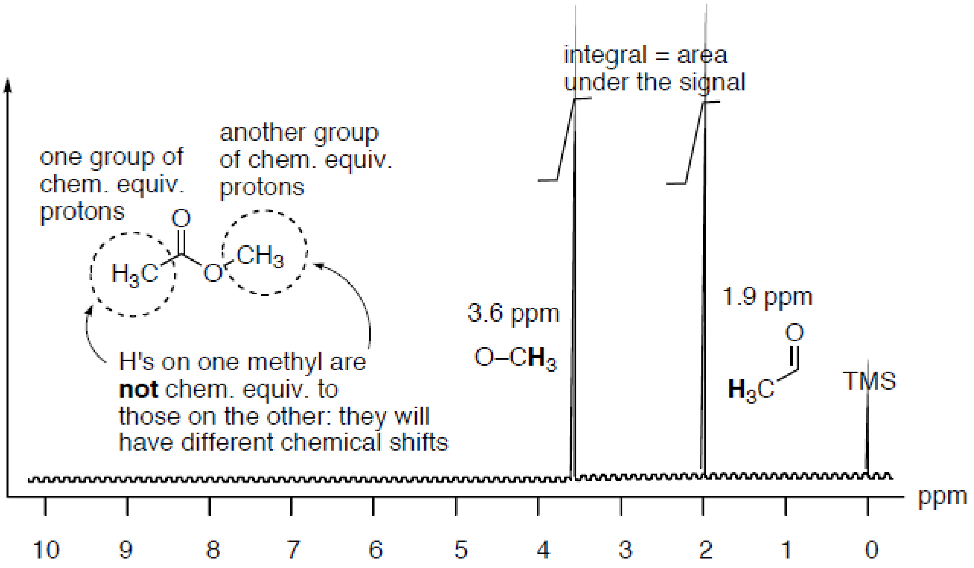
The ^1H NMR spectrum of methyl acetate



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Questions

1.Classify each of the following as organic or inorganic (not organic) compounds?

a) Sodium chloride, NaCl, in table salt

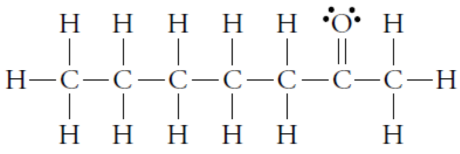
b) Hexane, C_6H_{14}, in gasoline

c) Ethyl butanoate, $CH_3CH_2CH_2CO_2CH_2CH_3$, in a pineapple

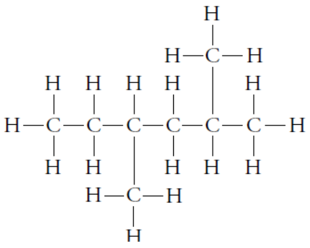
d) Water, H_2O, in your body

Solution: Organic compounds must have at least one carbon molecule in its molecule. Sodium Chloride, NaCl and water, H_2O does not contain any carbon in its molecule, so they are inorganic. Hexane, C6H14 and ethyl butanoate, $CH_3CH_2CH_2CO_2CH_2CH_3$ are organic compounds.

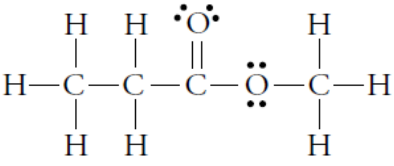
2. Identify each of these Lewis structures as representing either an alkane, alkene, alkyne, arene (aromatic), alcohol, carboxylic acid, aldehyde, ketone, ether, ester or amine?



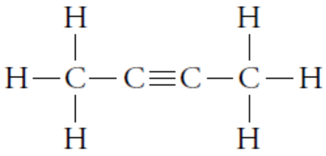
a)



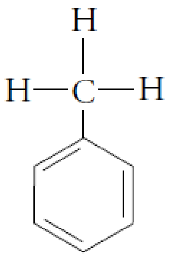
b)



c)



d)



e)

Solution: (a) Ketone (b) Alkane (c) Ester (d) Alkyne (e) Arene (aromatic)

3. Compounds that contain the______________ are called arenes or aromatics.

Solution: Benzene

4. The four smallest alkanes have the following general formulas: CH_4, C_2H_6, C_3H_8 and C_4H_{10}. Based on this trend what would be the formula for the alkane with 22 carbons?

