



# General chemistry (I)

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# *Atomic Theory and Structure*

Pure substances are classified as elements or compounds, but just what makes a substance possess its unique properties? How small a piece of salt will still taste salty? Carbon dioxide puts out fires, is used by plants to produce oxygen, and forms dry ice when solidified. But how small a mass of this material still behaves like carbon dioxide? Substances are in their simplest identifiable form at the atomic, ionic, or molecular level. Further division produces a loss of characteristic properties.

What particles lie within an atom or ion? How are these tiny particles alike? How do they differ? How far can we continue to divide them? Alchemists began the quest, early chemists laid the foundation, and modern chemists continue to build and expand on models of the atom.

## **Dalton's Model of the Atom**

More than 2000 years after Democritus, the English schoolmaster John Dalton (1766–1844) revived the concept of atoms and proposed an atomic model based on facts and experimental evidence (Figure 5.1). His theory, described in a series of papers published from 1803 to 1810, rested on the idea of a different kind of atom for each element. The essence of Dalton's atomic model may be summed up as follows:

1. Elements are composed of minute, indivisible particles called atoms.
2. Atoms of the same element are alike in mass and size.
3. Atoms of different elements have different masses and sizes.
4. Chemical compounds are formed by the union of two or more atoms of different elements.

5. Atoms combine to form compounds in simple numerical ratios, such as one to one, one to two, two to three, and so on.

6. Atoms of two elements may combine in different ratios to form more than one compound.

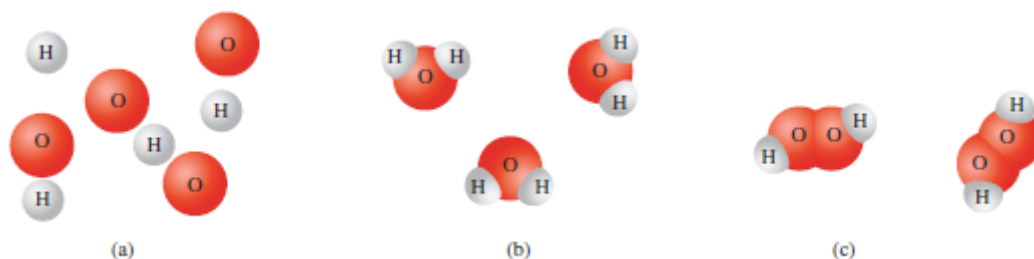


Fig 1.(a) Dalton's atoms were individual particles, the atoms of each element being alike in mass and size but different in mass and size from other elements. (b) and (c) Dalton's atoms combine in specific ratios to form compounds.

### Composition of Compounds

A large number of experiments extending over a long period have established the fact that a particular compound always contains the same elements in the same proportions by mass. For example, water always contains 11.2% hydrogen and 88.8% oxygen by mass (see Figure 1b). The fact that water contains hydrogen and oxygen in this particular ratio does not mean that hydrogen and oxygen cannot combine in some other ratio but rather that a compound with a different ratio would not be water. In fact, hydrogen peroxide is made up of two atoms of hydrogen and two atoms of oxygen per molecule and contains 5.9% hydrogen and 94.1% oxygen by mass; its properties are markedly different from those of water (see Figure 1c).

We often summarize our general observations regarding nature into a statement called a natural law. In the case of the composition of a compound, we use the law of definite composition, which states that a

compound always contains two or more elements chemically combined in a definite proportion by mass.

Let's consider two elements, oxygen and hydrogen, that form more than one compound. In water, 8.0 g of oxygen are present for each gram of hydrogen. In hydrogen peroxide, 16.0 g of oxygen are present for each gram of hydrogen. The masses of oxygen are in the ratio of small whole numbers, 16: 8 or 2: 1. Hydrogen peroxide has twice as much oxygen (by mass) as does water. Using Dalton's atomic model, we deduce that hydrogen peroxide has twice as many oxygen atoms per hydrogen atom as water. In fact, we now write the formulas for water as  $\text{H}_2\text{O}$  and for hydrogen peroxide  $\text{H}_2\text{O}_2$  as See Figure 1b and c.

The law of multiple proportions states atoms of two or more elements may combine in different ratios to produce more than one compound.

### **The Nature of Electric Charge**

You've probably received a shock after walking across a carpeted area on a dry day. You may have also experienced the static electricity associated with combing your hair and have had your clothing cling to you. These phenomena result from an accumulation of electric charge. This charge may be transferred from one object to another. The properties of electric charge are as follows:

1. Charge may be of two types, positive and negative.
2. Unlike charges attract (positive attracts negative), and like charges repel (negative repels negative and positive repels positive).
3. Charge may be transferred from one object to another, by contact or induction.
4. The less the distance between two charges, the greater the force of attraction between unlike charges (or repulsion between identical

charges). The force of attraction( $F$ ) can be expressed using the following equation:

$$F = kq_1q_2/ r^2$$

where  $q_1$  and  $q_2$  are the charges,  $r$  is the distance between the charges, and  $k$  is a constant.

### **.Discovery of Ions**

English scientist Michael Faraday (1791–1867) made the discovery that certain substances when dissolved in water conduct an electric current. He also noticed that certain compounds decompose into their elements when an electric current is passed through the compound. Atoms of some elements are attracted to the positive electrode, while atoms of other elements are attracted to the negative electrode. Faraday concluded that these atoms are electrically charged. He called them *ions* after the Greek word meaning “wanderer.”

Any moving charge is an electric current. The electrical charge must travel through a substance known as a conducting medium. The most familiar conducting media are metals formed into wires.

The Swedish scientist Svante Arrhenius (1859–1927) extended Faraday’s work. Arrhenius reasoned that an ion is an atom (or a group of atoms) carrying a positive or negative charge. When a compound such as sodium chloride is melted, it conducts electricity. Water is unnecessary.

Arrhenius’s explanation of this conductivity was that upon melting, the sodium chloride dissociates, or breaks up, into charged ions  $\text{Na}^+$  and  $\text{Cl}^-$ , the  $\text{Na}^+$  ions move toward the negative electrode (cathode), whereas the  $\text{Cl}^-$  ions migrate toward the positive electrode (anode). Thus positive ions are called cations, and negative ions are called anions.

From Faraday’s and Arrhenius’s work with ions, Irish physicist G. J. Stoney (1826–1911) realized there must be some fundamental unit of

electricity associated with atoms. He named this unit the electron in 1891. Unfortunately, he had no means of supporting his idea with experimental proof. Evidence remained elusive until 1897, when English physicist J. J. Thomson (1856–1940) was able to show experimentally the existence of the electron.

### **Subatomic Parts of the Atom**

The concept of the atom—a particle so small that until recently it could not be seen even with the most powerful microscope—and the subsequent determination of its structures and among the greatest creative intellectual human achievements. Any visible quantity of an element contains a vast number of identical atoms. But when we refer to an atom of an element, we isolate a single atom from the multitude in order to present the element in its simplest form. What is this tiny particle we call the atom? The diameter of a single atom ranges from 0.1 to 0.5 nanometer ( $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ ). Hydrogen, the smallest atom, has a diameter of about 0.1 nm. To arrive at some idea of how small an atom is, consider this dot (•), which has a diameter of about 1 mm, or  $1 \times 10^6 \text{ nm}$ . It would take 10 million hydrogen atoms to form a line of atoms across this dot. As inconceivably small as atoms are, they contain even smaller particles, the subatomic particles, including electrons, protons, and neutrons.

The development of atomic theory was helped in large part by the invention of new instruments. For example, the Crookes tube, developed by Sir William Crookes (1832–1919) in 1875, opened the door to the subatomic structure of the atom (Figure 2). The emissions generated in a Crookes tube are called cathode rays. J. J. Thomson demonstrated in 1897 that cathode rays

- (1) travel in straight lines,
- (2) are negative in charge,



(3) are deflected by electric and magnetic fields,  
(4) produce sharp shadows,  
and (5) are capable of moving a small paddle wheel. This was the experimental discovery of the fundamental unit of charge—the electron.

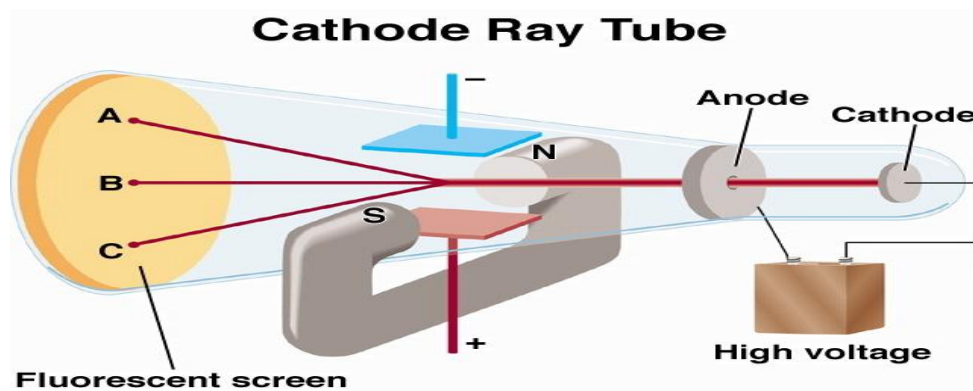


Fig 2. Crookes tube (cathode rays)

The electron( $e^-$ ) is a particle with a negative electrical charge and a mass of  $9.110 \times 10^{-28}$  g. This mass is the mass  $1/1837$  of a hydrogen atom. Although the actual charge of an electron is known, its value is too cumbersome for practical use and has therefore been assigned a relative electrical charge  $-1$  of the size of an electron has not been determined exactly, but its diameter is believed to be less than  $10^{-12}$  cm. Protons were first observed by German physicist Eugen Goldstein (1850–1930) in 1886. However, it was Thomson who discovered the nature of the proton. He showed that the proton is a particle, and he calculated its mass to be about 1837 times that of an electron. The proton (p) is a particle with actual mass of its  $1.673 \times 10^{-24}$  g. relative charge is  $(+1)$  equal in magnitude, but opposite in sign, to the charge on the electron. The mass of a proton is only very slightly less than that of a hydrogen atom.

Thomson had shown that atoms contain both negatively and positively charged particles. Clearly, the Dalton model of the atom was

no longer acceptable. Atoms are not indivisible but are instead composed of smaller parts. Thomson proposed a new model of the atom.

In the Thomson model of the atom, the electrons are negatively charged particles embedded in the positively charged atomic sphere. A neutral atom could become an ion by gaining or losing electrons. Positive ions were explained by assuming that the neutral atom loses electrons. An atom with a net charge +1 of (for example,  $\text{Na}^+$  or  $\text{Li}^+$ ) has lost one electron. An atom with a net charge of +3 (for example  $\text{Al}^{3+}$ ) has lost three electrons (Figure 3a). Negative ions were explained by assuming that additional electrons can be added to atoms. A net charge of (for example,  $\text{Cl}^-$  or  $\text{F}^-$ ) is produced by the addition of one electron. A net charge of -1 (for example,  $\text{Cl}^-$  or  $\text{F}^-$ ) requires the addition of one electron. A net charge of -2 (for example,  $\text{S}^{2-}$ ) requires the addition of two electrons (Figure 3b). The third major subatomic particle was discovered in 1932 by James Chadwick (1891–1974). This particle, the neutron (n), has neither a positive nor a negative charge and has an actual mass which is only very slightly greater than that of a proton. The properties of these three subatomic particles are summarized in Table 1.

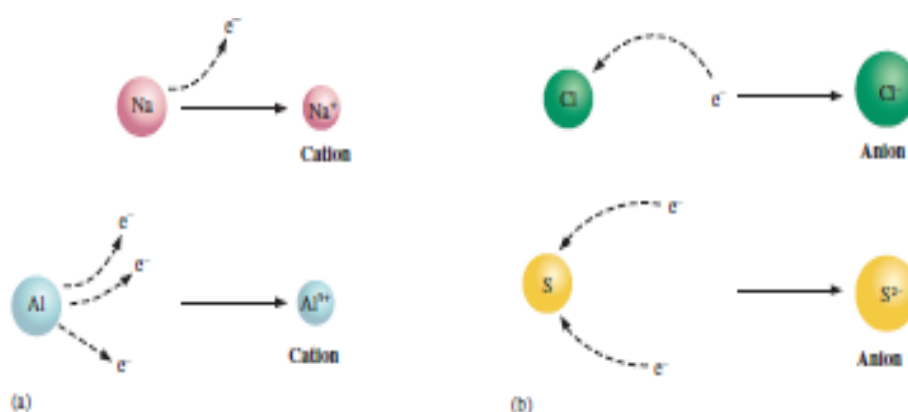


Fig. 3. Thomson model of the atom

Nearly all the ordinary chemical properties of matter can be explained in terms of atoms consisting of electrons, protons, and neutrons. The discussion of atomic structure that follows is based on the assumption

that atoms contain only these principal subatomic particles. Many other subatomic particles, such as mesons, positrons, neutrinos, and antiprotons, have been discovered, but it is not yet clear whether all these

Particles are actually present in the atom or whether they are produced by reactions occurring within the nucleus. The fields of atomic and high-energy physics have produced a long list of subatomic particles.

### Ions:

Positive ions were explained by assuming that a neutral atom loses electrons. Negative ions were explained by assuming that atoms gain electrons

Table 1. Electrical charge and relative mass of electrons, protons and neutrons.

Particle	Symbol	Relative electrical charge	Actual mass (g)
Electron	$e^-$	-1	$9.110 \times 10^{-28}$
Proton	p	+1	$1.673 \times 10^{-24}$
Neutron	n	0	$1.675 \times 10^{-24}$

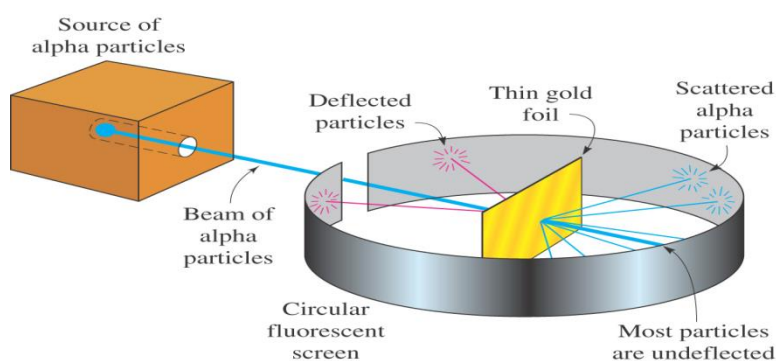
### The Nuclear Atom

The discovery that positively charged particles are present in atoms came soon after the discovery of radioactivity by Henri Becquerel (1852–1908) in 1896. Radioactive elements spontaneously emit alpha particles, beta particles, and gamma rays from their nuclei. By 1907 Rutherford found that alpha particles emitted by certain radioactive elements were helium nuclei.

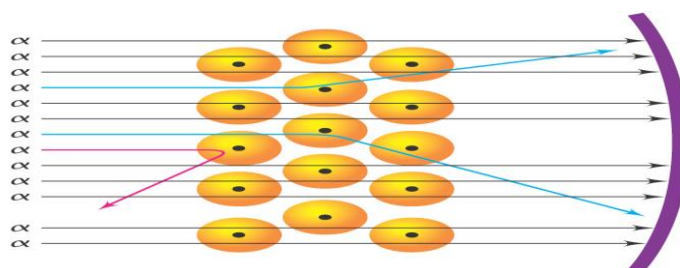
### Rutherford experiment

In 1911 performed experiments that shot a stream of alpha particles at a gold foil. Most of the alpha particles passed through the foil with little or

no deflection. He found that a few were deflected at large angles and some alpha particles even bounced back



An electron with a mass of  $1/1837$  amu could not have deflected an alpha particle with a mass of 4 amu. Rutherford knew that like charges repel. Rutherford concluded that each gold atom contained a positively charged mass that occupied a tiny volume. He called this mass the nucleus. Most of the alpha particles passed through the gold foil. This led Rutherford to conclude that a gold atom was mostly empty space.



### General Arrangement of Subatomic Particles

Rutherford's experiment showed that an atom had a dense, positively charged nucleus. Chadwick's work in 1932 demonstrated that the atom contains neutrons. Rutherford also noted that light, negatively charged electrons were present in an atom and offset the positive nuclear charge. Rutherford put forward a model of the atom in which a dense, positively charged nucleus is located at the atom's center. The negative electrons surround the nucleus. The nucleus contains protons and neutrons.

The atom and the location of its subatomic particles were devised in which each atom consists of a nucleus surrounded by electrons (see above). The nucleus contains protons and neutrons but does not contain electrons. In a neutral atom the positive charge of the nucleus (due to protons) is exactly offset by the negative electrons. Because the charge of an electron is equal to, but of opposite sign than, the charge of a proton, a neutral atom must contain exactly the same number of electrons as protons. However, this model of atomic structure provides no information on the arrangement of electrons within the atom. A neutral atom contains the same number of protons and electrons.

