Benha University, Faculty of Science, Chemistry Department

General Chemistry (Chm 100)

Part 1

For 1st year students

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Chapter 1

STOICHIOMETRY

Modern chemistry began when chemists recognized the importance of careful measurements and began to ask questions which could be answered quantitatively. **Stoichiometry** is the branch of chemistry that deals with the quantitative relationships between elements and compounds in chemical reactions. The atomic theory of matter is basic to this study.

Dalton's Atomic Theory

Many scientists from ancient times believed that all matter consists of atoms, but Dalton made the atomic theory quantitative by showing that it is possible to determine the relative masses of the atoms of different elements. The principle postulates of Dalton theory are:

1- Elements are composed of extremely small particles called atoms. All atoms of the same elements are alike, and atoms of different elements are different

2- The separation and union of atoms occur in chemical reactions. In the reactions, no atom is created or destroyed, and no atom of one element is converted into an atom of another element.

3- A chemical compound is the result of the combination of atoms of two or more elements in a simple numerical ratio.

Dalton believed that all atoms of a given element have equal atomic masses. Today we know that a given element may consist of several types

of atoms that differ in mass (isotopes). All atoms of the same element, however, react chemically in the same way.

The second postulate of Dalton's theory account for the **law of conservation of mass** which states that **"there is no detectable change in mass during the course of a chemical reaction."** So, the total of all the materials entering into a chemical reaction must equal the total mass of all the products of the reaction (balanced chemical equation).

The third postulate of the theory explains the **law of definite proportions** which states that **"a pure compound always contains the same elements combined by the same proportions by mass."**

On the basis of his theory, Dalton proposed a third law of chemical combination known as the **law of multiple proportions**. This law states that **"when two elements A and B form more than one compound, the amounts of A that are combined with a fixed amount of B are in a small whole-number ratio."** For example, carbon and oxygen form two compounds: carbon monoxide (CO) and carbon dioxide (CO_2), so the masses of oxygen that combined with fixed amount of carbon stand in the ratio of 2:1.

Atomic Weights

A very important aspect of Dalton's work is his attempt to determine the relative masses of atoms. Water is a compound which consists of 88.8% oxygen and 11.2% hydrogen by mass. It was fatherly found that one atom of oxygen is combined with two atoms of hydrogen. The oxygen atom therefore has a mass that is approximately 8 times the mass of two

hydrogen atoms or 16 times the mass of one hydrogen atom. Thus the oxygen atom has a relative mass of approximately 16.

It must be noted that two types of information are needed to apply Dalton's method successfully: (i) the combining ratio by mass of the elements in a compound and (ii) the combining ratio by numbers of atoms of these elements. The atomic combining ratios were not available to the chemists of Dalton's time and many years passed before the   methods of chemical analysis were discovered and accurate values of atomic masses were determined. At the present time they are determined by the use of instruments known as mass spectrophotometers rather than by means of chemical analysis.

Any relative atomic weight scale must be based on the arbitrary assignment of a value to one atom that is chosen as a standard. Dalton used the hydrogen atom as standard and assigned its value of 1. In latter years, chemists used naturally occurring oxygen as the standard and set its atomic weight to exactly 16. Today, a particular type of carbon atom, carbon-12 atom is employed as the standard and assigned a mass of exactly 12.

An element may occur in nature as a mixture of various types of atoms that have identical chemical properties but differ slightly in mass (isotopes). The atomic weight of such an element is an average values that takes into account the masses of these types of atoms and their relative abundances in nature.

Formulas

The chemical symbols that are assigned to the elements are used to write formulas that describe the atomic composition of compounds. The formula

of water is H_2O, which indicates that there are two atoms of hydrogen for every one atom of oxygen in the compound. The subscripts of the formula indicate the relative number of atoms of each type that are combined. If a symbol has no subscript, the number 1 is assigned.

A molecule is a particle formed from two or more atoms. Many (but not all) compounds occur in molecular form. In these cases, the formula gives the number of atoms of each type in a single molecule of the compound. Formulas of this type are sometimes called **molecular formula**. Both water and sulfuric acid, for examples, has the molecular formula H_2O and H_2SO_4 respectively.

The molecular formula of hydrogen peroxide, H_2O_2, indicates that there are two atoms of oxygen and two atoms of hydrogen in each molecule. Notice that the ratio of hydrogen atoms to oxygen atoms (2:2) is not the simplest whole number ratio (which is 1:1). A formula that is written using the simplest whole number ratio is called the **simplest formula** or **empirical formula**. The molecular formula of hydrogen peroxide is H_2O_2 while the empirical formula is HO.

For some compounds, the molecular and empirical formulas are the same; for examples: H_2O, H_2SO_4, CO_2 and NH_3. However, for many molecular compounds molecular and empirical formulas are different for examples

compound	Molecular formula	Empirical formula
hydrazine	N_2H_4	NH_2
benzene	C_6H_6	CH
Ethane	C_2H_6	CH_3
dichloroethane	$C_2H_4Cl_2$	CH_2Cl

Some compounds are not composed of molecules. For example sodium chloride is made up of ions (particles that bear positive or negative charges). The sodium and chloride ions form a crystal which composed of large numbers of these ions held together by the attractions between the dissimilar charges of the ions.

In the crystal, there is one sodium ion (Na^+) for every one chloride ion (Cl^-). The formula of the compound is NaCl which does not describe a molecule nor does it indicate that ions are paired. Rather, the formula gives the simplest ratio of Na and Cl atoms that produce the compound. The formula NaCl, therefore, is an empirical formula.

The formulas of ionic compounds are derived from the formulas of their ions. Since a crystal is electrically neutral, the total charge of positive ions must equal the total charge of the negative ions. For example in barium chloride, the formula of barium ion is Ba^{2+} and that of chloride ion is Cl^-. The Ba^{2+} ion and the $2Cl^-$ ions form $BaCl_2$.

The Mole

The atomic weight of fluorine (F) is 19.0 and of hydrogen is 1.0, which means that an atom of fluorine is 19 times than atom of hydrogen. If we take 100 fluorine atoms and 100 hydrogen atoms, the mass of the collection of fluorine atoms will be 19 times the mass of the collection of hydrogen atoms which is the ratio of their atomic weights.

Now, suppose that we take 19.0 g of fluorine and 1.0 g of hydrogen, the sample must contain the same number of atoms. In general, **a sample of any element that has a mass in grams numerically equal to the atomic weight of the element will contain the same number of atoms**. This number is called **Avogadro's number**. The value of Avogadro's number has been experimentally determined to be 6.02×10^{23}.

The amount of substance that contains Avogadro's number of element is called mole. The atomic weight of beryllium (Be), for example, is 9.01, thus 9.01 g of Be is a mole of Be and contain 6.02×10^{23} beryllium atoms.

Examples:

1-How many moles of aluminum (Al) are there in 125 g of Al? (the atomic weight of Al is 27.0)

Solution:

Since one mole of Al equals 27 g

So   X moles of Al equal 125 g

Then the number of moles of Al $= \dfrac{125 g of\ Al\ x\ one\ mol\ Al}{27.0 g of\ Al} = 4.63 mole Al$

2- How many moles and how many molecules are present in (a) 0.2 g of H_2, (b) 36 g of H_2O and (c) 98 g of H_2SO_4?

4- How many grams of gold (Au) constitute 0.25 mole of Au? (At.Wt. of Au = 197.0)

Solution:

Hence 1 mole of Au = 197.0 g

So   0.25 moles of Au = X g of gold

Then the No. of grams (X) of gold $= \dfrac{0.25 mol of Au x 197.0 g}{1 mol of Au} = 49.25$ g Au.

5- How many carbon atoms are there in 1.00 carat diamond?. Diamond is pure carbon and one carat is exactly 0.2 g (atomic weight of carbon = 12.01).

Solution

The question is: how many carbon atoms are there in 0.2 g of carbon?

Hence one mole of carbon = 12.01 g

So, 12.01 g of carbon contains Avogadro's number of carbon atoms

and, 0.200 g of C contains number equals X of C atoms

so, the number of C atoms (X) in 0.200 g carbon =

$$\frac{0.200\,g\,of\,C \times 6.022 \times 10^{23}\,C\,atoms}{12.01\,g\,of\,C} = 1.003 \times 10^{22} \text{ C atoms.}$$

What about compounds?

The formula weight of a substance is the sum of the atomic weights of all the atoms in the formula of the substance.

For example the formula weight of NaOH = 1x23 + 1x16 + 1x1 = 40.

Also the formula weight of $BaCl_2.2H_2O$ = 1x137.3 + 2x35.5 + 4x1 + 2x16 = 244.3.

A **molecular weight** is the sum of the atomic weights of the atoms that constitute a molecule. The formula weight of H_2O is 18 which is also the molecular weight of the substance since the formula describes the composition of water molecule. In case of NaCl, the formula weight is not the molecular weight since NaCl is an ionic compound and molecules of NaCl do not exist.

A mole of molecular substance consists of Avogadro's number of molecules. A mole of H_2O, therefore, has a mass of 18.0 g contains 6.022×10^{23} molecules. Since there two atoms of hydrogen and one atom of oxygen in H_2O molecule, a mole of H_2O molecules two moles of hydrogen atoms (2.0 g) and one mole of oxygen atom (16.0 g).

Derivation of Formulas

Data from chemical analysis of a compound are used to derive the empirical formula of the compound. The analysis gives the proportions by mass of the elements that make up the compound. The simplest or empirical formula indicates the relative numbers of atoms of various types that make up the compound. The derivation of empirical formula can be obtained following the following sequences:

1- If the data are given in terms of percentage composition, base the calculation on a 100 g sample of the compound. In this case, the number of grams of each element is equal to the percentage of the element present in the compound. There is no need to find percentage of the element if the data are given in terms of number of grams.

2- Convert the number of grams of each element to the number of moles of atoms of each atom. The number of moles equals the number of grams divided by the atomic weight.

3- Divide each of the values obtained in step 2 by the smallest value. If every number obtained in this way is not a whole number multibly each number by the same simple integer in such a way that whole number will result.

4- The whole numbers obtained in step 3 are the subscripts of the empirical formula.

Examples:

6- What is the empirical formula of compound that contains 43.6% P and 56.4% O? (atomic weights of P and O are 31.0 and 16.0 respectively).

Solution:

Assume that the sample has a mass of 100.0 g, thus there are 43.6 g of P and 56.4 g of O

The number of moles of P = 43.6 g / 31.0 = 1.41 mol P

The number of moles of O = 56.4 g / 16.0 = 3.53 mol O

Element	P	O	
No. of moles	1.41	3.53	dividing by smallest value
	1	2.5	multibly by 2 to get whole number
	2	5	

Thus the empirical formula is P_2O_5.

7- Caffeine, which occurs in coffee, tea and kola nuts, is a stimulant for the central nervous system. A 1.261 g sample of pure caffeine contains 0.624 g C, 0.065 g H, 0.364 g N and 0.208 g O. what is the empirical formula of caffeine?

Solutions:

Elements	C	H	N	O	
No. of moles	0.052	0.065	0.026	0.013	dividing by smallest value
	4	5	2	1	(Whole numbers are obtained)

Thus the empirical formula is $C_4H_5N_2O$.

The molecular formula of a compound can be derived from the empirical formula if the molecular weight of the compound is known

The molecular weight = n x empirical formula weight, where n is a whole number.

Example 8: One phosphorous oxide has an empirical formula P_2O_5, its molecular weight is 284. What is the molecular formula?

Solution:

The empirical formula weight = 2 x 31 + 5 x 16 = 142

Thus n = 284 / 142 = 2

Therefore, there are twice as many atoms of each kind present in the molecule, so the molecular formula is P_4O_{10}.

Example 9: The molecular weight of caffeine is 194 and the empirical formula is $C_4H_5N_2O$. What is the molecular formula?

Example 10: The compound glucose contains 40.0% C, 6.73% H and the rest is O. If its molecular weight is 180.2, what is the molecular formula?

Percentage Composition of Compounds

The percentage composition of a compound is readily calculated from its formula and from the atomic weights of the elements constitute the compound. The process is illustrated by the following examples.

Example 11: What is the percentage of Fe (At.Wt. 55.8) in Fe_2O_3?

Solution

One g mole of Fe_2O_3 = 2x55.8 + 3x16 = 159.6 g

The % of Fe = $\dfrac{2x55.8}{159.6} x100 = 69.92\%$ Fe in Fe_2O_3.

The % of O can be calculated in a similar way or by difference from 100%.

If the formula is not known, the percentage composition is frequently determined by chemical analysis. These data can be used to find the empirical formula of the compound.

Example 12: Nicotine is a compound that contains carbon, hydrogen and nitrogen. If 2.50 g sample of nicotine is burned in oxygen, 6.78 g of CO_2 ,

1.94 g of H_2O and 0.432 g of N_2 were produced. What is the percentage composition of nicotine?

Solution:

We first calculate the quantity of each element present in the 2.5 g sample. The C forms 6.78 g of CO_2, thus

One C forms one mole of CO_2

Then   12 g C forms 44 g of CO_2

X g C forms 6.78 g of CO_2 So, X = $\frac{6.78 x 12}{44}$ 1.85 g C

The % of C = $\frac{1.85 gC}{2.50 gnicotine} x100 = 74.0\%$ C in nicotine

In a similar way: 18 g of H_2O form 2.02 g of H, then

1.94 g H_2O form X g of H   So, X = $\frac{1.94 x 2.02}{18.0} = 0.218$ g H

The % of H = $\frac{0.218 gH}{2.50 gnicotine} x100 = 8.72$ % H in nicotine

Finally,   the % of N = $\frac{0.432 gN}{2.5 gNicotine} x100 = 17.3\%$ % N in nicotine.

Example 13: Find the empirical formula of nicotine.

Example 14: Silver sulfide (Ag_2S) occurs as the mineral argentite, which is an ore of silver. How many grams of silver are theoretically obtained from 250.0 g of an impure ore that is 70.00 % Ag_2S?

Example 15: What mass of copper (Cu) is theoretically obtained from 10.0 kg of chalcocite ore that is 25.0 % Cu_2S?

Chemical Equations

Chemical equations are representation of reactions in terms of symbols and formulas. They report the results of experimentation, for example carbon disulfide (CS_2) reacts with chlorine (Cl_2) to produce carbon tetra-chloride (CCl_4) and disulfur dichloride (S_2Cl_2). This is represented as:

$$CS_2 + Cl_2 \rightarrow CCl_4 + S_2Cl_2$$
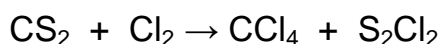
This equation is not quantitatively correct because only two chlorine atoms enter the reaction and six chlorine atoms produced which violates the law of conservation of mass. To balance the equation the number of chlorine molecules must be multiblied by three, so

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$
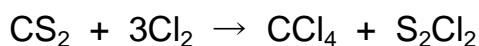
The simplest types of chemical equations are balanced by trial and error.

Example 16: Represent the following reactions by balanced chemical equations;

1- Reaction of steam with hot iron (Fe) to give magnetite (Fe_3O_4) and H_2

2- Complete combustion of ethane (C_2H_6) to give CO_2 and water vapor.

Problems based on chemical equations

Chemical equation can be interpreted in several different ways, for example the equation: $2H_2 + O_2 \rightarrow 2H_2O$ shows that two moles of H react with one mole of O to give two moles of water. In other way, it also shows that 2.02 g of H react with 32.0 g of O to give 36.0 g of water.

Example 17: Determine the number of moles of O_2 that reacted with 5.0 moles of ethane according to the equation:

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$
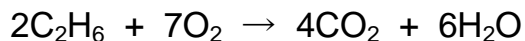
Solution: It is clear from the balanced equation that

7 moles of O_2 is required to react with 2.0 moles of ethane

so, X moles of O_2 is required to react with 5.0 moles of ethane

thus, the No. of moles of O_2 (X) = $\dfrac{5 \times 7}{2} = 17.5$ mol O_2.