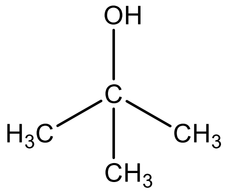
Solution: From CH_4, C_2H_6, C_3H_8 and C_4H_{10}, the general formula for alkane can be written as C_nH_{2n+2}.

Following the above general formula, condensed formula of alkane with 22 carbons will be $C_{22}H_{46}$.

5. In general, how do organic compounds differ from inorganic compounds?

Solution: Organic compounds, in general, differ greatly from inorganic compounds in seven respects:
a Organic compounds are usually combustible.
b Organic compounds, in general, have lower melting and boiling points.
c Organic compounds are usually less soluble in water.
d Several organic compounds may exist for a given formula. This is known as isomerism.
e Reactions of organic compounds are usually molecular rather than ionic. As a result, they are often quite slow.
f The molecular weights of organic compounds may be very high, often well over 1000.
g Most organic compounds can serve as a source of food for bacteria.

6. Name this molecule?



Solution: 2-methyl-2-propane

7.Distinguish primary, secondary and tertiary alcohols?

Solution: In primary alcohol-the carbon atom carrying-OH group is attached to one other carbon atom.

In secondary alcohol-the carbon atom carrying-OH group is attached to two other carbon atoms.

In tertiary alcohol-the carbon carrying the-OH group is attached to three other carbon atoms.

8. What is the difference between aliphatic and aromatic compound?

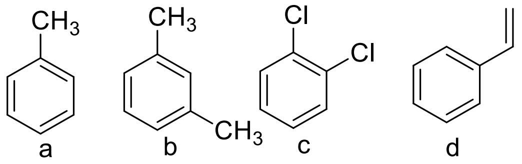
Solution: The *aromatic* organic compounds are all ring compounds or have cyclic groups of aromatic nature in their structure. The carbon atoms in these ring compounds have only one covalent bond, in contrast to those in aliphatic compounds with two.

9. Which alcohol is used as an antifreeze? How it is synthesized?

Solution: Methanol is used as an antifreeze. It is synthesized by the reaction of methane and steam as follows:

$$CH_4 + H_2O \xrightarrow[\text{catalyst}]{\Delta\ \text{pressure}} CH_3OH + H_2$$

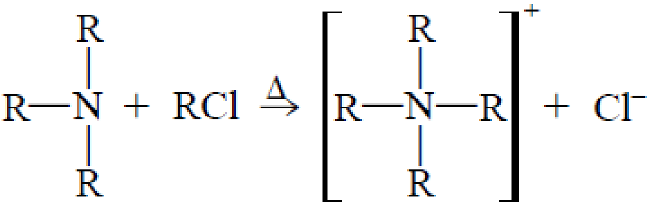
10. Name the following aromatic compounds?



Solution: a) Toluene b) Xylene c) o-Dichlorobenzene d) Styrene

11. How quaternary ammonium salts are formed?

Solution: Tertiary amines combine with alkyl halides to form *quaternary ammonium salts* as follows:



$$R-\underset{R}{\overset{R}{N}} + RCl \xrightarrow{\Delta} \left[R-\underset{R}{\overset{R}{N}}-R \right]^+ + Cl^-$$

The compounds formed are actually chloride salts and ionize to form a quaternary ammonium ion and a chloride ion. The quaternary ammonium salts have bactericidal properties that can be enhanced by the proper choice of the R groups.

12. Name two polyring hydrocarbons?

Solution: Naphthalene and Anthracene

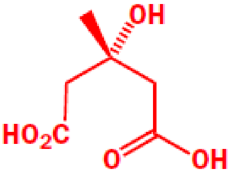
13. What is a stereo genic or chiral center?