### **Atomic Numbers of the Elements**

The atomic number of an element is the number of protons in the nucleus of an atom of that element. The atomic number determines the identity of an atom. For example, every atom with an atomic number of 1 is a hydrogen atom; it contains one proton in its nucleus. Every atom with an atomic number of 6 is a carbon atom; it contains 6 protons in its nucleus. Every atom with an atomic number of 92 is a uranium atom; it contains 92 protons in its nucleus. The atomic number tells us not only the number of positive charges in the nucleus but also the number of electrons in the neutral atom, since a neutral atom contains the same number of electrons and protons.

In the nuclear model of the atom, protons and neutrons are located in the nucleus. The electrons are found in the remainder of the atom (which is mostly empty space because electrons are very tiny). You don't need to memorize the atomic numbers of the elements because a periodic table is usually provided in texts, in laboratories, and on examinations. The atomic numbers of all elements are shown in the

periodic table on the inside front cover of this book and are also listed in the table of atomic masses on the inside front endpapers.

Atomic number  ${}_1\text{H}$  1 proton in the nucleus

Atomic number  ${}_6\text{C}$  6 protons in the nucleus

Atomic number  ${}_{92}\text{U}$  92 protons in the nucleus

### **Isotopes of the Elements**

Shortly after Rutherford's conception of the nuclear atom, experiments were performed to determine the masses of individual atoms. These experiments showed that the masses of nearly all atoms were greater than could be accounted for by simply adding up the masses of all the protons and electrons that were known to be present in an atom. This fact led to the concept of the neutron, a particle with no charge but with a mass about the same as that of a proton. Because this particle has no charge, it was very difficult to detect, and the existence of the neutron was not proven experimentally until 1932. All atomic nuclei except that of the simplest hydrogen atom contain neutrons. All atoms of a given element have the same number of protons. Experimental evidence has shown that, in most cases, all atoms of a given element do not have identical masses. This is because atoms of the same element may have different numbers of neutrons in their nuclei. Atoms of an element having the same atomic number but different atomic masses are called isotopes of that element. Atoms of the various isotopes of an element therefore have the same number of protons and electrons but different numbers of neutrons.

Three isotopes of hydrogen (atomic number 1) are known. Each has one proton in the nucleus and one electron. The first isotope (protium), without a neutron, has a mass number of 1; the second isotope

(deuterium), with one neutron in the nucleus, has a mass number of 2; the third isotope (tritium), with two neutrons, has a mass number of 3.

The three isotopes of hydrogen may be represented by the symbols  ${}_1^1\text{H}$ ,  ${}_1^2\text{H}$  and  ${}_1^3\text{H}$  and indicating an atomic number of 1 and mass numbers of 1, 2, and 3, respectively. This method of representing atoms is called isotopic notation. The subscript ( $Z$ ) is the atomic number; the superscript ( $A$ ) is the mass number, which is the sum of the number of protons and the number of neutrons in the nucleus. The hydrogen isotopes may also be referred to as hydrogen-1, hydrogen-2, and hydrogen-3.

Mass number

(sum of protons and neutrons in the nucleus)

**Z**

**E Symbol of element**

**A**

Atomic number (number of protons in the nucleus)

The mass number of an element is the sum of the protons and neutrons in the nucleus. Most of the elements occur in nature as mixtures of isotopes. However, not all isotopes are stable; some are radioactive and are continuously decomposing to form other elements. For example, of the seven known isotopes of carbon, only two, carbon-12 and carbon-13 are stable. Of the seven known isotopes of oxygen, only three  ${}^{16}_8\text{O}$ ,  ${}^{17}_8\text{O}$ , and  ${}^{18}_8\text{O}$ , are stable. Of the fifteen known isotopes of arsenic, only one is stable.  ${}^{75}_{33}\text{As}$  is the only one that is stable.

**Atomic Mass**

The mass of a single atom is far too small to measure on a balance, but fairly precise determinations of the masses of individual atoms can be made with an instrument called a mass spectrometer. The mass of a single

hydrogen atom is  $1.673 \times 10^{-24}$  g. However, it is neither convenient nor practical to compare the actual masses of atoms expressed in grams; therefore, a table of relative atomic masses using atomic mass units was devised. (The term atomic weight is sometimes used instead of atomic mass). The carbon isotope having six protons and six neutrons and designated carbon-12, or  $^{12}_6\text{C}$ , was chosen as the standard for atomic masses. This reference isotope was assigned a value of exactly 12 atomic mass units (amu). Thus, 1 atomic mass unit is defined as equal to exactly 1/12 of the mass of a carbon-12 atom. The actual mass of a carbon-12 atom is  $1.9927 \times 10^{-23}$  g and that of one atomic mass unit is  $1.6606 \times 10^{-24}$  g.

In the table of atomic masses, all elements then have values that are relative to the mass assigned to the reference isotope, carbon-12. Hydrogen atoms, with a mass of about 1/12 that of a carbon atom, have an average atomic mass of 1.00794 amu on this relative scale. Magnesium atoms, which are about twice as heavy as carbon, have an average mass of 24.305 amu. The average atomic mass of oxygen is 15.9994 amu.

Since most elements occur as mixtures of isotopes with different masses, the atomic mass determined for an element represents the average relative mass of all the naturally occurring isotopes of that element. The atomic masses of the individual isotopes are approximately whole numbers, because the relative masses of the protons and neutrons are approximately 1.0 amu each. Yet we find that the atomic masses given for many of the elements deviate considerably from whole numbers.

For example, the atomic mass of rubidium is 85.4678 amu, that of copper is 63.546 amu, and that of magnesium is 24.305 amu. The deviation of an atomic mass from a whole number is due mainly to the unequal occurrence of the various isotopes of an element.

The two principal isotopes of copper are  $^{63}_{29}\text{Cu}$  and  $^{65}_{29}\text{Cu}$ . Copper is used in everyday objects, and the Liberty Bell contains a mixture of these



two isotopes. It is apparent that copper-63 atoms are the more abundant isotope, since the atomic mass of copper, 63.546 amu, is closer to 63 than to 65 amu. The actual values of the copper isotopes observed by mass spectra determination are shown in the following table 2:

Table 2.

Isotope	Isotopic mass (amu)	Abundance (%)	Average atomic mass (amu)
$^{63}_{29}\text{Cu}$	62.9298	69.09	63.55
$^{65}_{29}\text{Cu}$	64.9278	30.91	

The average atomic mass can be calculated by multiplying the atomic mass of each isotope by the fraction of each isotope present and adding the results. The calculation for copper is

$$(62.9298 \text{ amu})(0.6909) = 43.48 \text{ amu}$$

$$(64.9278 \text{ amu})(0.3091) = \underline{20.07 \text{ amu}}$$

$$63.55 \text{ amu}$$

The atomic mass of an element is the average relative mass of the isotopes of that element compared to the atomic mass of carbon-12 (exactly 12.0000 amu). The relationship between mass number and atomic number is such that if we subtract the atomic number from the mass number of a given isotope, we obtain the number of neutrons in the nucleus of an atom of that isotope. For example, the fluorine atom ( $^{19}\text{F}$ ), atomic number 9, having a mass of 19 amu, contains 10 **neutrons**:

**mass number    atomic number    number of neutrons**

$$19 \quad 9 \quad 10$$

The atomic masses given in the table on the front endpapers of this book are values accepted by international agreement. You need not

memorize atomic masses. In the calculations in this book, the use of atomic masses rounded to four significant figures will give results of sufficient accuracy.

## **Modern Atomic Theory and the Periodic Table**

Chemists have the same dilemma when they study the atom. Atoms are so very small that it isn't possible to use the normal senses to describe them. We are essentially working in the dark with this package we call the atom. However, our improvements in instruments (X-ray machines and scanning tunneling microscopes) and measuring devices (spectrophotometers and magnetic resonance imaging, MRI) as well as in our mathematical skills are bringing us closer to revealing the secrets of the atom.

### **A Brief History**

In the last 200 years, vast amounts of data have been accumulated to support atomic theory. When atoms were originally suggested by the early Greeks, no physical evidence existed to support their ideas. Early chemists did a variety of experiments, which culminated in Dalton's model of the atom. Because of the limitations of Dalton's model, modifications were proposed first by Thomson and then by Rutherford, which eventually led to our modern concept of the nuclear atom. These early models of the atom work reasonably well—in fact, we continue to use them to visualize a variety of chemical concepts. There remain questions that these models cannot answer, including an explanation of how atomic structure relates to the periodic table. In this chapter, we will present our modern model of the atom; we will see how it varies from and improves upon the earlier atomic models.

### **Electromagnetic Radiation**

Scientists have studied energy and light for centuries, and several models have been proposed to explain how energy is transferred from place to place. One way energy travels through space is by electromagnetic radiation. Examples of electromagnetic radiation include light from the sun, X-rays in your dentist's office, microwaves from your microwave oven, radio and television waves, and radiant heat from your fireplace. While these examples seem quite different, they are all similar in some important ways. Each shows wavelike behavior, and all travel at the same speed in a vacuum ( $3.00 \times 10^8$  m/s).

Light is one form of electromagnetic radiation and is usually classified by its wavelength, as shown in Figure 4. Visible light, as you can see, is only a tiny part of the electromagnetic spectrum. Some examples of electromagnetic radiation involved in energy transfer outside the visible region are hot coals in your backyard grill, which transfer infrared radiation to cook your food, and microwaves, which transfer energy to water molecules in the food, causing them to move more quickly and thus raise the temperature of your food.

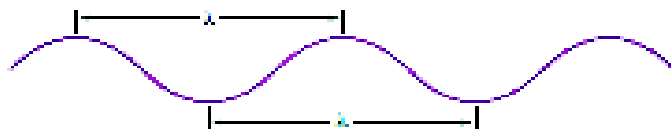


Fig. 4.

### **The Bohr Atom**

As scientists struggled to understand the properties of electromagnetic radiation, evidence began to accumulate that atoms could radiate light. At high temperatures, or when subjected to high voltages, elements in the gaseous state give off colored light. Brightly colored neon signs illustrate this property of matter very well. When the light emitted by a gas is passed through a prism or diffraction grating, a set of brightly colored lines called a line spectrum results (Figure 5). These colored lines

indicatethat the light is being emitted only at certain wavelengths, or frequencies, that correspondto specific colors. Each element possesses a unique set of these spectral lines that is different from the sets of all the other elements.

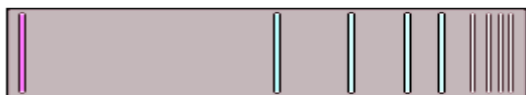


Fig. 5line spectrum

In 1912–1913, while studying the line spectrum of hydrogen, Niels Bohr(1885–1962), a Danish physicist, made a significant contribution to the rapidly growingknowledge of atomic structure. His research led him to believe that electrons existin specific regions at various distances from the nucleus. He also visualized the electronsas revolving in orbits around the nucleus, like planets rotating around the sun.

Bohr’s first paper in this field dealt with the hydrogen atom, which he described asa single electron revolving in an orbit about a relatively heavy nucleus. He applied theconcept of energy quanta, proposed in 1900 by the German physicist Max Planck(1858–1947), to the observed line spectrum of hydrogen. Planck stated that energyis never emitted in a continuous stream but only in small, discrete packets calledquanta.From this, Bohr theorized that electrons have several possible energies corresponding to several possible orbits at different distancesfrom the nucleus. Therefore an electron has to be in one specific energy level; it cannotexist between energy levels. In other words, the energy of the electron is said tobe quantized. Bohr also stated that when a hydrogen atom absorbed one or morequanta of energy, its electron would “jump” to a higher energy level.

Bohr was able to account for spectral lines of hydrogen this way. A number of energylevels are available, the lowest of which is called the

ground state. When an electron falls from a high energy level to a lower one (say, from the fourth to the second), a quantum of energy is emitted as light at a specific frequency, or wavelength<sup>5</sup>. This light corresponds to one of the lines visible in the hydrogen spectrum (Figure 5). Several lines are visible in this spectrum, each one corresponding to a specific electron energy-level shift within the hydrogen atom. The chemical properties of an element and its position in the periodic table depend on electron behavior within the atoms. In turn, much of our knowledge of the behavior of electrons within atoms is based on spectroscopy. Niels Bohr contributed a great deal to our knowledge of atomic structure by

(1) Suggesting quantized energy levels for electrons and

(2) Showing that spectral lines result from the radiation of small increments of energy (Planck's quanta) when electrons shift from one energy level to another.

Bohr's calculations succeeded very well in correlating the experimentally observed spectral lines with electron energy levels for the hydrogen atom. However, Bohr's methods of calculation did not succeed for heavier atoms. More theoretical work on atomic structure was needed.

In 1924, the French physicist Louis de Broglie suggested a surprising hypothesis:

All objects have wave properties. De Broglie used sophisticated mathematics to show that the wave properties for an object of ordinary size, such as a baseball, are too small to be observed. But for smaller objects, such as an electron, the wave properties become significant. Other scientists confirmed de Broglie's hypothesis, showing that electrons do exhibit wave properties. In 1926, Erwin Schrödinger, an Austrian physicist, created a mathematical model that described electrons as waves. Using Schrödinger's wave mechanics, we can determine the probability of finding an electron in a certain region around the nucleus of

the atom. This treatment of the atom led to a new branch of physics called wave mechanics or quantum mechanics, which forms the basis for our modern understanding of atomic structure. Although the wave-mechanical description of the atom is mathematical, it can be translated, at least in part, into a visual model. It is important to recognize that we cannot locate an electron precisely within an atom; however, it is clear that electrons are not revolving around the nucleus in orbits as Bohr postulated.

### **Energy Levels of Electrons**

One of the ideas Bohr contributed to the modern concept of the atom was that the energy of the electron is quantized—that is, the electron is restricted to only certain allowed energies. The wave-mechanical model of the atom also predicts discrete principal energy levels within the atom. These energy levels are designated by the letter  $n$ , where  $n$  is a positive integer (Figure 6). The lowest principal energy level corresponds to  $n=1$ , the next to  $n=2$  and so on. As  $n$  increases, the energy of the electron increases, and the electron is found on average farther from the nucleus. Each principal energy level is divided into sublevels, which are illustrated in Figure 7. The first principal energy level has one sublevel. The second principal energy level has two sublevels; the third energy level has three sublevels, and so on. Each of these sublevels contains spaces for electrons called orbitals.

In each sublevel the electrons are found within specified orbitals ( $s$ ,  $p$ ,  $d$ ,  $f$ ). Let's consider each principal energy level in turn. The first principal energy level  $n=1$  has one sublevel or type of orbital. It is spherical in shape and is designated as  $1s$ . It is important to understand what the spherical shape of the  $1s$  orbital means. The electron does *not* move around on the surface of the sphere, but rather the surface encloses a space where there is a 90% probability where the electron may be found.

It might help to consider these orbital shapes in the same way we consider the atmosphere. There is no distinct dividing line between the atmosphere and “space.” The boundary is quite fuzzy. The same is true for atomic orbitals. Each has a region of highest density roughly corresponding to its shape. The probability of finding the electron outside this region drops rapidly but never quite reaches zero. Scientists often speak of orbitals as electron “clouds” to emphasize the fuzzy nature of their boundaries. How many electrons can fit into a 1s orbital? To answer this question, we need to consider one more property of electrons. This property is called spin. Each electron appears to be spinning on an axis, like a globe. It can only spin in two directions.

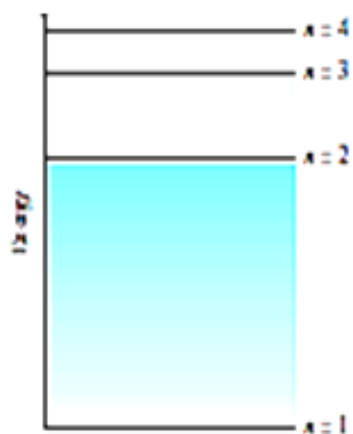


Fig.6



Fig.7

We represent this spin with an arrow  $\uparrow\downarrow$ . In order to occupy the same orbital, electrons must have opposite spins. That is, two electrons with the

same spin cannot occupy the same orbital. This gives us the answer to our question: An atomic orbital can hold a maximum of two electrons, which must have opposite spins. This rule is called the Pauli exclusion principle. The first principal energy level contains one type of orbital ( $1s$ ) that holds a maximum of two electrons. What happens with the second principal energy level ( $n=2$ ). Here we find two sublevels,  $2s$  and  $2p$ . Like  $1s$  in the first principal energy level, the  $2s$  orbital is spherical in shape but is larger in size and higher in energy. It also holds a maximum of two electrons. The second type of orbital is designated by  $2p$ . The  $2p$  sublevel consists of three orbitals  $2p_x$ ,  $2p_y$ ,  $2p_z$ , and the shape of  $p$  orbitals is quite different from the  $s$  orbitals, as shown in Figure 8.

