Section

General chemistry

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 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.

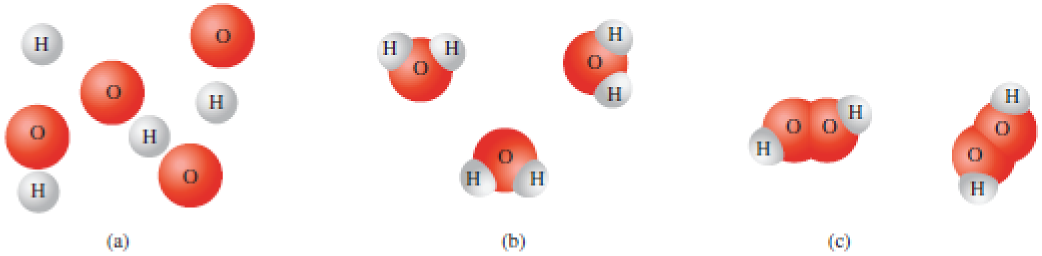


Fig 1.(a) Dalton's atoms were individual particles, the atoms of each element being alike in mass and size but different in mass and size from other elements. (b) and (c) Dalton's atoms combine in specific ratios to form compounds.

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 and for hydrogen peroxide H_2O_2 as See Figure 1 b 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 Na^+ and Cl^- , the Na^+ ions move toward the negative electrode (cathode), whereas the 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 structure stand 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 ($1 \text{ nm} = 1\text{x}10^{-9}$ 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 $1\text{x}10^{6}$ 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.

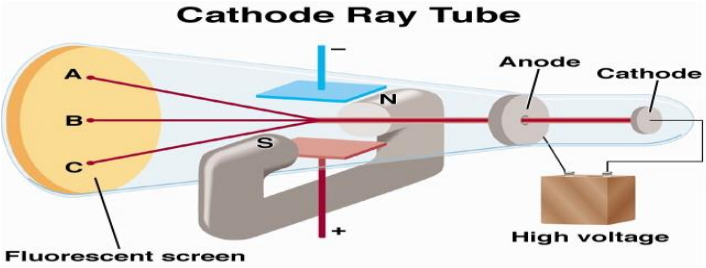


Fig 2. Crookes tube (cathode rays)

The electron **(e^-)** is a particle with a negative electrical charge and a mass of 9.110 x 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 than10^{-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 $1.673\text{x}10^{-24}$ *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, Na^+ or Li^+) has lost one electron. An atom with a net charge of +3 (for example 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, or) is produced by the addition of one electron. A net charge of -1(for example, Cl^- or F^-) 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.

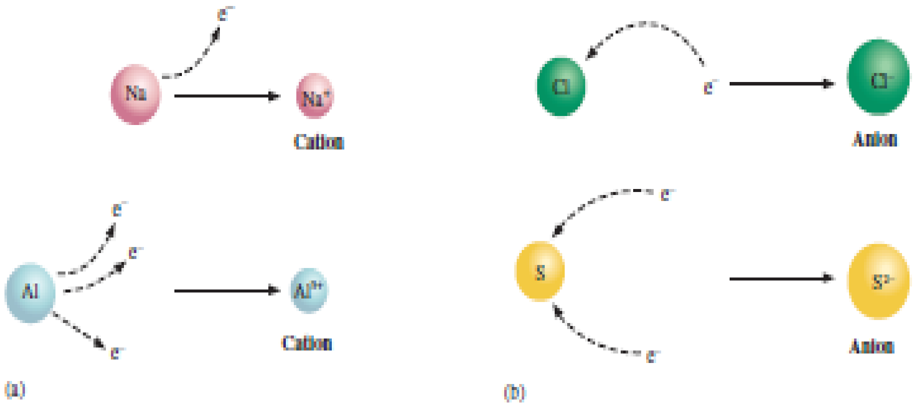


Fig. 3.Thomson model of the atom

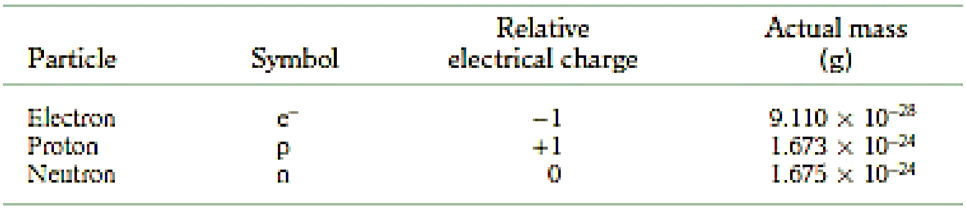
Nearly all the ordinary chemical properties of matter can be explained in terms of atoms consisting of electrons, protons, and neutrons. The discussion of atomic structure that follows is based on the assumption that atoms contain only these principal subatomic particles.

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.



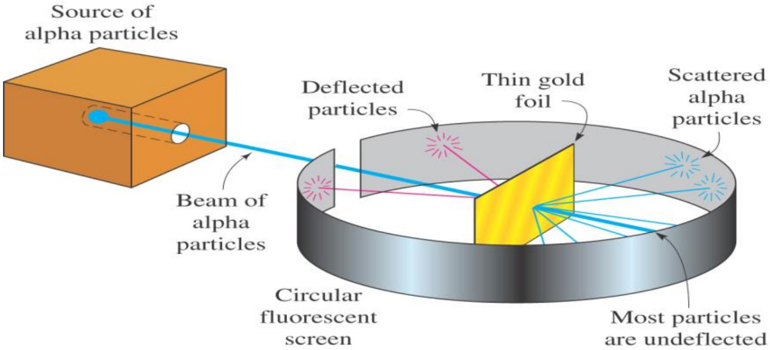
Particle	Symbol	Relative electrical charge	Actual mass (g)
Electron	e^-	−1	9.110×10^{-28}
Proton	p	+1	1.673×10^{-24}
Neutron	n	0	1.675×10^{-24}

The Nuclear Atom

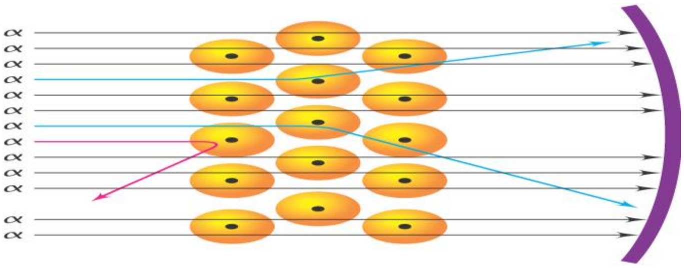
The discovery that positively charged particles are present in atoms came soon after the discovery of radioactivity by Henri Becquerel (1852–1908) in 1896. Radioactive elements spontaneously emit alpha particles, beta particles, and gamma rays from their nuclei By 1907 Rutherford found that alpha particles 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 $_1H$	1 proton in the nucleus
Atomic number $_6C$	6 proton in the nucleus
Atomic number $_{92}U$	92 proton 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 $_1^1H$, $_1^2H$ and $_1^3H$ 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 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 $^{16}{}_8O$ $^{17}{}_8O$ and$^{18}{}_8O$, are stable. Of the fifteen known isotopes of arsenic, is the only one that is stable. $^{75}{}_{33}As$. 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 x 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 ${}^{12}_{6}C$, 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 of the mass of a carbon-12 atom. The actual mass of a carbon-12 atom is 1.9927 x 10^{-23} *g* and that of one atomic mass unit is1.6606 x 10^{-24} g.

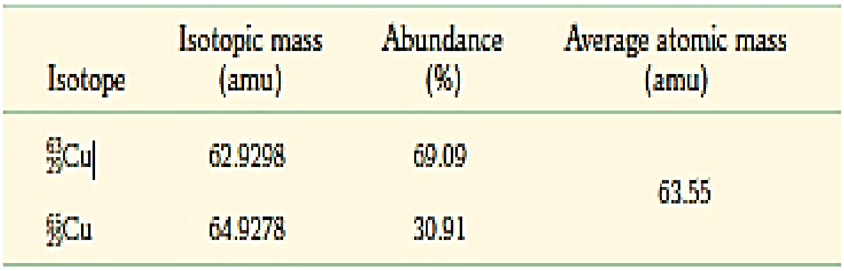
In the table of atomic masses, all elements then have values that are relative to the mass assigned to the reference isotope, carbon-12. Hydrogen atoms, with a mass of about 1/12 that of a carbon atom, have an average atomic mass of 1.00794 amu on this relative scale. Magnesium atoms, which are about 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 $^{63}_{29}$Cu and $^{65}_{29}$Cu. Copper used in everyday objects, and the Liberty Bell contains a mixture of these two isotopes. It is apparent thatcopper-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)
$^{63}_{29}$Cu	62.9298	69.09	63.55
$^{65}_{29}$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 amu)(0.6909) =43.48 amu

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

63.55 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}9F), atomic number 9, having a mass of 19 amu, contains 10 **neutrons:**

mass number	**atomic number**	**number of neutrons**
19	9	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 x 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.

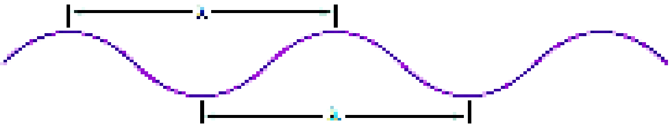


Fig. 4.

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

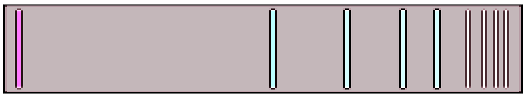


Fig. 5 line spectrum

In 1912–1913, while studying the line spectrum of hydrogen, Niels Bohr (1885–1962), a Danish physicist, made a significant contribution to the rapidly growing knowledge of atomic structure. His research led him to believe that electrons exist in specific regions at various distances from the nucleus. He also visualized the electrons as 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 as a single electron revolving in an orbit about a relatively heavy nucleus. He applied the concept of energy quanta, proposed in 1900 by the German physicist Max Planck (1858–1947), to the observed line spectrum of hydrogen. Planck stated that energy is never emitted in a continuous stream but only in small, discrete packets called quanta. From this, Bohr theorized that electrons have several possible energies corresponding to several possible orbits at different distances from the nucleus. Therefore an electron has to be in one specific energy level; it cannot exist between energy levels. In other words, the energy of the electron is said to be quantized. Bohr also stated that when a hydrogen atom absorbed one or more quanta 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 energy levels 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 5. 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 Schrqdinger, an Austrian physicist, created a mathematical model that described electrons as waves. Using Schrqdinger’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 1*s*. It is important to understand what the spherical shape of the 1*s* 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 1*s* 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.

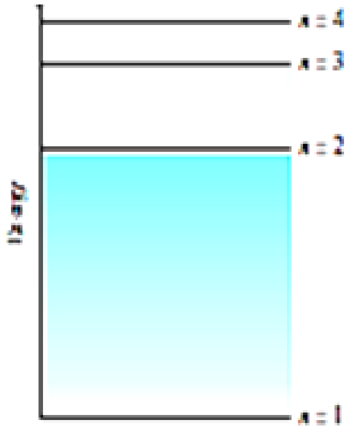


Fig.6

Fig.7

Were present this spin with an arrow ↑↓ . 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, 2*s* and 2*p*. Like 1*s* in the first principal energy level, the 2*s* 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 2*p*. The 2*p* 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.