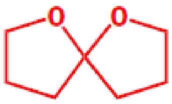
Solution: A carbon atom carrying four different groups is a stereo genic or chiral center.

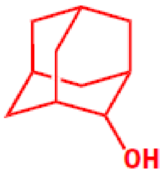
14. Which structures are called enantiomers?

Solution: We call two structures that are not identical but are mirror images of each other **enantiomers**.

15. Are the following compounds chiral?





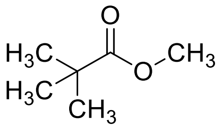


Solution: a) Chiral b) Achiral C) Achiral

16. The C-C triple bond stretch is too weak to be seen. Why?

Solution: A bond must have a permanent electric dipole to absorb IR light. IR light is an electromagnetic radiation and it can only interact with objects that have either a permanent electrostatic dipole or a permanent magnetic dipole. Clearly, C-C triple bond of an internal alkyne has no dipole moment, so it does not absorb IR radiation.

17. Predict the chemical shift for methyl pivalate ?



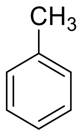
Solution: The t-butyl group protons (9Hs) will show around 1.2 ppm and O-CH_3 (Methoxy 3Hs) will show at 3.6-3.8 ppm.

18. Why TMS (Tetramethylsilane) is used as reference compound in NMR?

Solution: The electron density surrounding the protons in TMS molecule is unusually high. Consequently, these protons are highly shielded. Moreover, all 12Hs are chemically equivalent and they appear at the same position in an NMR spectrum.

19. Predict the NMR chemical shift of Toluene?

Solution. The structure of Toluene is



The aromatic 7Hs at around 7-7.5 ppm and CH_3 appear at around 2.3 ppm.

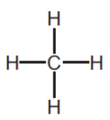
Advanced Questions

1. What functional group is characteristic of each of the following: alkenes, alcohols, aldehydes, ketones, acids, amines, ethers, esters, and aromatic compounds?

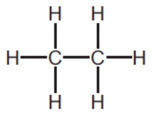
2. Draw the structure of ethene showing all atoms and all bonds

3. The structures of some alkanes, alkenes and alcohols are shown below. Identify them as saturated and unsaturated hydrocarbon?

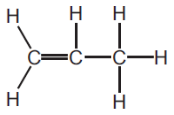
F



G



H



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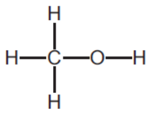

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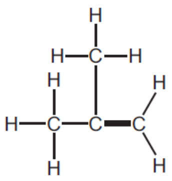
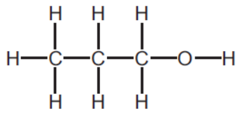
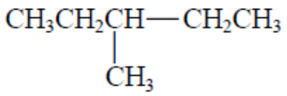


K

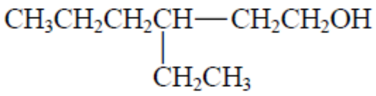


4. Give the structural formula for each of the following:
(*a*) 3-Nonene
(*b*) *n*-Octyl phenol
(*c*) Dimethyl ether
(*d*) 1,1,2-Trichloroethane
(*e*) Any PCB
(*f*) *n*-Pentanoic acid
(*g*) Isopropanol
(*h*) 2,4,6-Trinitrotoluene (TNT)

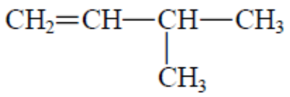
5. Name the following:



$CH_3CH_2\underset{CH_3}{\underset{|}{CH}}—CH_2CH_3$

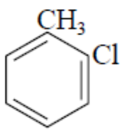


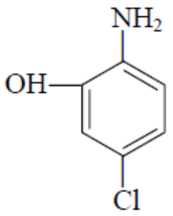
$CH_3CH_2CH_2\underset{CH_2CH_3}{\underset{|}{CH}}—CH_2CH_2OH$