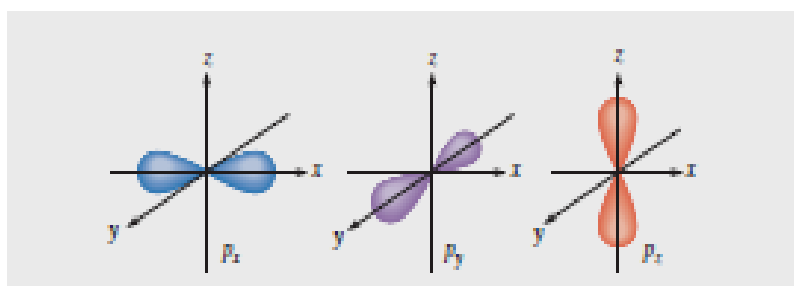


Fig.8

Each  $p$  orbital has two “lobes.” Remember, the space enclosed by these surfaces represents the regions of probability for finding the electrons 90% of the time. There are three separate  $p$  orbitals, each oriented in a different direction, and each  $p$  orbital can hold a maximum of two electrons. Thus the total number of electrons that can reside in all three  $p$  orbitals is six. To summarize our model, the first principal energy level of an atom has a  $1s$  orbital. The second principal energy level has a  $2s$  and three  $2p$  orbitals labeled  $2p_x$ ,  $2p_y$  and  $2p_z$ , as shown in Figure 9.



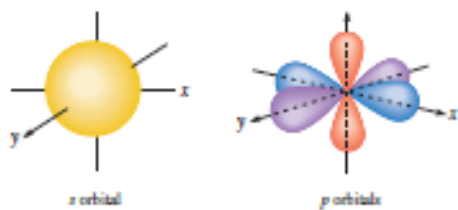


Fig.9

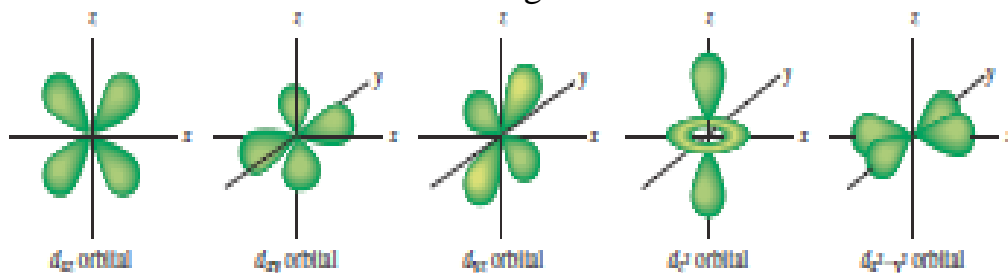


Fig.10.

The third principal energy level has three sublevels labeled  $3s$ ,  $3p$  and  $3d$ . The  $3s$  orbital is spherical and larger than the  $1s$  and  $2s$  orbitals. The  $3p_x$ ,  $3p_y$ ,  $3p_z$  orbitals are shaped like those of the second level, only larger. The five  $3d$  orbitals have the shapes shown in Figure 10. You don't need to memorize these shapes, but notice that they look different from the *s* or *p* orbitals. Each time a new principal energy level is added, we also add a new sublevel. This makes sense because each energy level corresponds to a larger average distance from the nucleus, which provides more room on each level for new sublevels containing more orbitals. The pattern continues with the fourth principal energy level. It has  $4s$ ,  $4p$ ,  $4d$ , and  $4f$  orbitals. There are one  $4s$ , three  $4p$ , five  $4d$ , and seven  $4f$  orbitals. The shapes of the *s*, *p*, and *d* orbitals are the same as those for lower levels, only larger. We will not consider the shapes of the orbitals. Remember that for all *s*, *p*, *d*, and *f* orbitals, the maximum number of electrons per orbital is two. We summarize each principal energy level:

$n = 1$	$1s$														
$n = 2$	$2s$	$2p$	$2p$	$2p$											
$n = 3$	$3s$	$3p$	$3p$	$3p$	$3d$	$3d$	$3d$	$3d$	$3d$						
$n = 4$	$4s$	$4p$	$4p$	$4p$	$4d$	$4d$	$4d$	$4d$	$4d$	$4f$	$4f$	$4f$	$4f$	$4f$	$4f$

The hydrogen atom consists of a nucleus (containing one proton) and one electron occupying a region outside of the nucleus. In its ground state, the electron occupies a  $1s$  orbital, but by absorbing energy the electron can become excited and move to a higher energy level.

### Atomic Structures of the First 18 Elements

We have seen that hydrogen has one electron that can occupy a variety of orbitals in different principal energy levels. Now let's consider the structure of atoms with more than one electron. Because all atoms contain orbitals similar to those found in hydrogen, we can describe the structures of atoms beyond hydrogen by systematically placing electrons in these hydrogen-like orbitals. We use the following guidelines:

1. No more than two electrons can occupy one orbital.
2. Electrons occupy the lowest energy orbitals available. They enter a higher energy orbital only when the lower orbitals are filled. For the atoms beyond hydrogen, orbital energies vary as  $s < p < d < f$  for a given value of  $n$ .
3. Each orbital in a sublevel is occupied by a single electron before a second electron enters.

For example, all three  $p$  orbitals must contain one electron before a second electron enters a  $p$  orbital. We can use several methods to represent the atomic structures of atoms, depending on what we are trying to illustrate. When we want to show both the nuclear makeup and the electron structure of each principal energy level (without orbital detail), we can use a diagram such as Figure 11.

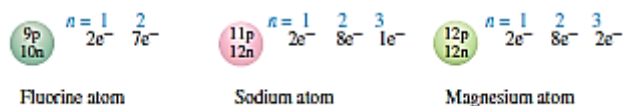
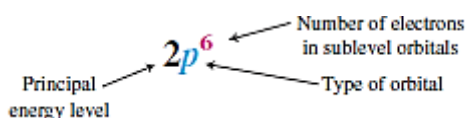


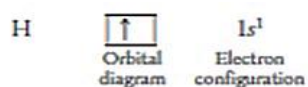
Fig. 11.

Often we are interested in showing the arrangement of the electrons in an atom in their orbitals. There are two ways to do this. The first method is called the electron configuration. In this method, we list each type of orbital, showing the number of electrons in it as an exponent. An electron configuration is read as follows:

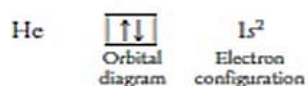


We can also represent this configuration with an orbital diagram in which boxes represent the orbitals (containing small arrows indicating the electrons when the orbital contains one electron, an arrow, pointing upward ( $\uparrow$ ) is placed in the box. A second arrow, pointing downward ( $\downarrow$ ) indicates the second electron in that orbital.

Let's consider each of the first 18 elements on the periodic table in turn. The order of filling for the orbitals in these elements is  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ , and  $4s$ . Hydrogen, the first element, has only one electron. The electron will be in the  $1s$  orbital because this is the most favorable position (where it will have the greatest attraction for the nucleus). Both representations are shown here:



Helium, with two electrons, can be shown as



The first energy level, which can hold a maximum of two electrons, is now full. An atom with three electrons will have its third electron in the second energy level. Thus, in lithium (atomic number 3),

the first two electrons are in the  $1s$  orbital, and the third electron is in the  $2s$  orbital of the second energy level.

Lithium has the following structure:



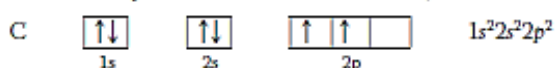
All four electrons of beryllium are  $s$  electrons:



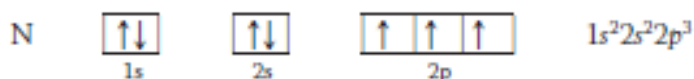
The next six elements illustrate the filling of the  $p$  orbitals. Boron has the first  $p$  electron. Because  $p$  orbitals all have the same energy, it doesn't matter which of these orbitals fills first:



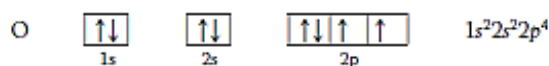
Carbon is the sixth element. It has two electrons in the  $1s$  orbital, two electrons in the  $2s$  orbital, and two electrons to place in the  $2p$  orbitals. Because it is more difficult for the  $p$  electrons to pair up than to occupy a second  $p$  orbital, the second  $p$  electron is located in a different  $p$  orbital. We could show this by writing  $2p_x^1 2p_y^1$  but we usually write it as  $2p^2$ : it is understood that the electrons are in different  $p$  orbitals. The spins on these electrons are alike, for reasons we will not explain here.



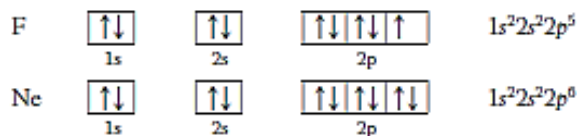
Nitrogen has seven electrons. They occupy the  $1s$ ,  $2s$ , and  $2p$  orbitals. The third  $p$  electron in nitrogen is still unpaired and is found in the  $2p_z$  orbital:



Oxygen is the eighth element. It has two electrons in both the  $1s$  and  $2s$  orbitals and four electrons in the  $2p$  orbitals. One of the  $2p$  orbitals is now occupied by a second electron which has a spin opposite the electron already in that orbital:

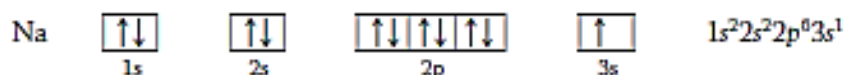


The next two elements are fluorine with nine electrons and neon with ten electrons:



With neon, the first and second energy levels are filled as shown in table 3. The second energy level can hold a maximum of eight electrons,  $2s^2 2p^6$ .

Sodium, element 11, has two electrons in the first energy level and eight electrons in the second energy level, with the remaining electron occupying the  $3s$  orbital in the third energy level



Magnesium (12), aluminum (13), silicon (14), phosphorus (15), sulfur (16), chlorine (17), and argon (18) follow in order. Table 4 summarizes the filling of the orbitals for elements 11–18. The electrons in the outermost (highest) energy level of an atom are called the valence electrons. For example, oxygen, which has the electron configuration of  $1s^2 2s^2 2p^4$  has electrons in the first and second energy levels. Therefore the second principal energy level is the valence level for oxygen. The  $2s$  and  $2p$  electrons are the valence electrons. In the case of magnesium ( $1s^2 2s^2 2p^6 3s^1$ ) the valence electrons are in the  $3s$  orbital, since these are outermost electrons.

Table.3

Number	Element	Orbitals			Electron configuration
		1s	2s	2p	
1	H	$\uparrow$			1s <sup>1</sup>
2	He	$\uparrow\downarrow$			1s <sup>2</sup>
3	Li	$\uparrow\downarrow$	$\uparrow$		1s <sup>2</sup> 2s <sup>1</sup>
4	Be	$\uparrow\downarrow$	$\uparrow\downarrow$		1s <sup>2</sup> 2s <sup>2</sup>
5	B	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>
6	C	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>
7	N	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$   $\uparrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>
8	O	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>
9	F	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>
10	Ne	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>

Table. 4.

Number	Element	Orbitals					Electron configuration
		1s	2s	2p	3s	3p	
11	Na	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow$		1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>
12	Mg	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$		1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>
13	Al	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>1</sup>
14	Si	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>2</sup>
15	P	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$   $\uparrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>3</sup>
16	S	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>4</sup>
17	Cl	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>5</sup>
18	Ar	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup>

## Electron Structures and the Periodic Table

We have seen how the electrons are assigned for the atoms of elements 1–18. How do the electron structures of these atoms relate to their position on the periodic table?

To answer this question, we need to look at the periodic table more closely. The periodic table represents the efforts of chemists to organize the elements logically. Chemists of the early nineteenth century had sufficient knowledge of the properties of elements to recognize similarities among groups of elements. In 1869, Dimitri Mendeleev (1834–1907) of Russia and Lothar Meyer (1830–1895) of Germany independently published periodic arrangements of the elements based on increasing atomic masses. Mendeleev's arrangement is the precursor to the modern periodic table, and his name is associated with it. The modern

periodic table is shown in Figure 12 and on the inside front cover of the book. Each horizontal row in the periodic table is called a period, as shown in Figure 12. There are seven periods of elements. The number of each period corresponds to the outermost energy level that contains electrons for elements in that period. Those in Period 1 contain electrons only in energy level 1, while those in Period 2 contain electrons in levels 1 and 2. In Period 3, electrons are found in levels 1, 2, and 3, and so on. Elements that behave in a similar manner are found in groups or families. These form the vertical columns on the periodic table. Several systems exist for numbering the groups. In one system, the columns are numbered from left to right using the numbers 1–18. However, we use a system that numbers the columns with numbers and the letters A and B, as shown in Figure 12.

The A groups are known as the representative elements. The B groups and Group 8 are called the transition elements. In this notebook we will focus on the representative elements. The groups (columns) of the periodic table often have family names. For example, the group on the far right side of the periodic table (He, Ne, Ar, Kr, Xe and Rn) is called the noble gases. Group 1A is called the alkali metals, Group 2A the alkaline earth metals, and Group 7A the halogens. How is the structure of the periodic table related to the atomic structures of the elements?

Period	1A	2A	Transition Metals (B groups)										3A	4A	5A	6A	7A	8A
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	8B										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Uup			118 Uuo

Fig. 12

The chemical behavior and properties of elements in a particular family must therefore be associated with the electron configuration of the elements. The number for the principal energy level is different. This is expected since each new period is associated with a different energy level for the valence electrons. The electron configurations for elements beyond these first 18 become long and tedious to write. We often abbreviate the electron configuration using the following notation:



Look carefully at Figure 14 and you will see that the  $p$  orbitals are full at the noble gases. By placing the symbol for the noble gas in square brackets, we can abbreviate the complete electron configuration and focus our attention on the valence electrons. To write the abbreviated electron configuration for any element, go back to the previous noble gas and place its symbol in square brackets. Then list the valence electrons. Here are some examples:



The sequence for filling the orbitals is exactly as we would expect up through the  $3p$  orbitals. The third energy level might be expected to fill with  $3d$  electrons before electrons enter the  $4s$  orbital, but this is not the case. The behavior and properties of the next two elements, potassium (19) and calcium (20), are very similar to the

1A	2A	3A	4A	5A	6A	7A	Noble gases
1 H $1s^1$							2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$	5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
11 Na $3s^1$	12 Mg $3s^2$	13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$

Fig. 13.



elements in Groups 1A and 2A, respectively. They clearly belong in these groups. The other elements in Group 1A and Group 2A have electron configurations that indicate valence electrons in the  $s$  orbitals (Figure 13).

The early chemists classified the elements based only on their observed properties, but modern atomic theory gives us an explanation for why the properties of elements vary periodically. For example, as we “build” atoms by filling orbitals with electrons, the same orbitals occur on each energy level. This means that the same electron configuration reappears regularly for each level. Groups of elements show similar chemical properties because of the similarity of these outermost electron configurations.

This periodic table illustrates these important points:

1. The number of the period corresponds with the highest energy level occupied by electrons in that period.
2. The group numbers for the representative elements are equal to the total number of outermost electrons in the atoms of the group. For example, elements in Group 7A always have the electron configuration  $nS^2, nP^5$ . The  $d$  and  $f$  electrons are always in a lower energy level than the highest energy level and so are not considered as outermost (valence) electrons.
3. The elements of a family have the same outermost electron configuration except that the electrons are in different energy levels.

### **Metals, Nonmetals, and Metalloids**

The elements can be classified as metals, nonmetals, and metalloids. Most of the elements are metals. We are familiar with them because of their widespread use in tools, construction materials, automobiles, and so on. But nonmetals are equally useful in our everyday

life as major components of clothing, food, fuel, glass, plastics, and wood. Metalloids are often used in the electronics industry. The metals are solids at room temperature (mercury is an exception). They have high luster, are good conductors of heat and electricity, are malleable (can be rolled or hammered into sheets), and are ductile (can be drawn into wires). Most metals have a high melting point and a high density. Familiar metals are aluminum, chromium, copper, gold, iron, lead, magnesium, mercury, nickel, platinum, silver, tin, and zinc. Less familiar but still important metals are calcium, cobalt, potassium, sodium, uranium, and titanium.

**Metals** have little tendency to combine with each other to form compounds. But many metals readily combine with nonmetals such as chlorine, oxygen, and sulfur to form compounds such as metallic chlorides, oxides, and sulfides. In nature, minerals are composed of the more reactive metals combined with other elements. A few of the less reactive metals such as copper, gold, and silver are sometimes found in a native, or free, state. Metals are often mixed with one another to form homogeneous mixtures of solids called alloys. Some examples are brass, bronze, steel, and coinage metals.