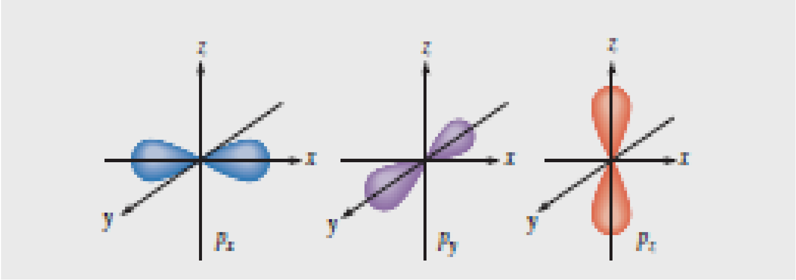


Fig.8

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 1*s* orbital. The second principal energy level has a 2*s* and three 2*p* orbitals labeled $2p_x$, $2p_y$ and $2p_z$, as shown in Figure 9.

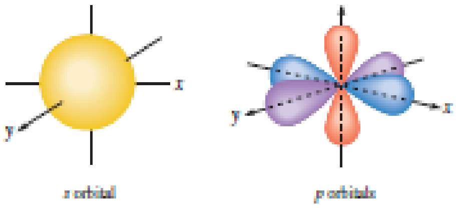


Fig.9

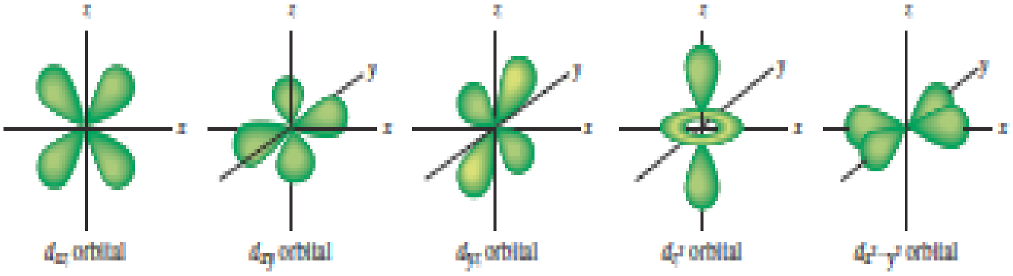
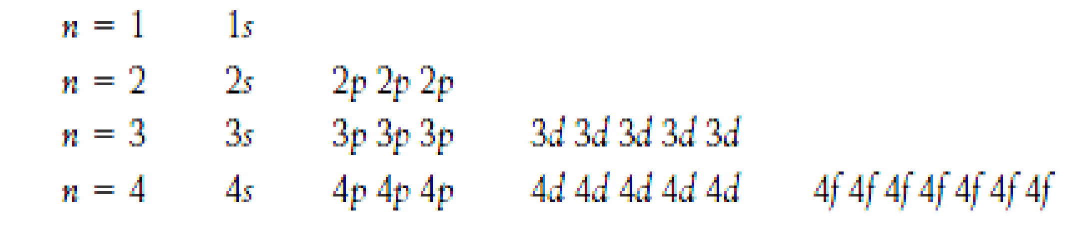


Fig.10.

The third principal energy level has three sublevels labeled 3s,3p and 3*d*. The 3*s* orbital is spherical and larger than the 1*s* and 2*s* orbitals. The 3p$_x$ 3p$_y$, 3p$_z$ orbitals are shaped like those of the second level, only larger. The five 3*d* 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 4*s*, 4*p*, 4*d*, and 4f orbitals. There are one 4*s*, three 4*p*, five 4*d*, 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 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 1*s* 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.

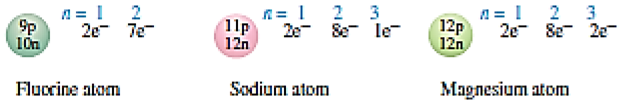
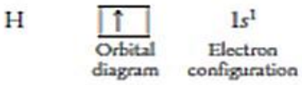


Fig. 11.

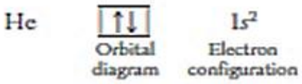
Often we are interested in showing the arrangement of the electrons in an atom in their orbitals. There are two ways to do this. The first method is called the electron configuration. In this method, we list each type of orbital, showing the number of electrons in it as an exponent. An electron configuration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

We can also represent this configuration with an in which boxes represent the orbitals (containing small arrows indicating the electrons when the orbital contains one electron, an arrow, pointing upward (↑) is placed in the box. A second arrow, pointing downward (↓) 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 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 4*s*. Hydrogen, the first element, has only one electron. The electron will be in the 1*s* orbital because this is the most favorable position (where it will have the greatest attraction for the nucleus). Both representations are shown here:

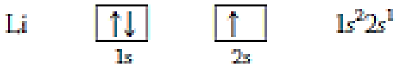


Helium, with two electrons, can be shown as

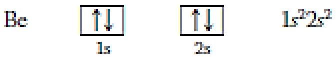


The first energy level, which can hold a maximum of two electrons, is now full. An atom with three electrons will have its third electron in the second energy level. Thus, in lithium (atomic number 3), the first two electrons are in the 1*s* orbital, and the third electron is in the 2*s* orbital of the second energy level.

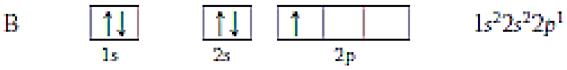
Lithium has the following structure:



All four electrons of beryllium are *s* electrons:

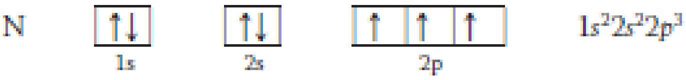


The next six elements illustrate the filling of the *p* orbitals. Boron has the first *p* electron. Because *p* orbitals all have the same energy, it doesn't matter which of these orbitals fills first:



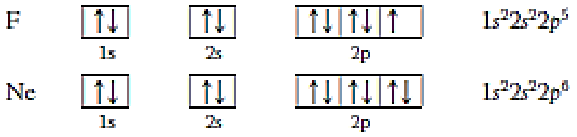
Carbon is the sixth element. It has two electrons in the 1*s* orbital, two electrons in the 2*s* orbital, and two electrons to place in the 2*p* orbitals. Because it is more difficult for the *p* electrons to pair up than to occupy a second *p* orbital, the second *p* electron is located in a different *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 1*s*, 2*s*, and 2*p* orbitals. The third *p* electron in nitrogen is still unpaired and is found in the $2p_z$ orbital:



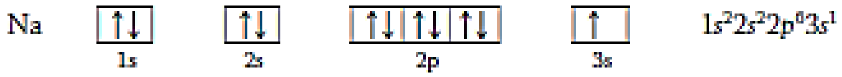
Oxygen is the eighth element. It has two electrons in both the 1*s* and 2*s* orbitals and four electrons in the 2*p* orbitals. One of the 2*p* orbitals is now occupied by a second electron which has a spin opposite the electron already in that orbital:

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



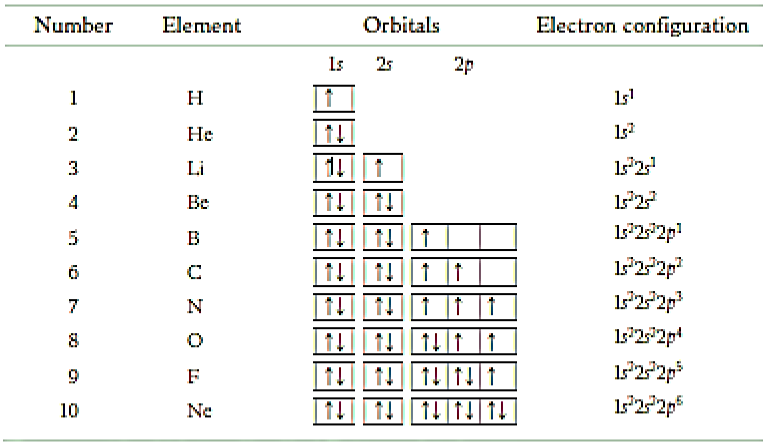
With neon, the first and second energy levels are filled as shown in table 3. The second energy level can hold a maximum of eight electrons, $2s^2$ $2p^6$.

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 3*s* orbital in the third energy level



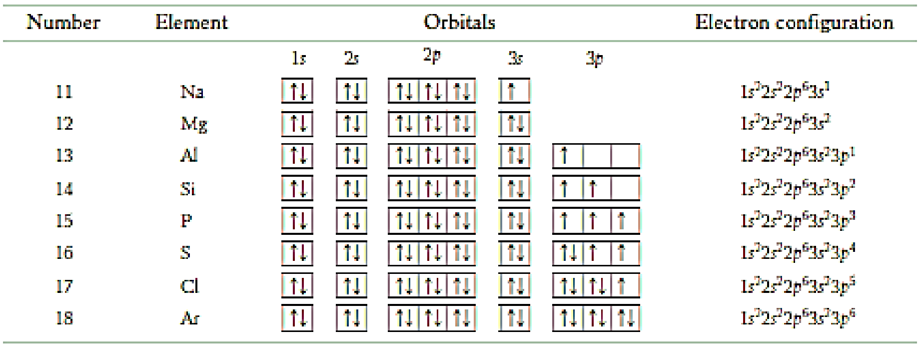
Magnesium (12), aluminum (13), silicon (14), phosphorus (15), sulfur (16), chlorine (17), and argon (18) follow in order. Table 4 summarizes the filling of the orbitals for elements 11–18. The electrons in the outermost (highest) energy level of an atom are called the valence electrons. For example,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

Table. 3



Number	Element	Orbitals 1s	Orbitals 2s	Orbitals 2p	Electron configuration
1	H	↑			$1s^1$
2	He	↑↓			$1s^2$
3	Li	↑↓	↑		$1s^2 2s^1$
4	Be	↑↓	↑↓		$1s^2 2s^2$
5	B	↑↓	↑↓	↑	$1s^2 2s^2 2p^1$
6	C	↑↓	↑↓	↑ ↑	$1s^2 2s^2 2p^2$
7	N	↑↓	↑↓	↑ ↑ ↑	$1s^2 2s^2 2p^3$
8	O	↑↓	↑↓	↑↓ ↑ ↑	$1s^2 2s^2 2p^4$
9	F	↑↓	↑↓	↑↓ ↑↓ ↑	$1s^2 2s^2 2p^5$
10	Ne	↑↓	↑↓	↑↓ ↑↓ ↑↓	$1s^2 2s^2 2p^6$

Table. 4.