$CH_2{=}CH—\underset{CH_3}{\underset{|}{CH}}—CH_3$

$CH_3CH_2CH_2COOH$

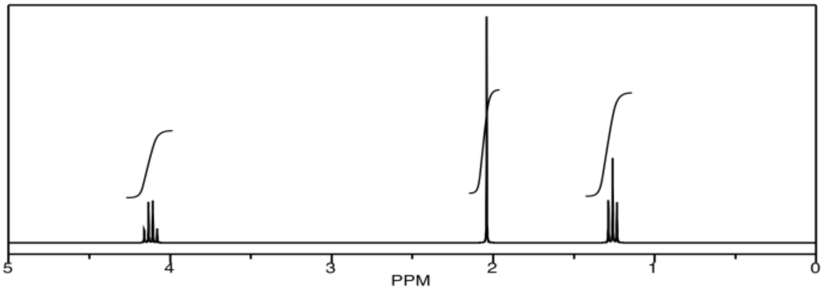




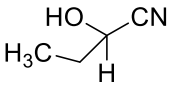
6. Rank the following compounds from most volatile
(*a*) Benzene
(*b*) Phenol
(*c*) Chloroform
(*d*) Bromoform

(*e*) Trichloroethene
(*f*) 1,1,1-Trichloroethane
(*g*) Tetrachloroethene (also called perchloroethene)

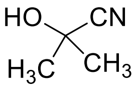
7. Predict the structure from the following NMR spectrum?



8. Identify the following as chiral or achiral?

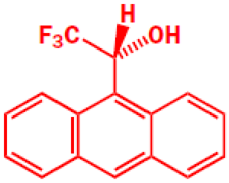


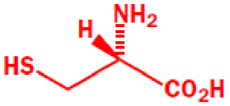
a



b

9. Assign, R or S , to each of the following compounds?

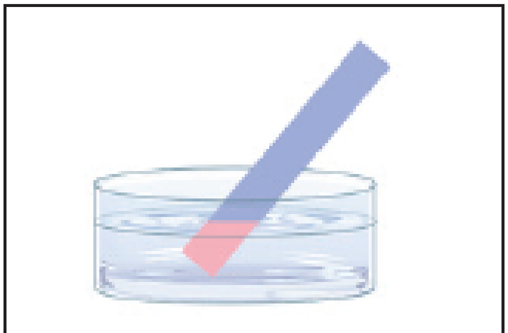




Acids and Bases

Acids

Acids are a special group of compounds with a set of common properties. This helps to distinguish them from other compounds. Thus, if you had a number of compounds and you were wondering whether these were acids or otherwise, you could identify them by their properties. But what exactly are the properties? Think about the last time you tasted lemons. Did they taste sour, sweet, or bitter? Lemons taste sour. This is a property of acids. Another property of acids is that they turn blue litmus paper red. Litmus paper is an **indicator**, which is a substance that changes color depending on how acidic or basic something is. If blue litmus paper turns red when it is dipped into a solution, then the solution is an acid. Another property of acids that many people are familiar with is their ability to cause burns to skin. This is why it is a bad idea to play with battery acid or other acids.



Acids cause blue litmus paper to turn red

Introduction to Chemistry by Tracy Poulsen

Acetic acid (CH_3COOH) is a component of vinegar, hydrochloric acid (HCl) is stomach acid, phosphoric acid (H_3PO4) is commonly found in dark soda pop, sulfuric acid H_2SO_4 is used in car batteries and formic acid HCOOH is what causes the sting in ant bites. For all of these acids, the chemical formula of an acid begins with one or more hydrogen atoms. Acids dissolve in water to make H+ ions. Because they make ions (charged particles) when they are dissolved, acids will also conduct electricity when they are dissolved in water.