Example 18: Chlorine can be prepared by the reaction:

$$MnO_2 \ + \ 4HCl \ \rightarrow \ MnCl_2 \ + \ Cl_2 \ + \ 2H_2O$$

(a): how many grams of HCl are required to react with 25.0 g of MnO_2?

(b): how many grams of Cl_2 are produced by the reaction?

Example 19: The amount of carbon monoxide (CO) in a sample of gas is determined by the reaction: $I_2O_5 \ + \ 5CO \ \rightarrow \ I_2 \ + \ 5CO_2$.

If a gas sample liberates 0.192 g of I_2, how many grams of CO were present in the sample?

The limiting reactant

In some cases, quantities are given for two or more reactants. For example when asking: how many moles of H_2O can be prepared from 2 moles of H and 2 moles of O_2 by the equation: $2H_2 \ + \ O_2 \ \rightarrow \ 2H_2O$. In such case more O_2 has been supplied than can be used. When all H_2 has been consumed, the reaction will stop. Thus the amount of H_2 supplied limits the reaction and is called the limiting reactant.

Whenever the quantities of two or more reactants are given, we must determine which one limits the reaction. This can be done as follows:

1- Calculate the number of moles of each of the given reactants.

2- Divide each value by the coefficient of the chemical equation.

3- the smallest number obtained pertains to the limiting reactant. Use the quantity of this reactant to solve the problem.

Example 20: How many moles of H_2 can be theoretically prepared from 4.00 mol of Fe and 5.00 mol of H_2O according to the equation:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$
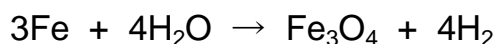
Solution: First determine the limiting reactant

1- For Fe: the number of moles given in the problem is 4.00 and the coefficient of Fe in chemical equation is 3. Thus the amount of Fe given is 4.00 mol Fe / 3mol Fe = 1.33 times the amount specified in the chemical equation.

2- In a similar case, the amount of H_2O is 5.00 mol H_2O / 4 mol H_2O = 1.25 times the amount specified in the chemical equation.

From l & 2, the limiting reactant is the H_2O.

Thus, the No. of moles of H_2 = 5.00 mol $H_2Ox \dfrac{4 mol H_2}{4 mol H_2O}$ = 5.0 mol H2.

Example 21: How many grams of N_2F_4 can be theoretically prepared from 4.00 g of NH_3 and 14.0 g of F_2?. The chemical equation for the reaction is:

$$2NH_3 + 5F_2 \rightarrow N_2F_4 + 6HF$$
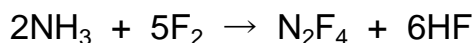
Percent yield:

Actually the quantity of the product obtained from the reaction is less than the amount calculated. This is due to part of the reactants do not react, or this part of the reactants react in a different way (side reactions) or that not all of the product is recovered. The percent yield is given by:

$$Percent\ yield = \frac{actual yield}{theoretical} x100\ \%$$

Stoichiometry of Reactions in Solution

Many chemical reactions are carried out in aqueous solutions. The quantities of reactants in this case are usually stated in terms of solution concentration.

The molarity (M) of a solution is the number of moles of substance (solute) dissolved in one liter of solution. The relation between mass (m) of dissolved solute, molarity (M) and the volume (V) in ml of solution is given by:

$$\text{Mass (g)} = \frac{M x Molecular weight x volume}{1000}$$

While the number of moles (n) is given by

$$n = \frac{mass}{molar mass} \text{ mol}$$

Example 22: How many moles of $AgNO_3$ are present in 25.0 ml of 0.600 M $AgNO_3$ solution?

Example 23: How many grams of NaOH are required to prepare 0.250 liter of 0.300 M solution?

Example 24: Soda mint tablet contains $NaHCO_3$ as an antacid. One tablet requires 34.5 ml of 0.138 M HCl solution for complete reaction. Determine the number of grams of $NaHCO_3$ that one tablet contains.

Chapter 2

ATOMIC STRUCTURE

Modern atomic theory has provided a foundation upon which modern chemistry has been built. An understanding of atomic structure and the ways in which atoms interact is central to understanding the chemistry. Individual atoms cannot be weighed, measured or examined directly. Indirect evidence, therefore, has been used to develop the atomic theory

Electron

In Dalton's theory, atoms were regarded as the smallest possible unit of matter. At the end of 19th century, it began to appear that the atom itself might be composed of even smaller particles. This change in viewpoint was obtained by experiments with electricity.

Attempts to pass an electric current through a vacuum led to the discovery of **cathode ray**. Two electrodes are sealed in a glass tube from which air is almost completely removed. When a high voltage was applied across these electrodes, rays stream from the cathode.

Intensive studies on the cathode rays showed that the rays are streams of fast-moving, negatively charged particles. These particles were called electrons. The electrons which originate from different metals used as cathode are the same no matter what material is used.

The streams of electrons that constitute a cathode ray are attracted toward the positive plate when two oppositely charged plates are placed on either sides of them (Figure 1). So, the rays are deflected from their usual straight-line path in presence of electric field. The extent of deflection depends on:

1- The size of the charge of the particle (*e*); the higher the size of the charge, the more the deflection.

2- The mass of the particle (*m*); particle with a large mass is deflected less than one with a small mass.

A cathode ray tube with an electric field perpendicular to the direction of the cathode rays and an external magnetic field. The symbols N and S denote the north and south poles of the magnet. The cathode rays will strike the end of the tube at A in the presence of a magnetic field, at C in the presence of an electric field, and at B when there are no external fields present or when the effects of the electric field and magnetic field cancel each other.

Fig.1: Deflection of cathode rays (a) in a magnetic field, (b) with magnetic   and electric fields balanced and (c) in an electric field.

By studying the deflection of cathode rays in electric and magnetic fields, J. Thomson determined the value of *e/m* for the electron which was:

e/m = -1.7588 x 10^8 C/g

where C represents the **coulomb** which is the unit of electric charge.

The first precise measurement of the charge of electron was made by Millikan in 1909. in his experiment (Fig.2), electrons are produced by the action of X-ray on the molecules of which air is composed. Very small drops of oil pick up electrons and acquire electric charges. The oil drops are allowed to settle between two horizontal plates, and the mass of a single drop is determined by measuring its rate of fall.
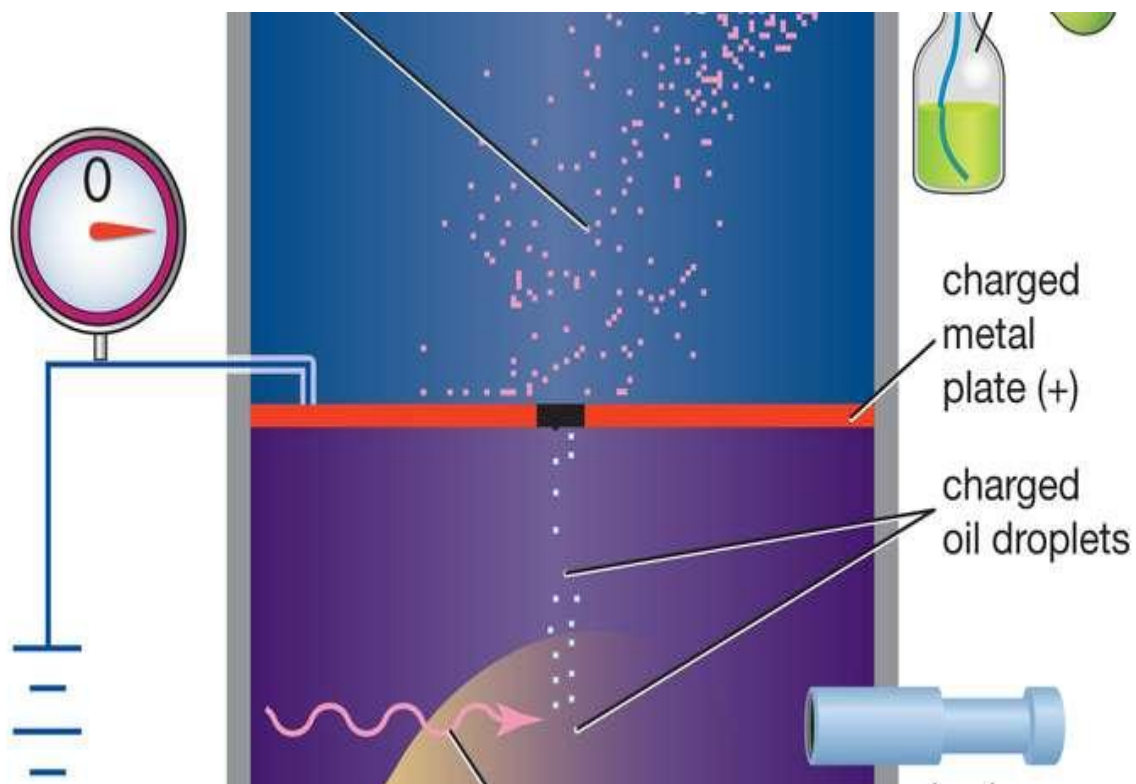
Fig.(2): Millikan's determination of the charge on the electron.

When the plates are charged, the rate of fall of the drop is altered because the negatively charged drop is attracted to the positive plate. Measurement of the rate of fall in these cases enables calculation of the charge on the drop. Since a given drop can pick up one or more electrons, the charges calculated in this way are not identical. They are, however, all simple

multiples of the same value, which is assumed to be the charge on a single electron: $e = -1.6022 \times 10^{-19}$ C.

The mass of an electron can be calculated from the value of *e/m* and the value of *e*:

$$m = \frac{e}{e/m} = \frac{-1.6022 \times 10^{-19}}{-1.7588 \times 10^{8}} = 9.1096 \times 10^{-28} g$$

The Proton

If one or more electrons are removed from a neutral atom, the residue has a positive charge equal to the sum of the negative charges of the removed electrons. Positive particles of this type (positive ions) are formed in an electric discharge tube when cathode rays rip electrons from the atom of the gas present in the tube. The positive ions move toward the cathode and if holes are made in this electrode, the positive ions pass through them. These streams of positive ions are called positive rays (Fig.3)
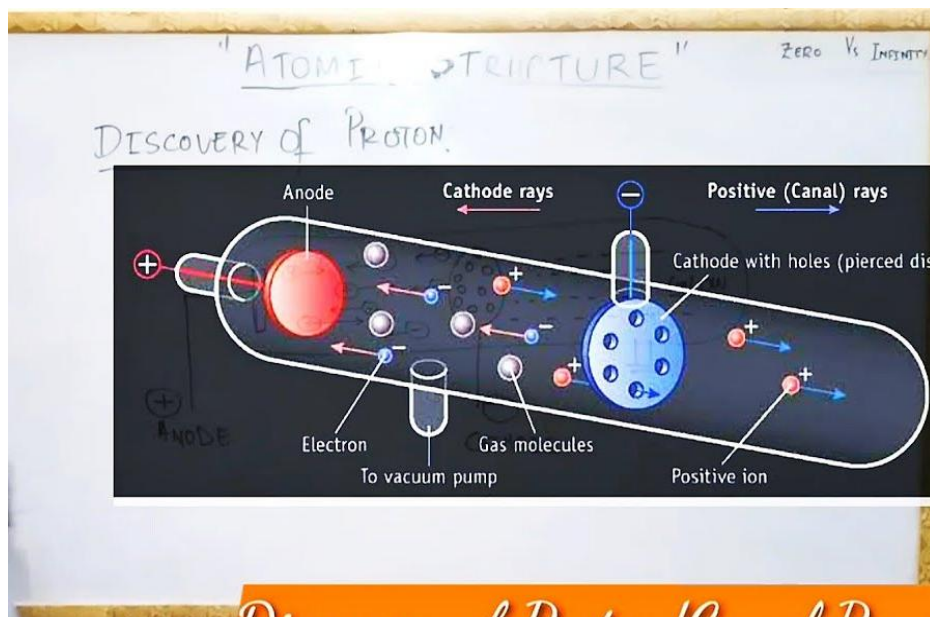
Fig.3: Positive rays

The deflection of positive rays in electric and magnetic fields was studied and the values of e/m were determined by using the same method used in the study of cathode rays. When different gases are used in the electric discharge tube, different types of positive ions are produced. When hydrogen gas is used, a positive particle results that has the smallest mass (and hence the largest e/m value):

$$e/m = + 9.5791 \times 10^4 \text{ C/g}$$

These particles, now called **protons**, are assumed to be a component of all atoms. The proton has a charge equal in magnitude to that of the electron but opposite in sign:

$$e = + 1.6022 \times 1x^{-19} \text{ C.}$$

This charge is called the unit electrical charge. The proton is said to have a unit positive charge and the electron, a unit negative charge.

The mass of neutron, which is 1836 times the mass of the electron, can be calculated from these data:

$$m = \frac{e}{e/m} = \frac{+1.6022x10^{-19}}{+9.5791x10^4} = 1.6726x10^{-24}g$$

The Neutron

Since atoms are electrically neutral, a given atom must contain as many electrons as protons. To account for the total mass of atoms, Rutherford in 1920 postulated the existence of uncharged particles. Because this particle is uncharged, it is difficult to detect and characterize. In 1932, Chadwick proved the existence of **neutron**. He was able to calculate the mass of neutron from the data of certain nuclear reactions. Chadwick showed that the mass of neutron is very slightly larger than that of the proton. The neutron has a mass of 1.6726×10^{-24} g and is electrically neutral.

The Nuclear Atom

Certain atoms are unstable, spontaneously emit rays and change into atoms with different chemical identity. This process is called *radioactivity*. In subsequent years, Rutherford explained the nature of three types of rays emitted by natural radioactive substances. These rays are:

1- Alpha rays (α): consists of particles that carry 2+ charges and have a mass approximately four times that of proton. α particles have speed about 0.05 times the speed of light. They consist of two protons and two neutrons.

2- Beta rays (β): streams of electrons that travel at approximately 0.4 timed the speed of light.

3- Gamma radiation (γ): is essentially a high energetic form of light. They are uncharged, travel with the speed of light and are similar to X-rays.

In 1911, Rutherford did experiments in which α particles were used to investigate the structure of the atom. A beam of α particles was directed against a very thin foil of gold, platinum, silver or copper where it was found that the large majority of the α particles went directly through the foil, some were deflected from the straight-line path and a few recoiled back toward their source (Fig.4).
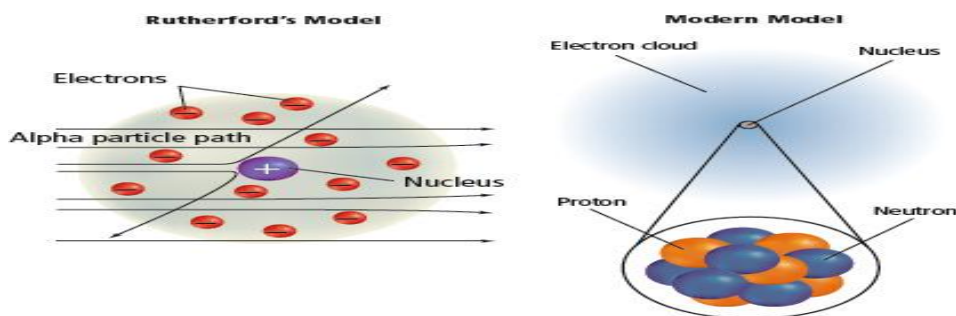
Rutherford explained the results of these experiments by assuming that:

- Nucleus exists in the centre of atom

- Most of the mass and all of the positive charge of the atom are concentrated in the nucleus.

- The electrons are outside the nucleus and in rapid motion around it.

The nucleus is now believed to contain protons and neutrons, which together account for the mass of the nucleus. Since an atom is electrically neutral, the number of positive charge (protons) equals the number of negative charge (electrons).

Atomic Symbols

An atom is identified by two numbers, the atomic and the mass number:

1- **The atomic number; (Z)**: is the number of unit positive charges on the nucleus (the number of protons in the nucleus).Since an atom is electrically neutral, it also indicates the number of extra-nuclear electrons in an uncombined atom.