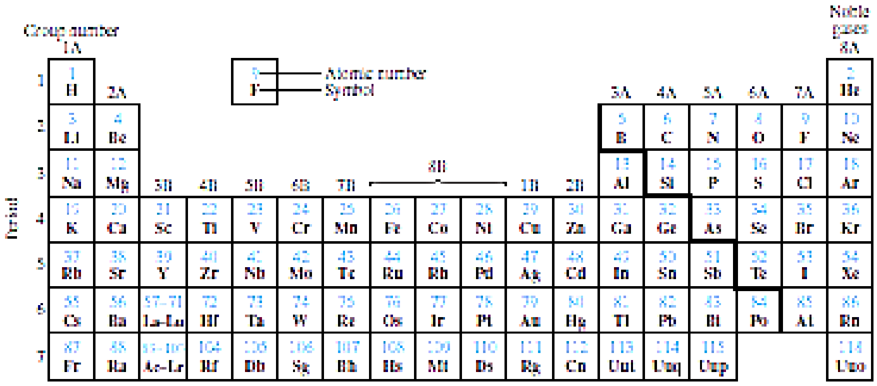
Number	Element	Orbitals 1s	Orbitals 2s	Orbitals 2p	Orbitals 3s	Orbitals 3p	Electron configuration
11	Na	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑		$1s^2 2s^2 2p^6 3s^1$
12	Mg	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓		$1s^2 2s^2 2p^6 3s^2$
13	Al	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^2 3p^1$
14	Si	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^2$
15	P	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^3$
16	S	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑	$1s^2 2s^2 2p^6 3s^2 3p^4$
17	Cl	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑	$1s^2 2s^2 2p^6 3s^2 3p^5$
18	Ar	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	$1s^2 2s^2 2p^6 3s^2 3p^6$

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?



Group number

Noble gases

1 — Atomic number
H — Symbol

Period	1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	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											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 Uut	114 Uuq	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:

$$\mathrm{Na} \qquad [\mathrm{Ne}]3s^1$$

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:

B	$1s^22s^22p^1$	$[\mathrm{He}]2s^22p^1$
Cl	$1s^22s^22p^63s^23p^5$	$[\mathrm{Ne}]3s^23p^5$
Na	$1s^22s^22p^63s^1$	$[\mathrm{Ne}]3s^1$

The sequence for filling the orbitals is exactly as we would expect up through the 3*p* orbitals. The third energy level might be expected to fill with 3*d* electrons before electrons enter the 4*s* 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

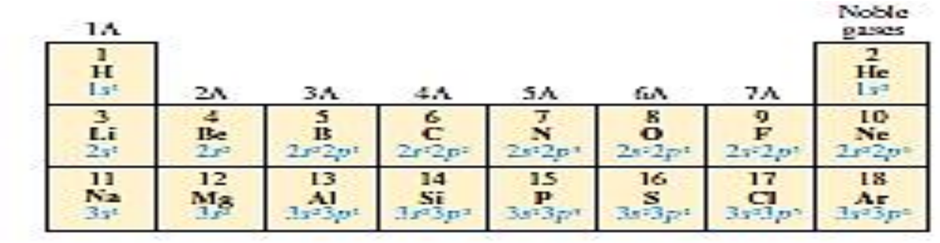


Fig.13.

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.

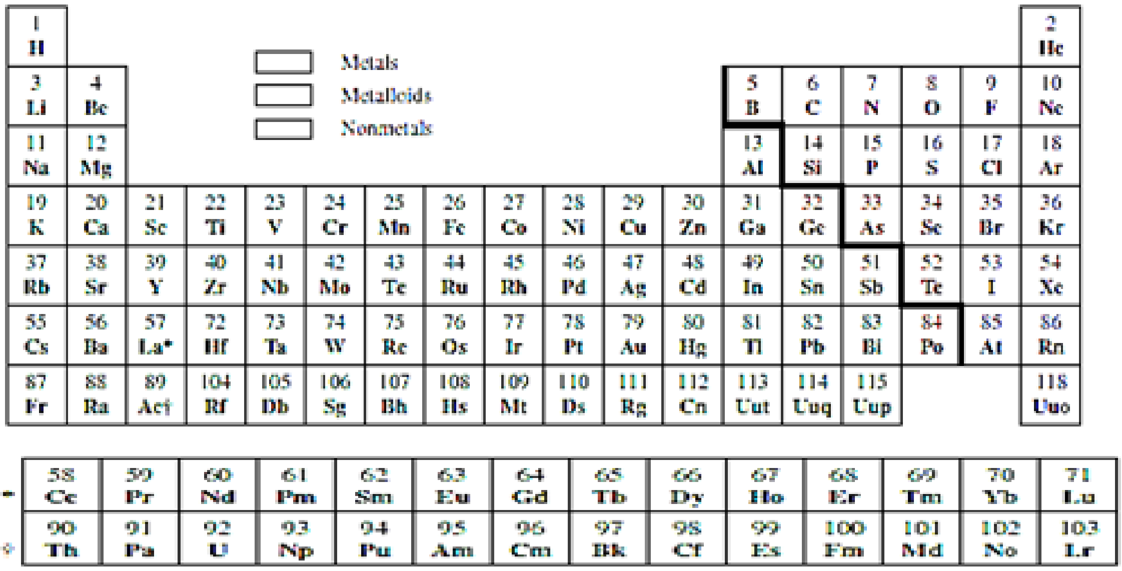
Several elements (boron, silicon, germanium, arsenic, antimony, tellurium, and polonium) are classified as **metalloids** and have properties that are intermediate between those of metals and those of nonmetals. Certain metalloids, such as boron, silicon, and germanium, are the raw materials for the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

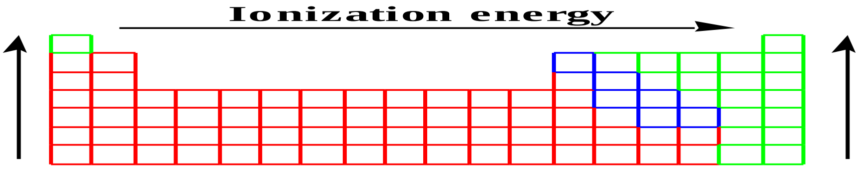
Ionization Energy:

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

Na + ionization energy → Na^- + e^-

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.

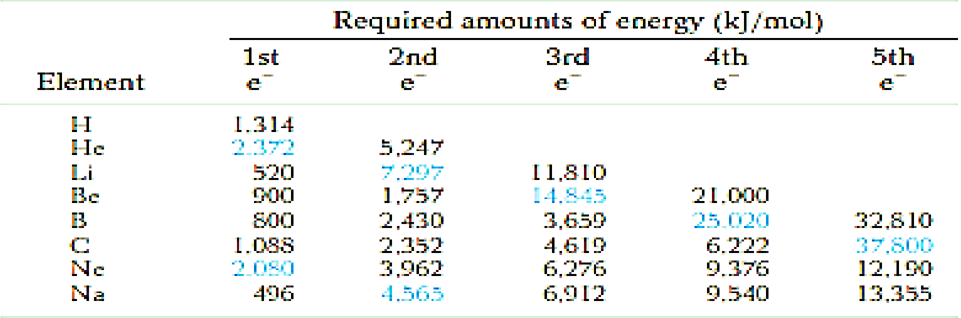
Table 8 gives the ionization energies for the removal of one to five electrons from several elements. The table shows that even higher amounts of energy are needed to remove the second, third, fourth, and fifth electrons. This makes sense because removing electrons leaves fewer electrons attracted to 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 6*s* electron much more easily than the metal lithium gives up its 2*s* 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.

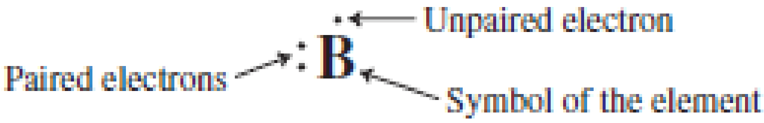


	Required amounts of energy (kJ/mol)				
Element	1st e^-	2nd e^-	3rd e^-	4th e^-	5th e^-
H	1,314				
He	2,372	5,247			
Li	520	7,297	11,810		
Be	900	1,757	14,845	21,000	
B	800	2,430	3,659	25,020	32,810
C	1,088	2,352	4,619	6,222	37,800
Ne	2,080	3,962	6,276	9,376	12,190
Na	496	4,565	6,912	9,540	13,355

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.

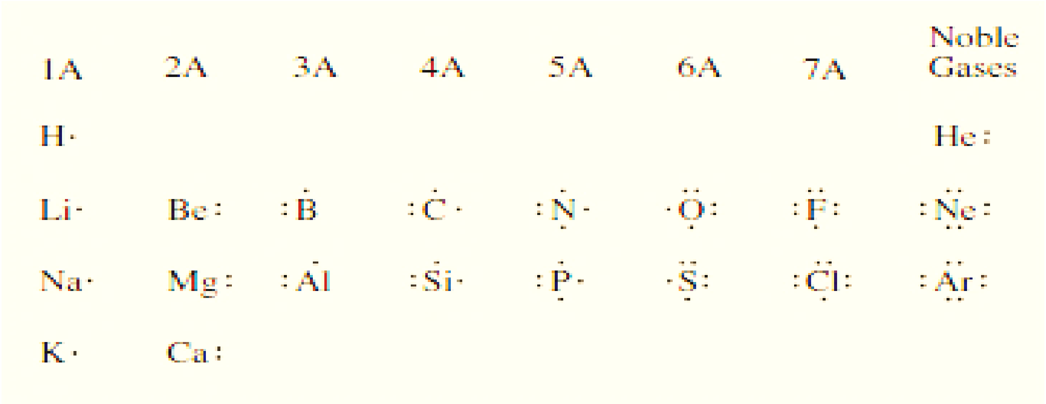
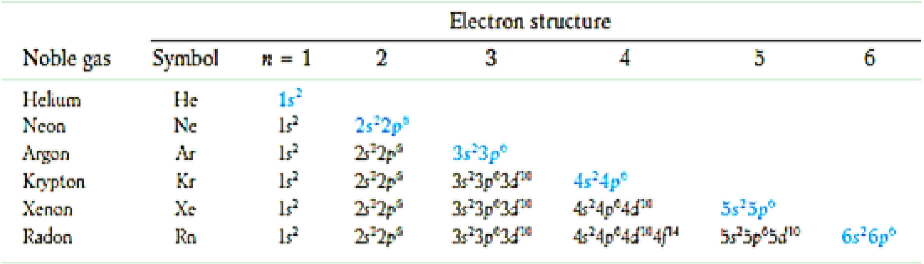


Fig.16

The ionic bond:

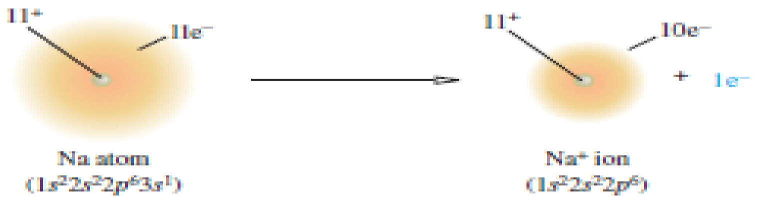
The chemistry of many elements, especially the representative ones, is to attain an outer electron structure like that of the chemically stable noble gases. With the exception of helium, this stable structure consists of eight electrons in the outermost energy level (Figure 6).

Table. 6.