Bases

There is one common base that some may have had the opportunity to taste: milk of magnesia, which is a slightly soluble solution of magnesium hydroxide. This substance is used for acid indigestion. Flavorings have been added to improve the taste, otherwise it would have a bitter taste when you drink it. Other common bases include substances like Windex, Drano, oven cleaner, soaps and many cleaning other products. A bitter taste is one property you will have to take for granted. Bases also tend to have a slippery feel. This matches what you have experienced with soaps and detergents. As with acids, bases have properties that allow us to distinguish them from other substances. We have learned that acids turn blue litmus paper red. Bases turn red litmus paper blue. Notice that the effect of the indicator is the opposite of that of acids.

Most acids have formulas that start with H. On the other hand, most of the bases we will be using in this course have formulas that end with –OH. These bases contain the polyatomic ion called hydroxide. When bases dissolve in water, they produce hydroxide (OH-) ions. Because they dissolve into charged particles, bases will also conduct electricity when they are dissolved.

Arrhenius Acids

Take a look at all of the following chemical equations. What do you notice about them? What is common for each of the equations below?

Hydrochloric acid: $HCl(aq) \rightarrow H+(aq) + Cl-(aq)$

Nitric acid: $HNO_3(aq) \rightarrow H+(aq) + NO3-(aq)$

Perchloric acid: $HClO_4(aq) \rightarrow H+(aq) + ClO4-(aq)$

One of the distinguishable features about acids is the fact that acids produce H+ ions in solution. If you notice in all of the above chemical equations, all of the compounds dissociated to produce H+ ions. This is the one main, distinguishable characteristic of acids and the basis for the Arrhenius definition of acids. An **Arrhenius acid** is a substance that produces H+ ions in solution.

Arrhenius Bases

In contrast, an Arrhenius **base** is a substance that releases OH- ions in solution. Many bases are ionic substances made up of a cation and the anion hydroxide, OH-. The dissolving equation for the base sodium hydroxide, NaOH, is shown below:

$$NaOH(s) \rightarrow Na^+(aq) + OH-(aq)$$

Barium hydroxide produces a similar reaction when dissociating in water:

$$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2\ OH-(aq)$$

The production of OH- ions is the definition of bases according to the Arrhenius.

Conjugate Acids and Bases

A **conjugate acid** contains one more H atom and one more + charge than the base that formed it.

A **conjugate base** contains one less H atom and one more - charge than the acid that formed it.

Let us take the example of bicarbonate ions reacting with water to create carbonic acid and hydronium ions.

HCO_3^- + H_2O → H_2CO_3 + OH^-

base + acid → Conj A + Conj B

We see that HCO_3^- becomes H_2CO_3. It has one more H atom and one more + charge (-1 + 1 = 0). So, H_2CO_3 is the conjugate acid of HCO_3^-.

The H_2O becomes OH^-. It has one less H atom and one more – charge. So, OH^- is the conjugate base of H_2O.

Conjugate Acid-Base Pairs

All acids have a conjugate base. All bases have a conjugate acid. Acids "donate" H+ when they react. This is most easily seen when they dissociate in water:
$H_2SO_4 + H_2O => HSO-4 + H_3O^+$
In this example, sulfuric acid (H_2SO_4) is an acid because it "donates" H+ to the water. It becomes the hydrogen sulfite ion (HSO^{-4}) which is the conjugate base of sulfuric acid.
The same idea applies to a base:
$NH_3 + H_2O <=> NH^{+4} + OH-$
Ammonia (NH_3) is a base because is "accepts H+ from water to come its conjugate acid, the ammonium ion (NH^{+4}).

pH Scale

We have been discussing what makes an acid or a base and what properties acids and bases have. It is frequently useful to compare how acidic or basic a solution is in comparison to other solutions. A couple of ways to do this is to compare [H+] to [OH-] or to find the pH of a solution.