2- **The mass number**; (**A**): is the total number of protons and neutrons (called **nucleons**) in the nucleus of the atom. The number of neutrons can be obtained as: number of neutrons = $A - Z$.

The mass number is the total number of nucleons in a nucleus and not the mass of the nucleus, so it must be a whole number.

 An atom of an element is designed by the chemical symbol for the element summarized as $_Z$**symbol**^{A}. For example the chemical symbol of chlorine is $_{17}Cl^{35}$ indicating that chlorine has 17 protons (Z) and 18 neutrons ($A - Z$) in the nucleus and 17 extra-nuclear electrons Z).

Isotopes

All atoms of a given element have the same atomic number. However, some elements consist of several types of atoms that differ from one another in mass number. **Atoms that have the same atomic number but different mass number are called *isotopes*.**

Two isotopes of chlorine, for example, occur in nature; $_{17}Cl^{35}$ and $_{17}Cl^{37}$. The atomic compositions of these isotopes are:

	protons	neutrons	electrons
$_{17}Cl^{35}$	17	18	17
$_{17}Cl^{37}$	17	20	17

Both of them have the same number of protons and electrons but differ in the number of neutrons. Isotopes, therefore, differ in the number of neutrons in the nucleus, which means that they differ in atomic mass.

The chemical properties of an atom depend principally upon the number of protons and electrons that the atom contains. Isotopes of the same elements, therefore, have very similar chemical properties. Most elements have more than one natural isotopes except few elements such as sodium, beryllium or fluorine.

Isobars: are atoms of different elements that have the same mass number but different atomic numbers. Thus $_{16}S^{36}$ and $_{18}Ar^{36}$ are isobars. The total number of nucleons in each of the isobars is the same, but numbers of protons and neutrons are different:

	Protons	neutrons	electrons
$_{16}S^{36}$	16	20	16
$_{18}Ar^{36}$	18	18	18

The mass spectrometer:

An instrument used to determine (i) the types of isotopes present in an element, (ii) the exact atomic mass of these isotopes and (iii) the relative amount of each isotopes present. Essential features of the instrument are shown in Fig.5
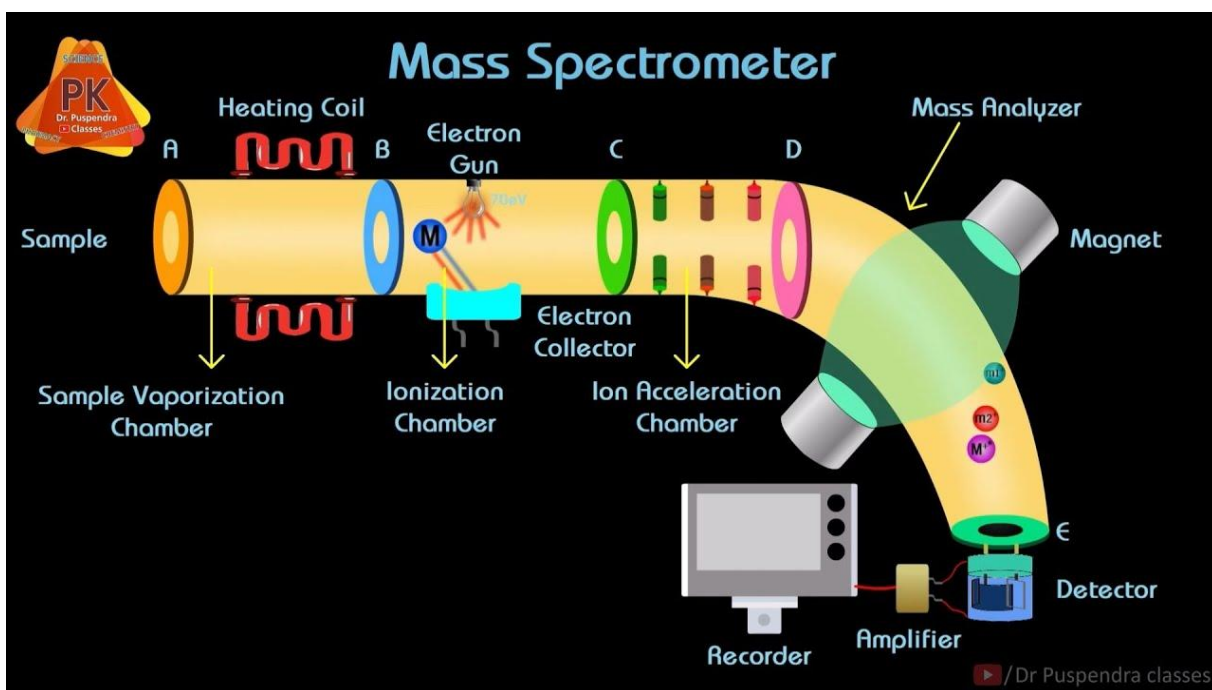
Fig.5: Essential features of a mass spectrometer

In this experiment:

1. Positive ions are produced from vaporized materials by bombardment with electrons.
2. The ions are accelerated by electric field and pass through the slit with high velocity

3- The beam of ions is the passed through a magnetic field where it is deflected and takes a circular path. The radius of this circular path depends on the value of *e/m*.

Atomic Weights

The atomic mass unit (*u*) is defined as one-twelfth ($1/12^{th}$) of the mass of $_6C^{12}$. The masses of proton, neutron and electrons based on this scale are:

Particle	Mass in grams	Mass in amu
Electron	9.109535×10^{-28} g	**0.0005485803 u**
Proton	1.672649×10^{-24} g	**1.007276 u**
Neutron	**1.674954×10^{-24} g**	**1.008665 u**

Atomic masses are determined by the use of the mass spectrometer. Most elements occur in nature as a mixture of isotopes. In this case the instrument can be used to determine the relative amount of each isotope as well as the atomic mass of each one. For example chlorine consists of 75.77% $_{17}Cl^{35}$ (mass, 34.969 u) and 24.23% $_{17}Cl^{37}$ (mass, 36.966 u). Any sample of chlorine from a natural source consists of these two isotopes in this proportion,

The atomic weight of the element is the weighted average of the atomic masses of the natural isotopes given by:

$$atomic\ mass = \sum (abundance)(mass)$$

Thus for chlorine

$_{17}Cl^{35}$ (0.7577)(34.969 u) = 26.496 u

$_{17}Cl^{37}$ (0.2423)(36.966 u) = 8.957 u

Thus the atomic mass   = 35.453 u

Example 1: What is the atomic mass of magnesium? The element consists of 78.99% $_{12}Mg^{24}$ (mass, 23.99 u), 10% $_{12}Mg^{25}$ (mass, 24.99 u) and 11.01% $_{12}Mg^{26}$ (mass, 25.98 u).

Example 2: Carbon occurs in nature as a mixture of $_6C^{12}$ (mass, 12.00 u) and $_6C^{13}$ (mass, 13.003 u). If the atomic weight of carbon is 12.011 u, what is the percent of $_6C^{12}$ in natural carbon.

Solution:

Let X is the abundance of $_6C^{12}$ then ($1 - X$) is the abundance of $_6C^{13}$. Thus

$$(X)(12.00) + (1 - X)(913.003) = 12.011$$

then, $12.000X + 13.003 - 13.003X = 12.011$

so, $X = 0.989$

then the percent of $_6C^{12}$ in nature is 98.9%

Electromagnetic Radiation

Radio waves, infrared, visible light, ultraviolet and X-rays are types of electromagnetic radiation. EMR travels through space in wave motion as shown in figure.

The following terms are used to describe these waves:

1- **The wavelength (λ)**: the distance between two similar two similar points on two successive waves.

2- **The amplitude (a)**: it is the height of the crest. The intensity of the radiation is proportional to the square of the amplitude (a^2).

3- **The frequency (v)**: the number of waves that pass a given point in a second. For a given type of radiation: $v = \dfrac{C}{\lambda}$ where C is the velocity at which radiation travel (velocity of light).

The electromagnetic spectrum is shown in Fig.5. Radio waves have very long wavelengths, infrared waves have moderate wavelengths and gamma (γ) rays have extremely wavelengths. White light (visible light) consists of radiation with wavelengths in the range 400 nm to 750 nm (1 nm = 10^{-9} m = 10^{-7} cm).
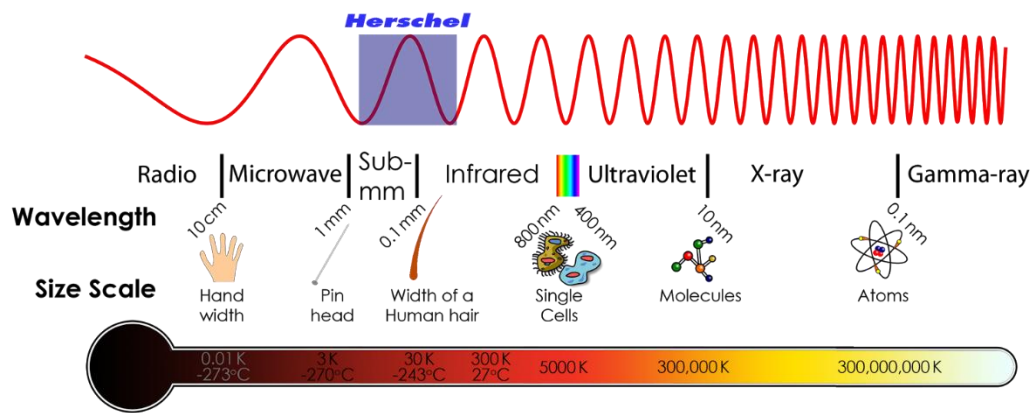
Fig.6: Electromagnetic radiation

In 1900, Max Planck proposed the quantum theory of radiant energy. Planck suggested that radiant energy could be absorbed or given off only in definite quantities, called quanta. The energy of quantum, **E**, is proportional to the frequency (*v*) of the radiation: $E = h\nu$.
The proportionality constant, *h*, is Planck's constant, 6.6262 x 10^{-34} J.s.

Since *E* and *v* are directly proportional and v and λ are inversely proportional, so, the wavelength of high energy radiation must be short and the frequency must be high. On the other hand, low energy radiation has low frequency and long wavelength.

Atomic Spectra

When a ray of light is passed through a prism, the ray is refracted. The amount that a wave is refracted depends upon its wavelength. A wave with a short wavelength is bent more than one of long wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a wide band called a *continuous spectrum*. The spectrum is a rainbow of colors.

When gases or a vapor of a chemical substance are heated in an electric arc or a Bunsen flame, light is emitted. If a ray of this light is passed through a prism, a **line spectrum** is produced (Fig.7). This spectrum consists of a limited number of colored lines, each of which corresponds to different wavelength of light. The spectrum of each element is unique.
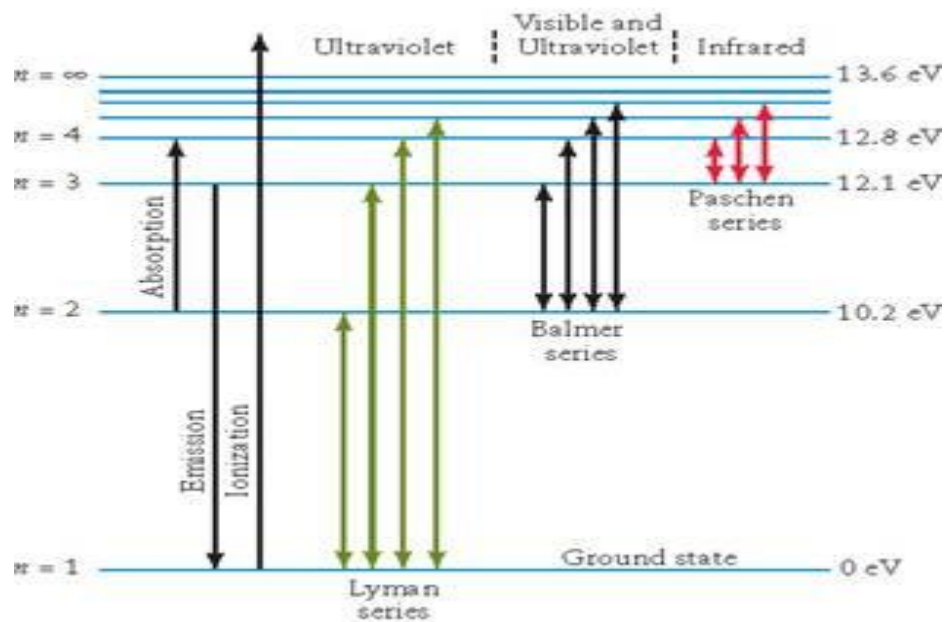
Fig.7: **Atomic Spectra**

The frequencies corresponding to the lines in the visible region of the hydrogen spectrum are given by the equation:

$$v = \frac{c}{\lambda} = (3.289 x 10^{15} / s)(\frac{1}{2^2} - \frac{1}{n^2}), n = 3,4,5,...$$

This relation was derived by Balmer from experimental observation.

In 1913, Niels Bohr proposed a theory for the electronic structure of the hydrogen atom which explained the line spectrum of this element. Bohr's theory includes the following points:

1- The electron of the hydrogen atom can exist only in certain spherical orbits (called the energy levels or shells). These shells are arranged concentrically around the nucleus and is designated by letters (K, L, M, N, O, …) or a value of n (1, 2, 3, 4, 5, ….).

2- The electron has a definite energy characteristic of its orbit. The K shell (n = 1), has the smallest radius and electron in this level has the lowest possible energy. With increasing distance from the nucleus, the radius of the shell and the energy of an electron in the shell increase. The electron cannot have an energy that would place it between the permissible shells.

3- Electron in the K shell is in the condition of lowest possible energy (ground state). When the atoms are excited (heated in an electric arc or Bunsen flame), electrons absorb energy and jump to outer levels, which are higher energy state.

4- When an electron falls back to lower level, it emits a definite amount of energy in the form of a quantum of light. The light quantum has a definite frequency (and wavelength) and produces a characteristic line. Each spectral line corresponds to a definite electron transition.

Bohr derived an equation for the energy that an electron would have in each orbit (E_{orbit}).

$$E_{orbit} = - \frac{(2.179 \times 10^{-18} J)}{n^2} \; ; \; n = 1, 2, 3, …$$

According to Planck's equation, the energy of a photon is equal to $h\nu$. So,

$$h\nu = E_o - E_i \qquad \text{(for } E_o \rightarrow E_i)$$

where E_o is the energy of the outer level and E_i is the energy of the inner level.

$$\therefore h\nu = \frac{(-2.179 x10^{-18}J)}{n_o^{\ 2}} - \frac{(-2.179 x10^{-18}J)}{n_o^{\ 2}} = (2.179 x10^{-18}J)(\frac{1}{n_i^{\ 2}} - \frac{1}{n_o^{\ 2}})$$

since $h = 6.6262 \times 10^{-34}$ J.s, then $\quad \nu = (3.289 x10^{15}/s)(\frac{1}{n^2_i} - \frac{1}{n_o^{\ 2}})$

This equation is the same as the equation derived by Balmer from experimental data.

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The Bohr theory is highly successful in interpreting the spectrum of hydrogen, but it fails to explain the spectra of many electron atoms.

Example 3: What are the frequency and wavelength of the line in H atom that corresponds to electron transition from n = 3 to n = 2 levels?

Atomic Number and the Periodic Law

Many attempts were done by early chemists to study the chemical and physical similarities that exist between elements. In 1817-1829, Dobereiner stated that sets of three elements such as (Ca, Sr, Ba), (Li, Na, K) or (Cl, Br, I) have similar properties and the atomic weight of the middle element is approximately equal to the average atomic weights of the other two elements. He called these elements (**Triades**)

In further studies (1863 - 66), Newlands proposed the **law of octaves**, which stated that" **when the elements are listed by increasing atomic weights, the eighth elements is similar to the first, the ninth to the second, and so forth".**

The modern periodic classification of the elements stems from the work of Lother Meyer and Mendeleev (1869). Mendeleev proposed a periodic law

which stated that "**when the elements are studied in order of increasing atomic weight, similarities in properties recur periodically**". Mendeleev table listed the element in such a way that similar elements appeared in vertical columns called groups. (table1).