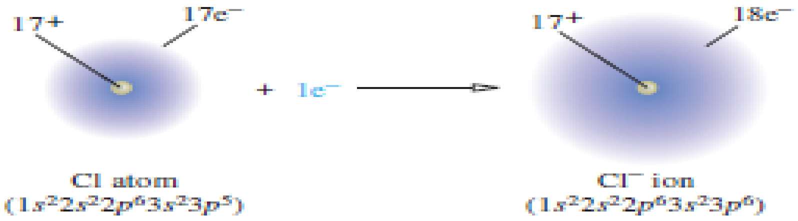
		Electron structure					
Noble gas	Symbol	$n = 1$	2	3	4	5	6
Helium	He	$1s^2$					
Neon	Ne	$1s^2$	$2s^2 2p^6$				
Argon	Ar	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$			
Krypton	Kr	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6$		
Xenon	Xe	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}$	$5s^2 5p^6$	
Radon	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 3*s* 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 + signs and is written as a superscript after the symbol of the element Na^+. A chlorine atom with seven electrons in the third energy level needs one electron to pair up with its one unpaired 3*p* electron to attain the stable outer electron structure of argon. By gaining one electron, the chlorine atom becomes a chloride ion 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 3*s* electron from the sodium atom transfers to the half-filled 3*p* orbital in the chlorine atom to form a positive sodium ion and a negative chloride ion. The compound sodium chloride results because the Na^+ and 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).

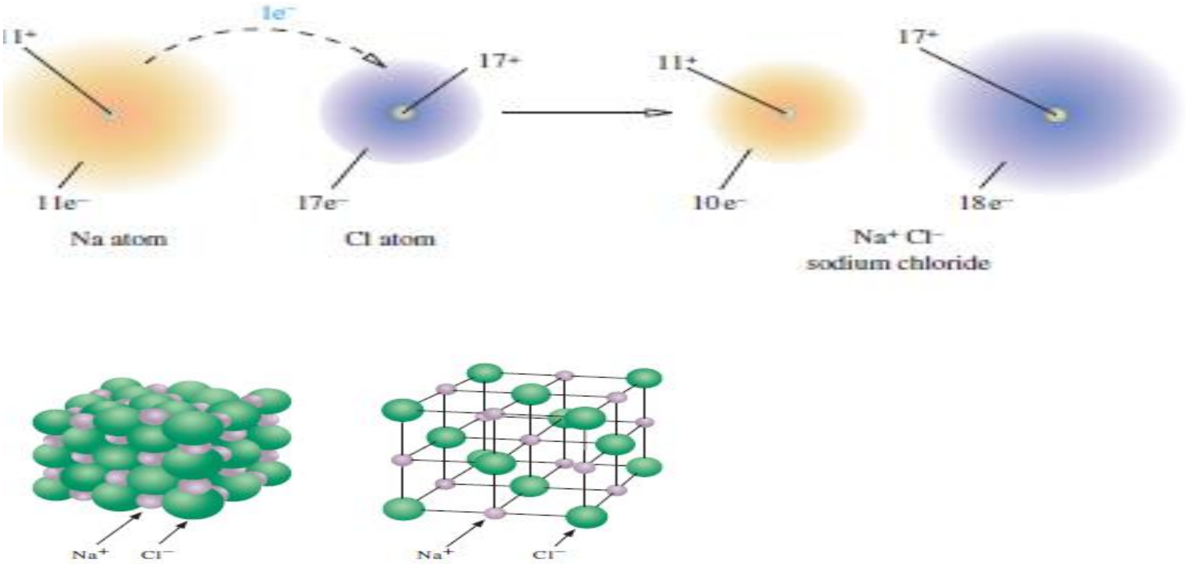


Fig.17.

The Lewis representation of sodium chloride formation is;

$$\mathrm{Na\cdot} + \mathrm{\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:} \longrightarrow \mathrm{Na^{+}} + \left[\mathrm{:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:}\right]^{-}$$

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 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.

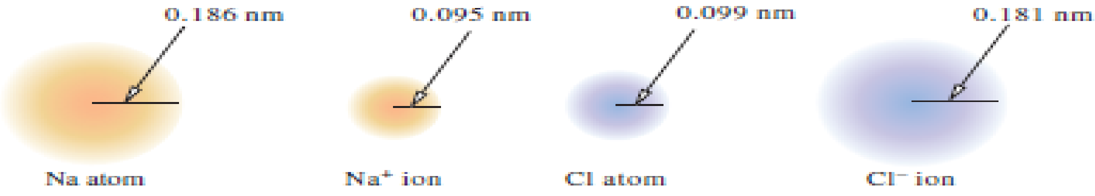
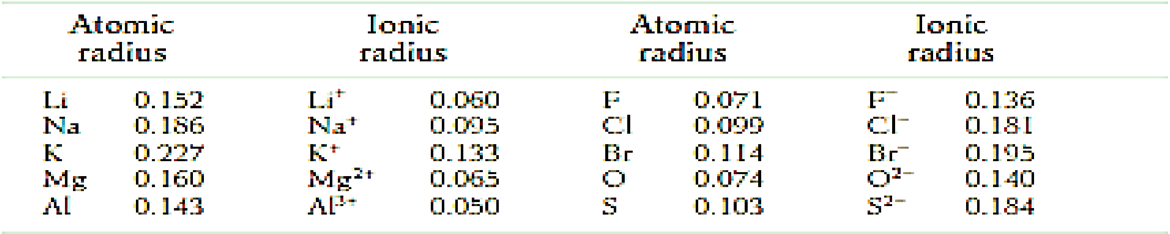


Fig. 18.

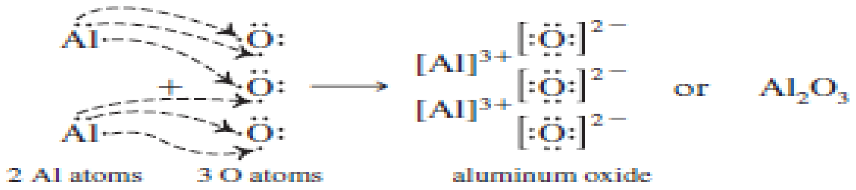
Table. 7.



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

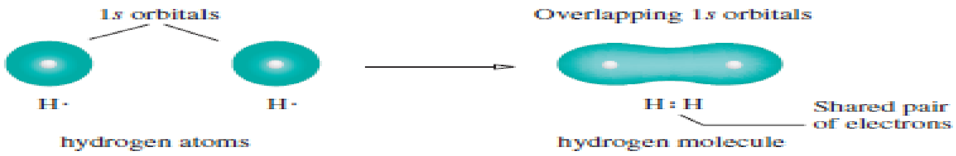
Formation of aluminum oxide Al_2O_3 from its elements.



The covalent bond: sharing electrons

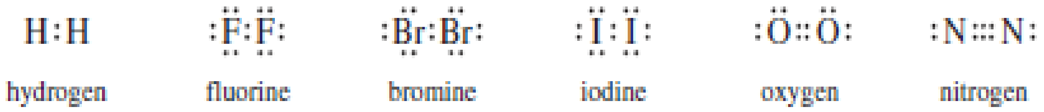
Some atoms do not transfer electrons from one atom to another to form ions. Instead they form a chemical bond by sharing pairs of electrons between them. A covalent bond consists of a pair of electrons shared between two atoms. This bonding concept was introduced in 1916 by G. N. Lewis. In the millions 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 H_2 involves the overlapping and pairing of 1*s* 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 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 3*p* electron orbital of one chlorine atom overlaps the unpaired 3*p* 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 H_2 oxygen nitrogen O_2 fluorine F_2 bromine Br_2 and iodine 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.

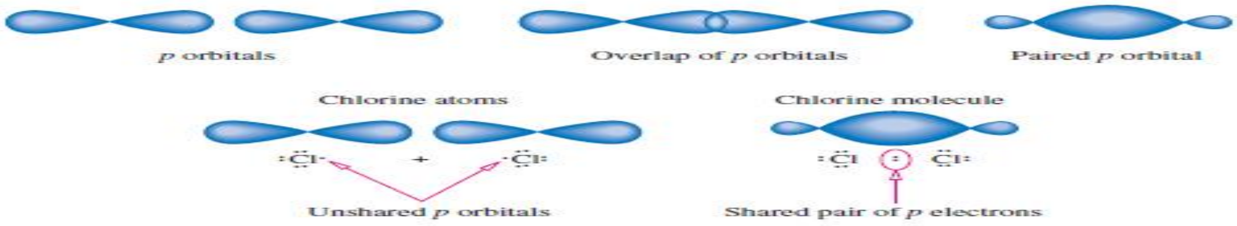


Fig.19

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, δ.

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.

$$\mathbf{X + e^{-} \rightarrow X^{-} + energy}$$

- 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.

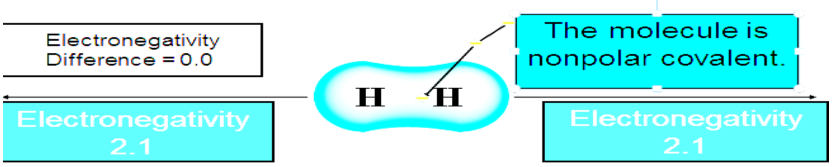
This charge difference is a result of the unequal attractions the atoms have for their shared electron pair.

Relating bond type to electronegativity difference

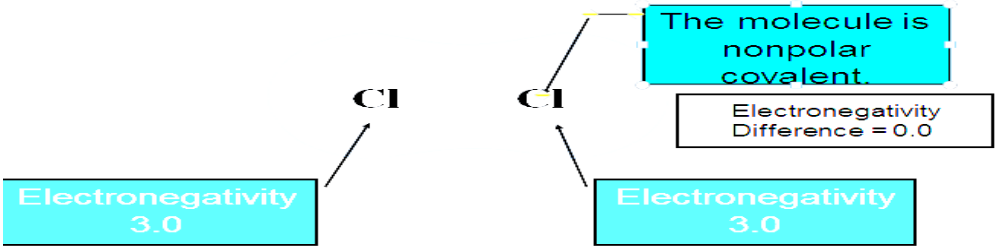
The polarity of a bond is determined by the difference in electronegativity values of the atoms forming the bond.

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

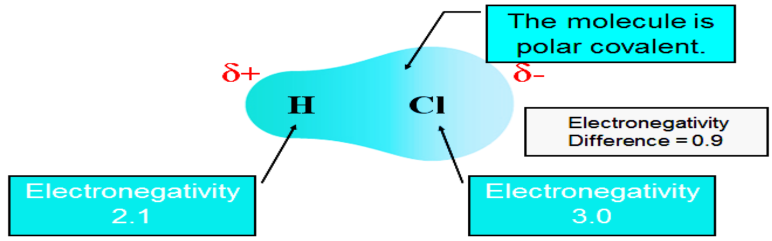
If the electronegativities are the same, the bond is nonpolar covalent and the electrons are shared equally.