**Nonmetals**, unlike metals, are not lustrous, have relatively low melting points and densities, and are generally poor conductors of heat and electricity. Carbon, phosphorus, sulfur, selenium, and iodine are solids; bromine is a liquid; and the rest of the nonmetals are gases. Common nonmetals found uncombined in nature are carbon (graphite and diamond), nitrogen, oxygen, sulfur, and the noble gases (helium, neon, argon, krypton, xenon, and radon). Nonmetals combine with one another to form molecular compounds such as carbon dioxide, methane, butane, and sulfur dioxide. Fluorine, the most reactive nonmetal, combines readily with almost all other elements.

Several elements (boron, silicon, germanium, arsenic, antimony, tellurium, and polonium) are classified as **metalloids** and have properties that are intermediate between those of metals and those of nonmetals. Certain metalloids, such as boron, silicon, and germanium, are the raw materials for the semiconductor devices that make the electronics industry possible.

## **The Formation of Compounds from Atoms**

### **Periodic Trends in Atomic Properties**

Although atomic theory and electron configuration help us understand the arrangement and behavior of the elements, it's important to remember that the design of the periodic table is based on observing properties of the elements. Before we use the concept of atomic structure to explain how and why atoms combine to form compounds, we need to understand the characteristic properties of the elements and the trends that occur in these properties on the periodic table. These trends allow us to use the periodic table to accurately predict properties and reactions of a wide variety of substances (Fig. 14).

In the above section, we classified elements as metals, nonmetals, or metalloids. The heavy stair-step line beginning at boron and running diagonally down the periodic table separates the elements into metals and nonmetals. Metals are usually lustrous, malleable, and good conductors of heat and electricity. Nonmetals are just the opposite—nonlustrous, brittle, and poor conductors. Metalloids are found bordering the heavy diagonal line and may have properties of both metals and nonmetals. Most elements are classified as metals. Metals are found on the left side of the stair-step line, while the nonmetals are located toward the upper right of the table. Note that hydrogen does not fit into the division of metals and nonmetals. It displays nonmetallic properties under normal conditions,

even though it has only one outermost electron like the alkali metals. Hydrogen is considered to be a unique element. It is the chemical properties of metals and nonmetals that interest us most. Metals tend to lose electrons and form positive ions, while nonmetals tend to gain electrons and form negative ions. When a metal reacts with a nonmetal, electrons are often transferred from the metal to the nonmetal.

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac†	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup			118 Uuo
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

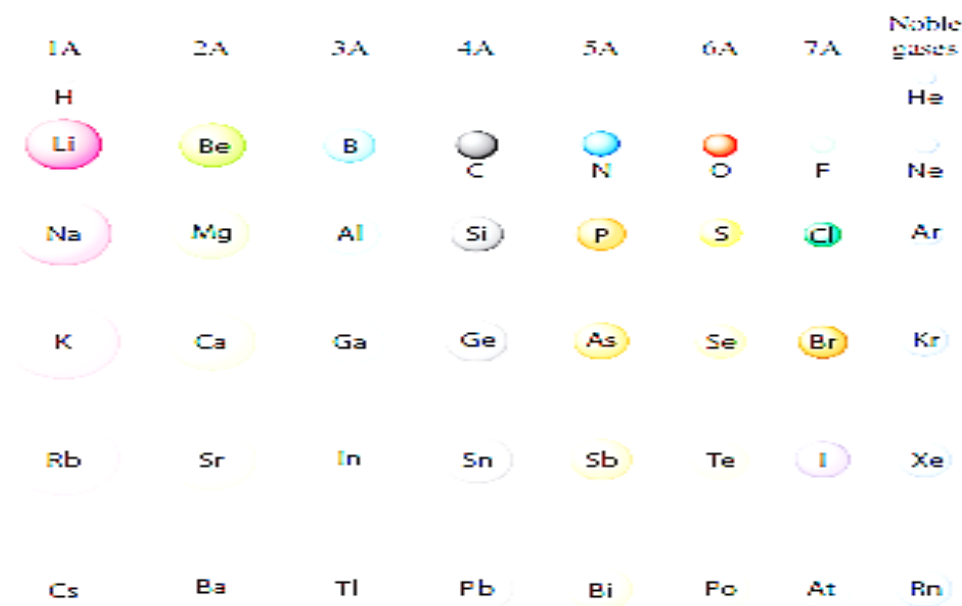
Fig. 14.

### Atomic Radius;

The relative radii of the representative elements are shown in Figure 15. Notice that the radii of the atoms tend to increase down each group and that they tend to decrease from left to right across a period.

The increase in radius down a group can be understood if we consider the electron structure of the atoms. For each step down a group, an additional energy level is added to the atom. The average distance from the nucleus to the outside edge of the atom must increase as each new energy level is added. The atoms get bigger as electrons are placed in these new higher-energy levels.

Understanding the decrease in atomic radius across a period requires more thought, however. As we move from left to right across a period, electrons within the same block are being added to the same principal energy level. Within a given energy level, we expect the orbitals to have about the same size. We would then expect the atoms to be about the same size across the period. But each time an electron is added, a proton is added to the nucleus as well. The increase in positive charge (in the nucleus) pulls the electrons closer to the nucleus, which results in a gradual decrease in atomic radius across a period as seen from the following:



**Fig.15**

**Ionization Energy:**

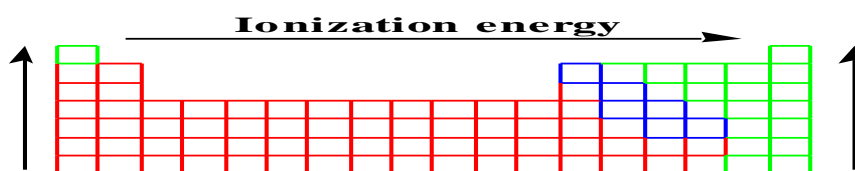
The **ionization energy** of an atom is the energy required to remove an electron from the atom. For example,



The first ionization energy is the amount of energy required to remove the first electron from an atom, the second is the amount required to remove the second electron from that atom, and so on.

Table 8 gives the ionization energies for the removal of one to five electrons from several elements. The table shows that even higher amounts of energy are needed to remove the second, third, fourth, and fifth electrons. This makes sense because removing electrons leaves fewer electrons attracted to the same positive charge in the nucleus. The data in Table 5 also show that extra-large ionization energy (blue) is needed when an electron is removed from a noble gas-like structure, clearly showing the stability of the electron structure of the noble gases.

First ionization energies have been experimentally determined for most elements.



Metals don't behave in exactly the same manner. Some metals give up electrons much more easily than others. In the alkali metal family, cesium gives up its 6s electron much more easily than the metal lithium gives up its 2s electron. This makes sense when we consider that the size of the atoms increases down the group. The distance between the nucleus and the outer electrons increases and the ionization energy decreases. The most chemically active metals are located at the lower left of the periodic table.

Nonmetals have relatively large ionization energies compared to metals. Nonmetals tend to gain electrons and form anions. Since the nonmetals are located at the right side of the periodic table, it is not surprising that ionization energies tend to increase from left to right across a period. The most active nonmetals are found in the upper right corner of the periodic table (excluding the noble gases).

Table .5.

Element	Required amounts of energy (kJ/mol)				
	1st e <sup>-</sup>	2nd e <sup>-</sup>	3rd e <sup>-</sup>	4th e <sup>-</sup>	5th e <sup>-</sup>
H	1.314				
He	2.372	5.247			
Li	520	7.297	11.810		
Be	900	1.757	14.845	21.000	
B	800	2.430	3.659	25.020	32.810
C	1.088	2.352	4.619	6.222	37.800
Ne	2.080	3.962	6.276	9.376	12.190
Na	496	4.565	6.912	9.540	13.355

## Lewis Structures of Atoms

Metals tend to form cations (positively charged ions) and nonmetals form anions (negatively charged ions) in order to attain a stable valence electron structure. For many elements this stable valence level contains eight electrons (two *s* and six *p*), identical to the valence electron configuration of the noble gases. Atoms undergo rearrangements of electron structure to lower their chemical potential energy (or to become more stable). These rearrangements are accomplished by losing, gaining, or sharing electrons with other atoms. For example, a hydrogen atom could accept a second electron and attain an electron structure the same as the noble gas helium. A fluorine atom could gain an electron and attain an electron structure like neon. A sodium atom could lose one electron to attain an electron structure like neon. The valence electrons in the outermost energy level of an atom are responsible for the electron activity that occurs to form chemical bonds.

The Lewis structure of an atom is a representation that shows the valence electrons for that atom. American chemist Gilbert N. Lewis (1875–1946) proposed using the symbol for the element and dots for electrons. The number of dots placed around the symbol equals the number of *s* and *p* electrons in the outermost energy level of the atom. Paired dots represent paired electrons; unpaired dots represent unpaired electrons. For example, **H**· is the Lewis symbol for a hydrogen atom  $1S^1$ , **B** is the Lewis symbol for a boron atom, with valence electrons  $2S^2, 2P^1$

In the case of boron, the symbol represents the boron nucleus and the  $1S^2$  electrons ; the dots represent only the electrons  $2S^2, 2P^1$



The Lewis method is used not only because of its simplicity of expression but also because much of the chemistry of the atom is directly associated with the electrons in the outermost energy level. Figure 16 shows Lewis structures for the elements hydrogen through calcium.

1A	2A	3A	4A	5A	6A	7A	Noble Gases
H·							He :
Li·	Be :	·Ḃ	·Ċ·	·Ṅ·	·Ȯ:	·Ḟ:	·Nė:
Na·	Mg :	·Al̇	·Si̇·	·Ṗ·	·Ṡ:	·Cl̇:	·Aṙ:
K·	Ca :						

Fig.16

### The ionic bond:

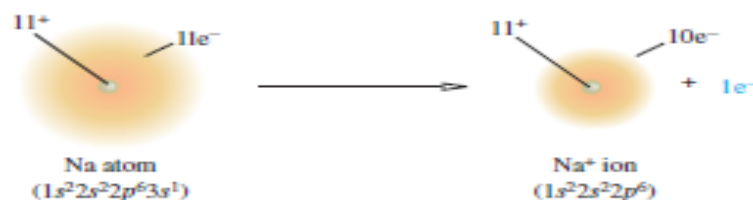
The chemistry of many elements, especially the representative ones, is to attain an outer electron structure like that of the chemically stable noble gases. With the exception of helium, this stable structure consists of eight electrons in the outermost energy level (Figure 6).

Table.6.

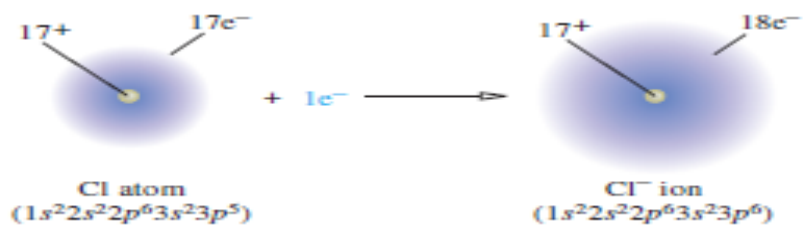
Noble gas	Symbol	Electron structure					
		$n = 1$	2	3	4	5	6
Helium	He	$1s^2$					
Neon	Ne	$1s^2$	$2s^2 2p^6$				
Argon	Ar	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$			
Krypton	Kr	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6$		
Xenon	Xe	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}$	$5s^2 5p^6$	
Radon	Rn	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10} 4f^{14}$	$5s^2 5p^6 5d^{10}$	$6s^2 6p^6$



Let's look at the electron structures of sodium and chlorine to see how each element can attain a structure of 8 electrons in its outermost energy level. A sodium atom has 11 electrons: 2 in the first energy level, 8 in the second energy level, and 1 in the third energy level. A chlorine atom has 17 electrons: 2 in the first energy level, 8 in the second energy level, and 7 in the third energy level. If a sodium atom transfers or loses its 3s electron, its third energy level becomes vacant, and it becomes a sodium ion with an electron configuration identical to that of the noble gas neon. This process requires energy:



An atom that has lost or gained electrons will have a positive or negative charge, depending on which particles (protons or electrons) are in excess. Remember that a charged particle or group of particles is called an ion. By losing a negatively charged electron, the sodium atom becomes a positively charged particle known as a sodium ion. The charge +1, results because the nucleus still contains 11 positively charged protons and the electron orbitals contain only 10 negatively charged electrons. The charge is indicated by a plus + sign and is written as a superscript after the symbol of the element  $\text{Na}^+$ . A chlorine atom with seven electrons in the third energy level needs one electron to pair up with its one unpaired 3p electron to attain the stable outer electron structure of argon. By gaining one electron, the chlorine atom becomes a chloride ion  $\text{Cl}^-$  a negatively charged particle containing 17 protons and 18 electrons. This process releases energy:



Consider sodium and chlorine atoms reacting with each other. The  $3s$  electron from the sodium atom transfers to the half-filled  $3p$  orbital in the chlorine atom to form a positive sodium ion and a negative chloride ion. The compound sodium chloride results because the  $\text{Na}^+$  and  $\text{Cl}^-$  ions are strongly attracted to each other by their opposite electrostatic charges. The force holding the oppositely charged ions together is called an ionic bond (Figure 17).

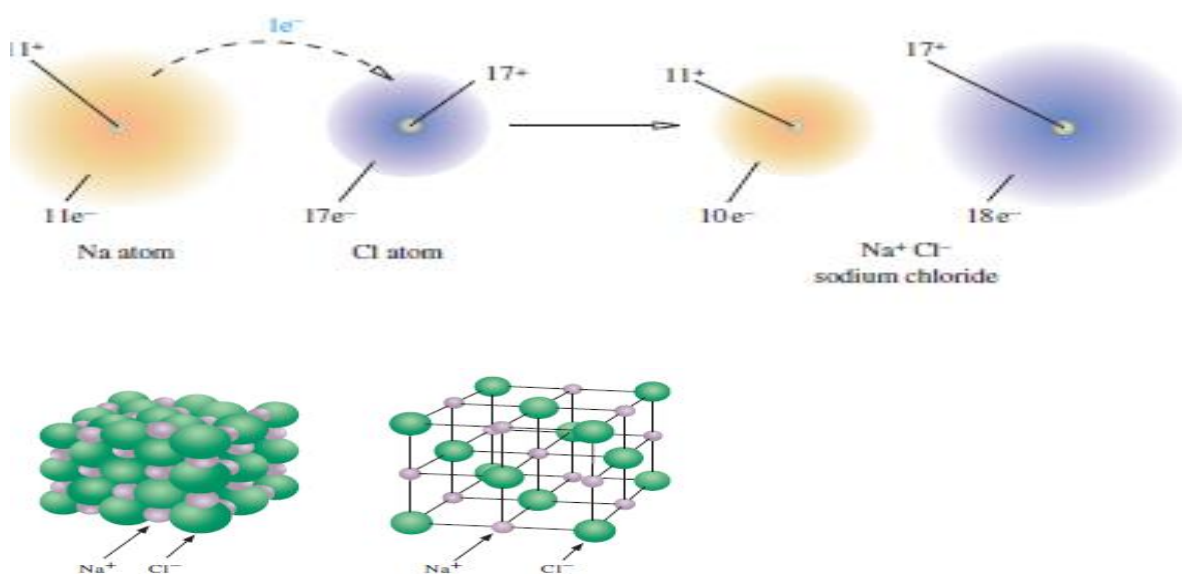
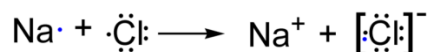


Fig.17.

The Lewis representation of sodium chloride formation is;



The chemical reaction between sodium and chlorine is a very vigorous one, producing considerable heat in addition to the salt formed. When energy is released in a chemical reaction, the products are more stable than the reactants. Note that in  $\text{NaCl}$  both atoms attain a noble gas electron structure. Sodium chloride is made up of cubic crystals in which

each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions, except at the crystal surface. A visible crystal is a regularly arranged aggregate of millions of these ions, but the ratio of sodium to chloride ions is, 1:1 hence the formula NaCl. The cubic crystalline lattice arrangement of sodium chloride is shown in Figure 18.

Figure 18 contrasts the relative sizes of sodium and chlorine atoms with those of their ions. The sodium ion is smaller than the atom due primarily to two factors:

- (1) The sodium atom has lost its outermost electron, thereby reducing its size; and
- (2) the 10 remaining electrons are now attracted by 11 protons and are thus drawn closer to the nucleus. Conversely, the chloride ion is larger than the atom because (1) it has 18 electrons but only 17 protons and (2) the nuclear attraction on each electron is thereby decreased, allowing the chlorine atom to expand as it forms an ion.