Relationship between [H^+] and [OH^-]

We have learned that acids and bases are related to hydrogen ions [H+] and hydroxide ions [OH-]. Both of these ions are present in both acids and bases. However, they are also present in pure water. Water self-ionizes according to the following reaction:

$$H2O(l)\square\ H+(aq) + OH-(aq)$$

The equilibrium expression for this reaction would be:

$$Kw=[H+]\ [OH-]$$

The equilibrium constant for this particular equilibrium is Kw, meaning the equilibrium constant for water. From experimentation, chemists have determined that in pure water, $[H+] =1x10^{-7}$ M and $[OH-]=1x10^{-7}$ M. If you substitute these values into the equilibrium expression, you find that $Kw=1x10^{-14}$. Any solution which contains water, even if other things are added, will shift to establish this equilibrium. Therefore, for any solution, the following relationship will always be true:

$$Kw=1x10^{-14}=[H+]\ [OH-]\ @\ 25°C$$

We can describe whether a solution is acidic, basic, or neutral according to the concentrations in this equilibrium.

If [H+] = [OH-], the solution is neutral (such as in pure water)

If [H+] > [OH-], the solution is acidic. This means that $[H+] > 1x10^{-7}$ M.

Review Question

Suppose acid is added to some water, and [H+] is measured to be $1x10^{-4}$ M. What would [OH-] be?

Solution: substitute what we know into the equilibrium expression:
$Kw=1x10^{-14}=[H+]\ [OH-]$
$1x10^{-14}=[1x10^{-4}]\ [OH-]$
To isolate [OH-], divide by sides by 1x10-4.
These leaves, **$[OH-]=1x10^{-10}$ M**
Note that because [H+] > [OH-], the solution must be acidic.

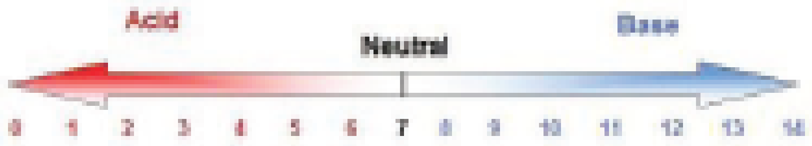
pH Scale

A Danish chemist named Soren Sorensen developed a shorter method for expressing acid strength or hydrogen ion concentration with a non-exponential number. He named his method **pH**. The p from pH comes from the German word *potenz* meaning "power or the exponent of". Sorensen's idea that the pH would be a simpler number to deal with in terms of discussing acidity level led him to a formula that relates pH and [H+]:

pH = - log [H+]

If the hydrogen ion concentration is between 1.0 M and 1.0x10-14, the value of the pH will be between 0 and 14.

The pH scale developed by Sorensen is a logarithmic scale, which means that a difference of 1in pH units indicates a difference of a factor of 10 in the hydrogen ion concentrations. A difference of 2 in pH units indicates a difference of a factor of 100 in the hydrogen ion concentrations. Not only is the pH scale a logarithmic scale but by defining the pH as the *negative* log of the hydrogen ion concentration, the numbers on the scale get smaller as the hydrogen ion concentration gets larger. For example, pH=1is a stronger acid than pH=2 and, it is stronger by a factor of 10 (the difference between the pH's is 1). The closer the pH is to 0 the greater the concentration of [H+] ions and therefore the more acidic the solution. The closer the pH is to 14, the higher the concentration of OH- ions and the stronger the base.



The pH Scale.

Introduction to Chemistry by Tracy Poulsen

Review Question

Calculate the pH of a solution given that $[H^+]$ =0.01 M?
Solution: pH = - log (0.01)
pH = 2

Neutralization

Neutralization is a reaction between an acid and a base that produces water and a salt. The general reaction for the neutralization reaction is shown below.

acid + base → salt + water

In this section, we will be writing the products of neutralization reactions.

Acids are a combination of hydrogen ions (H+) and an anion. Examples include HCl, HNO3. Bases can be a combination of metal cations and hydroxide ions, OH-. Examples include NaOH, KOH, and Mg(OH)2. According to the Arrhenius definitions of acids and bases, the acid will contribute the H+ ion that will react to neutralize the OH- ion, contributed by the base, to produce neutral water molecules. All acid-base reactions produce salts. The anion from the acid will combine with the cation from the base to form the ionic salt. Look at the following equations. What do they have in common?