In order to make similar elements appear under one another, Mendeleev had to leave blanks for undiscovered elements in his table. On the basis of his system, he predicted the properties of three of the missing elements. The subsequent discovery of scandium, gallium and germanium, each of which was found to have properties much like those predicted by Mendeleev, indicating the validity of his periodic system. The existence of the noble gases (He, Ne, Ar, Kr, Xe and Rn) was unforeseen by Mendeleev. But, after their discovery (1892 - 98), these elements readily fitted into the periodic table.

Mendeleev's Periodic Table of Elements

Some problems faced the periodic classification of elements according to increasing atomic weight, for example, the position of iodine (I) (see table 1). Subsequent studies of the periodic classification showed that some fundamental property other than atomic weight is the cause of the observed periodicity. It was proposed that this fundamental property is related to atomic number which was, at that time, a serial number derived from the periodic system.

The discovery of X-ray and the work of Moseley (1913) solved the problem of determination of atomic number. When high energy cathode rays are focused on a target, X-rays are produced (Fig. 9). Different X-ray spectra result when different elements are used as targets; each spectrum consists of only a few lines.
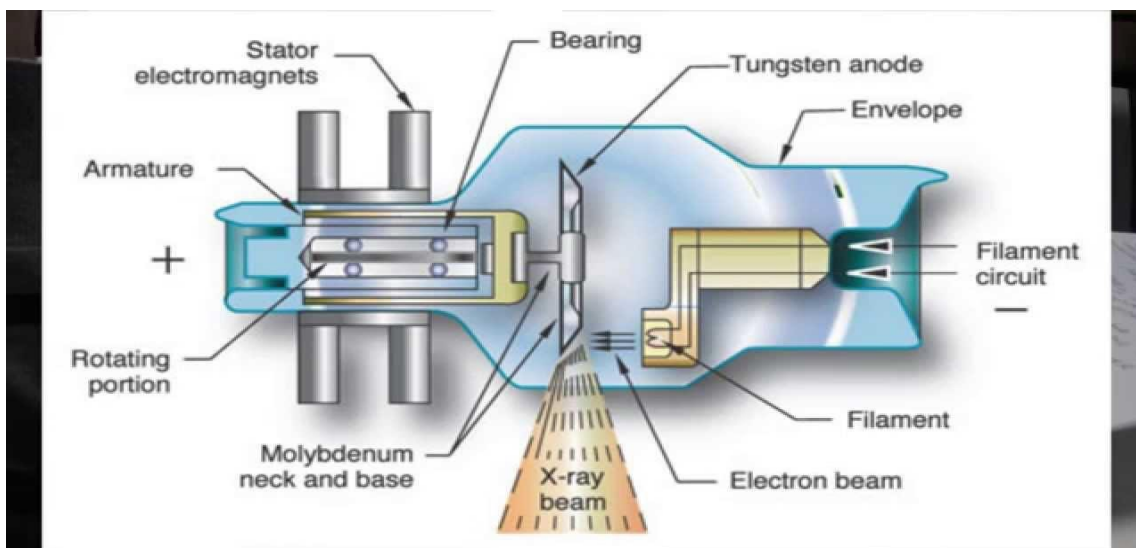
Fig.9: X-ray tube

By changing the target, Moseley studied the X-ray spectra of 38 elements with atomic numbers between 13 (aluminum, Al) and 79 (gold; Au). Using

the corresponding spectral line of each element, he found that there is a linear relationship between the square root of the frequency ($\sqrt{\nu}$) of the line and the atomic number of the element.

Moseley was able, therefore, to assign the correct atomic number to any element on the basis of its X-ray spectrum. In this way he settled the problem involving the classification of elements that have atomic weights out of line with those of their neighbor (K, Ni and I). He also stated that there should be 14 elements in the series from $_{58}$Ce to $_{71}$Lu (found in the bottom in table 1), and he established that these elements should follow lanthanum in the periodic table (now known as lanthanides). On the basis of Moseley's work, the periodic law was refined as: **the physical and chemical properties of the elements are periodic function of atomic number.**

At the present time, the most popular form of the periodic table is that shown in the outer cover of this book. The periods consist of elements that are arranged in horizontal rows in the table. Elements of similar physical and chemical properties (called **groups** or families) appear in vertical column.

The first period consists of only two elements, hydrogen and helium. Subsequent periods have 8, 8, 18, 18 and 32 elements. Each complete period begins with an alkali metals (group 1 A) which are highly reactive metals and ends with noble gases (group 0) which are of low reactivity. The elements before the noble gases (except for the first period) are halogens (group VII A) which are very reactive nonmetals.

A general trend for each period (except for the first one) is the starting with an alkali metal, the properties change from element to element. The

metallic properties fade and are gradually replaced by nonmetallic characters. After a highly reactive nonmetal (a halogen), each complete period ends with a noble gas.

Wave Mechanics

Bohar regarded the electron as a charged particle in motion, and he assumed that both position and momentum of electron can be precisely determined. He derived the theory from the laws of classical physics that pertain to the behavior of charged particles. It soon became evident that this approach was inadequate and that a new one is needed. Heisenberg's **uncertainty principle** stated that: **it is impossible to determine simultaneously the exact position and exact momentum of a body as small as the electron.**

In 1924, de Broglie proposed that; in the same way that light has both a wave and a particle-like character, electrons and other particles have wave properties. The energy of a photon of light (E) is given by:

$$E = h\nu$$

where ν is the frequency and h is Planck's constant.

Since $\nu = c/\lambda$ where c is the speed of light and λ is the wavelength, so

$$E = h\frac{c}{\lambda} \text{ J/p}$$

Using Einstein.s equation, $E = mc^2$ where m is the effective mass of the photon, we get

$$mc^2 = h\frac{c}{\lambda} \quad \text{so,} \quad \lambda = \frac{h}{mc} = \frac{h}{p} \quad \text{where is the momentum.}$$

According to de Broglie, a similar equation can be used to assign a wavelength to an electron:

$$\lambda = \frac{h}{mv}$$

where *m* is the mass of electron and *v* its velocity.

Schrodinger equation

It is the basis of wave mechanics. The equation is written in terms of a wave function Ψ for an electron. If an electron is considered as a wave moves in three directions x, y and z, the amplitude of the wave at any point is given by:

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\Psi \qquad (1)$$

using the symbol ∇ instead of the three partial differentials, we get

$$\nabla^2 \Psi = -\frac{4\pi^2}{\lambda^2}\Psi \qquad (2)$$

using the de Broglie equation $\lambda = \frac{h}{mv}$ we get

$$\nabla^2 \Psi = -\frac{4\pi^2 m^2 v^2}{h^2}\Psi \quad \text{or} \quad \nabla^2 \Psi + \frac{4\pi^2 m^2 v^2}{h^2}\Psi = 0 \qquad (3)$$

however, the total energy of the system *E* is made up of the kinetic energy *K* and the potential energy *V*; $E = K = V$ or $K = E - V$

but the kinetic energy

$$K = \frac{1}{2}mv^2 \text{ so } \frac{1}{2}mv^2 = E - V \text{ and } v^2 = \frac{2}{m(E-V)} \qquad (4)$$

substituting for v^2 in equation (3) gives the well-known form of the Schrödinger equation:

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0 \qquad (5)$$

Acceptable solutions to the wave equation (solutions which are physically possible) must have the following properties:

1- Ψ must be continuous.

2- Ψ must be finite.

3- Ψ must be single valued

4- the probability of finding an electron at a point x, y, z is Ψ^2.

5- the probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one, so:

$$\int_{-\infty}^{+\infty}\Psi^2 dxdydz = 1$$

Several wave functions called Ψ_1, Ψ_2, Ψ_3, .. will satisfy these conditions and is called an orbital (instead of orbit in Bohar theory). **Orbital is the volume in space where there is a high probability of finding the electron.** Each of these has a corresponding energy E_1, E_2, E_3, … In hydrogen atom, the single electron normally occupies the lowest of the energy level E_1. This is called the ground state.

Quantum Numbers

In wave mechanics, the electron distribution of an atom containing a number of electrons is divided into *shells*. The shells consist of one or more *subshells*, and the subshells composed of one or more *orbitals*. The electron of an atom is identified by a set of four quantum numbers:

1- The principal quantum number, *n*: It identifies the shell, or level, to which electron belongs. These shells are regions where the probability of finding an electron is high. The values of *n* = 1, 2, 3, ……

2- The subsidiary quantum number ,*l*,: It is the number of subshells in the principle shell. The values of *l* = 0, 1, 2, …(n-1). When *n* = 1, there is only one value of *l* (0). When *n* = 2, there are two subshells that have *l* values of 0 and 1. When *n* = 3, there three *l* values; 0, 1 and 2.

Other symbols are used to denote subshells which are letters instead of numbers:

$$l = 0, 1, 2, 3, 4, 5, ...$$

$$notation = s, p, d, f, g, h......$$

Each subshell consists of one or more orbitals. The number of orbitals in a subshell is given by the equation: *number of orbitals = 2l + 1.*

In any l = o subshell, for example, there is 2(0) + 1 = 1 orbital. In any l = 1 subshell; there are 2(1) + 1 = 3 orbitals and so on. In other words:

$$notation = s, p, d, f, g, ...$$

$$l = 0, 1, 2, 3, 4, ...$$

number of orbitals = 1, 3, 5, 7, 9

3- Magnetic orbital quantum number , m_l: Each orbital within a given subshell is identified by the magnetic orbital quantum number. For any sub shell, the values of m_l are given as:

$$m_l = +l, +(l-1), ..., 0, ...-(l-1), -l$$

Notice that the values of m_l are derived from l, and that the values of l are derived from n. The quantum numbers for the orbitals of the first four shells are given in table 2.

Table (2)

Shell (n)	Subshell (l)	Orbitals (m_l)	Subshell notation	No.of orbitals per subshell
1	0	0	1s	1
2	0	0	2s	1
	1	+1, 0, -1	2p	3
3	0	0	3s	1
	1	+1, 0, -1	3p	3
	2	+2, +1, 0, -1, -2	3d	5
4	**0**	**0**	**4s**	**1**
	1	**+1, 0, -1**	**4p**	**3**

	2	+2, +1, 0, -1, -2	4d	5
	3	+3, +2, +1, 0, -1, -2, -3	4f	7

The subsidiary quantum number (l) describes the shape of the orbital occupied by the electron. When $l = 0$, (s orbital) the orbital is spherical. The value of the wave function Ψ, and hence the probability of finding the electron Ψ^2 depend only on the distance r from the nucleus. The boundary surface diagram of s orbital is as shown in figure.

When $l = 1$ (p orbital), the wave function Ψ depends on the distance from the nucleus and on the direction in space (x, y or z). There are three possible values of the magnetic quantum number ($m_l = $ -1, 0 and +1). There are, therefore, three orbitals which are identical in energy, shape and size and differ only in their direction in space. The boundary surface diagrams of the p orbitals are shown in figure 10.

(b)
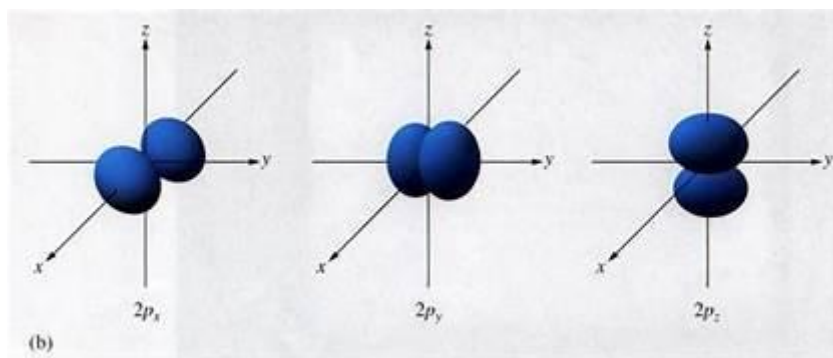
Fig. 10: Boundary surface diagrams of the 2p orbitals

When $l = 2$ (d orbital), the wave function depends both on the distance from the nucleus and the direction in space and have five sets of solutions corresponding to $m_l = $ -2, -1, 0, +1, +2. Thus, there five degenerate orbitals

differ only in the direction in space. The boundary surface diagrams of the *d* orbitals are shown in figure 11.

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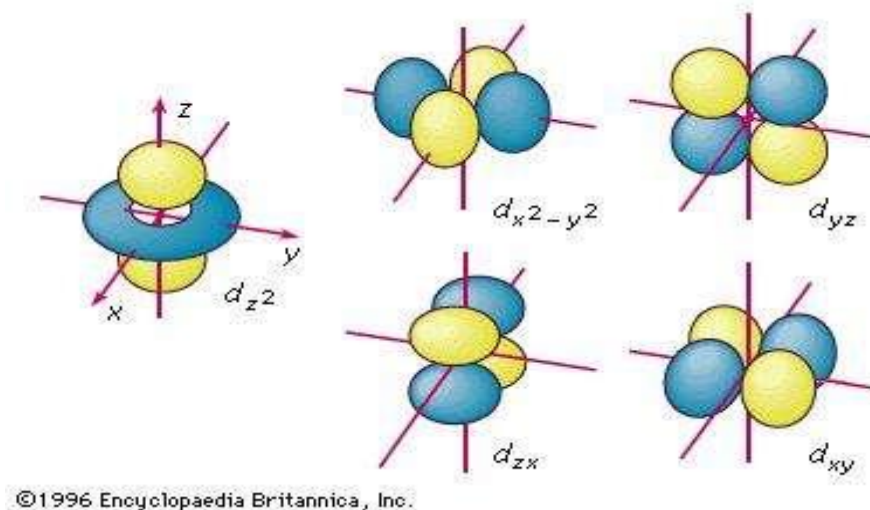
Fig.11: Boundary surface diagrams of 3*d* orbitals.

4- Magnetic spin quantum number, *m*$_s$: It is necessary to describe an electron completely. An electron has magnetic properties that are like those of a charged particle which spin on an axis. A spinning electron has a magnetic field associated with it. The magnetic spin quantum number of an electron can have one of the two values: ms = +1/2 or − 1/2.

Two electrons that have different *m*$_s$ values (one +1/2 and the other -1/2) are said to have opposite spins. The spin magnetic moments of these two electrons cancel each other. Each orbital can held two electrons with opposite spins.

Each electron, there for, may be described by a set of four quantum numbers:

1- *n* gives the shell and the relative average distance of the electron from the nucleus.

2- *l* gives the subshell and the shape of the orbital for the electron.

3- m_l shows the orientation of the orbital.

4- m_s refers to the spin of the electron

Exclusion principal of Pauli: states that "**no two electrons in the same atom may have identical sets of all four quantum numbers**". Even if two electrons have the same values of *n*, *l* and m_l they will differ in their m_s values. Quantum numbers for the orbitals of the first four shells are given in table 2. The maximum number of electrons that shell can hold is given by **2n²**.

Example: write the four quantum numbers of:

        i-   The two electrons in He atom.

        ii-   The third electron in carbon atom.

Solution: i-The four quantum numbers of the first electron in He are (100)

The four quantum numbers of the first electron in He are $(100\text{-}\frac{1}{2})$

ii- The four quantum numbers of the third electron are $(200\frac{1}{2})$

Orbital Filling and Hund's Rule

The way electrons are arranged in an atom is called electron configuration of the atom. For the first 18 elements, the ground-state electrons occupy the shells by increasing value of **n**, and within the shell by increasing value of **l**. In case of elements with atomic numbers higher than 18, the situation is slightly different.

Two ways to indicate the electron configuration of an atom. In the orbital diagram, each orbital is indicated by a dash and the electron is represented by an arrow either pointing up ↑or down ↓ to represent the

direction of electron spin (m_s either +1/2 or -1/2). In the electronic notation, the electron configuration of an atom is summarized by using the symbols $1s$, $2s$, $2p$,…etc to indicate *subshell*, and superscripts are added to indicate the number of electrons in each subshell. .