We have seen that when sodium reacts with chlorine, each atom becomes an ion. Sodium chloride, like all ionic substances, is held together by the attraction existing between positive and negative charges. An ionic bond is the attraction between oppositely charged ions.

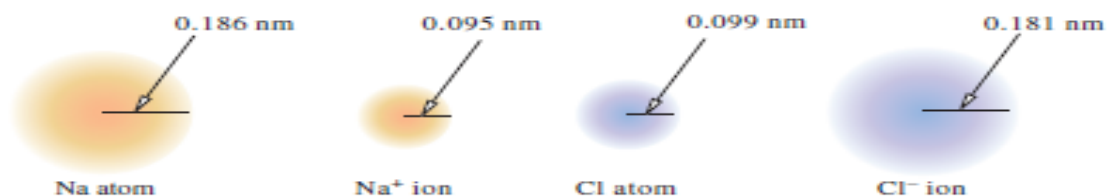


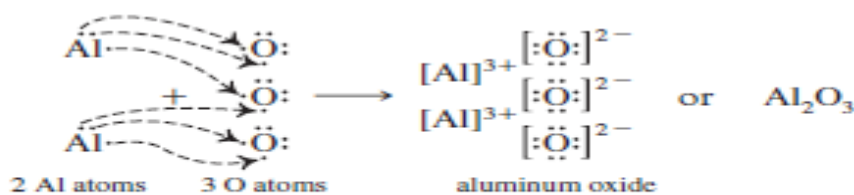
Fig. 18.

Table.7.

Atomic radius		Ionic radius		Atomic radius		Ionic radius	
Li	0.152	Li <sup>+</sup>	0.060	F	0.071	F <sup>-</sup>	0.136
Na	0.186	Na <sup>+</sup>	0.095	Cl	0.099	Cl <sup>-</sup>	0.181
K	0.227	K <sup>+</sup>	0.133	Br	0.114	Br <sup>-</sup>	0.195
Mg	0.160	Mg <sup>2+</sup>	0.065	O	0.074	O <sup>2-</sup>	0.140
Al	0.143	Al <sup>3+</sup>	0.050	S	0.103	S <sup>2-</sup>	0.184

Ionic bonds are formed whenever one or more electrons are transferred from one atom to another. Metals, which have relatively little attraction for their valence electrons, tend to form ionic bonds when they combine with nonmetals. It's important to recognize that substances with ionic bonds do not exist as molecules. In sodium chloride, for example, the bond does not exist solely between a single sodium ion and a single chloride ion. Each sodium ion in the crystal attracts six near-neighbor negative chloride ions; in turn, each negative chloride ion attracts six near-neighbor positive sodium ions (see Figure 18). A metal will usually have one, two, or three electrons in its outer energy level. In reacting, metal atoms characteristically lose these electrons, attain the electron structure of a noble gas, and become positive ions. A nonmetal, on the other hand, is only a few electrons short of having a noble gas electron structure in its outer energy level and thus has a tendency to gain electrons. In reacting with metals, nonmetal atoms characteristically gain one, two, or three electrons; attain the electron structure of a noble gas; and become negative ions. The ions formed by loss of electrons are much smaller than the corresponding metal atoms; the ions formed by gaining electrons are larger than the corresponding nonmetal atoms. The dimensions of the atomic and ionic radii of several metals and nonmetals are given in Table 7.

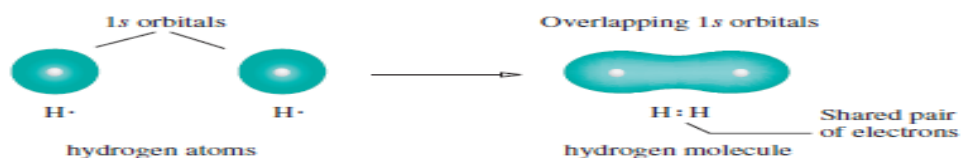
Formation of aluminum oxide  $\text{Al}_2\text{O}_3$  from its elements.



### The covalent bond: sharing electrons

Some atoms do not transfer electrons from one atom to another to form ions. Instead they form a chemical bond by sharing pairs of electrons between them. A covalent bond consists of a pair of electrons shared between two atoms. This bonding concept was introduced in 1916 by G. N. Lewis. In the millions of known compounds, the covalent bond is the predominant chemical bond. True molecules exist in substances in which the atoms are covalently bonded. It is proper to refer to molecules of such substances as hydrogen, chlorine, hydrogen chloride, carbon dioxide, water, or sugar. These substances contain only covalent bonds and exist as aggregates of molecules. We don't use the term molecule when talking about ionic ally bonded compounds such as sodium chloride, because such substances exist as large aggregates of positive and negative ions, not as molecules (Figure 18).

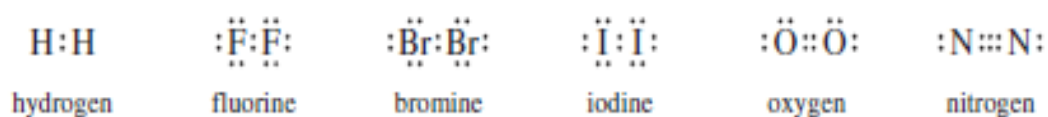
A study of the hydrogen molecule gives us an insight into the nature of the covalent bond and its formation. The formation of a hydrogen molecule  $\text{H}_2$  involves the overlapping and pairing of 1s electron orbitals from two hydrogen atoms.



Each atom contributes one electron of the pair that is shared jointly by two hydrogen nuclei. The orbital of the electrons now includes both hydrogen nuclei, but probability factors show that the most likely place to

find the electrons (the point of highest electron density) is between the two nuclei. The two nuclei are shielded from each other by the pair of electrons, allowing the two nuclei to be drawn very close to each other.

The formula for chlorine gas  $\text{Cl}_2$  is when the two atoms of chlorine combine to form this molecule; the electrons must interact in a manner similar to that shown in the hydrogen example. Each chlorine atom would be more stable with eight electrons in its outer energy level. But chlorine atoms are identical, and neither is able to pull an electron away from the other. What happens is this: The unpaired  $3p$  electron orbital of one chlorine atom overlaps the unpaired  $3p$  electron orbital of the other atom, resulting in a pair of electrons that are mutually shared between the two atoms. Each atom furnishes one of the pair of shared electrons. Thus, each atom attains a stable structure of eight electrons by sharing an electron pair with the other atom. The pairing of the  $p$  electrons and the formation of a chlorine molecule is illustrated in figure 19. Neither chlorine atom has a positive or negative charge, because both contain the same number of protons and have equal attraction for the pair of electrons being shared. Other examples of molecules in which electrons are equally shared between two atoms are hydrogen  $\text{H}_2$  oxygen  $\text{O}_2$  fluorine  $\text{F}_2$  bromine  $\text{Br}_2$  and iodine  $\text{I}_2$ . Note that more than one pair of electrons may be shared between atoms:



The Lewis structure given for oxygen does not adequately account for all the properties of the oxygen molecule.

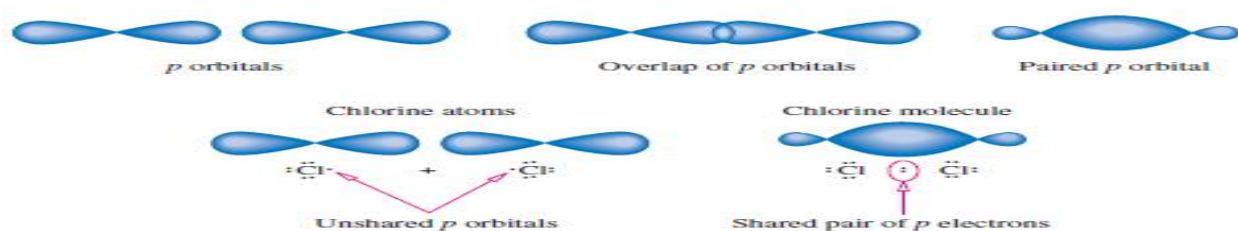


Fig.19

In writing structures, we commonly replace the pair of dots used to represent a shared pair of electrons with a dash (—). One dash represents a single bond; two dashes, a double bond; and three dashes, a triple bond. The six structures just shown may be written thus:



The ionic bond and the covalent bond represent two extremes. In ionic bonding the atoms are so different that electrons are transferred between them, forming a charged pair of ions. In covalent bonding, two identical atoms share electrons equally. The bond is the mutual attraction of the two nuclei for the shared electrons. Between these extremes lie many cases in which the atoms are not different enough for a transfer of electrons but are different enough that the electron pair cannot be shared equally. This unequal sharing of electrons results in the formation of a polar covalent bond.

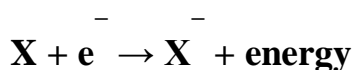
### Electronegativity:

When two different kinds of atoms share a pair of electrons, a bond forms in which electrons are shared unequally. One atom assumes a partial positive charge and the other a partial negative charge with respect to each other. This difference in charge occurs because the two atoms exert unequal attraction for the pair of shared electrons. The attractive force that an atom of an element has for shared electrons in a molecule or

polyatomic ion is known as its electronegativity. Elements differ in their electronegativities. For example, both hydrogen and chlorine need one electron to form stable electron configurations. They share a pair of electrons in hydrogen chloride HCl. Chlorine is more electronegative and therefore has a greater attraction for the shared electrons than does hydrogen. As a result, the pair of electrons is displaced toward the chlorine atom, giving it a partial negative charge and leaving the hydrogen atom with a partial positive charge. Note that the electron is not transferred entirely to the chlorine atom (as in the case of sodium chloride) and that no ions are formed. The entire HCl molecule is electrically neutral. A partial charge is usually indicated by the Greek letter delta,  $\delta$ .

### **Electron Affinity**

The amount of energy released or spent when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion.



- If the two atoms that constitute a covalent bond are identical, then there is equal sharing of electrons.
- This is called nonpolar covalent bonding.
- If the two atoms that constitute a covalent bond are not identical, then there is unequal sharing of electrons.
- This is called polar covalent bonding.
- One atom assumes a partial positive charge and the other atom assumes a partial negative charge.

This charge difference is a result of the unequal attractions the atoms have for their shared electron pair.

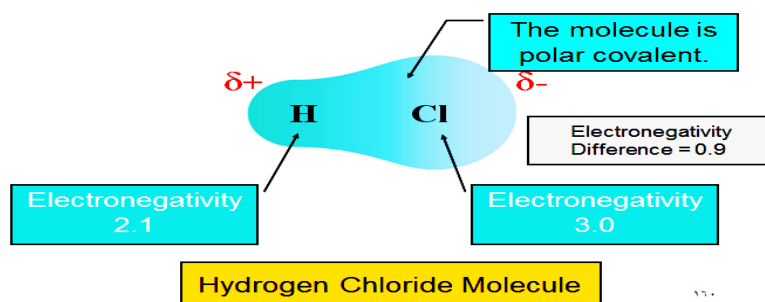
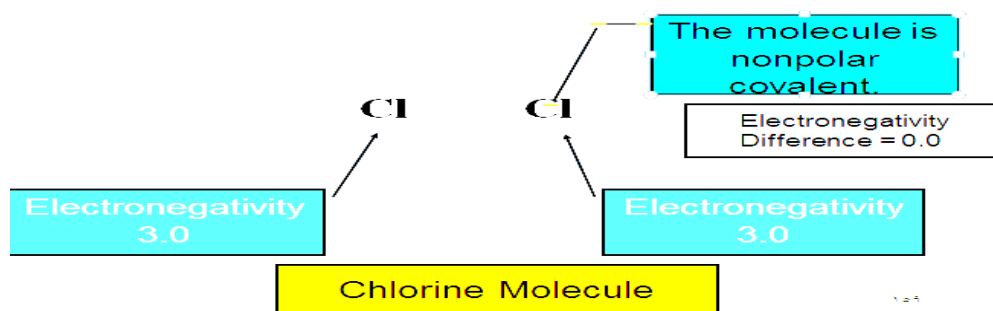
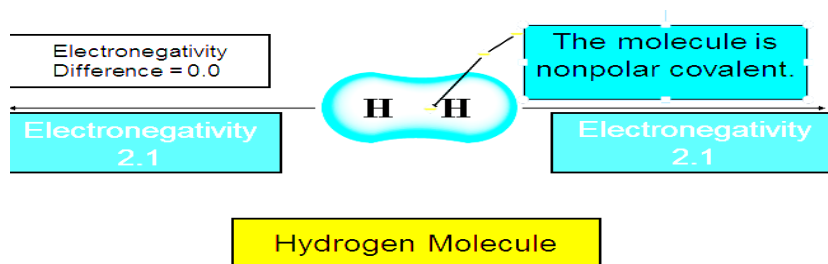
### **Relating bond type to electronegativity difference**

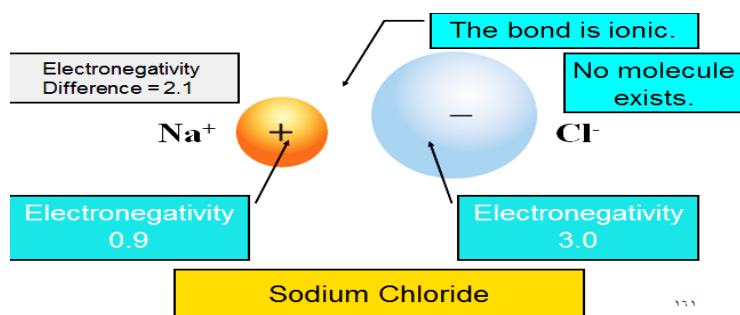


The polarity of a bond is determined by the difference in electronegativity values of the atoms forming the bond.

Electronegativity Difference ( $\Delta$ )	Bond
$\Delta \geq 2$	Ionic
$0.4 < \Delta < 2$	Polar covalent
$\Delta \leq 0.4$	Nonpolar covalent

If the electronegativities are the same, the bond is nonpolar covalent and the electrons are shared equally.





**Molecular Polarity:**

Polar bonds occur when two bonded atoms differ in their electronegativities. Such is the case in HCl where chlorine is more electronegative than hydrogen resulting in a polar H-Cl bond. As seen in Figure 21, the partial negative charge ( $-\delta$ ) is on the more electronegative atom (Cl); the partial positive charge ( $+\delta$ ) resides on the less electronegative atom (H). The bond polarity is indicated by an arrow ( $\leftrightarrow$ ), with the plus sign indicating the partial positive charge ( $+\delta$ ) on the less electronegative atom, and the arrow pointing to the partial negative charge ( $-\delta$ ) end of the bond. A molecule that has polar bonds may or may not be polar. If electron density is concentrated at one end of the molecule, as in HCl, the result is a polar molecule. A polar molecule is a permanent dipole with a partial negative charge ( $-\delta$ ) where the electron density is concentrated, and a partial positive ( $+\delta$ ) charge at the opposite end, as illustrated in Figure 20. If the polar bonds are oriented so that their polarities cancel each other, such as in  $\text{CO}_2$ , a nonpolar molecule results.



Fig.20

The net dipole moment of a molecule is the sum of its bond dipoles. A diatomic molecule is, of course, linear. If its atoms differ in

electronegativity, then the bond and the molecule will be polar, with the partial negative charge at the more electronegative atom, as in HCl (figure 20).

### Polarity of Molecules:

Water, H<sub>2</sub>O, has two polar bonds and, because of its geometry, is a polar molecule

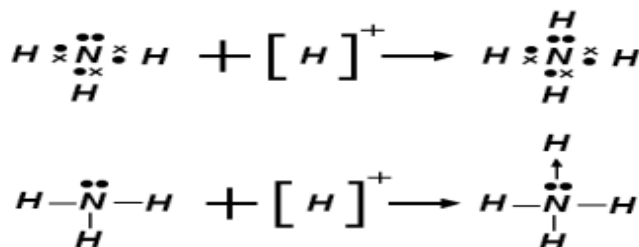


### The coordinate covalent bond:

A covalent bond (dative) in which one of the atoms donates both electrons. Properties do not differ from those of a normal covalent bond. A coordinate covalent bond is usually shown with an arrow.



**Example 2:** Ammonium ion NH<sub>4</sub><sup>+</sup>



**Example 3:** Hydronium ion H<sub>3</sub>O<sup>+</sup>

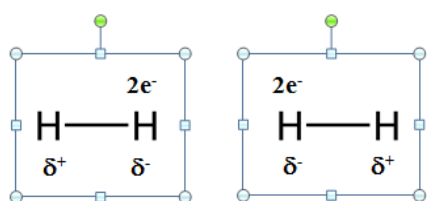


### London (Dispersion) Forces:

London forces, also known as dispersion forces, occur in all molecular substances. They result from the attraction between the positive

and negative ends of induced (nonpermanent) dipoles in adjacent molecules. An induced dipole is caused in one molecule when the electrons of a neighboring molecule are momentarily unequally distributed, resulting in a temporary dipole in the first molecule.