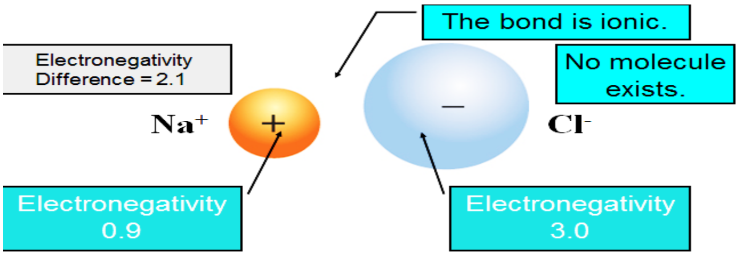
Hydrogen Molecule



Chlorine Molecule



Hydrogen Chloride Molecule



Sodium Chloride

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 (- δ) is on the more electronegative atom (Cl); the partial positive charge (+δ) resides on the less electronegative atom (H). The bond polarity is indicated by an arrow (↔), with the plus sign indicating the partial positive charge (+δ) on the less electronegative atom, and the arrow pointing to the partial negative charge (- δ) 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 (- δ) where the electron density is concentrated, and a partial positive (+δ) 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 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:

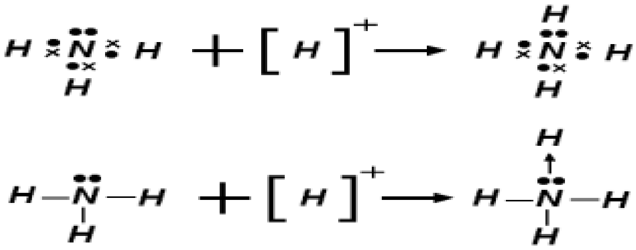
Water, H_2O, has two polar bonds and, because of its geometry, is a polar molecule

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.

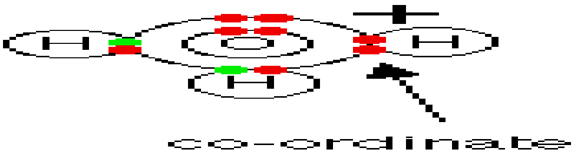
Example 1: $:C\vdots\vdots O: \rightarrow C\overset{\leftarrow}{=}O$

Example 2: Ammonium ion NH_4^+



+

Example 3: Hydronium ion H_3O^+



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.

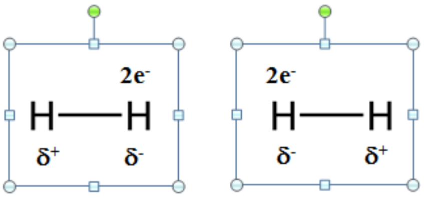


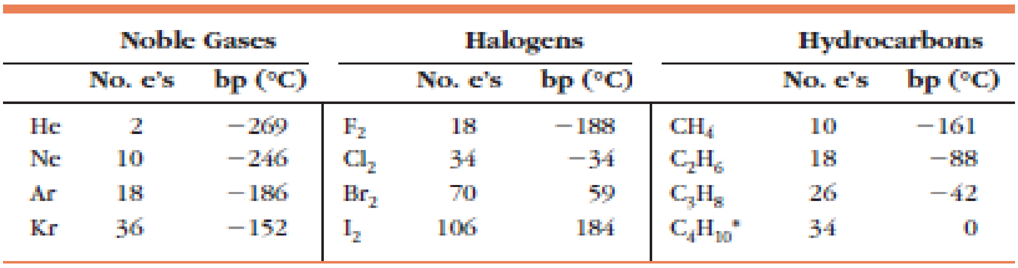
Fig. 21

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's	bp (°C)		No. e's	bp (°C)		No. e's	bp (°C)
He	2	−269	F_2	18	−188	CH_4	10	−161
Ne	10	−246	Cl_2	34	−34	C_2H_6	18	−88
Ar	18	−186	Br_2	70	59	C_3H_8	26	−42
Kr	36	−152	I_2	106	184	C_4H_{10}*	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_2 (bp =34 °C) compared with F_2 (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_2 (59 °C) is higher than that of Cl_2 (-34 °C), indicating stronger London forces among Br_2 molecules than among Cl_2 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_5H_{12}) 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-dimethylpropane molecule does not allow as much close contact.

pentane, bp = 36.0 °C

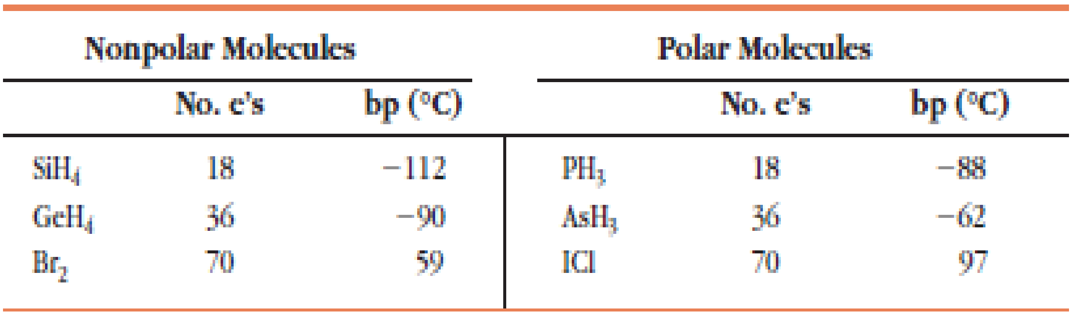
2,2-dimethylpropane, bp = 9.5 °C

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_2 (97 °C) with dipole-dipole attractions and nonpolar Br_2 (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).

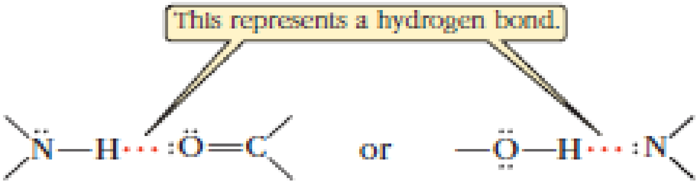
Table. 9.



Nonpolar Molecules			Polar Molecules		
	No. e's	bp (°C)		No. e's	bp (°C)
SiH_4	18	−112	PH_3	18	−88
GeH_4	36	−90	AsH_3	36	−62
Br_2	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-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.

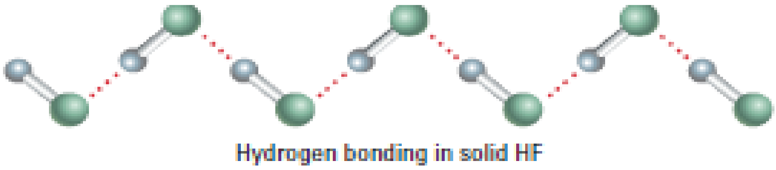
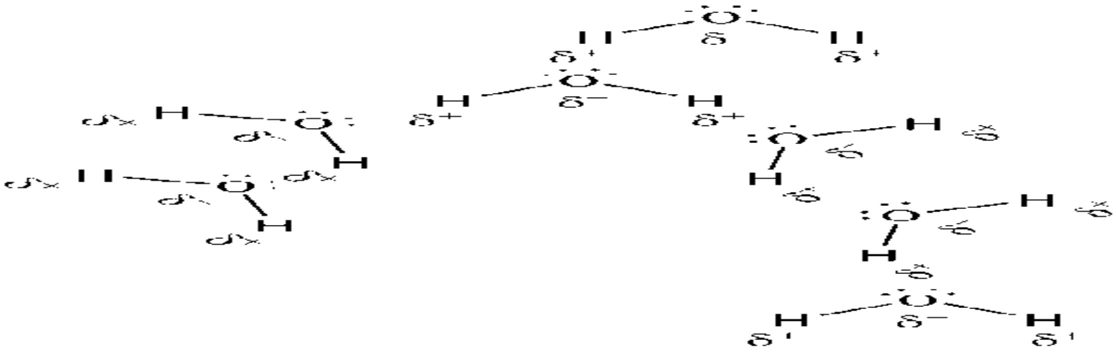
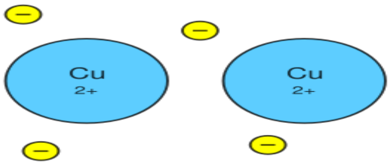


Fig.22

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: CH_4, NH_3, H_2S, H_2Se, H_2Te, PH_3, HF, and HCl. But H_2O is a liquid at room temperature, indicating a strong degree of intermolecular attraction.



Metallic BondingThe “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.

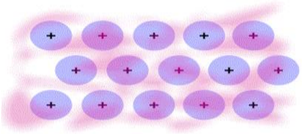


Fig.23.

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 descirbe3 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 at5 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.

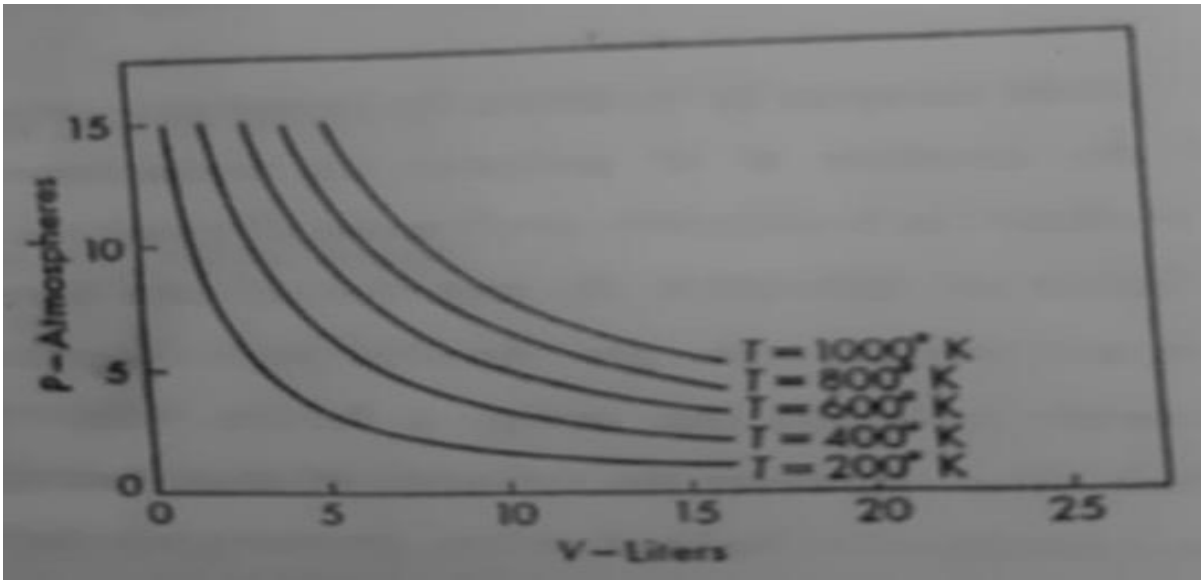
Boyle's Law

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 x 103 Pa, its pressure was increased to 1.5 x 104Pa at a constant temperature. What will be the new volume of the gas?