In hydrogen atom ($_1$H), the single electron occupies a $1s$ orbital ($n = 1$, $l = 0$, $m_l = 0$ and m_s is 1/2). The electronic notation for the H atom is $1s^1$. The helium atom ($_2$He) has two electrons with opposite spins in the $1s$ orbital and the electronic notation of He atom is $1s^2$. The $n = 1$ shell is now filled. The lithium atom ($_3$Li) has a pair of electrons in the $1s$ orbital plus one electron in the $2s$ orbital ($n = 2$, $l = 0$, $m_l = 0$ and $m_s = 1/2$) and the electron notation is $1s^2 2s^1$. In a similar way, the electronic notation of beryllium atom ($_4$Be) is $1s^1 2s^2$ and that for boron ($_5$B) is $1s^2 2s^2 2p^1$.

In case of carbon atom ($_6$C), two questions arise: does the sixth electron occupy the $2p$ orbital that already holds one electron, or does it occupy another orbital? What is the spin orientation of the sixth electron? Hund's rule of **maximum multiplicity** provides the answer. The rule states that "**the electrons are distributed among the orbitals of a subshell in a way that gives the maximum number of unpaired electrons with parallel spins**". The term parallel spins means that all the unpaired electrons spin in the same direction.

In carbon atom, there fore, each of the $2p$ electrons occupies a separate orbital, and these two electrons have the same spin orientation as shown in the orbital diagram. In general, it can be seen that:

1- The number of electrons in the outer shell (**valence shell**) is equal to the number of main group (A). The number of electrons in the valence shell is known as **valence electrons**.

2- The noble gases (group 0) have eight electrons in their valence shell (complete octet) except (He) which has only two.

3- The number of period in which element is present is equal to the principle quantum number (*n*).

The electron configuration of atoms can be derived by adding an electron to the outer shell to the next atom (taking into account Hund's rule). This is known as **aufbau** principle.

All the orbitals of a given subshell have equivalent energies. Thus, all 3p orbitals have the same energy and are said to be degenerate, also are the 3d orbitals. For a given value of (*n*), the energies increase in the order s< p< d < f. Sometimes, the energies of different orbitals from different shells overlap, for example, the 4s orbital has a lower energy than the 3d orbital. The aufbau order of energy levels is shown in figure 12.

Electron configuration can be derived from the diagram shown in figure by successive filling the orbitals starting at the bottom of the chart and proceeding upward. The electron configurations of the elements, based on this process, are given at the end of this chapter.

The diagonal rule for electron filling order.

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p
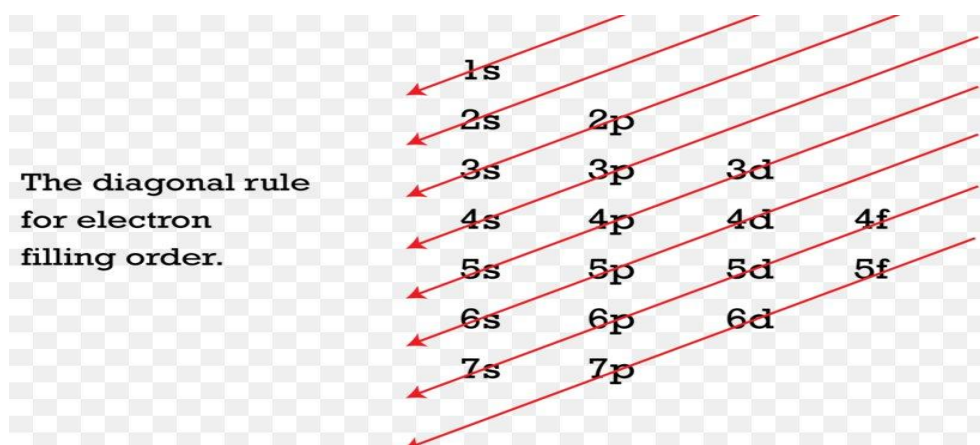
Figure 12: *Aufbau* order of atomic orbitals.

Half-filled and Filled Subshells

There are few exceptions from the standard pattern of aufbau process. For example, chromium (24Cr) is $3d^44s^2$ according to aufbau principle, whereas the experimentally derived configuration is $3d^54s^1$. This is due to the extra stability of half-filled subshells. In a similar way copper (29Cu) has the predicted notation $3d^94s^2$, whereas the experimentally derived configuration is $3d^{10}4s^1$. This is due to the extra stability of the completely filled subshells.

Chapter 3

Geometry of Chemical Molecules (Valence-Shell Electron-Pair Repulsion Theory) (VSEPR)

Predicting the Shapes of Molecules

There is no direct relationship between the formula of a compound and the shape of its molecules. The shapes of these molecules can be predicted from their Lewis structures along with the **valence-shell electron-pair repulsion (VSEPR) theory**.

Lewis structure

Lewis structures, also known as **Lewis dot formulas** are diagrams that show the bonding between atoms of   a molecule,   as   well   as   the lone pairs of electrons that may exist in the molecule. A Lewis structure can be drawn for any covalently bonded molecule, as well as coordination compounds.

Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

Electron counting

The total number of electrons represented in a Lewis structure is equal to the sum of the numbers of valence electrons on each individual atom. Non-valence electrons are not represented in Lewis structures.

Once the total number of available electrons has been determined, electrons must be placed into the structure according to these steps:

1. The atoms are first connected by single bonds.
2. If t is the total number of electrons and n the number of single bonds, $t-2n$ electrons remain to be placed. These should be placed as lone pairs: one pair of dots for each pair of electrons available. Lone pairs should initially be placed on outer atoms (other than hydrogen) until each outer atom has *eight* electrons in bonding pairs and lone pairs; extra lone pairs may then be placed on the central atom. When in doubt, lone pairs should be placed on more electronegative atoms first.
3. Once all lone pairs are placed, atoms (especially the central atoms) may not have an octet of electrons. In this case, the atoms must form a double bond; a lone pair of electrons is moved to form a second bond between the two atoms. As the bonding pair is shared between the two atoms, the atom that originally had the lone pair still has an octet; the other atom now has two more electrons in its valence shell.

Lewis structures for polyatomic ions may be drawn by the same method. When counting electrons, negative ions should have extra electrons placed in their Lewis structures; positive ions should have fewer electrons than an uncharged molecule. When the Lewis structure of an ion is written, the entire structure is placed in brackets, and the charge is written as a superscript on the upper right, outside the brackets.

A simpler method has been proposed for constructing Lewis structures, eliminating the need for electron counting: the atoms are drawn showing the valence electrons; bonds are then formed by pairing up valence electrons of the atoms involved in the bond-making process, and anions and cations are formed by adding or removing electrons to/from the appropriate atoms.

A trick is to count up valence electrons, then count up the number of electrons needed to complete the octet rule (or with hydrogen just 2 electrons), then take the difference of these two numbers. The answer is the number of electrons that make up the bonds. The rest of the electrons just go to fill all the other atoms' octets.

The following are examples for some molecules:

Lewis Electron Dot Structures

What are Lewis Structures?

Lewis Structure diagrams show how the valence electrons in molecules are distributed about their atoms - as bonds and lone pairs.

?

EXAMPLE:

:C̈l—N̈—C̈l:
|
:C̈l:
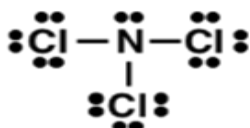
The Lewis Structure for NCl_3 shows how the 26 valence electrons are distributed about its atoms.

Interpret:

— Shared e⁻ pair

⋮ Unshared e⁻ pair

Dashes represent bonds and two dots represent unshared electrons.

Assumption:
Lewis Structures are based on the assumption that covalently-bonded atoms will share electrons with each other.

The Octet Rule:
Noble Gases (Ne, Ar, Kr, etc.) have 8 valence electrons (VEs) and are very stable. Atoms of other elements will share VEs with each other to acquire a stable octet. This e⁻ sharing results in a covalent bond.

:F̈:

:F̈—

Fluorine has 7 VEs. To obtain 8 VEs, it shares its one unpaired e⁻ with another atom, thus forming a bond to it.

Double and Triple Bonds:
Sometimes a double or triple bond is formed.

:N̈:

—N̈—
|
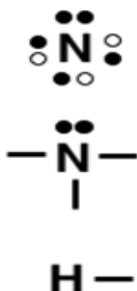
Nitrogen has 5 VEs. To obtain 8 VEs, it often shares its three unpaired e⁻ with other atoms, thus forming three bonds.

Ö=Ö   :C≡O:

H—

Hydrogen follows the **Duet Rule**.

Double Bond (4 shared e⁻s)   Triple Bond (6 shared e⁻s)

Formal charge

In general, the formal charge of an atom can be calculated using the following formula:

$$\text{Formal charge} = \left(\begin{array}{c}\text{number of valence}\\ \text{electrons in the}\\ \text{neutral atom}\end{array}\right) - \left(\begin{array}{c}\text{number of valence}\\ \text{electrons around the}\\ \text{atom in the molecule}\end{array}\right)$$

$$\text{Formal charge} = \left(\begin{array}{c}\text{number of valence}\\ \text{electrons in the}\\ \text{neutral atom}\end{array}\right) - \frac{1}{2}\left(\begin{array}{c}\text{number of electrons}\\ \text{in covalent bonds}\end{array}\right) - \left(\begin{array}{c}\text{number of electrons}\\ \text{in lone pairs}\end{array}\right)$$

Group number

remember that these electrons are shared by the atoms in the bond

OR

$$\text{Formal charge} = (\text{Group number}) - \left(\begin{array}{c}\text{number of}\\ \text{covalent bonds}\end{array}\right) - \left(\begin{array}{c}\text{number of electrons}\\ \text{in lone pairs}\end{array}\right)$$

STEP-BY-STEP METHOD

$$\ddot{O} = C = \ddot{O}$$

$$formal\ charge = VE - NE - \frac{BE}{2}$$

$VE = 6$
$NE = 4$
$BE = 4$

We now substitute the values and we have:

$$formal\ charge = 6 - 4 - \frac{4}{2} = 0$$

formal charge of oxygen (left) = 0

$$\ddot{O} = C = \ddot{O}$$

Resonance

For some molecules and ions, it is difficult to determine which lone pairs should be moved to form double or triple bonds, and two or more different *resonance* structures may be written for the same molecule or ion. In such cases it is usual to write all of them with two-way arrows in between.

When this situation occurs, the molecule's Lewis structure is said to be a resonance structure, and the molecule exists as a resonance hybrid. Each of the different possibilities is superimposed on the others, and the molecule is considered to have a Lewis structure equivalent to some combination of these states.

The nitrate ion (NO_3^-), for instance, must form a double bond between nitrogen and one of the oxygens to satisfy the octet rule for nitrogen. However, because the molecule is symmetrical, it does not matter *which* of the oxygens forms the double bond. In this case, there are three possible resonance structures. Expressing resonance when drawing Lewis structures may be done either by drawing each of the possible resonance forms and placing double-headed arrows between them or by using dashed lines to represent the partial bonds (although the latter is a good representation of the resonance hybrid which is not, formally speaking, a Lewis structure).

When comparing resonance structures for the same molecule, usually those with the fewest formal charges contribute more to the overall resonance hybrid. When formal charges are necessary, resonance structures that have negative charges on the more electronegative elements and positive charges on the less electronegative elements are favored.

The resonance structure should not be interpreted to indicate that the molecule switches between forms, but that the molecule acts as the average of multiple forms.

Example

The formula of the nitrite ion is NO^{-2}.
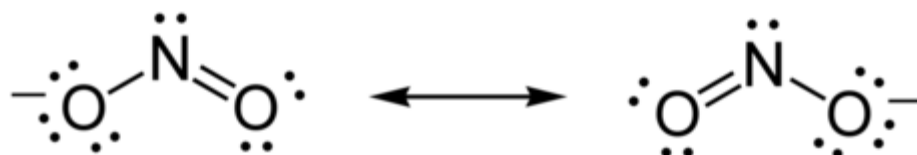
Geometry of inorganic molecules

The VSEPR theory assumes that each atom in a molecule will achieve a geometry that minimizes the repulsion between electrons in the valence shell of that atom. The following tables illustrate many examples
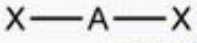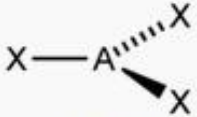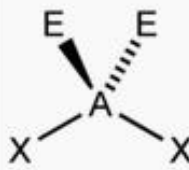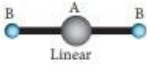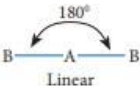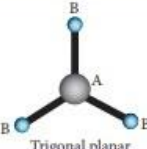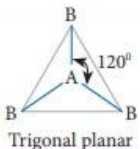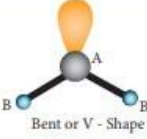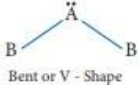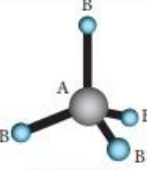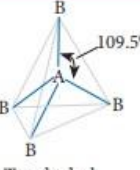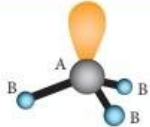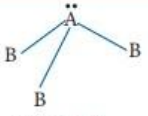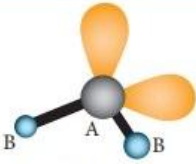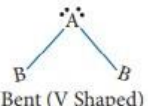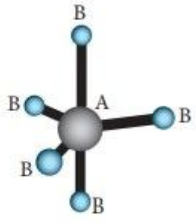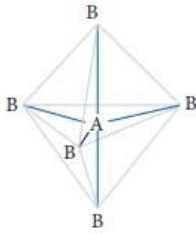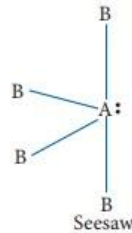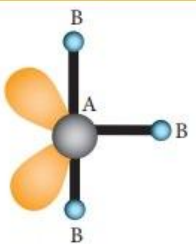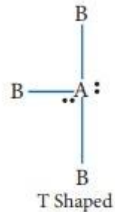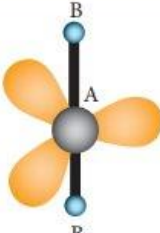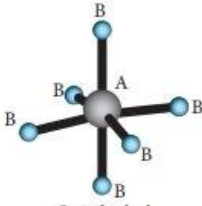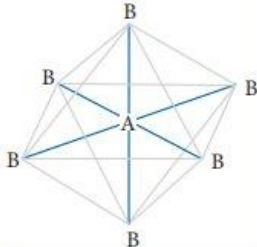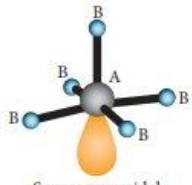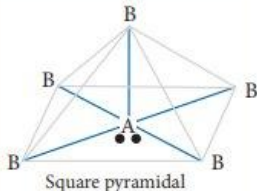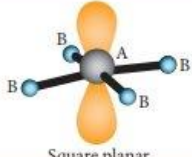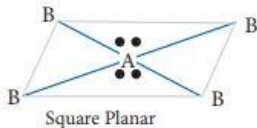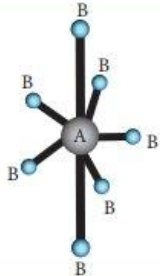
Steric No.	Basic geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
2	X—A—X Linear (CO_2)			
3	Trigonal planar (BCl_3)	Bent (SO_2)		
4	Tetrahedral (CH_4)	Trigonal pyramidal (NH_3)	Bent (H_2O)	
5	Trigonal bipyramidal (PCl_5)	Seesaw (SF_4)	T-shaped (ClF_3)	Linear (I_3^-)
6	Octahedral (SF_6)	Square pyramidal (BrF_5)	Square planar (XeF_4)	

Table 10. 6 Shapes of molecules predicted by VSEPR theory.