Figure 21, illustrates how one  $H_2$  molecule with a momentary unevenness in its electron distribution can induce a dipole in a neighboring  $H_2$  molecule. This kind of shift in electron distribution in a molecule is known as polarization.



**Fig. 21**

Due to polarization, even noble gas atoms, molecules of diatomic gases such as oxygen, nitrogen, and chlorine (all of which must be nonpolar), and nonpolar hydrocarbon molecules such as  $CH_4$  and  $C_2H_6$  have these fleeting dipoles. Such London forces are the only noncovalent interactions among nonpolar molecules.

London forces range in energy from approximately 0.05 to 40 kJ/mol. Their strength depends on how readily electrons in a molecule can be polarized, which depends on the number of electrons in a molecule and how tightly they are held by nuclear attraction. In general, electrons are more easily polarized when the molecule contains more electrons and the electrons are less tightly attracted to the nucleus; London forces increase with increased number of electrons in a molecule. Thus, large molecules with many electrons, such as  $Br_2$  and  $I_2$ , are relatively polarizable. In contrast, smaller molecules ( $F_2$ ,  $N_2$ ,  $O_2$ ) are less polarizable because they have fewer electrons. When we look at the boiling points of several

groups of nonpolar molecules (Table 8), the effect of the total number of electrons becomes readily apparent:

Boiling points increase as the total number of electrons increases. (This effect also correlates with molar mass—the heavier an atom or molecule, the more electrons it has.) For a liquid to boil, its molecules must have enough energy to overcome monovalent intermolecular attractive forces among the molecules.

Table 8.

Noble Gases			Halogens			Hydrocarbons		
	No. e <sup>-</sup> s	bp (°C)		No. e <sup>-</sup> s	bp (°C)		No. e <sup>-</sup> s	bp (°C)
He	2	-269	F <sub>2</sub>	18	-188	CH <sub>4</sub>	10	-161
Ne	10	-246	Cl <sub>2</sub>	34	-34	C <sub>2</sub> H <sub>6</sub>	18	-88
Ar	18	-186	Br <sub>2</sub>	70	59	C <sub>3</sub> H <sub>8</sub>	26	-42
Kr	36	-152	I <sub>2</sub>	106	184	C <sub>4</sub> H <sub>10</sub> <sup>*</sup>	34	0

Thus, the boiling point of a liquid depends on the nature and strength of intermolecular forces. If more energy is required to overcome the intermolecular attractions between molecules of liquid A than the intermolecular attractions between molecules of liquid B, then the boiling point of A will be higher than that of B. As noted in Table 11, such is the case for Cl<sub>2</sub> (bp = 34 °C) compared with F<sub>2</sub> (bp = -188 °C) due to weaker London forces between diatomic fluorine molecules than between diatomic chlorine molecules. Conversely, weaker intermolecular attractions result in lower boiling points. For example, the boiling point of Br<sub>2</sub> (59 °C) is higher than that of Cl<sub>2</sub> (-34 °C), indicating stronger London forces among Br<sub>2</sub> molecules than among Cl<sub>2</sub> molecules.

Interestingly, molecular shape can also play a role in London forces. Two of the isomers of pentane—straight-chain pentane and 2,2-dimethylpropane (both with the molecular formula C<sub>5</sub>H<sub>12</sub>)—differ in boiling point by 27 °C. The linear shape of the pentane molecule allows close contact with adjacent molecules over its entire length, resulting in stronger

London forces, while the more compact 2,2-dimethylpropanemolecule does not allow as much close contact.



### Dipole-Dipole Attractions:

Because polar molecules have permanent dipoles, a noncovalent interaction called a dipole-dipole attraction is created between two polar molecules or between two polar groups in the same large molecule. Molecules that are permanent dipoles attract each other when the partial positive region of one is close to the partial negative region of another.

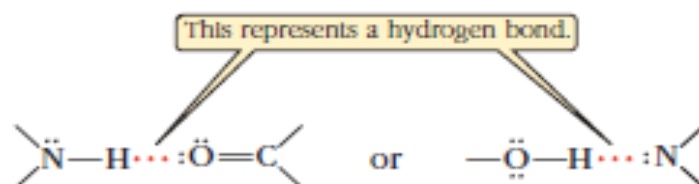
The boiling points of several nonpolar and polar substances with comparable numbers of electrons, and therefore comparable London forces, are given in Table 9. In general, the more polar its molecules, the higher the boiling point of a substance, provided the London forces are similar (molecules with similar numbers of electrons). The lower boiling points of nonpolar substances compared with those of polar substances in Table 9.4 reflect this relationship. Dipole-dipole forces range from 5 to 25 kJ/mol, but London forces (0.05 to 40 kJ/mol) can be stronger. For example, the greater London forces in HI cause it to have a higher boiling point (-36 °C) than HCl (-85 °C), even though HCl is more polar. When London forces are similar, however, a more polar substance will have stronger intermolecular attractions than a less polar one. An example of this is the difference in boiling points of polar Cl<sub>2</sub> (97 °C) with dipole-dipole attractions and nonpolar Br<sub>2</sub> (59 °C) with only London forces, even though the substances have approximately the same London forces due to their similar number of electrons (Table 12).

Table.9.

Nonpolar Molecules			Polar Molecules		
	No. e's	bp (°C)		No. e's	bp (°C)
SiH <sub>4</sub>	18	-112	PH <sub>3</sub>	18	-88
GeH <sub>4</sub>	36	-90	AsH <sub>3</sub>	36	-62
Br <sub>2</sub>	70	59	ICl	70	97

### Hydrogen Bonds:

A hydrogen bond is an especially significant type of noncovalent interaction due to a special kind of dipole-dipole force. A hydrogen bond is the attraction between a partially positive hydrogen atom covalently bonded to F, N, or O and a lone electron pair on a small, very electronegative atom (generally F, O, or N). The H atom and the lone pair may be in two different molecules or in different parts of the same large molecule. Electron density within molecules shifts toward F, O, or N because of their high electronegativity, giving these atoms partial negative charges. As a result, a hydrogen atom bonded to the nitrogen, oxygen, or fluorine atom acquires a partial positive charge. In a hydrogen bond, a partially positive hydrogen atom bonded covalently to one of the electronegative atoms (X) is attracted electrostatically to the negative charge of a lone pair on the other atom (Z). Hydrogen bonds are typically shown as dotted lines ( . . . ) between the atoms:



The hydrogen bond forms a “bridge” between a hydrogen atom and a highly electronegative atom. This type of bridge from hydrogen to a lone pair on nitrogen or on oxygen plays an essential role in determining the

folding (three-dimensional structure) of large protein molecules. The greater the electronegativity of the atom connected to H, the greater the partial positive charge on H and hence the stronger the hydrogen bond. The H atom is very small and its partial positive charge is concentrated in a very small volume, so it can come very close to the lone pair to form an especially strong dipole-dipole force through hydrogen bonding. Hydrogen-bond strengths range from 10 to 40 kJ/mol, which is less than for covalent bonds. However, a great many hydrogen bonds often occur in a sample of matter, and the overall effect can be very dramatic. An example of this effect can be seen in the melting and boiling points of ethanol. This chapter began by noting the very different melting and boiling points of ethanol and dimethyl ether, both of which have the same molecular formula,  $C_2H_6O$ , and thus the same number of electrons and roughly the same London forces. Both molecules are polar (dipole moment  $\neq 0$ ), so there are dipole-dipole forces in each case. The differences in melting and boiling points arise because of hydrogen bonding in ethanol. The OH bonds in ethanol make intermolecular hydrogen bonding possible, while this is not possible in dimethyl ether because it has no O-H bonds. The hydrogen halides also illustrate the significant effects of hydrogen bonding (Figure 22). The boiling point of hydrogen fluoride, HF, the lightest hydrogen halide, is much higher than expected. This is attributed to hydrogen bonding, which does not occur significantly in the other hydrogen halides.

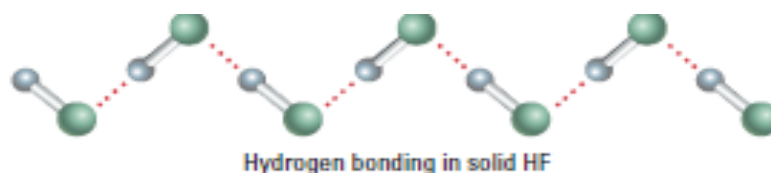
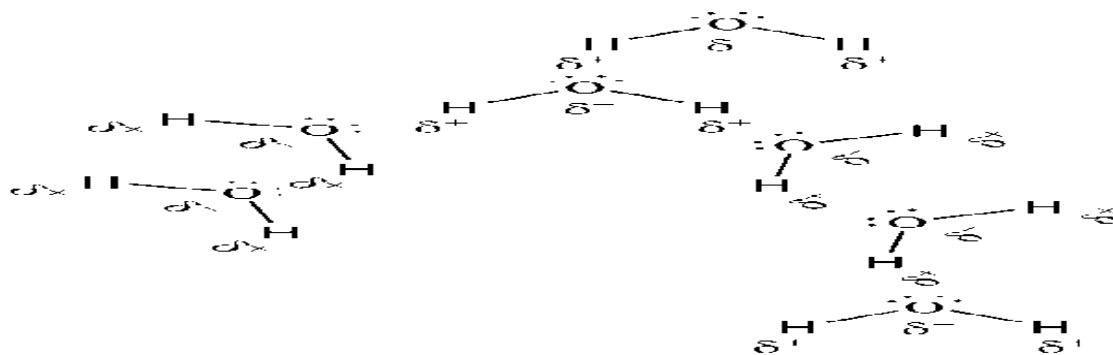


Fig.22

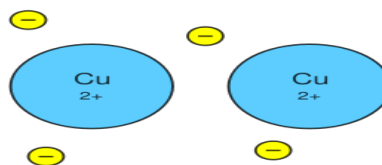
Hydrogen bonding is especially strong among water molecules and is responsible for many of the unique properties of water. Hydrogen



compounds of oxygen's neighbors and family members in the periodic table are gases at room temperature:  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{Te}$ ,  $\text{PH}_3$ ,  $\text{HF}$ , and  $\text{HCl}$ . But  $\text{H}_2\text{O}$  is a liquid at room temperature, indicating a strong degree of intermolecular attraction.



### Metallic Bonding The “Sea of Electrons” Model:



Due to low electronegativities, low effective nuclear charges and large diffuse orbitals, electrons can flow freely from one atom to the next.

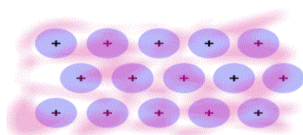


Fig.23.

Metals behave as though metal cations exist in a “sea” of mobile electrons—the valence electrons of all the metal atoms. Metallic bonding is the nondirectional attraction between positive metal ions and the surrounding sea of negative charge (valence electrons). Each metal ion has a large number of near neighbors. The valence electrons are spread throughout the metal’s crystal lattice, holding the positive metal ions together. When an electric field is applied to a metal, these valence electrons move toward the positive end of the field, and the metal conducts electricity. The mobile valence electrons provide a uniform charge distribution in a metal lattice, so the positions of the positive ions

can be changed without destroying the attractions among positive ions and electrons. Thus, most metals can be bent and drawn into wire. Conversely, when we try to deform an ionic solid, which consists of a lattice of positive and negative ions, the crystal usually shatters because the balance of positive ions surrounded by negative ions, and vice versa, is disrupted.

To visualize how bonding electrons behave in a metal, first consider the arrangement of electrons in an individual atom far enough away from any neighbor so that no bonding occurs. In such an atom the electrons occupy orbitals that have definite energy levels. In a large number of separated, identical atoms, all of the energy levels are identical. If the atoms are brought closer together, however, they begin to influence one another. The identical energy levels shift up or down and become bands of energy levels characteristic of the large collections of metal atoms (Figure 23). An energy band is a large group of orbitals whose energies are closely spaced and whose average energy is the same as the energy of the corresponding orbital in an individual atom. In some cases, energy bands for different types of electrons (s, p, d, and so on) overlap; in other cases there is a gap between different energy bands.

Within each band, electrons fill the lowest energy orbitals much as electrons fill orbitals in atoms or molecules. The number of electrons in a given energy band depends on the number of metal atoms in the crystal. In considering conductivity and other metallic properties, it is usually necessary to consider only valence electrons, as other electrons all occupy completely filled bands in which two electrons occupy every orbital. In these bands, no electron can move from one orbital to another, because there is no empty spot for it.

# State of Matter

## Gases, Liquids, and Solids

Matters exist in three distinct physical states gas, liquids, and solid. Of these, gaseous state is the easiest to describe both experimentally and theoretically. A gas has neither definite shape nor volume. A liquid, on the other hand has a definite volume but no definite shape. Liquids and gases are both termed Fluids. A solid is defined as possessing both definite volume and definite shape at a given temperature and pressure. The particular state of a substance is determined by the temperature and pressure under which it exists. However, within certain limits of temperature and pressure, a substance may exist in more than one state at the same time. In fact, under special conditions a substance may exist in all three states simultaneously.

## Gases

### Ideal Gas Laws

In ideal gases, the volume occupied by the molecules is negligible compared with the total volume of the container at all pressures and temperatures and the intermolecular force of attraction is extremely small under all conditions. For real gases, both of these factors are appreciable, the magnitude of each depend on the nature, the temperature, and pressure of the gas. An ideal gas is a hypothetical one, as all actual gases contain molecules that occupy a definite volume and exert attractions between each other. However the influence of these

factors becomes negligible, and the gas is considered to be ideal, at low pressures and relatively high temperatures, condition under which the free space within the gas is large and the attractive forces between molecules are small.

### **Boyle's Law**

Boyle studied the relationship between the pressure of a trapped gas and its volume and recognized from his data that the product of the pressure and volume of for the trapped air sample was constant within the accuracies of his measurements. This behavior can be represented by the equation:

$$PV = K_1$$

or  $P = K_1/V,$

and is called Boyle's Law states that " the volume of a given quantity of a gas at constant temperature varies inversely with the applied pressure "  $K_1$  is constant at a specific temperature for a given amount of the gas. When the pressure of a gas is plotted against the volume, a family of curves is obtained as that shown in following figure. Each curve corresponds to a different fixed temperature and is known as an isotherm. The higher curves correspond to the higher temperatures.

Isothermal plot of P versus V according to Boyle's law

**Problem:** A 1.53-L sample of a gas at a pressure of  $5.6 \times 10^3$  Pa, its pressure was increased to  $1.5 \times 10^4$  Pa at a constant temperature. What will be the new volume of the gas ?

**Solution:** According to Boyle's law

$$P_1V_1 = P_2V_2$$

$$5.6 \times 10^3 \times 1.53 = 1.5 \times 10^4 \times V_2$$

$$V_2 = \frac{5.6 \times 10^3 \times 1.53}{1.5 \times 10^4} = 0.57 \text{ L}$$

### Charles or Gay-Lussac's Law

Charles found that "the volume of a given quantity of a gas at constant pressure increases linearly with the temperature of the gas ". That is, a plot of the volume of a gas (at constant pressure) versus its temperature (in °C) gives a straight line, see the following figure. A very interesting feature of these plots is that the volume of all gases extrapolate to zero at the same temperature,  $-273^\circ\text{C}$ . However, it was Gay-Lussac who first found that for the increase in volume for each degree centigrade rise in temperature was equal to  $1/273$  of the volume of the gas at  $0^\circ\text{C}$ .

Plots of V versus T (in °C or K) for several gases.

If we designate  $V_0$  as the volume of a gas at 0°C and V its volume at any given temperature  $t^\circ\text{C}$ , then in terms of Gay-Lussac finding V may be written as:

$$V = V_0 + (1/273) V_0$$

$$= V_0 \{1 + t/273\}$$

$$= V_0 \{272+t\}/273$$

On the absolute or Kelvin scale, the temperature  $-273.^\circ\text{C}$  is defined as 0 K, which leads to the relation.

$$T (\text{K}) = t(^{\circ}\text{C}) + 273$$

Then the Gay-Lussac's relation becomes simply

$$V/V_0 = T/T_0$$

Or generally

$$V_1/V_2 = T_1/T_2$$

That is "the volume of a given quantity of a gas at constant pressure is directly proportional to the absolute temperature", or that

$$V = k_2 T$$

Where  $k_2$  is a proportionality factor dependent on pressure and the amount of the gas. The above statement and relation are the expressions of Charles or Gay-Lussac's law of volumes.

**Problem:**

A sample of a gas at  $^{\circ}\text{C}$  and 1 atm. has a volume of 2.28 L. What volume will this gas occupy at  $38^{\circ}\text{C}$  and 1 atm.