Solution: According to Boluyl's law

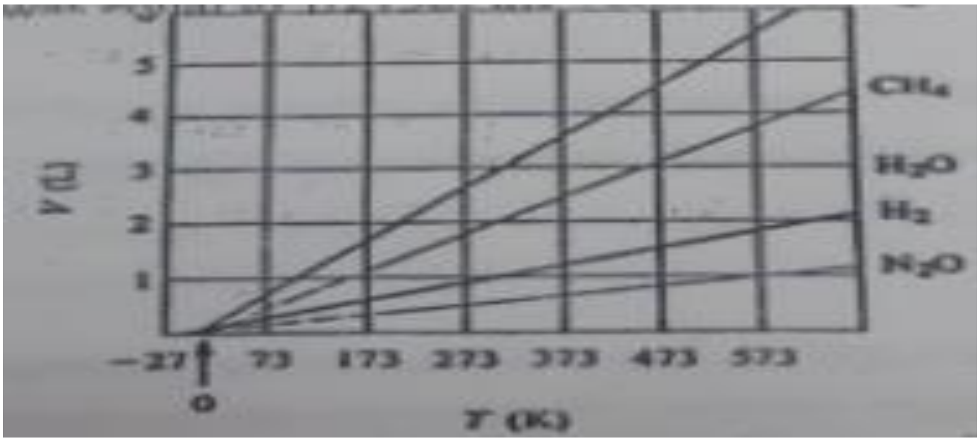
$$P_1V_1 = P_2V_2$$

$5.6 \times 103 \times 1.53 = 1.5 \times 104 \times V_2$

$V_2 = 5. \times 103 \times 1.53 / 1.5 \times 104 = 0.57$ L

Charles or Bay-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 ^{o}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^{o}C. However, it was Gay-Lussac who first found that for the increase in volume for each degree centigrade rise is temperature was equal to 1/273of the volume of the gas at 0^{o}C.



Plots of V versus T (in ^{o}C or K) for several gases.

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

$$V = V_o + (1/273)\ V_o$$

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

$$= V_o\ \{272+t)/273$$

On the absolute or Kelvin scale, the temperature -273. ^oC is defined as 0 K, which leads to the relation.

$$T\ (K) = t(^oC) + 273$$

Then the Gay-Lussac's relation becomes simply

$$V/V_o = T/T_o$$

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 ^oC and 1 atm. has a volume of 2.28 L. What volume will this gas occupy at 38^oC and 1 atm.

Solution From Charles law we have

$$V_1/V_2 = T_1/T_2$$

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

$V_2 = 2.58 \times 311/288$

$V_2 = 2.79$ 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 $V = k_3n$

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:

$$V / V_1 = T / T^{/}$$
$$\mathbf{V_1 = VT / T^{/}}$$

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,

$$P^{/} V^{/} T = PV T^{/}$$

$$PV/T = P^{/} V^{/} / T^{/}$$

Or

$$PV/T = P^{/} V^{/} / T^{/} = \text{Constant} = R$$

For n gram mole of gas

$$PV = nRT$$

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=PV /nT

If we compensate for the volume in liters and the pressure in the atmosphere, then:
R = 22.4 x 1/273 = 0.082 [liter of atmosphere / degree of Gram]
If instead of volume in cubic centimeters and pressure in the atmosphere, then:
R = 22400 x 1/273 = 82 [atmosphere / degree Cm^3]
If the volume is estimated in cubic centimeters and pressure in debt, then:
R = 22400 x 76 x 13.6 x 980.6 / 273 = 8.314 x 107 [Erg/°G]
Since Joule = 107 Erg, (R = 8.314 Joule degree^{-1} 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 ^{o}C and a pressure of 1.5 atm. Calculate the moles of 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

$$P_1V_1 = nRT = P_2V_2$$

$$P_2 = P_1V_1/V_2$$

$$= 1.68 \text{ x } 3.5/1,35 = 4.4 \text{ atm.}$$

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

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

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

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:

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

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:

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

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

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

where n_{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,

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

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

Similarly, $P_2 = X_2P\ _{Total}$ - $P_3 = X_3P_{Total}$ - $P_4 = X_4P_{Total}$, and so on, where X_1, X_2, X_3,.... 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.,

$$X_1 + X_2 + X_3 + ... = 1$$

Problem: A sample of 46 L of oxygen at 25^{o}C and 1 atm. was pumped along with 12 L of helium at 25^{o}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^{o}C

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

$n = PV/RT$

$nO_2 = 1.0 \times 46 / (0.082 \times 298) = 1.9$ mol

$nO_2 = 10 \times 12 / (0.082 \times 298) = 0.49$ mol

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

$P = nRT/V$

$P_O = 1.9 \times 0.082 \times 298/ 50 = 9.3$ atm.

$PH_2 = 0.49 \times 0.082 \times 298/ 5.0 = 2.4$ atm.

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

$P_{Total} = PO_2 + PH_2$

$= 9.3 + 2.4 = 11.7$ atm

$XO_2 = PO_2/P_{Total} = 156/743 = 0.21$

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. His 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 and be the rates of diffusion (or effusion) of two gases, and p_1 and p_2 be their respective densities, then: where M_1 and M_2 are the molecular or atomic weights of the two gases, respectively.

$$f_1 /f_2 \qquad \surd\ d_2/d_1$$

According to this law, the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density. If f_1 and $f_2$represents the rates of diffusion of two gases whose densities under the given conditions are d_1 and d_2 respectively, then:

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

$$f_1/f_{2_1} \quad = \quad \surd\ M_2/M_1$$

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.

$$t_2/t_1= \quad \surd\, d_2/ d_1 \quad = \quad \surd\ M_2/M_1$$

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

<u>Example:</u> :

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.

<u>Solution</u>:

Molecular weight of oxygen = 32

Molecular weight of hydrogen = 2

Density of oxygen related to hydrogen $d_1 = 32/2 = 16$

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

$$1.44/1.80 = d_2/16$$

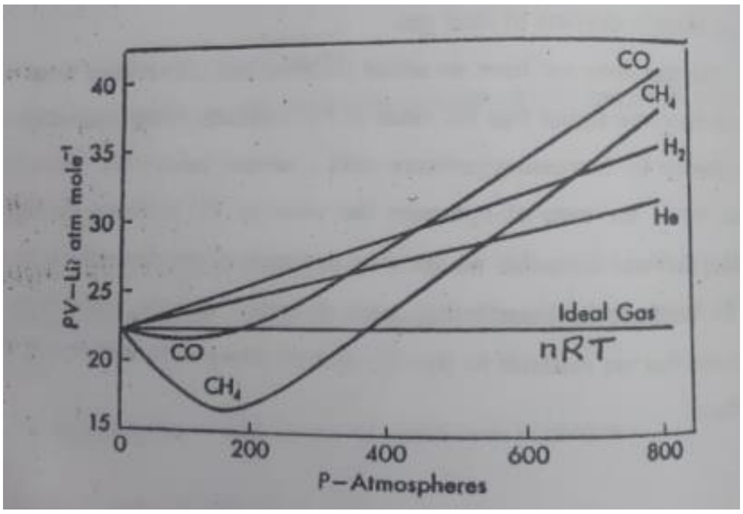
Real Gases

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:

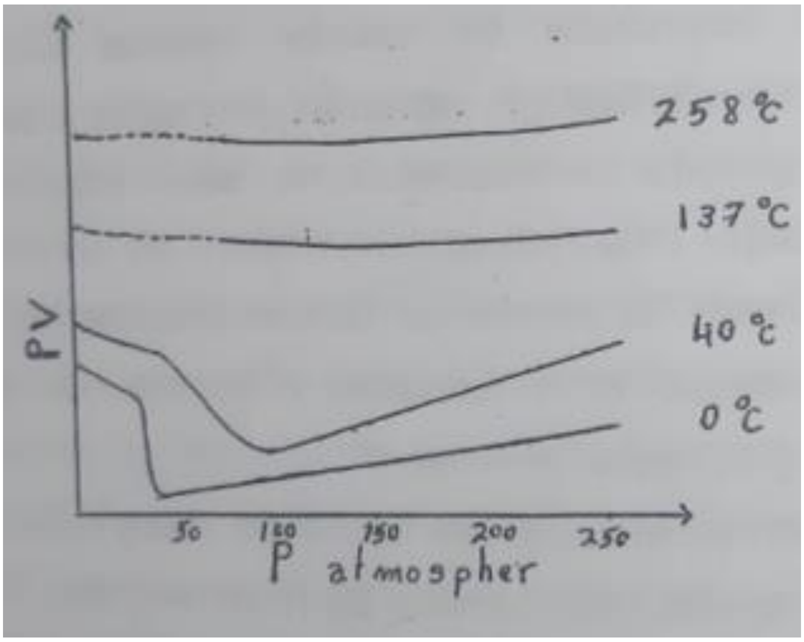
firstly, that the value of volume is less than is consistent with Boyle's law, that is, when gas is compressed, its volume decreases by a greater amount than is consistent with Boyle's law due to the presence of another factor, which is the attraction between the particles increase in impact when the 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 (-80ºC 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^{o}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**

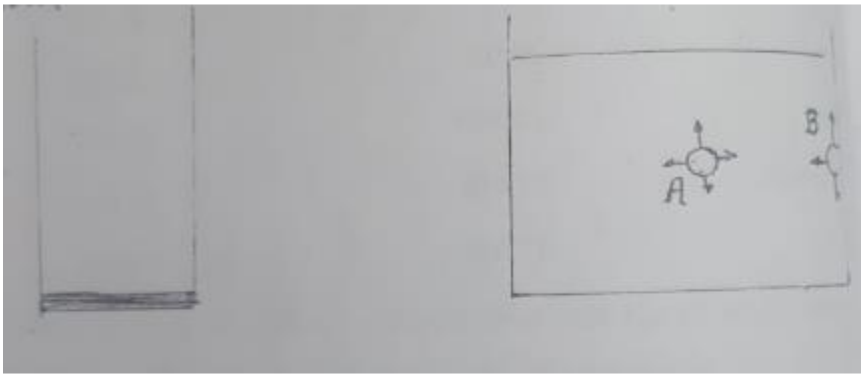
Gas	Molecular weight	Volume 1mol at 0^oC and 1 atm.
Hydrogen	2.016	22.724
Nitrogen	28.020	22.405
Oxygen	32.000	22.394
Carbon dioxide	44.010	22.264
Ammonia	17.030	22.084

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 if the molecules came 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 add to the measured pressure is proportional to n^2. If V is the volume occupied by 1 mole of gas then:

$n \propto 1/V$ and $n^2 \propto 1/V^2$

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

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 ab/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:

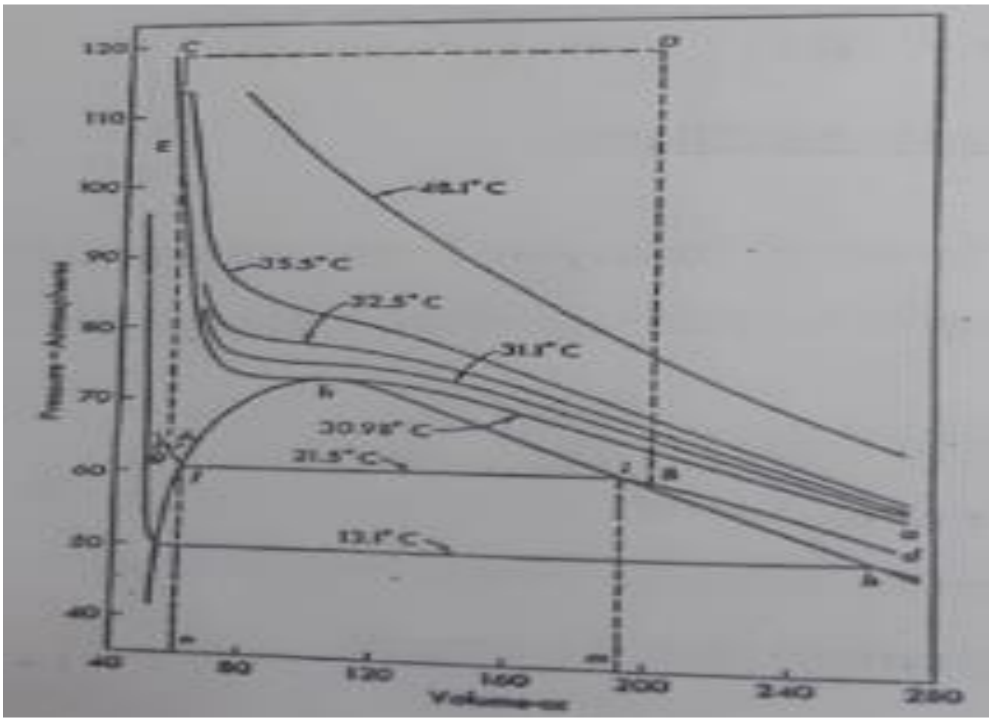
$$PV = RT + Pb$$

The Liquefaction of Gases

The Critical State:

At the beginning of the nineteenth century a number of gases such as carbon dioxide, sulpher 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 dioxid. 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 pause 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.