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
2	AB_2	2	-	Linear	$180°$ Linear	$BeCl_2$, $HgCl_2$, CO_2, CS_2, HCN, BeF_2
3	AB_3	3	-	Trigonal planar	$120°$ Trigonal planar	BF_3, BCl_3, NO_3^-, BF_3, CO_3^{2-}
	AB_2L	2	1	Bent or V - Shape	Bent or V - Shape	HCHO, SO_2, O_3, $PbCl_2$, $SnBr_2$
4	AB_4	4	-	Tetrahedral	$109.5°$ Tetrahedral	CH_4, CCl_4, CCl_2F_2, SO_4^{2-}, ClO_4^-, NH_4^+

	AB_3L	3	1	pyramidal	pyramidal	NH_3, PF_3, ClO_3^-, H_3O^+,
	AB_2L_2	2	2	Bent (V Shaped)	Bent (V Shaped)	H_2O, OF_2, SCl_2
5	AB_5	5	-	Trigonal bipyramidal	Trigonal bipyramidal	PCl_5, ASF_5, SOF_4
	AB_4L	4	1	Seesaw	Seesaw	SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$
	AB_3L_2	3	2	T shaped	T Shaped	BrF_3, ClF_3,

Number of electron Pairs	Molecule	No.of bond pairs	No.of. lone pairs	Shape	Molecular geometry	Examples
	AB_2L_3	2	3	Linear	Linear	XeF_2, I_3^-, IF_2^-
	AB_6	6	-	Octathedral		SF_6, IOF_5,
6	AB_5L	5	1	Square pyramidal	Square pyramidal	BrF_5, IF_5, TeF_5^-, $XeOF_4$,
	AB_4L_2	4	2	Square planar	Square Planar	XeF_4, ICl_4^-
7	AB_7	7	-		pentagonal bi-pyramidal	IF_7

Incorporating Double and Triple Bonds Into the VSEPR Theory

Compounds that contain double and triple bonds raise an important point: The geometry around an atom is determined by the number of places in the valence shell of an atom where electrons can be found, not the number of pairs of valence electrons. Consider the Lewis structures of carbon dioxide (CO_2) and the carbonate (CO_3^{2-}) ion, for example.
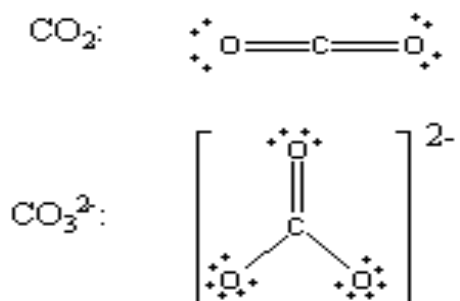
There are four pairs of bonding electrons on the carbon atom in CO_2, but only two places where these electrons can be found. (There are electrons in the C=O double bond on the left and electrons in the double bond on the right.) The force of repulsion between these electrons is minimized when the two C=O double bonds are placed on opposite sides of the carbon atom. The VSEPR theory therefore predicts that CO_2 will be a linear molecule, just like BeF_2, with a bond angle of 180°.

The Lewis structure of the carbonate ion also suggests a total of four pairs of valence electrons on the central atom. But these electrons are concentrated in three places: The two C-O single bonds and the C=O double bond. Repulsions between these electrons are minimized when the three oxygen atoms are arranged toward the corners of an equilateral triangle. The CO_3^{2-} ion should therefore have a trigonal-planar geometry, just like BF_3, with a 120° bond angle.

The Role of Nonbonding Electrons in the VSEPR Theory

To understand why, we have to recognize that nonbonding electrons take up more space than bonding electrons. Nonbonding electrons need to be close to only one nucleus, and there is a considerable amount of space in which nonbonding electrons can reside and still be near the nucleus of the atom. Bonding electrons, however, must be simultaneously close to two nuclei, and only a small region of space between the nuclei satisfies this restriction.

Because they occupy more space, the force of repulsion between pairs of nonbonding electrons is relatively large. The force of repulsion between a pair of nonbonding electrons and a pair of bonding electrons is somewhat smaller, and the repulsion between pairs of bonding electrons is even smaller.

The figure below can help us understand why nonbonding electrons are placed in equatorial positions in a trigonal bipyramid.
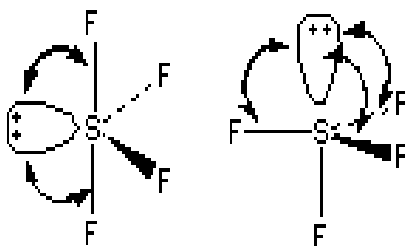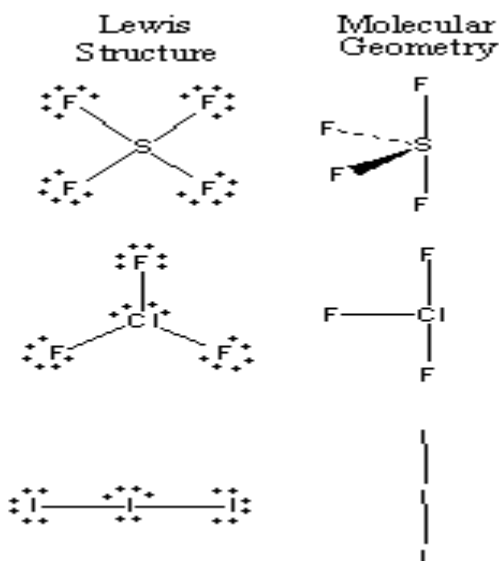

If the nonbonding electrons in SF_4 are placed in an axial position, they will be relatively close (90°) to three pairs of bonding electrons. But if the nonbonding electrons are placed in an equatorial position, they will be 90° away from only two pairs of bonding electrons. As a result, the repulsion between nonbonding and bonding electrons is minimized if the nonbonding electrons are placed in an equatorial position in SF_4.

The results of applying the VSEPR theory to SF_4, ClF_3, and the I_3^- ion are shown in the figure below.

Lewis Structure   Molecular Geometry

When the nonbonding pair of electrons on the sulfur atom in SF_4 is placed in an equatorial position, the molecule can be best described as having a *see-saw* or *teeter-totter* shape. Repulsion between valence electrons on the chlorine atom in ClF_3 can be minimized by placing both pairs of nonbonding electrons in equatorial positions in a trigonal bipyramid. When this is done, we get a geometry that can be described as *T-shaped*. The Lewis structure of the triiodide (I_3^-) ion suggests a trigonal bipyramidal distribution of valence electrons on the central atom. When the three pairs of nonbonding electrons on this atom are placed in equatorial positions, we get a *linear* molecule.

Molecular geometries based on an octahedral distribution of valence electrons are easier to predict because the corners of an octahedron are all identical.

Hybridization

Molecular geometry can also be predicted from the type of hybridization taking place within the atomic orbitals of the interacting atoms. This can be summarized as given in the following Table:

VSEPR					Hybridization			
ECC	Bonding Pair	Lore Pair	Electron Distribution Electron geometry domain		Atomic orbitals	Type of Hybridization	Number of Hybrid orbitals	Shape/Geometry
2	2	0		linear	s, p	sp	2	linear
3	3	0		Trigonal planar	s, p, p	sp²		Trigonal planar
	2	1		Trigonal planar	s, p, p	sp²	3	Bend V shape
4	4	0		Tetrahedral	s, p, p, p	sp³	4	Tetrahedral
	3	1		Tetrahedral	s, p, p, p	sp³	4	Trigonal pyrimidal
	2	2		Tetrahedral	s, p, p, p	sp³	4	Bend V shape
5	5	0		Trigonal Bipyrimidal	s, p, p, p, d	dsp³	5	Trigonal Bipyrimidal
	4	1		Trigonal Bipyrimidal	s, p, p, p, d	dsp³	5	Seesaw
	3	2		Trigonal Bipyrimidal	s, p, p, p, d	dsp³	5	T shape
	2	3		Trigonal Bipyrimidal	s, p, p, p, d	dsp³	5	Linear
6	6	0		Octahedral	s, p, p, p, d, d	d²sp³	6	Octahedral
	5	1		Octahedral	s, p, p, p, d, d	d²sp³	6	Square pyrimidal
	4	2		Octahedral	s, p, p, p, d, d	d²sp³	6	Square planar

Chapter 4

Chemical Bonding

Atoms are trying to reach the most stable (lowest-energy) state that they can. Many atoms become stable when their valence shell is filled with electrons or when they satisfy the octet rule (by having eight valence electrons). If atoms don't have this arrangement, they'll "want" to reach it by gaining, losing, or sharing electrons via bonds.

Ions and ionic bonds

Some atoms become more stable by gaining or losing an entire electron (or several electrons). When they do so, atoms form **ions**, or charged particles. Electron gain or loss can give an atom a filled outermost electron shell and make it energetically more stable.

Forming ions

Ions come in two types. **Cations** are positive ions formed by losing electrons. For instance, a sodium atom loses an electron to become a sodium cation. Negative ions are formed by electron gain and are called **anions**. Anions are named using the ending "-ide": for example, the anion of chlorine is called chloride.

When one atom loses an electron and another atom gains that electron, the process is called **electron transfer**. Sodium and chlorine atoms provide a good example of electron transfer.

Sodium (Na) only has one electron in its outer electron shell, so it is easier (more energetically favorable) for sodium to donate that one electron than to find seven more electrons to fill the outer shell..

Chlorine (Cl), on the other hand, has seven electrons in its outer shell. In this case, it is easier for chlorine to gain one electron than to lose seven, so it tends to take on an electron and become Cl⁻

Neutral Atom

loss of
electron(s)

gain of
electron(s)

Cation

Anion
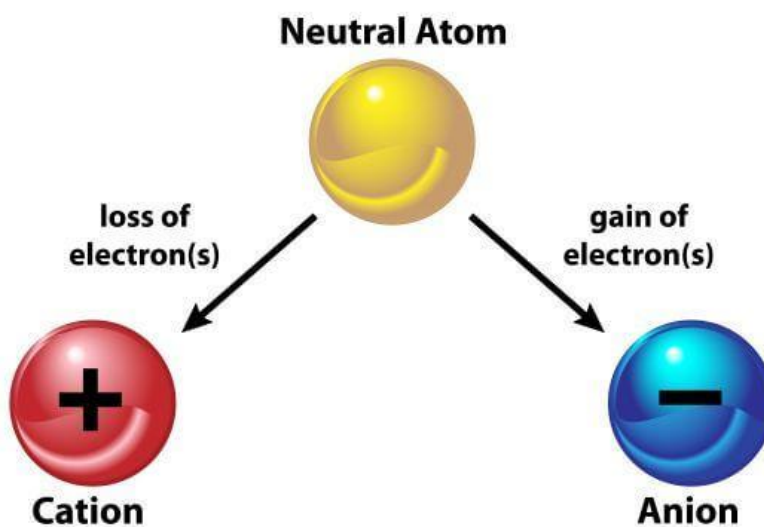
For example, when a *sodium atom* meets a *chlorine atom,* the sodium donates one valence electron to the chlorine. This creates a *positively-charged sodium ion* and a *negatively-charged chlorine ion.* The electrostatic attraction between them forms an ionic bond, resulting in a stable ionic compound called *sodium chloride* .

Na   Cl   Na+   Cl-
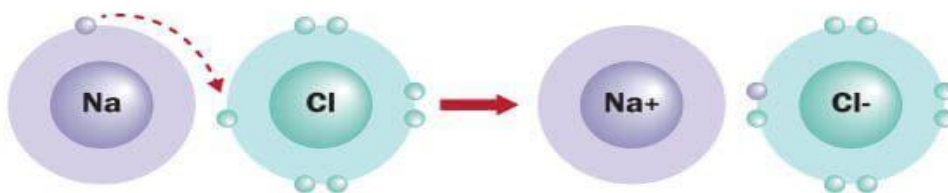
When sodium and chlorine are combined, sodium will donate its one electron to empty its shell, and chlorine will accept that electron to fill its shell. Both ions now satisfy the octet rule and have complete outermost shells. Because the number of electrons is no longer equal to the number of protons, each atom is now an ion and has a +1 or −1 .

Many other common reactions lead to the formation of ionic bonds. Calcium burns in oxygen to form calcium oxide:

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$
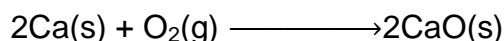
Assuming that the diatomic O_2 molecule first splits into separate oxygen atoms, we can represent the reaction with Lewis symbols:

$$\cdot \text{Ca} \cdot + \quad \cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \cdot \quad \longrightarrow \quad \text{Ca}^{2+} \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:^{2-}$$
$$[\text{Ar}]4s^2 \quad 1s^2 2s^2 2p^4 \qquad [\text{Ar}] \qquad [\text{Ne}]$$
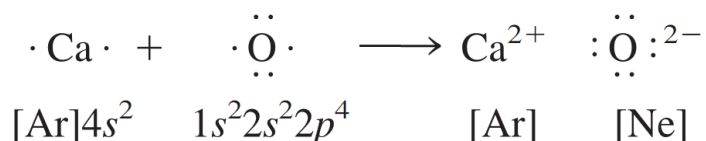
There is a transfer of two electrons from the calcium atom to the oxygen atom. Note that the resulting calcium ion (Ca^{2+}) has the argon electron configuration, the oxide ion (O^{2-}) is isoelectronic with neon, and the compound (CaO) is electrically neutral.

In many cases, the cation and the anion in a compound do not carry the same charges. For instance, when lithium burns in air to form lithium oxide (Li_2O), the balanced equation is

$$4\text{Li}(s) + O_2(g) \longrightarrow 2\text{Li}_2O(s)$$
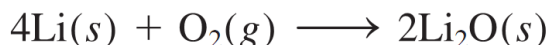
Using Lewis dot symbols, we write

$$2 \cdot \text{Li} + \quad \cdot \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \cdot \quad \longrightarrow \quad 2\text{Li}^+ \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}:^{2-} \text{ (or Li}_2\text{O)}$$
$$1s^2 2s^1 \quad 1s^2 2s^2 2p^4 \qquad [\text{He}] \qquad [\text{Ne}]$$
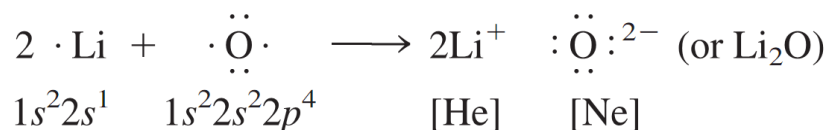
In this process, the oxygen atom receives two electrons (one from each of the two lithium atoms) to form the oxide ion. The Li^+ ion is isoelectronic with helium.

When magnesium reacts with nitrogen at elevated temperatures, a white solid compound, magnesium nitride (Mg_3N_2), forms:

$$3\text{Mg}(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

or

$$3 \cdot \text{Mg} \cdot \; + \; 2 \cdot \overset{..}{\underset{.}{\text{N}}} \cdot \;\longrightarrow\; 3\text{Mg}^{2+} \quad 2 : \overset{..}{\underset{..}{\text{N}}} :^{3-} \;(\text{or } \text{Mg}_3\text{N}_2)$$

$$[\text{Ne}]3s^2 \qquad 1s^2 2s^2 2p^3 \qquad\quad [\text{Ne}] \qquad\quad [\text{Ne}]$$
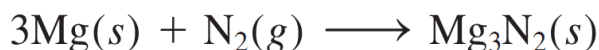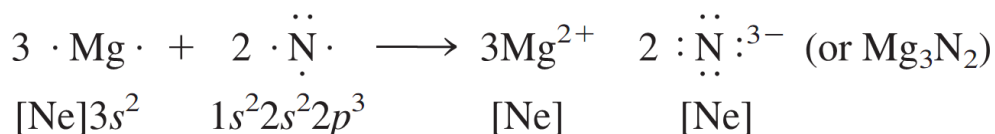
The reaction involves the transfer of six electrons (two from each Mg atom) to two nitrogen atoms. The resulting magnesium ion (Mg^{2+}) and the nitride ion (N^{3-}) are both isoelectronic with neon. Because there are three +2 ions and two -3 ions, the

charges balance and the compound is electrically neutral.