**Solution** From Charles law we have

$$V_1/V_2 = T_1/T_2$$

$$2.58/V_2 = (273+15)/(273+38)$$

$$V_2 = 2.58 \times 311 / 288$$

$$V_2 = 2.79 \text{ L}$$

**Pressure Law;**

If the volume of a fixed mass of gas is maintained constant, its pressure was found to be directly proportional to the absolute temperature. It was also found that the relative change in pressure with temperature at constant volume is identical with the relative change in volume with temperature at constant pressure.

$$P_1 = P_0 (1 + t_1/273)$$

$$P_2 = P_0 (1 + t_2/273)$$

Upon dividing equations then the result is

$$P_1/p_2 = \frac{(1 + t_1/273)}{(1 + t_2/273)} =$$

$$= T_1/T_2$$

### Avogadro's Law

Avogadro postulated that "equal volumes of different gases at the same temperature and pressure contain the same number of molecules or atoms". This can be stated mathematically as  $V = k_3 n$

When  $V$  is the volume of the gas  $n$  the number of moles, and  $k_3$  a proportionality constant dependent on the pressure and temperature of the gas. This equation states that "for a gas at constant temperature of the pressure the volume is directly proportional to the number of moles of the gas".

### The Ideal Gas law

Boyle's and Charles's laws can be combined in an expression which represents the relationship between the pressure, volume and temperature of a given mass of gas, such an expression is known as the equation of state. If a certain mass (1gram mole) of gas has initially a volume  $V$  at a pressure  $P$  and temperature  $T$ , when the pressure is changed to  $P'$  and the temperature to  $T'$  the volume will be  $V'$ . The relationship between these quantities may be deriving in the following manner.

I) if the pressure is kept constant at  $P$  and the temperature is altered from  $T$  to  $T'$ , the volume will then change from  $V$  to the final value of  $V_1$ .

Applying Charles's law equation (9) it follows that:

$$V/V_1 = T/T'$$

$$V_1 = VT/T'$$



II) Suppose the temperature is maintained at  $T'$  while the pressure is change from  $P$  to  $P_1$  and the accompanying volume to  $V_1$  according to Boyle's law (constant temperature  $T'$ ) change to  $V'$ .

$$P/P' = V' / V_1$$

substitution

$$P'/P = V' / V_1 = V' T / VT'$$

So,

$$P' V' T = P V T'$$

$$P V / T = P' V' / T'$$

Or

$$P V / T = P' V' / T' = \text{Constant} = R$$

For  $n$  gram mole of gas

$$P V = n R T$$

IF Avogadro's law holds precisely, so, equation frequently referred to as the ideal gas equation.

### **Evaluation of the gas constant:**

The value of this constant can be set from the general equation as follows:

$$R = P V / n T$$

If we compensate for the volume in liters and the pressure in the atmosphere, then:

$$R = 22.4 \times 1/273 = 0.082 \text{ [liter of atmosphere / degree of Gram]}$$

If instead of volume in cubic centimeters and pressure in the atmosphere, then:

$$R = 22400 \times 1/273 = 82 \text{ [atmosphere / degree Cm}^3\text{]}$$

If the volume is estimated in cubic centimeters and pressure in debt, then:

$$R = 22400 \times 76 \times 13.6 \times 980.6 / 273 = 8.314 \times 10^7 \text{ [Erg/}^\circ\text{G]}$$

Since Joule =  $10^7$  Erg, ( $R = 8.314 \text{ Joule degree}^{-1} \text{ mol}^{-1}$ )

Since the price = 4.18 joules,  $R = 8.314 / 4.18 = 1.99$  (the degree of  $-1$  mole  $-1$ )

As for the value of one molecule R, it is equal to  $R/N$ , where N is the number of Avogadro.

As an alternative to the previous treatment, we find that the laws of Boyle and Charles describe the behavior of the gas to determine how the volume of a certain amount of gas changes with the change of pressure and temperature. Thus, an equation can be written on the formula:

$$V = f(P, T)$$

**Problem:** A sample of hydrogen gas has a volume of 89.65 L at a temperature of  $0^\circ\text{C}$  and a pressure of 1.5 atm. Calculate the moles of  $\text{H}_2$  present in this gas sample.

Solution: From the ideal gas law we have

$$\begin{aligned} n &= PV/RT \\ &= 1.5 \times 8.56 / (0.082 \times 273) \\ &= 0.57 \text{ mol} \end{aligned}$$

**Problem:** A sample of ammonia gas with a volume of 3.5 L and at a pressure of 1.68 atm. is compressed a volume of 1.35 L at constant temperature. Calculate the final pressure.

**Solution:** Using the ideal gas law, at constant temperature

$$P_1V_1 = nRT = P_2V_2$$

$$P_2 = P_1V_1/V_2$$

$$= 1.68 \times 3.5/1.35 = 4.4 \text{ atm.}$$

**Problem:** A sample of methane gas that has a volume of 3.8 L at 5°C is heated to 86°C at constant pressure. Calculate the new volume.

**Solution:** Using the ideal gas law, at constant pressure

$$V_1T_1 = nR/P = V_2/T_2$$

$$V_2 = (T_2/T_1)V_1 = 3.8 \times (359.15/278.15) = 4.9 \text{ L}$$

### **Dalton's Law of Partial Pressures:**

It is summarized in the statement: For a mixture of gases in a container, the total pressure exerted is the sum of the partial pressures that each gas would exert if it occupies alone the whole volume of the container". This statement, known as Dalton's Law of Partial Pressures, can be expressed as follows:

$$P_{\text{Total}} = P_1 + P_2 + P_3 + \dots$$

This equation is strictly applicable to a mixture of ideal gases, although the deviations exhibited by actual gases are not large. Of important attention those gases are not reacted chemically. If each of the gases present in the mixture behaves ideally, it is possible to write for each of the gases separately occupying the vessel of volume  $V$ . Where the subscripts refer to the individual gases. The pressures  $P_1, P_2, P_3$  and so on are called Partial Pressures, that is the pressure that each gas would exert if it were alone in the container. Assuming that each gas behaves ideally, the partial pressure of each gas can be calculated from the ideal gas law:

$$P_1 = n_1RT/V, P_2 = n_2RT/V, P_3 = n_3RT/V, \dots\dots$$

The total pressure of the mixture,  $P_{\text{Total}}$ , can be represented as

$$\begin{aligned} P_{\text{Total}} &= n_1RT/V + n_2RT/V + n_3RT/V + \dots\dots \\ &= (n_1 + n_2 + n_3 + \dots\dots) RT/V \\ &= n_{\text{Total}} (RT/V) \end{aligned}$$

where  $n_{\text{Total}}$  is the sum of the numbers of moles of the various gases. Thus, for a mixture of ideal gases, it is the total number of moles of particles that is important, not the identity or composition of individual gas particles.

Dalton's law can be put in another form by dividing the partial vapor pressure of each constituent of the gas mixture by the total pressure. That is,

$$\begin{aligned} P_1/P_{\text{Total}} &= (n_1RT/V)/(n_{\text{Total}} RT/V) \\ &= n_1/n_{\text{Total}} \end{aligned}$$

$$= X$$

Or  $P_1 = X_1 p_{\text{Total}}$

Similarly,  $P_2 = X_2 P_{\text{Total}}$  -  $P_3 = X_3 P_{\text{Total}}$  -  $P_4 = X_4 P_{\text{Total}}$ , and so on, where  $X_1, X_2, X_3, \dots$  are the mole fractions of the gas constituents 1,2,3, ..., respectively. It should be mentioned here that the sum of the mole fractions of the constituent gases of the mixture is equal to one i.e.,

$$X_1 + X_2 + X_3 + \dots = 1$$

**Problem:** A sample of 46 L of oxygen at 25°C and 1 atm. was pumped along with 12 L of helium at 25°C and 1 atm. into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C

Solution; First we have to calculate the number of moles of each gas using the ideal gas law, thus

$$n = PV/RT$$

$$n_{\text{O}_2} = 1.0 \times 46 / (0.082 \times 298) = 1.9 \text{ mol}$$

$$n_{\text{O}_2} = 10 \times 12 / (0.082 \times 298) = 0.49 \text{ mol}$$

Second we will calculate the partial pressures of each gas using again the same equation, thus:

$$P = nRT/V$$

$$P_{\text{O}_2} = 1.9 \times 0.082 \times 298 / 5.0 = 9.3 \text{ atm.}$$

$$P_{\text{H}_2} = 0.49 \times 0.082 \times 298 / 5.0 = 2.4 \text{ atm.}$$

And the total pressure of the mixture from Dalton's law will be

$$P_{\text{Total}} = P_{\text{O}_2} + P_{\text{H}_2}$$

$$= 9.3 + 2.4 = 11.7 \text{ atm}$$

$$X_{\text{O}_2} = P_{\text{O}_2}/P_{\text{Total}} = 156/743 = 0.21$$

## Graham's law

Diffusion is the term used to describe the mixing of gases. The rate of diffusion is the rate of mixing of gases. Diffusion is the term used to describe the passage of a gas through a tiny orifice into evacuated chamber. The rate of effusion measures the speed at which the gas is transferred into the chamber.

Thomas Graham found experimentally that different gases diffuse through a tube or effuse from a fine orifice in a container at different rates dependent on the densities or molecular weights of the gas. He states that: "at constant temperature and pressure the rates of diffusion or effusion of various gases vary inversely as the square roots of their densities or molecular weights". Thus if we let  $r_1$  and  $r_2$  be the rates of diffusion (or effusion) of two gases, and  $\rho_1$  and  $\rho_2$  be their respective densities, then: where  $M_1$  and  $M_2$  are the molecular or atomic weights of the two gases, respectively.

$$r_1/r_2 = \sqrt{\rho_2/\rho_1}$$

According to this law, the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density. If  $r_1$  and  $r_2$  represents the rates of diffusion of two gases whose densities under the given conditions are  $\rho_1$  and  $\rho_2$  respectively, then:

Since the density of a gas (directly proportional to its molecular weight equation (28) becomes :

$$f_1/f_2 = \sqrt{M_2/M_1}$$

where  $M_1$  and  $M_2$  are the molecular weights of the two gases. It follows from Graham's law of diffusion, that a light gas will diffuse rapidly than a heavy one, as a result of this law, determination of gas densities can be obtained by measuring the time required for a definite volume of the gas to diffuse through hole in a thin metal plate. The time required for a known volume of gas to pass through the hole is inversely proportional to its rate of diffusion. If the times for the two gases are  $t_1$  and  $t_2$ , then by equations.

$$t_2/t_1 = \sqrt{d_2/d_1} = \sqrt{M_2/M_1}$$

Hence, either the density or the molecular weight of the unknown gas can be determined.

**Example:** :

The time for a certain volume of gas to stream through a small hole was 1.44 min., under exactly the same conditions, an equal volume of oxygen took 1.8 min. to pass through

Calculate the approximate density of the gas relative to hydrogen.

**Solution:**

$$\text{Molecular weight of oxygen} = 32$$

$$\text{Molecular weight of hydrogen} = 2$$

$$\text{Density of oxygen related to hydrogen } d_1 = 32/2 = 16$$

If the density of the gas is  $d_2$ , then by equation;

$$1.44/1.80 = d_2/16$$

## Real Gases

### Deviation from ideal behavior:

Amagat was the first to demonstrate by experience that Boyle's law does not apply to gases under high pressure, as the deviation from this law is not small except under pressure that does not exceed atmospheric pressure, but if the pressure exceeds that much and the temperature decreases then the difference between the behavior of gases and the ideal state is most evident. This difference becomes clear if the relationship between  $PV$  and pressure on the gas is drawn ( $P$ ). In the ideal case when the gas follows the Boyle Law, the value of ( $PV$ ) and pressure is represented by a straight line parallel to the pressure axis. But such behavior is not observed only in one case, which is the case of ideal gas.

This gas does not have an actual presence and it is evident from the curves shown in the given figure that the value of  $PV$  decreases in the case of nitrogen and carbon dioxide by increasing pressure until a certain value after which it starts to increase, but in the case of hydrogen the value of  $PV$  increases directly without decreasing first and from this we see. The deviation of gas depends on its nature, as gases that facilitate its liquefaction, such as carbon dioxide, have large deviation unlike gases that are difficult to liquefy, such as nitrogen. Deviation was interpreted according to:

firstly, that the value of volume is less than is consistent with Boyle's law, that is, when gas is compressed, its volume decreases by a

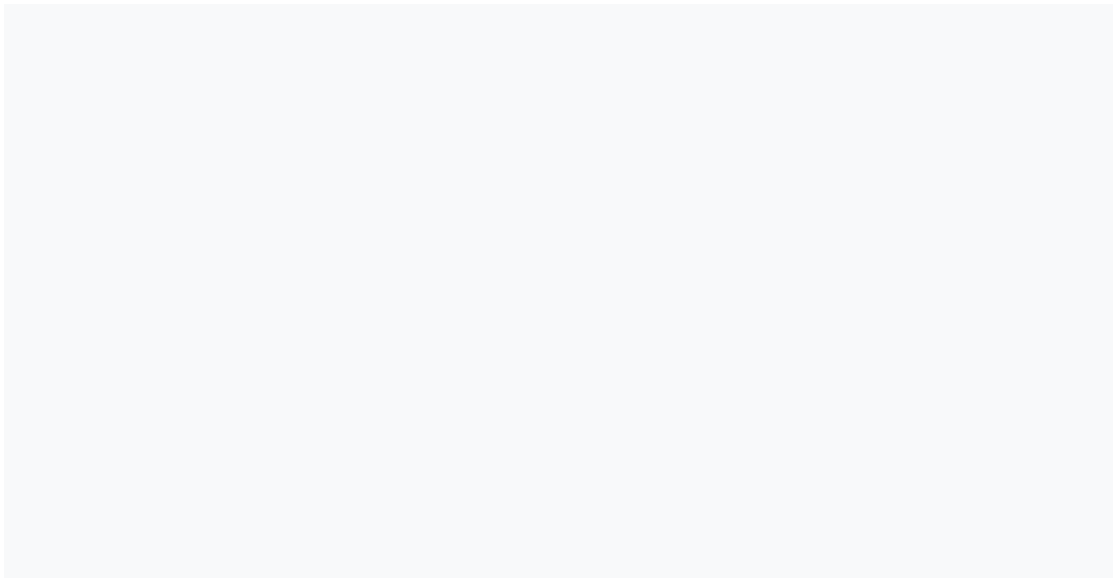


greater amount than is consistent with Boyle's law due to the presence of another factor, which is the attraction between the particles increase in impact when the gas temperature approaches the liquefaction point. The increase in the value of  $(PV)$  can be explained by the increase in pressure after it reaches its minimum value, that the volume of gas does not decrease by increasing the pressure to the extent that is consistent with Boyle's law, as a result of the appearance of the forces of repulsion between molecules when they approach each other under high pressure. The deviation of gases from Boyle's law is much lower at low pressures as the curve approaches the ideal gas line, and therefore it can be said that gas deviation can fade under low pressures and at high temperatures

**Effect of temperature on then deviation of gases:**

It was found that if experiments were carried out on nitrogen gas, for example, at different temperatures, the deviation increases with decreasing temperatures, as is the case with hydrogen and similar gases such as helium and neon. If experiments were conducted at low temperatures, they behave like nitrogen gas and carbon dioxide. For example, if the hydrogen cools to (-80°C and this is known as the "Inversion point"), it behaves like a normal gas path and from this we conclude that the behavior of the gas depends on the temperature of the experiment in relation to the degree at which the gas liquefaction occurs.

As is the case with carbon dioxide, the deviation is greatly reduced with a rise in temperature, as can be seen from following figure and increased with decrease. The reason is that the value of  $PV$  decreases firstly, that the value of  $(PV)$  decreases firstly, that the value of volume is less than is consistent with Boyle's law, that is, when gas is compressed, its volume decreases by a greater amount than is consistent with Boyle's law due to the presence of another factor, which is the attraction between The particles increase in impact when the gas temperature approaches the liquefaction point. The increase in the value of  $(PV)$  can be explained by the increase in pressure after it reaches its minimum value, that the volume of gas does not decrease by increasing the pressure to the extent that is consistent with Boyle's law, as a result of the appearance of the forces of repulsion between molecules when they approach each other under high pressure. The deviation of gases from Boyle's law is much lower at low pressures as the curve approaches the ideal gas line, and therefore it can be said that gas deviation can fade under low pressures and at high temperatures.



### **Deviation about Charle's law:**

In addition to the deviation from Boyle's law, real gases exhibit departures from Charle's law, this is apparent from the fact that the shape of the PV curves in the above figure change with temperature. In general, deviation from the ideal behavior is greater the higher the pressure and the closer the temperature are to that at which liquefaction is possible.