$HClO_4 + NaOH \rightarrow NaClO4 + HOH$

$H_2SO_4 + 2\ KOH \rightarrow K_2SO4 + 2\ HOH$

(Note: HOH is the same as H2O)

No matter what the acid or the base may be, the products of this type of reaction will always be a salt and water. The H+ ion from the acid will neutralize the OH- ion from the base to form water. The other product is a salt formed when the cation of the base combines with the anion of the acid. Remember, the total charge on the salt MUST be zero. You must have the correct number of cations and anions to cancel out the charges of each.

Titration

For acid-base neutralization reactions, the typical laboratory procedure for determining the stoichiometric amounts of acid and/or base in the reaction is to complete a titration. As we go through this section, we will use some of the prior knowledge we have obtained about acids and bases, chemical reactions, and molarity calculations, to apply them to the concept of titrations.

An **indicator** is a substance that changes color at a specific pH and is used to indicate the pH of the solution. Litmus paper is a paper that has been dipped in an indicator. The litmus paper is called an indicator because it is used to indicate whether the solution is an acid or a base. If the red litmus paper turns blue, the solution is basic (pH > 7), if the blue litmus turns red the solution is acidic (pH < 7).

The Titration Process

Titration, by definition, is the addition of a known concentration of base (or acid) to a solution of acid (or base) of unknown concentration. Since both volumes of the acid and base are known, the concentration of the unknown solution is then mathematically determined. So, what does one do in a titration? When doing a titration, you need to have a few pieces of equipment. A **buret** is used to accurately dispense the volume of the solution of known concentration (either the base or the acid). A flask is used to hold a known, measured volume of the unknown concentration of the other solution (either the acid or the base). If the basic solution was in the buret, you would first read the volume of base in the buret at the beginning. You would add the base to the flask containing the acid until all of the acid has reacted and then read the volume of base in the buret again. To see how much was added, you would subtract the initial volume from the final volume.

In a titration, just enough base is added to completely react with all of the acid, without extra base being added. This is called the **equivalence point** because you have added equal moles of acid and base. For most acids and bases, this point is difficult to see, because the acid and base reactants as well as the salt and water products have no color. This is where indicators come in. An **indicator** is used to determine the equivalence of the titration. A few drops of the indicator are added to the flask before you begin the titration. If an appropriate indicator has been chosen, the indicator will only react and change color (and stay color changed) when all of the other acid has reacted. Therefore, the indicator will change color immediately after enough base was added to completely react with all of the acid (the equivalence point).

Buffers

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added. A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).

How Buffer Works

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3COOH\ (aq) + H_2O \longrightarrow H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+\ (aq) + CH_3COO^-\ (aq) \longrightarrow CH_3COOH\ (aq) + H_2O$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3CCO^-$$

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$H_3O^+ + NH_3 \longrightarrow NH_4^+ + H_2O$$

Questions

1. If the final hydrogen ion concentration is $1x10^{-12}$ M, we can calculate the final hydroxide ion concentration?
Solution: Kw=$1x10^{-14}$=[H+] [OH-]
$1x10^{-14}$=[$1x10^{-12}$] [OH-]
To isolate [OH-], divide by sides by $1x10^{-12}$.
This leaves, **[OH-]=$1x10^{-2}$ M**
Note that because [H+] < [OH-], the solution must be basic.