Electrostatic (Lattice) Energy

Lattice energy (U) is the energy required to completely separate one mole of a solid ionic compound into gaseous ions.

$$E = k\frac{Q_+ Q_-}{r}$$

Q+ is the charge on the cation

Q- is the charge on the anion

r is the distance between the ions

E is the potential energy

MgF_2	2957	Q: +2,-1
MgO	3938	Q: +2,-2
LiF	1036	$r\,F^- < r\,Cl^-$
LiCl	853	

Lattice energy increases as Q increases and/or and when r decreases.

Table: Lattice energies and melting points of some alkali and alkaline earth metal halides and oxides

Compound	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
LiBr	787	550
LiI	732	450
NaCl	788	801
NaBr	736	750
NaI	686	662
KCl	699	772
KBr	689	735
KI	632	680
$MgCl_2$	2527	714
Na_2O	2570	Sub*
MgO	3890	2800

Covalent bonds

Another way atoms can become more stable is by sharing electrons (rather than fully gaining or losing them), thus forming **covalent bonds**. Covalent bonds are more common than ionic bonds in the molecules of living organisms.

For instance, covalent bonds are key to the structure of carbon-based organic molecules like our DNA and proteins. Covalent bonds are also found in smaller inorganic molecules.

As an example of covalent bonding, let's look at water. A single water molecule, consists of two hydrogen atoms bonded to one oxygen atom. Each hydrogen shares an electron with oxygen, and oxygen shares one of its electrons with each hydrogen:
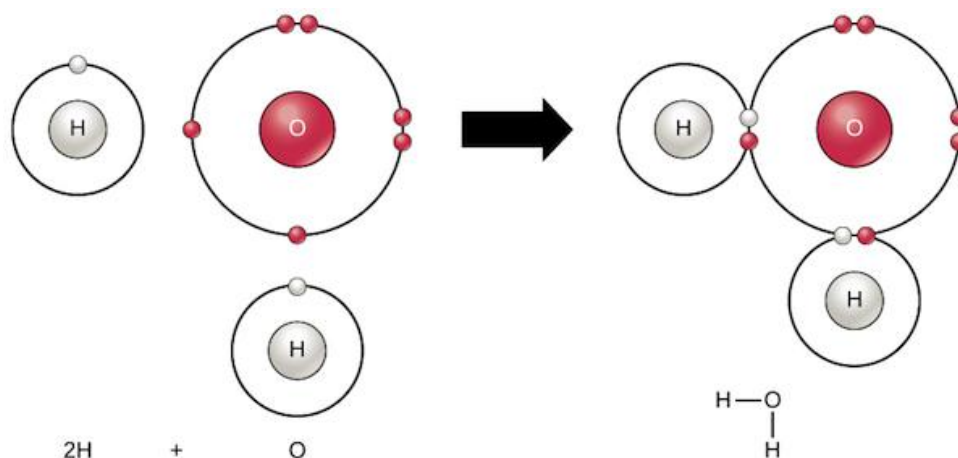
Hydrogen atoms sharing electrons with an oxygen atom to form covalent bonds, creating a water molecule

In the F_2 and H_2O molecules, the F and O atoms achieve a noble gas configuration by sharing electrons:

$$8e^-\ 8e^- \qquad\qquad 2e^-\ 8e^-\ 2e^-$$

In a single bond, two atoms are held together by one electron pair. Double bonds formed when two atoms share two or more pairs of electrons. (covalent double

bond). Double bonds are found in molecules of carbon dioxide (CO_2) and ethylene (C_2H_4):

$$\ddot{O} :: C :: \ddot{O} \quad \text{or} \quad \ddot{O}=C=\ddot{O}$$

$8e^- \quad 8e^- \quad 8e^-$

$$\begin{array}{cc} H & H \\ & \ddot{C} :: \ddot{C} \\ H & H \end{array} \quad \text{or} \quad \begin{array}{cc} H & H \\ C=C \\ H & H \end{array}$$

$8e^- \quad 8e^-$
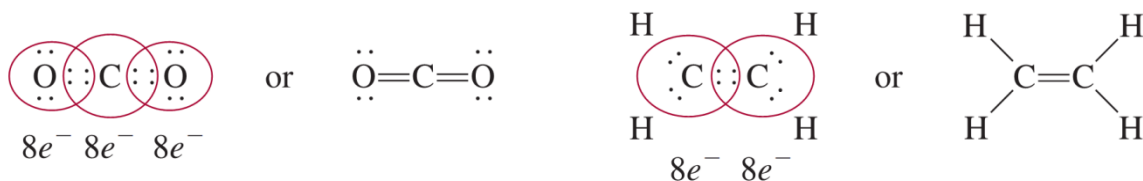
A triple bond forms when two atoms share three pairs of electrons, as in the nitrogen molecule (N_2):

$$: N ::: N : \quad \text{or} \quad : N{\equiv}N :$$

$8e^- \quad 8e^-$
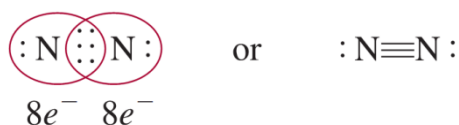
The acetylene molecule (C_2H_2) also contains a triple bond, in this case between two carbon atoms:

$$H : C ::: C : H \quad \text{or} \quad H{-}C{\equiv}C{-}H$$

$8e^- \quad 8e^-$
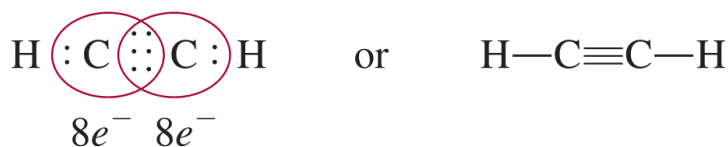
Multiple bonds are shorter than single covalent bonds. Bond length is defined as the distance between the nuclei of two covalently bonded atoms in a molecule. The triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds (triple bonds < double bonds < single bonds).

74 pm   161 pm

H_2 HI   Bond length (in pm)
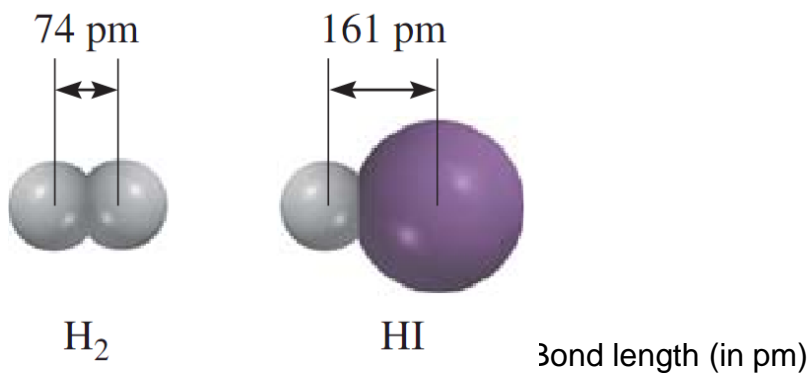
Polar covalent bonds

There are two basic types of covalent bonds: polar and nonpolar. In a **polar covalent bond**, the electrons are unequally shared by the atoms and spend more time close to one atom than the other. Because of the unequal distribution of electrons between the atoms of different elements, slightly positive ($δ+$) and slightly negative ($δ–$) charges develop in different parts of the molecule.

In a water molecule (above), the bond connecting the oxygen to each hydrogen is a polar bond. Oxygen is a much more **electronegative** atom than hydrogen, meaning that it attracts shared electrons more strongly, so the oxygen of water bears a partial negative charge (has high electron density), while the hydrogens bear partial positive charges (have low electron density).

In general, the relative electronegativities of the two atoms in a bond – that is, their tendencies to "hog" shared electrons – will determine whether a covalent bond is polar or nonpolar. Whenever one element is significantly more electronegative than the other, the bond between them will be polar, meaning that one end of it will have a slight positive charge and the other a slight negative charge.

Nonpolar covalent bonds

Nonpolar covalent bonds form between two atoms of the same element, or between atoms of different elements that share electrons more or less equally. For example, molecular oxygen is nonpolar because the electrons are equally shared between the two oxygen atoms.

Another example of a nonpolar covalent bond is found in methane CH_4. Carbon has four electrons in its outermost shell and needs four more to achieve a stable octet. It gets these by sharing electrons with four hydrogen atoms, each of which provides a single electron. Reciprocally, the hydrogen atoms each need one additional electron to fill their outermost shell, which they receive in the form of shared electrons from carbon. Although carbon and hydrogen do not have

exactly the same electronegativity, they are quite similar, so carbon-hydrogen bonds are considered nonpolar.
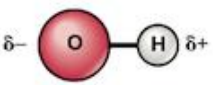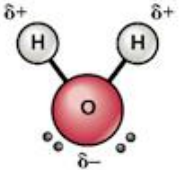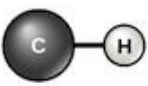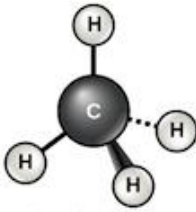
	Bond type	Molecular shape
Water	δ− O—H δ+ Polar covalent	δ+ H H δ+ O δ− Bent
Methane	C—H Nonpolar covalent	H H C H H Tetrahedral

Table showing water and methane as examples of molecules with polar and nonpolar bonds, respectively.

The Electronegativities of Common Elements

Electronegativity is a relative concept; Linus Pauling devised a method for calculating relative electronegativities of most elements.

Increasing electronegativity

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	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	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Increasing electronegativity

Figure: The electronegativities of common elements

In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each

group, electronegativity decreases with increasing atomic number, and increasing metallic character.

Classification of bonds by difference in electronegativity

Difference in electronegativity	Bond Type
0	Covalent
≥ 2	Ionic
0 < and <2	Polar Covalent

Increasing difference in electronegativity

Covalent   Polar Covalent   Ionic

share e⁻   partial transfer of e⁻   transfer e⁻
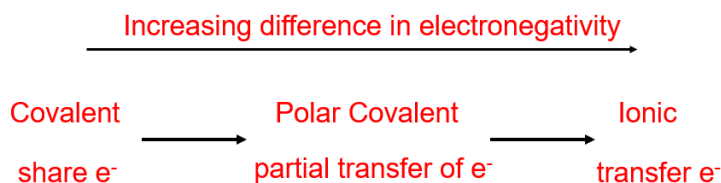
Example: Classify the following bonds as ionic, polar covalent, or covalent: The bond in CsCl; the bond in H_2S; and the NN bond in H_2NNH_2.

Cs – 0.7   Cl – 3.0   3.0 – 0.7 = 2.3   Ionic

H – 2.1   S – 2.5   2.5 – 2.1 = 0.4   Polar Covalent

N – 3.0   N – 3.0   3.0 – 3.0 = 0   Covalent

Hydrogen bonds and London dispersion forces

Covalent and ionic bonds are both typically considered strong bonds. However, other kinds of more temporary bonds can also form between atoms or molecules. Two types of weak bonds often seen in biology are hydrogen bonds and London dispersion forces.

Not to be overly dramatic, but without these two types of bonds, life as we know it would not exist! For instance, hydrogen bonds provide many of the life-sustaining properties of water and stabilize the structures of proteins and DNA, both key ingredients of cells.

Hydrogen bonds

The *hydrogen bond* is a special dipole-dipole interaction between they hydrogen atom in a polar N-H, O-H, or F-H bond and an electronegative O, N, or F atom.
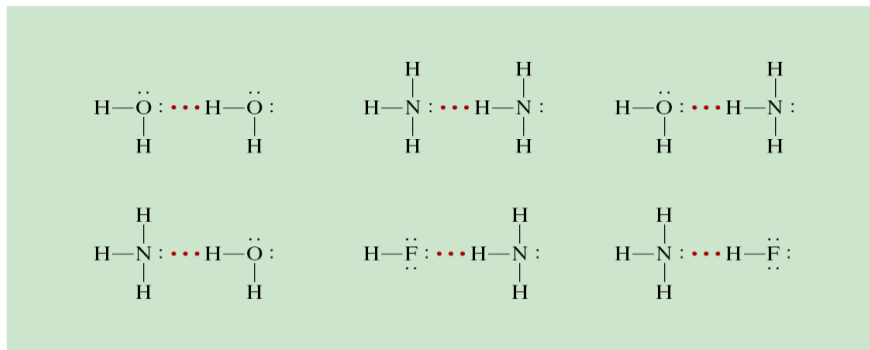
In a polar covalent bond containing hydrogen (e.g., an O-H bond in a water molecule), the hydrogen will have a slight positive charge because the bond electrons are pulled more strongly toward the other element. Because of this slight positive charge, the hydrogen will be attracted to any neighboring negative charges. This interaction is called a **hydrogen bond**.

Hydrogen bonds are common, and water molecules in particular form lots of them. Individual hydrogen bonds are weak and easily broken, but many hydrogen bonds together can be very strong.

London dispersion forces

Like hydrogen bonds, **London dispersion forces** are weak attractions between molecules. However, unlike hydrogen bonds, they can occur between atoms or molecules of any kind, and they depend on temporary imbalances in electron distribution.

How does that work? Because electrons are in constant motion, there will be some moments when the electrons of an atom or molecule are clustered together, creating a partial negative charge in one part of the molecule (and a partial positive charge in another). If a molecule with this kind of charge imbalance is very close to another molecule, it can cause a similar charge redistribution in the

second molecule, and the temporary positive and negative charges of the two molecules will attract each other.

Hydrogen bonds and London dispersion forces are both examples of **van der Waals forces**, a general term for intermolecular interactions that do not involve covalent bonds or ions. Some textbooks use the term "van der Waals forces" to refer only to London dispersion forces, so make sure you know what definition your textbook or teacher is using.

Metallic bonding

In metallic bonding, bonding electrons are delocalized over a lattice of atoms. By contrast, in ionic compounds, the locations of the binding electrons and their charges are static. The free movement or delocalization of bonding electrons leads to classical metallic properties such as luster (surface light reflectivity), electrical and thermal conductivity, ductility, and high tensile strength.