### **Deviation from Avogadro's law**

The accuracy of Avogadro's law may be tested by determining the volume occupied by 1 mole of gas at  $0^{\circ}\text{C}$  and 1 atm. pressure. If the law is exactly true, the volume would be independent of the nature of the gas, but the results in the following Table which shows that this is not true.

Table : **Test of Avogadro's law**

Gas 0°C and 1 atm.	Molecular weight	Volume 1 mol at
Hydrogen	2.016	22.724
Nitrogen	28.020	22.405
Oxygen	32.000	22.394
Carbon dioxide	44.010	22.264
Ammonia	17.030	22.084

As before, the largest deviations are shown by the most easily liquefiable gases, e.g. ammonia and carbon dioxide. The departure from ideal behavior increases with decreasing temperature and pressure.

### **Causes of deviations from ideal gas law**

In order to adapt the ideal gas law equation to the behavior of real gases, attractive and repulsive forces between molecules should be taken into consideration. For this purpose Van der Waal derived an equation which fulfills such requirements. Consider a molecule in the interior of a gas; it is surrounded by other molecules equally distributed in all directions (see the following figure A) so that they exert no resultant attractive force on the molecule under consideration.

As the molecule approaches the wall of the containing vessel, the uniform average distribution of the molecules comes on one side (Fig. B). So that a force is exerted in order to pull the molecule inwards. When a molecule is about to strike the walls of the containing vessel and thus contribute its share towards the total gas pressure, the molecules in the bulk of the gas exert a force having the effect of pulling the molecule away from the wall. The measured pressure  $P$  is thus less than the ideal pressure required by the kinetic theory.

### **Correction of Pressure**

Correction factor to the observed pressure in order to obtain the ideal pressure. The attractive force exerted on a single molecule about to strike the walls is proportional to the number  $a$  of molecules  $n$ , per unit volume in the bulk of the gas, further the number of molecules striking the walls is also proportional to this number  $n$ , so that the total attraction force, which is related to the correction term to be added to the measured pressure is proportional to  $n^2$ . If  $V$  is the volume occupied by 1 mole of gas then:

$$n \propto 1/V \quad \text{and} \quad n^2 \propto 1/V^2$$

Or the attractive force  $\propto 1/V^2$

$$\text{Corrected (ideal) pressure} = P + a / V^2$$

### **Correction of Volume**

The effect of combined repulsive and attractive forces is to give the molecules an appreciable size, and hence the space available for their movement is less than the actual volume  $V$  of the gas. In order to obtain the ideal volume therefore it is necessary to subtract an appropriate correction term  $b$  from the total volume. It was found that the value of  $(b)$  is not equal to the size of the molecules themselves, and this is what this volume is called by the non-compressible volume (uncompressed volume), the compressible volume is  $(V-b)$ . This size is known as the Incompressible volume, and the compressible volume is  $(V-b)$ .

This correction term was found to be equal to four times the actual volume of the molecules, is given the symbol,  $b$ , thus, corrected (ideal) volume  $(V - b)$ .

The product of the ideal pressure and ideal volume derived in this manner may be expected to equal to  $RT$ , as given for an ideal gas, hence,

$$(P + a/V^2) (V - b) = RT$$

### **Applicability of the Van der Waals equation:**

At low pressure, so that  $P$  is small and  $V$  is large, values of  $Pb$  and  $a/V^2$  may be neglected in comparison with  $a/V$  so that equation reduces to:

$$PV = RT - a/V$$

At high pressures, the last two terms on the right of equation being of opposite sign and approximately equal magnitude may be neglected in comparison with the other two terms. The Van der Waals equation then becomes:

$$PV = RT + Pb$$

## **The Liquefaction of Gases**

### **The Critical State:**

At the beginning of the nineteenth century a number of gases such as carbon dioxide, sulphur dioxide, ammonia, etc. . . were liquefied by the simultaneous use of high pressure and low temperature. Further by allowing compressed liquid carbon dioxide to evaporate, the temperature was lowered sufficiently for the solid to be obtained. The same principle

was used at the present time in the manufacture of (dry ice) as solid carbon dioxide.

The essential conditions for the liquefaction of gases were discovered by Andrews (1869); as the result of a study of the pressure – volume– temperature relationship of carbon dioxide. A definite amount of the gas was enclosed in a glass tube kept at a constant temperature and volume at different Pressures, were measured, the results for a series of temperatures were plotted in the form of isotherms as shown in Fig.

The maximum temperature at which a gas can be liquefied is referred to as the critical temperature, and the pressure required to cause liquefaction at this temperature is the critical pressure.

**Critical Temperature:** It is the temperature above which it is impossible to liquefy gas no matter how great pressure is applied.

**Critical Pressure:** it is the minimum pressure necessary to bring about liquefaction at the critical temperature.

**Critical Volume:** It is the volume occupied by one mole of a gas at the critical temperature and pressure.

### **Kinetic Theory of Ideal Gases**

The kinetic molecular theory is a simple model that attempts to explain the properties of an ideal gas. This model is based on speculations about the behavior of the individual gas molecules. The postulates of the kinetic molecular theory can be stated as follows:

(1) Gases consist of minute particles usually molecules. Molecules of any gas are similar in shape and size.

(2) The particles are in constant motion. The collision of the particles with the walls of the container is the cause of the pressure exerted by the gas.

(3) Gas molecules are assumed to be perfectly elastic, i.e., there is no net change in momentum upon collision.

(4) The pressure exerted by the gas molecules is caused by the bombardment of molecules with the wall of the container.

(5) The gas molecules are so small compared to the intermolecular distance that the volume of the individual particles can be assumed to be negligible.

(6) The particles are assumed to exert no forces on each other, they are assumed neither to attract nor to repel each other.

(7) The average kinetic energy of a collision of the gas particles is assumed to be directly proportional to the Kelvin (absolute) temperature of the gas.



Of course, real gases do not conform to these assumptions, but we will see that these postulates do indeed explain ideal gas behavior.

Consider a cubic container filled with  $n$ , molecules of a gas, all with molecular mass  $m$  and velocity  $u$ . The velocity  $u$  may be resolved into its three components along  $x, y$ , and  $z$  axes, as shown in the figure.

### Resolution of velocity along $x, y$ , and $z$ -axes

If we designate these velocity components by  $u_x$ ,  $u_y$ , and  $u_z$ , respectively, then

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

where  $u$  is called the root mean square velocity. Suppose that the molecule of mass  $m$  is moving in the  $x$ -direction to the right with velocity  $u_x$ . It will strike the  $yz$ -plane with a momentum " $mu_x$ " and, since the collision is elastic, it will rebound with velocity  $-u_x$  and momentum  $-mu_x$ . Since the number of shocks per second in this direction is  $(u_x/L)$  on one of the cubic sides, the change in the amount of movement per second as a result of shocks on one side of the cube is  $2 mu_x (u_x/L) = 2mu_x^2/L$  ( $g \text{ cm s}^{-2}$  or dyne)

Analogous change in the momentum take place in the  $y$  and  $z$  directions, and these are given by  $mu_y^2/L$  and  $mu_z^2/L$  per molecule per second, respectively. Form these:

$$= 2mu_x^2/L + 2mu_y^2/L + 2mu_z^2/L$$

$$= (2m/L) (u_x^2 + u_y^2 + u_z^2)$$

$$= (2m/L) u^2$$

As there are  $n$  molecules in the cube, the change in momentum per second for all of them will be given by:  $(2nm/L) u^2$ . According to Newton's Law of motion, the rate of change of momentum is equal to the force acting consequently.

Force due to collisions of a single molecule =  $2mu^2/L$  dynes. Each of the molecules in the cube will exert a similar force, so that total force due to collisions of  $n$  molecules =  $2m/L (u_1^2 + u_2^2 + \dots + u_n^2)$  dynes where  $u_1, u_2, \dots, u_n$  are the velocities of the individual molecules.

$$2nm u^2/L$$

So that total force due to collisions of  $n$  molecules =  $2nm u^2/L$  dynes since the pressure is the force per unit area, and the total area of the cube =  $6L^2$ , the total pressure exerted by all the molecules is given by:

$$\text{Pressure} = \frac{2 n m u^2}{L} \times \frac{1}{6L^2} = \frac{n m u^2}{3L^3} \text{ dynes cm}^{-2}$$

But  $L^3$  is the volume of the cube,  $V$ , and so

$$P = \frac{n m u^2}{3V}$$

Or  $PV = \frac{1}{3} n m u^2$

This is if we assume that the particles move with the same speed, the previous equation was written on the following form:

$$PV = \frac{1}{3} n m u^2, \quad K_e = \frac{1}{2} m u^2$$

$$PV = \frac{2}{3} n \left( \frac{1}{2} m u^2 \right) = \frac{2}{3} n K_e \quad [K_e \text{ is the kinetic energy of single molecule}]$$

## **Liquids state**

A liquid may be considered as a continuation of the gas phase into the region of small volumes and very high molecular attractions. The cohesive forces in a liquid must be stronger than those in a gas even at high pressures, for they are high enough to keep the molecules confined to a definite volume. Still, the molecules within the liquid must not be thought of as rigid fixed. They have some freedom of motion, but this motion is considerably restricted, and hence the mean free path is much shorter than in the gas phase. If a liquid, such as water, is sealed in an evacuated tube, a certain amount will evaporate to form vapor. This vapor will exert a pressure just as any gas does, and provided the temperature is maintained constant, equilibrium will be established between the liquid and the vapor phases. The vapor pressure established is characteristic for each liquid and is constant at any given temperature, it is known as the saturated vapor pressure of the liquid. The saturated vapor pressure increases continuously with temperature and equals 1 atmosphere at the normal boiling point of the liquid.

### **Properties of liquids**

#### **Vaporization:**

Liquids are different the gases molecules. Both liquid and gas molecules are in permanent motion. Most liquid molecules have average velocities; little molecules have a velocity higher than the average velocity value. These molecules overcome the forces of attraction and can

leave the surface of liquid and hence, vapor, at the given temperature and pressure.

At certain point approach an equilibrium state between the numbers of molecules evaporate and condensed molecules, since the condensation process is accompanying the evaporation one. The pressure at this point is called vapor pressure. This phenomenon is called surface phenomena.

### **Boiling:**

The boiling process is characterized about the evaporation. Boiling is not a surface phenomenon and occur at constant temperature and began the all the liquid to transfers to vapor, and its pressure is equal to the outer pressure. Water is boiling at 100 °C at 1 atm (760 mmHg). As the pressure increased the boiling point increased and versa.

Water boil at 102 °C at 816 mmHg and boil at 52 °C when the pressure at 100 mmHg.

### **Surface Tension**

A molecule in the interior of a liquid is completely surrounded by other molecules and so on the average it is attracted equally in all directions. On the molecule in the surface there is a resultant attraction inwards, because the number of molecules per unit volume is greater in the liquid than in the vapor.

As a sequence of this inward pull, the surface of the liquid always tends to contract to smallest possible area, it is for this reason that drops of liquid and bubbles of gas become spherical, as far as feasible for the surface area is then a minimum for the given volume. In order to extend the surface area, it is necessary to do work to bring molecules from the

bulk of the liquid into the surface against the inward attractive force. The work required to increase the area by  $1\text{Cm}^2$  is called the surface energy, as a result of the tendency to contract, a surface behaves as if it were in a state of tension. The surface tensions equal numerically and dimensionally to the surface energy. Thus, surface energy expressed as  $\text{erg}/\text{Cm}^2$  this equivalent to  $\text{dynes}/\text{Cm}$  which is the unit of surface tension. It is frequently stated that, because surface has a spontaneous tendency to contract, it behaves like a stretched elastic membrane.

### **Viscosity**

Liquid exhibit the resistance to flow a property which is known as viscosity. In general it is the property which opposes (resist) the relative motion of adjacent layers of the liquid and so it may be regarded as internal friction. The viscosity in poises or  $\text{dynes}/\text{Cm}^2/\text{Sec}$ . If a liquid in capillary and we affect with a force (difference of pressure), the liquid not flow as one unit with the same velocity, but the liquid consist several layers, each layer has own velocity deferent of the other layer, since the layer in contact to the wall of capillary is static approximately (velocity  $\sim 0$ ) and the velocity of other layers increases as far from each other till the center of capillary. As we moved to the other capillary wall the velocity decreased in result it happened a friction between the deferent layers of liquid. This resistance of flow and the friction expressed as viscosity.

## Solids

Solids differ from liquids and gases in possessing both definite volume and definite shape. The stability of a solid is not due to any difference in compactness between solids and liquid states, for the density of a substance in the solid state may actually be less than that of the corresponding liquid, as in the case of ice and water. The definite shape of a solid is to be ascribed rather to the fact that the structure units, instead of being in random motion like the molecules of a liquid or a gas, are confined to definite positions of equilibrium within the crystal of the solid, positions about which the particles may vibrate but which they cannot really leave.

Solid substance is frequently classified as either crystalline or amorphous. A crystalline solid is one in which the constituent structural units are arranged in a definite geometrical configuration characteristic of the substance. This configuration repeats itself with definite periodicities in three dimensions, resulting in a substance having long-range order. Amorphous substance, on the other hand, although possessing many of the attributes of a solid such as definite shape and certain rigidity and hardness, do not show definite configurationally arrangement or order extending for any distance.

### **Crystallization and Fusion:**

A pure liquid on being cooled at constant pressure suffers a decrease in the average translational energy of its molecules, and hence its temperature drops until the freezing point is reached. At this temperature, the attractive forces of the molecules are sufficient to

overcome the translational energy, and the molecules are forced to arrange themselves in a geometric pattern which is characteristic for each substance. When crystallization starts, heat is evolved, this heat evolution arrests temperature drop, and the temperature of the mixture of solid and liquid remains constant as long as both phases are present. Further removal of heat results merely in the crystallization of more liquid, until finally the whole mass solidifies. Only then the temperature begins to fall again on cooling. The amount of heat evolved per mole of substance is called the heat of

### **Crystallization of the substance:**

The reverse of crystallization is the fusion or melting of the solid. As the pure solid is heated, its average vibration energy increases until at the melting point some particles are vibrating with sufficient energy to overcome the confining forces. The solid then begins to fuse. The solid then begins to fuse. For a given pressure, the temperature at which this occurs is the same as the crystallization temperature. To accomplish further fusion, heat must be supplied to compensate the loss of the particles with high energy. The amount of heat, which is absorbed to accomplish the transition of one mole of the solid to one mole of the liquid, is known as the heat of fusion. This amount of heat is equal in magnitude, but is opposite in sign, to the heat of crystallization of the substance.

### **X-ray diffraction study:**

Bragg and Laue have been made some research to study the installation of crystalline and demonstrated those studies. The levels of the atoms in the crystal serve as surfaces for measuring X-ray diffraction.

Knowing the amount of diffraction can assign those distances and then find out the structure of crystallization. Several other studies have been conducted to study the structure of the crystals by measuring the amount of light reflection from surfaces. Including possible the crystal angles and then the distribution of atoms in the way. From the results reached by this study to know the structure of crystallized salts. There cubic crystals and other monoclinic and a third, Hexagonal and so on.

Sodium chloride for example NaCl not formed from molecules but it was found that NaCl is crystal of regular cubic cells. Where ions of  $\text{Cl}^-$  and  $\text{Na}^+$  occupied sequence positions separated with equal Spacing.

### **Vapor pressure of solids:**

Many solids give off vapor at ordinary temperatures just as liquid do. This is evident from their odors such as naphthalene. As the solid is heated the vapor pressure increases and when it becomes just greater than the pressure of the atmosphere the solid cannot be heated in an open vessel to a temperature higher than its melting point as in case of liquid which cannot be raised temperature above boiling point. At this stage the temperature remains constant and the heat supplied is used in converting the solid into vapor. When the entire solid is converted into vapor the temperature begins to increase with further supply of heat. Solid carbondioxid have a vapor pressure of 1 atm., at  $-78\text{ }^\circ\text{C}$  and temperature  $-56\text{ }^\circ\text{C}$  its vapor pressure is more than 5 atm. And that in the solid state are forces of attraction between molecules reached the maximum degree,



which determines the action and its capacity to escape from the mutual attraction forces field.

Thus, the vapor pressure of solids is very small, but will have non-existent in most cases, but in the case of heated the solid and the molecules have amounted of energy in results, the vapor pressure of solid material increases. The vapor pressure is depended on forces of attraction between molecules and this in turn depends on the types of crystals and structure of the materials (molecular crystals), which arise from the union of atoms of the elements in a way electro sharing bonds. Since the attraction forces between their molecules are relatively weak.

For the ionic crystals such as NaCl crystals consisting positive ions and the other negative. The strength of correlation between them very large and thus the vapor pressure is very small and has a high melting point.

**Sublimation of solid substances:**

Transfer of solid state to gas state without pass through liquid state.