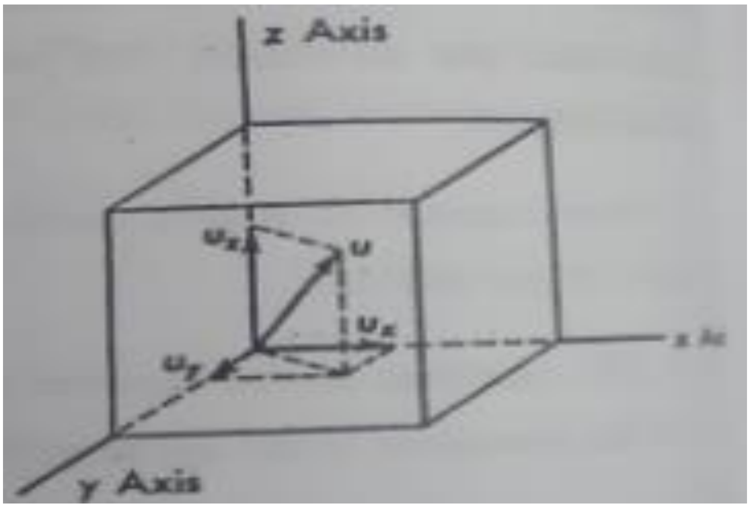
(5) The gas molecules are so small compared to the intermolecular distance that the volume of the individual particles can be assumed to be negligible.

(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

$$u^2 = u^2_x + u^2_y + u^2_z$$

where u is called the root mean square velocity. Suppose that the molecule of mass m is moving in the x-direction o the right with velocity u^2. It will strike the yz-plane with a momentum "mux" and, since the collision is elastic, it will rebound with velocity - ux and momentum - mux. Since the number of shocks per second in this direction is (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 mx (x/L) = $2mx^2/L$ (g cm s^{-2} or dyne)

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

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

$$= (2m/L)(u^2_x + u^2_y + u^2_z)$$

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

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 exact a similar force, so that total force due to collisions of n molecules = $2m/L\,(u_1^2 + u_2^2 +. .+ u^2 n)$ dynes where u_1 , u_2 , . . . u_n are the velocities of the individual molecules.

$$2nmu^2/L$$

So that total force due to collisions of n molecules=$2nmu^{-2}/L$ 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 molecule is given by:

$$\text{Pressure} = 2\,n\,mu^{-2} / L\ x6L^2 = n\,m\,u^{-2} / 3L^3 \text{ dynes cm}^{\overset{---}{-2}}$$

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

$$P = m\,n\,u^2/3V$$

Or $\qquad PV = 1/3\ m\,n\,u^2$

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

$PV = 1/3\ nm\,u^2$, $\qquad K_e = 1/2\ mu^2$

$PV = 2/3\ n\,(1/2\ mu^2) = 2/3\ n\,K_e$ [K_e 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 n 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:

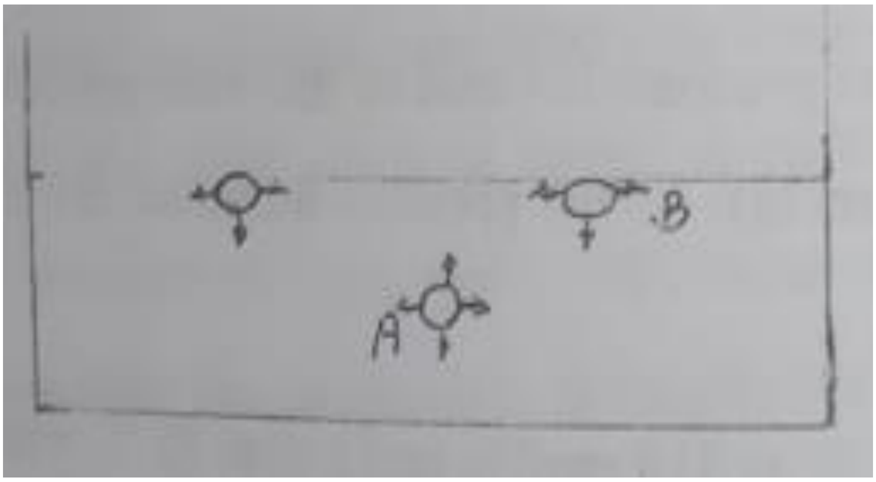
The boiling process is characterized about the evaporation. Boiling is not a surface phenomenon and occur at constant temperature and began the all the liquid to transfers to vapor, and its pressure is equal to the outer pressure. Water is boiling at 100 ^{o}C at 1 atm (760 mmHg). As the pressure increased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

Water boil at 102 ^{o}C at 816 mmHg and boil at 52 ^{o}C when the pressure at 100 mmHg.

Surface Tension

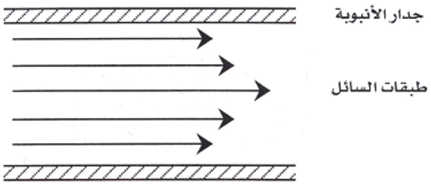
A molecule in the interior of a liquid is completely surrounded by other molecules and so on the average it is attracted equally in all directions. On the molecule in the surface there is a resultant attraction inwards, because the number of molecules per unit volume is greater in the liquid than in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

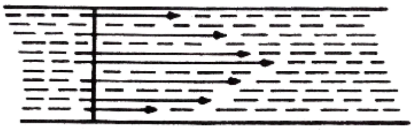
As a sequence of this inward pull, the surface of the liquid always tends to contract to smallest possible area, it is for this reason that drops of liquid and bubbles of gas become spherical, as far as feasible for the surface area is then a minimum for the given volume. In order to extend the surface 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 1Cm^2 is called the surface energy, as a results 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 erg/Cm^2 this equivalent to dynes/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 dynes/Cm^2/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 ~ 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 altitudes 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

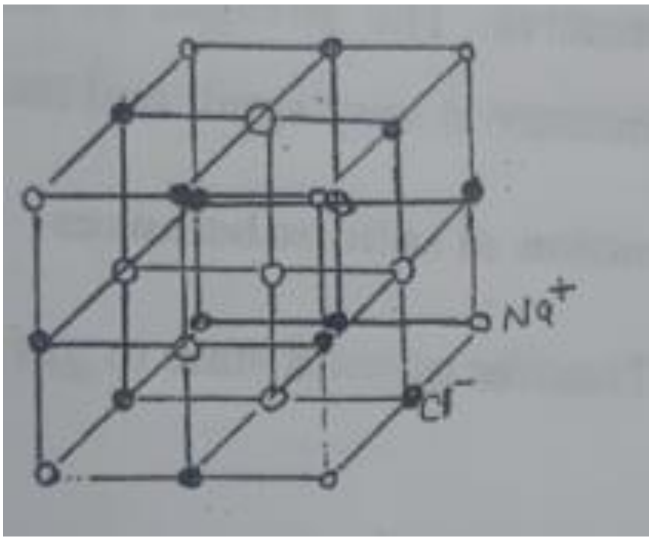
Crystallization of the substance:

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 lose 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 Cl^- and 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 ^{o}C and temperature -56 ^{o}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.

HOMOGENOUS CHEMICAL EQUILIBRIUM

Chemical equilibrium

It is the familiar and well established fact that many reactions do not go to completion. They proceed to a certain point and then apparently ceases, often leaving considerable amounts of unaffected reactants. The remarkable fact is that under any given set of temperature, pressure, and concentration, the point at which any reaction seems to stop is always the same i.e. there exists at this point among the concentrations of the various reactants and products of any reaction a relationship which is definitely fixed. When a reaction reaches this stage in the course, it is said to be in equilibrium.

Some of chemical reactions proceed with high speed such as neutralization reactions and precipitation reactions (spontaneous reactions). While some other reactions proceed slowly such as interaction of oxygen and hydrogen at normal temperatures and in the absence of catalyst. But the greater are gaseous reactions, inorganic and organic in solutions reactions happened with reasonable speed.

The rate of chemical reactions not depends only on the nature of interacting substances but also depend on other factors:

Temperature
Catalysts
Concentrations (pressure in case of gases)
Stirring

Effect of temperature:

Vant Hoff was found that when the temperature of reaction increased by (10 ^{o}C) the rate of reaction increased four times. This is due to the interaction between reactants substances that to happen it must collide with each other and increasing the temperature leads to increase of particles energy movement and activity increased and thus to the possibility of increasing the number of effective colloid of them.

For example interaction between O_2 and H_2 not happened at normal temperature. While the interaction with reasonable speed at more than 600 ^oC.

Effect of concentration (pressure):

Increasing of the reactants concentration lead to increasing the chance of number of collides between the reactant molecules, in result increasing the reaction rate. Doubling the concentration of one of the substance interacting or both lead to increasing the reaction velocity four times for Example:

$Na_2S_2O_3 + HCl \rightarrow 2NaCl + SO_2 + H_2O + S$

In the reaction under study, if a certain amount of HCl acid to different solutions from the reaction mixture, the turbidity for sulfur separation was observed faster in the concentrated solutions faster than in diluted solutions. The increased pressure serves as an increased focus in the case of gaseous reactions.

Effect of Stirring and surface of interface:

This effect is apparent in the reactions where the interaction occur at interface between the reacted phases, for instance when a solid dissolve in a liquid that the rate of its solubility increases with stirring of the mixture, i.e increase the interface. Likewise, if the powdered sulfur is scattered on the surface of mercury, the two materials interact slowly, and if the two materials are mixed and scrubbed very strongly, the interaction between them takes place very quickly. It was also found that the greater the surface area exposed between the reactants, the faster the reaction occurred. Crushed iron, for example, rusts faster than iron found in large, cohesive masses.

Effect of catalysts:

Many chemical reactions can increase speed in the presence of trace amounts of materials that do not interfere in the reaction known catalytic helps the rate of reaction without consumption of catalyst.