This can be summarize in the following figure:

Ionic Bonding

$Na + Cl \longrightarrow Na^+ + Cl^- \longrightarrow NaCl$

Covalent Bonding

$H + H \longrightarrow H:H$

Hydrogen Molecule

$H + O + H$

Water Molecule

Metallic Bonding

Sea Electron

Metal Core

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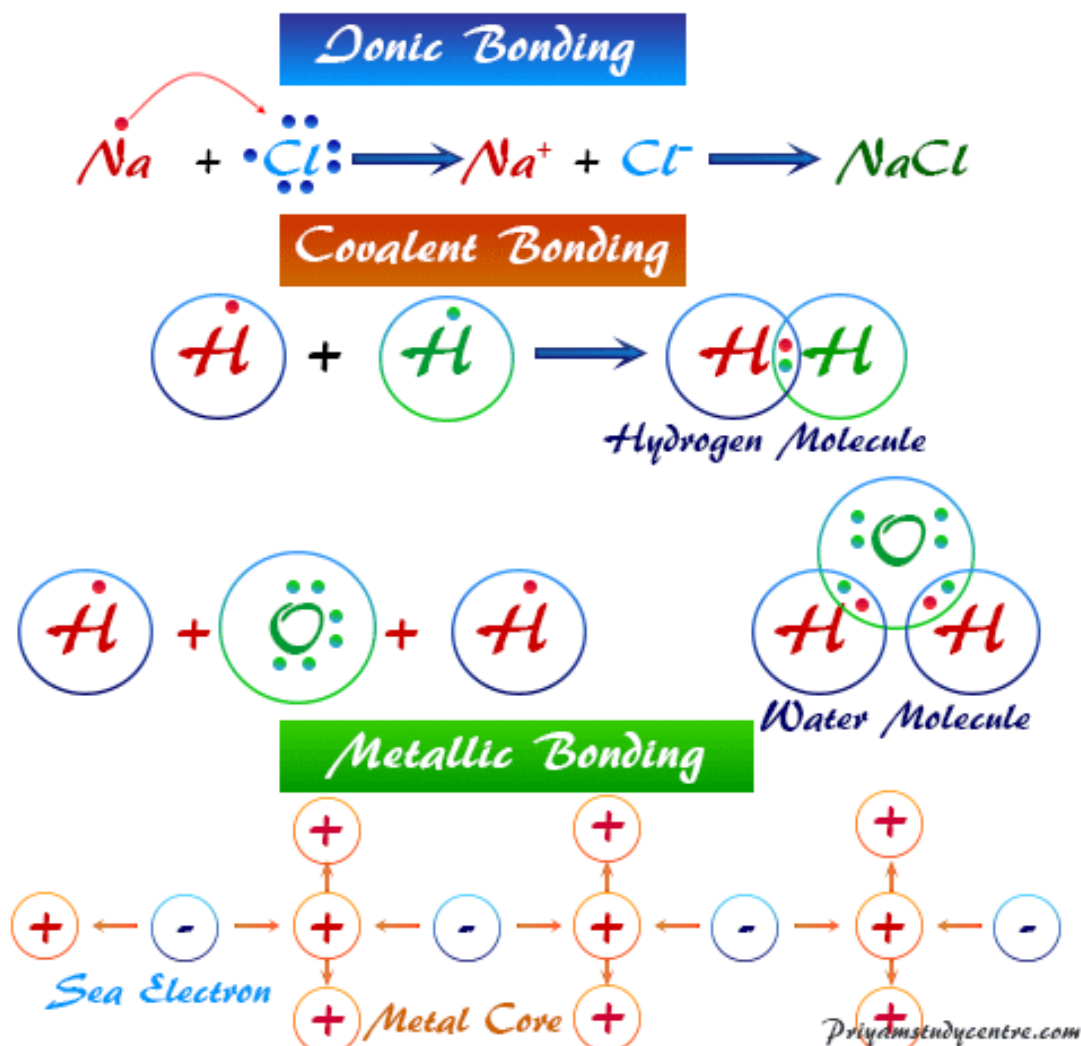
Some selected problems

What are the main postulates of Dalton theory?

The principle postulates of Dalton theory are:

1- Elements are composed of extremely small particles called atoms. All atoms of the same elements are alike, and atoms of different elements are different

2- The separation and union of atoms occur in chemical reactions. In the reactions, no atom is created or destroyed, and no atom of one element is converted into an atom of another element.

3- A chemical compound is the result of the combination of atoms of two or more elements in a simple numerical ratio.

What is meant by the law of conservation of mass?

The second postulate of Dalton's theory account for the **law of conservation of mass** which states that "***there is no detectable change in mass during the course of a chemical reaction.***" So, the total mass of all the materials entering into a chemical reaction must equal the total mass of all the products of the reaction (balanced chemical equation).

What is meant by the law of multiple proportions?

This law states that "***when two elements A and B form more than one compound, the amounts of A that are combined with a fixed amount of B are in a small whole-number ratio.***" For example, carbon and oxygen form two compounds: carbon monoxide (CO) and carbon dioxide (CO_2), so the masses of oxygen that combined with fixed amount of carbon stand in the ratio of 2:1.

What is meant by molecular and empirical formula? Give example.

The formula which gives the number of atoms of each type in a single molecule of the compound is called ***molecular formula***. Both water and sulfuric acid, for examples, has the molecular formula H_2O and H_2SO_4 respectively.

The formula which gives the simplest whole number ratio is called the **simplest formula** or **empirical formula**. The molecular formula of hydrogen peroxide is H_2O_2 while the empirical formula is HO.

The compound glucose contains 40.0% C and 6.73% H. If its molecular weight is 180.2, what is the molecular formula?

Nicotine is a compound that contains carbon, hydrogen and nitrogen. If 2.50 g sample of nicotine is burned in oxygen, 6.78 g of CO_2 and 1.94 g of H_2O were produced. What is the percentage composition of nicotine? Find the empirical formula of nicotine.

Solution:

We first calculate the quantity of each element present in the 2.5 g sample. The C forms 6.78 g of CO_2, thus

      One C forms one mole of CO_2

Then   12 g C $\longrightarrow$ 44 g of CO_2

      X g C $\longrightarrow$ 6.78 g of CO_2 So, X = $\dfrac{6.78 \times 12}{44}$ 1.85 g C

    The % of C = $\dfrac{1.85\, g\, C}{2.50\, g\, nicotine} \times 100 = 74.0\%$ C in nicotine

In a similar way: 18 g of H_2O form 2.02 g of H, then

        1.94 g H_2O form X g of H   So, X = $\dfrac{1.94 \times 2.02}{18.0} = 0.218$ g H

    The % of H = $\dfrac{0.218\, g\, H}{2.50\, g\, nicotine} \times 100 = 8.72$ % H in nicotine

The weight of nitrogen = 2.5 − (1.85 + 0.218) = 0.432 g N

Finally,   the % of N = $\dfrac{0.432\, g\, N}{2.5\, g\, Nicotine} \times 100 = 17.3\%$ % N in nicotine.

Find the empirical formula of nicotine.

Elements	C	H	N

Weight:	1.85 g	0.218 g	0.432 g
No. of moles	$\dfrac{1.85}{12}$	$\dfrac{0.218}{1}$	$\dfrac{0.432}{14}$
	0.154	0.218	0.031
dividing by least value	$\dfrac{0.154}{0.031}$	$\dfrac{0.218}{0.031}$	$\dfrac{0.031}{0.031}$
	4.97	7.03	1.00
this can be rounded to	5	7	1

thus the empirical formula of nicotine is C_5H_7N

1.261 g sample of pure organic compound contains 0.624 g C, 0.065 g H, 0.364 g N and 0.208 g O. what is the molecular formula of this compound if its molecular weight is 194?

Solutions:

Elements	C	H	N	O	
No. of moles	0.052	0.065	0.026	0.013	dividing by smallest value
	4	5	2	1	(Whole numbers are obtained)

Thus the empirical formula is $C_4H_5N_2O$.

The molecular weight = n x empirical formula weight, where n is a whole number.

Thus 194 = n x (4x12 + 5x1 + 2x14 + 1x16) = n x 97

So, n = 2.0   thus the molecular formula is $C_8H_{10}N_4O_2$

One phosphorous oxide has an empirical formula P_2O_5, its molecular weight is 284. What is the molecular formula?

Solution:

The empirical formula weight = 2 x 31 + 5 x 16 = 142

Thus n = 284 / 142 = 2

Therefore, there are twice as many atoms of each kind present in the molecule, so the molecular formula is P_4O_{10}.

Represent the following reactions by balanced chemical equations:

1- Reaction of steam with hot iron (Fe) to give magnetite (Fe_3O_4) and H_2

2- Complete combustion of ethane (C_2H_6).

3- Neutralization of aluminum hydroxide by sulfuric acid.

4- Reaction of manganese dioxide and hydrochloric acid to give manganese chloride, chlorine and water.

5- Reaction of iodine pentaoxide with carbon monoxide to give iodine and carbon dioxide.

Chlorine can be prepared by the reaction:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

(a): how many grams of Cl_2 are prepared from 0.325 mole of MnO_2?

(b): how many grams of HCl are reacted in this case?

The amount of carbon monoxide (CO) in a sample of gas is determined by the reaction: $I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$.

If a gas sample liberates 0.192 g of I_2, how many grams of CO were present in the sample?

Solution

From the balanced chemical equation: $I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$

	5 moles of CO produce	one mole of I_2
thus	5x 28 g of CO produce	2x 126.90 g of I_2
so	x g of CO produce	0.192 g of I_2

$$\therefore X = \frac{0.192 \, x5x28}{2x126.90} = 0.106 \text{ g of CO}$$

Parathion is a toxic compound which is used as insecticide, its molecular formula is $C_{10}H_{14}O_5NSP$. What are the percent compositions of C, N, S and P?

How much does 4.98×10^{-6} mol of Cu weigh?

Solution:

The No. of moles of Cu $= \dfrac{mass}{molarmass}$

Then 4.98×10^{-6} mol of Cu $= \dfrac{weight}{63.5}$

So the weight of Cu $= 4.98 \times 10^{-6} \times 63.5 = 3.16 \times 10^{-4}$ g of Cu

What is the nature of cathode rays?

Cathode rays are streams of fast-moving, negatively charged particles. These particles were called electrons. The electrons which originate from different metals used as cathode are the same no matter what material is used.

What is meant by isotope and isobar? Give examples

Isotopes are atoms that have the same atomic number but different mass number.

Two isotopes of chlorine, for example, occur in nature; $_{17}Cl^{35}$ and $_{17}Cl^{37}$. The atomic compositions of these isotopes are:

	protons	neutrons	electrons
$_{17}Cl^{35}$	17	18	17
$_{17}Cl^{37}$	17	20	17

Isotopes of the same elements have very similar chemical properties.

Isobars are atoms of different elements that have the same mass number but different atomic numbers.

Thus $_{16}S^{36}$ and $_{18}Ar^{36}$ are isobars. The total number of nucleons in each of the isobars is the same, but numbers of protons and neutrons are different:

	Protons	neutrons	electrons
$_{16}S^{36}$	16	20	16
$_{18}Ar^{36}$	18	18	18

Copper (Cu) occurs on earth as an isotopic mixture of 69.09 % ^{63}Cu (mass = 62.930 amu) and 30.91 % ^{65}Cu (mass = 64.930 amu). What is the atomic mass of copper?

Carbon occurs in nature as a mixture of $_{6}C^{12}$ (mass, 12.00 u) and $_{6}C^{13}$ (mass, 13.003 u). If the atomic weight of carbon is 12.011 u, what is the percent of $_{6}C^{12}$ in natural carbon.

Solution:

Let X is the abundance of $_{6}C^{12}$ then ($1 - X$) is the abundance of $_{6}C^{13}$. Thus

$$(X)(12.00) + (1 - X)(913.003) = 12.011$$

then, $12.000X + 13.003 - 13.003X = 12.011$

so, $X = 0.989$

then the percent of $_{6}C^{12}$ in nature is 98.9%

Certain radio station broadcasts on a frequency 980 KHz. What is the wavelength of the electromagnetic wave broadcast by the station?

Solution:

$\ominus \lambda = \dfrac{c}{v}$ where c = velocity of light = 3 x108 m/s and v = frequency

$$\therefore \lambda = \dfrac{3.00x10^8 m/s}{980x10^3 s^{-1}} = 306 \ \text{m}$$

What is the wavelength (in nm) of blue light which has frequency of 6.60 x10¹⁴ Hz?

What are the frequency and wavelength of the line in H atom that corresponds to electron transition from n = 3 to n = 2 levels?

Solution:

$$\ominus v = (3.289x10^{15} s^{-1})(\dfrac{1}{n_i^2} - \dfrac{1}{n_o^2}) = (3.289x10^{15} s^{-1})(\dfrac{1}{2^2} - \dfrac{1}{3^2}) = 4.658x10^{14} s^{-1}$$

$$\ominus \lambda = \dfrac{c}{v} = \dfrac{2.998x10^8 ms^{-1}}{4.658x10^{14} s^{-1}} = 6.563x10^{-7} m = 656.3nm$$

Give short account on: (i) Heisenberg's uncertainty principle

(ii) Dual nature of electron.

(i) Heisenberg's uncertainty principle states that: **it is impossible to determine simultaneously the exact position and exact momentum of a body as small as the electron.**

(ii) de Broglie proposed that electrons and other particles have wave properties. The energy of a photon of light (E) is given by:

$$E = hv$$

where v is the frequency and h is Planck's constant.

Since $v = c/\lambda$ where c is the speed of light and λ is the wavelength, so

$$E = h\dfrac{c}{\lambda} \ \text{J/p}$$

Using Einstein's equation, $E = mc^2$ where *m* is the effective mass of the photon, we get

$$mc^2 = h\frac{c}{\lambda} \quad \text{so,} \quad \lambda = \frac{h}{mc} = \frac{h}{p} \quad \text{where is the momentum.}$$

According to de Broglie, a similar equation can be used to assign a wave-length to an electron:

$$\lambda = \frac{h}{mv}$$

where *m* is the mass of electron and *v* its velocity.

What are the conditions required for acceptable solutions to Schrödinger equation? What is meant by orbital in this case?

Acceptable solutions to the wave equation $\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E-V)\Psi = 0$ must have the following properties:

1- Ψ must be continuous.   2- Ψ must be finite.

3- Ψ must be single valued

4- the probability of finding an electron at a point x, y, z is Ψ^2.

5- the probability of finding the electron over all the space from plus infinity to minus infinity must be equal to one, so:

$$\int_{-\infty}^{+\infty} \Psi^2 dxdydz = 1$$

Several wave functions called Ψ_1, Ψ_2, Ψ_3, .. will satisfy these conditions and is called an orbital. **Orbital is the volume in space where there is a high probability of finding the electron.**

What are the four quantum numbers used for specifying electrons in atoms? What is the physical significance of each?

Each electron can be described by a set of four quantum numbers:

1- Principal quantum number (*n*) which gives the shell and the relative average distance of the electron from the nucleus.

2- Secondary quantum number (*l*) which gives the subshell and the shape of the orbital for the electron.

3- Magnetic quantum number (m_l) which shows the orientation of the orbital.

4- Spin quantum number (m_s) refers to the spin of the electron

State the Pauli's exclusion principle.

Exclusion principal of Pauli**:** states that "**no two electrons in the same atom may have identical sets of all four quantum numbers**".

Write the four quantum numbers of:

       iii-   The two electrons in He atom.

       iv-   The third electron in carbon atom.

Solution: i-The four quantum numbers of the first electron in He are (1001/2)

The four quantum numbers of the first electron in He are $(100\text{-}\frac{1}{2})$

ii- The four quantum numbers of the third electron are $(200\frac{1}{2})$

Write the ground state electronic configuration of : Si (z = 14), Se (34) and V (23).

Which of the following sets of quantum numbers are impossible for an electron in an atom:

a- 4, 2, 0, +1/2   b- 3, 3, -3, -1/2   c- 1, 0, 0, 1

d- 1, 0, 0, -1/2   e- 2, 0, -1, +1/2   f- 3, 1, 1, -1/2.

Where in the periodic table do you find the elements with the highest first ionization energies? Explain.

Answer:

In general, the ionization energy increases across the period, so the highest element in ionization energy lies in the right hand side of the periodic table (noble gases). On the other hand, the ionization energy decreases down the group. So, the highest element of ionization energy lies in the upper right hand side of the periodic table.

For each of the following pairs of atoms state which would be expected to have the higher electron affinity, and explain why:

a- F and Cl   b- F and Ne   c- Li and F.

Answer:

a- Both F and Cl atoms has seven electrons in the outer most shell and needs one electron to get complete octet. But the radius of F atom is smaller than that of Cl atom, so the coming electron is more attracted to F atom than to Cl atom. Thus F atom has more electron affinity than Cl atom.

b- F atom has seven electrons in the outer most shell and needs one electron to get complete octet, while Ne atom has eight electrons in outer shell and is completely octet and has no electron affinity.

c- Li has only one electron in the outer shell and tends to lose it to get the electronic configuration of the nearest noble gas He). So Li atom has very low electron affinity compared to F atom.

For each of the following pairs of atoms state which would be expected to have the higher ionization energy, and explain why:

a- K and Rb   **b- Al and Cl**   **c- Li and F.**

Answer:

a- Since the ionization energy decreases down the group due to increasing atomic radius and decreasing the effect of charge on the outer electron, so Rb has lower ionization energy than K.

b- Since the ionization energy increases across the period due decreasing atomic radius and increasing the effect of charge on the outer electron, so Cl has higher ionization energy than Al.

c- Li has only one electron in the outer shell and tends to lose it to get the electronic configuration of the nearest noble gas He). Also, the radius of Li atom is much greater than that of F atom, so Li atom has very low ionization energy compared to F atom.