2. What would be the [H+] for a grapefruit found to have a [OH-] of $1.26x10^{-11}$? What is [H+] and is the solution acidic, basic, or neutral?
Solution: Kw=$1x10^{-14}$=[H+] [OH-]
$1x10^{-14}$=[H+] [$1.26x10^{-11}$]
To isolate [H+], divide by sides by $1.26x10^{-11}$.
This leaves, **[H+] =$7.94x10^{-4}$ M**
Also, the solution must be acidic because [H+] > [OH-]

3. Calculate the pH of saliva with [H+] =$1.58x10^{-6}$ M?
Solution: pH = - log ($1.58x10^{-6}$)
pH = 5.8

4. Calculate the pH of a solution with $[OH-]=7.2x10^{-4}$ M?
Solution: In order to find pH, we need [H+].
$Kw=1x10^{-14}=[H+]\ [OH-]$
$1x10^{-14}=[H+]\ [7.2x10^{-4}]$
To isolate [H+], divide by sides by $7.2x10^{-4}$.
This leaves, $[H+]=1.39x10^{-11}$ M
We can now find the pH
$pH = - \log (1.39x10^{-11})$

5. Compare lemon juice (pH=2.5) to milk (pH=6.5). Answer each of the following:
a) Label each as acidic, basic, or neutral
b) Which has a higher concentration of H+ ions?
c) How many times more H+ does that solution have?

Solution: a) Both lemon juice and milk are acidic, because their pH's are less than 7. (*Note: milk is only very slightly acidic as its pH is very close to 7)
b) The lower the pH, the higher the concentration of H+ ions. Therefore, lemon juice has more H+.
c) Each step down on the pH scale increases the H+ concentration by 10 times. It is 4 steps down on the pH scale to go from 6.5 to 2.5. Therefore, lemon juice has 10x10x10x10 or 10,000 times more H+ ions than milk.

6. Complete the following neutralization reactions.
(a) H2SO4 + Ba(OH)2 →
(b) HCOOH + Ca(OH)2 →
(c) HCl + NaOH →

Solution: (a) The H+ in H_2SO_4 will combine with the OH- part of $Ba(OH)_2$ to make water. The salt produced is what is formed when Ba^{2+} (the cation from the base) combines with $SO4^{2-}$(the anion from the acid). These have charges of +2 and -2, so the formula for this compound is BaSO4. Before it is balanced, the reaction is:
$H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + H_2O$
After balancing, we get:
$\mathbf{H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2\ H_2O}$
(b) The H+ in HCOOH will combine with the OH- part of $Ca(OH)_2$ to make water. The salt produced is what is formed when Ca2+ (the cation from the base) combines with COOH- the anion from the acid). These have charges of +2 and -1, so the formula for this compound is $Ca(COOH)_2$.
Before it is balanced, the reaction is:
$HCOOH + Ca(OH)_2 \rightarrow Ca(COOH)_2 + H2O$
After balancing, we get:
$\mathbf{2\ HCOOH + Ca(OH)_2 \rightarrow Ca(COOH)_2 + 2\ H_2O}$
(c) The H+ in HCl will combine with the OH- part of NaOH to make water. The salt produced is what is formed when Na+ (the cation from the base) combines with Cl the anion from the acid). These have charges of +1 and -1, so the formula for this compound is NaCl.
Before it is balanced, the reaction is:

$HCl + NaOH \rightarrow NaCl + H_2O$
The reaction is already balanced, so we are done.

Advanced Questions

1. What is the Arrhenius definition of an acid?
2. In saturated limewater, $[H+] = 3.98 \times 10^{-13}$ M.
a) Find $[OH]-$
b) What is the pH?
c) Is the solution acidic, basic, or neutral?
3. A solution contains 4.33×10^{-8} M hydroxide ions. What is the pH of the solution?
4. During the course of the day, human saliva varies between being acidic and basic. If $[OH-] = 3.16 \times 10^{-8}$ M,
a) Find $[H+]$
b) What is the pH?
c) Is the solution acidic, basic, or neutral?
5. Write a balanced reaction for each of the following neutralization reactions:
$HNO_3 + KOH \rightarrow$
$HClO_4 + NH_4OH \rightarrow$
$H_2SO_4 + NaOH \rightarrow$
$HNO_3 + NH_4OH \rightarrow$
$HF + NH_4OH \rightarrow$
$HC_2H_3O_2 + KOH \rightarrow$
$HCl + KOH \rightarrow$
6. What is an indicator? What is it used for?
7. What is an equivalence point?