Interactions are divided in terms of their occurrence to the two main types:

Irreversible reactions:

These reactions occur in one direction and the products have not chance to interact with each other once more. For instance, one of gas evolved from or one of the products coming out of the scope of interaction volatilization or sedimentation.

Example, $NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow$

The same occur when $Na_2CO_3 + HCl \rightarrow NaCl + H_2O + CO_2\uparrow$

In these reactions are consistent with the amounts outputs perfectly with the equation of the interaction of computational, that the reactants consumed completely.

Reversible reactions:

These reactions do not take place in one direction only until completeness, but the resulting materials remain in the reaction space and partially unite with each other to form the original materials. Accordingly, the quantities of the products are not quantitatively compatible with what is required by the reaction equation.

For example, $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

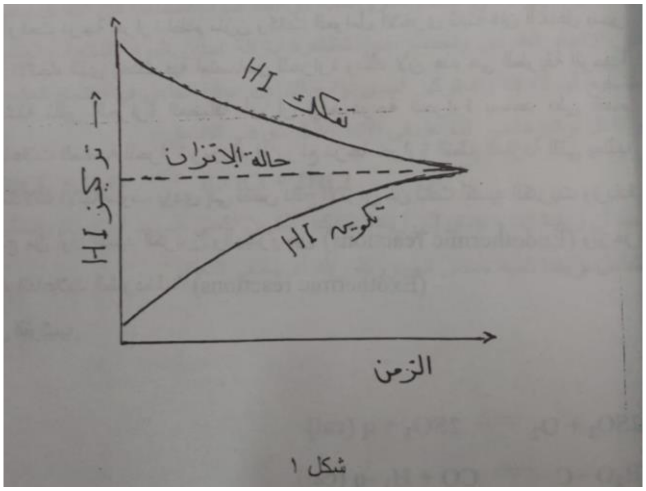
It was found that a 2/3 from both acid and alcohol including interaction and 1/3 with no matter how long interaction. This is due to the ethyl acetate and water; the resulting products interact with each other again to form acetic acid and alcohol. A state of equilibrium is reached when the reactions (forward and backward) speeds are equal.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Examples of these reactions: iodine and hydrogen union to form hydrogen iodide at a temperature of 450°C. Analysis of the reaction mixture at the end of the interaction found that 67% of the hydrogen iodide - 12% hydrogen and 12%. Unlike when interacting with H_2 and I_2 to form HI at the same degree of heat that always found the mixture containing 67% of hydrogen iodide.

The following curve illustrates the relation between the concentration of HI against time for both reaction (formation and dissociation of HI).

Example, $H_2 + I_2 \rightleftharpoons 2\,HI$



شكل ١

The le Chatelier-Braum principle

This rule is used in the descriptive study of the effect of different factors such as temperature, pressure and degree of focus on different equilibrium states and states that if a change occurs in one of the factors that affect a system in equilibrium, the system modifies itself to equilibrium so that it nullifies or reduces the effect of this change.

Thus, if pressure is applied to a system, the tendency of the stress will be to decrease the volume, and hence that reaction. In the ammonia equilibrium the combination of nitrogen and hydrogen to form ammonia is attended by a volume decrease from two molar volumes to one molar volume and hence accordingly to the Le Chatellier principle we may accept the formation of ammonia to be favored by an increase in total pressure.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In the system will take place which will favor the smaller volume.

Again when a reaction is endothermic, i.e. absorbs heat, addition of heat should_favor it, and the reaction should proceed to a greater extent at higher temperatures. Conversely when a reaction is exothermic we may expect the addition of heat would tend to inhibit the reaction, and hence at higher temperatures the reaction should tend to reverse itself. The latter behavior is shown by the ammonia synthesis reaction, which is exothermic.

Effect of temperature:

When the temperature increases for a system in equilibrium state and the other factors are constant, the reaction proceeds in the direction where the heat absorb. According to Le Chetelier principle increase the temperature inhibit the first reaction (exothermic) and favor the second reaction (endothermic).

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + Q\ \text{Kcal.}$$

$$H_2O + C \rightleftharpoons CO + H_2 - Q\text{KCal}$$

Effect of pressure:

When the pressure act on a system in equilibrium state, the system tend to retune back to its original value of pressure. Thus the system proceeds into the side of low volume (low number molecules) products.

$$2NO_{2(gas)} \rightleftharpoons N_2O_{4(gas)}$$

Increasing the pressure leads to increase of N_2O_4. In other word, increasing of pressure help to complete the gases reactions.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4\ (s) + 4\ H_2\ (g)$$

For such reaction the pressure has not effect since the reaction not accompanied with any change of the volume.

Effect of concentration:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2\ HCl$$

In this reaction it was found that the addition of water lead to the high turbidity and added of HCl acid lead to disappearance of turbidity.

Applications on Le Chetelier principle

Exothermic reactions:

Synthesis of ammonia

$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}$

This reaction is in equilibrium state at certain outer pressure and at constant temperature. According to Le Chetelier principle if the pressure increased the system adjusts itself to remove this effect. Thus the number of molecules of the system decreased. Since 4 volumes of H_2 and N_2 give 2 volumes of NH_3. Increasing the pressure leads to the decrease of volume. In results the system shifted to interact of other amount of N_2 and H_2, thus increasing the amount of ammonia in the system.

The reverse process was happened when the pressure on the system is reduced. On the other hand, this reaction is exothermic. Thus elevate temperature will favors the backward reaction (decomposition of ammonia). While the decreasing of temperature leads to increasing the forward reaction (formation of ammonia). According to Le' Chatelier principle**,**

a) Decrease of temperature shifted the equilibrium toward ammonia formation (Exothermic reaction).

b) Rise the pressure shifted the equilibrium toward ammonia formation (reaction accompanied by decrease of volume).

Without a catalyst ammonia synthesis proceeds at an extremely slow rate even at very high temperatures. An increase in temperature reduces the equilibrium content of the ammonia. Consequently, a catalyst which increases the rate synthesis at low temperatures must be used.

Iron is used to employ as a catalyst and obtained from the reduction of Fe_2O_3 and Fe_3O_4. Furthermore, it was found that in the industrial processes that to obtain high mass products of ammonia need addition of heat from outside source.

Endothermic reactions:

$$N_2 + O_2 \rightleftharpoons 2NO - QKCal$$

From this equation its clear that the reaction is endothermic reaction. According to, Le Chetelier principle that increasing temperature led to increasing of nitric oxide and versa. On the other hands the pressure not affect on such reaction since the number of products molecules equal of reactants, i.e. not accompanied with volume change.

Decomposition of PCl_5:

$$\mathbf{PCl_5 \rightleftharpoons PCl_3 + Cl_2 - QKCal}$$

The reaction given is endothermic one and according to Le Chetelier principle that increasing temperature led to decomposition of PCl_5 while when the temperature decrease the union of PCl_3 and Cl_2 is occurred to form PCl_5. On the other hand this reaction is accompanied by increasing in volume. In results the decrease of pressure will be lead to reaction complete, and the raise of pressure favor the reverse reaction.

Physical Changes

1- Melting of solids:

Solid body was in equilibrium state with its molt at the melting point, the volume of molt more than volume of solid in most cases. In the same time this process accompanied with absorb of heat.

Solid $\rightleftharpoons$ liquid - heat

According to Le Chetelier principle that increasing temperature led to transform of solid to liquid, while with increasing of pressure the liquid freezes.

The ice is an exception to this because its volume is greater than the volume of water. If the pressure increases, then the ice turns into a liquid, that is, the melting point of the ice decreases with increasing pressure.

2- Boling:

Liquid also in equilibrium state with its vapor at boiling point

Liquid $\rightleftharpoons$ Vapor - heat

Since, the volume of vapor larger than of liquid, therefore increasing the pressure leads to condensation of vapor. If we need boiling the liquid under new pressure it must raise the temperature as the process of evaporation absorbent. Raise the temperature leads to the evaporation of the liquid either leads to reduced steam.

The Law of Mass Action

It has been mentioned before that the degree of concentration is one of the most important factors that affect the speed of chemical reactions. The degree of concentration in the case of gases can be replaced by pressure where the pressure is proportional to the degree of concentration.

Guldberg and Waage studied the effect of the degree of concentration on chemical reactions in quantitative terms and announced in the year 1867 the law of mass action that shows the relationship between the concentration of the reactants and the resulting materials. This law states that at a constant temperature, the speed of the chemical reaction is proportional in direct proportion to the active mass of the reactants; they are usually replaced by degrees of molecular concentration (number of gram particles per liter M/L) Molar concentration.

With the aid of this principle may now be define the relations which obtain among the concentrations of reactants and products at equilibrium. According to the law of mass action, the rate of the direct reaction U_1 in the reversible process

$$A + B + .. \rightleftharpoons . \qquad C = D + ..$$

must at any time be proportional to [A] [B] concentration of A, B, …. etc. Therefore:

$$U_1 \alpha [A] [B] \quad .....$$

$$U_1 = K_1 [A] [B]$$

where K_1 is proportionality constant of known as the specific rate constant for the direct reaction. Similarly U_2, the rate of the reverse reaction is given at any instant by the expression.

$$U_2 = K_2 [C] [B] \quad . . . . .$$

Where K_2 is the proportionality constant for the reverse reaction.

Since at equilibrium the two rates must be equal, then for the conditions of chemical equilibrium we have that:

$$U_1 = U_2 \quad . . . . .$$

$$K_1 [A] [B] = K_2 [C] [D] \quad \text{and}$$

$$[C] [D]/ [A] [B] = \underline{K_1/} K_2 = K_C$$

According to above equation the ratio of the product of the concentrations of resultants to the product of the concentrations of reactants is equal to equilibrium to the ratio of the two velocity constants, and hence must be equal to another constant K_C is known as the equilibrium constant of the particular reaction.

The subscript C is used to indicate that in equation is expressed in concentration units, e.g. mole per liter. When more than a single molecule of a substance is involved in a reaction equation, is no larger proportional to the reacting species, but to the concentration of the given substance raised to the power of the number of molecules of substances participating. Thus for the reaction:

$$\alpha A + ßB + . . . = cC + dD \; . . .$$

The rates become

$$U_1 \; \alpha \; [A]^{\alpha} [B]^{ß} \quad . . . . .$$

$$U_1 = K_1 [A]^{\alpha} [B]^{ß}$$

$$U_2 = K_2 [C]^{c} [D]^{d}$$

$[C]^c [D]^d / [A]^\alpha [B]^ß \quad = \quad K_1 / K_2 \quad = \quad K_C$

This equation gives the most general definition of the equilibrium constant. By convention the concentrations of products are always placed in the numerator of the equilibrium constant expression, the concentrations of reactants in the denominator.

If we represent by P_A , P_B , P_C and P_D this partial pressure of the respective gaseous species present in equilibrium, then for an equilibrium such as given in we may write;

$P^c{}_C \; P^d{}_D / P^\alpha{}_A \; p^ß{}_B \quad = \; K_1 / K_2 \; = \; K_P$ . . . . . .

where K_P is the equilibrium constant in terms of partial pressure. The pressure may be expressed in any desired unites, usually at atmospheres.

In general K_P and K_C for a gaseous reaction are not the same numerically. A relation between these two constancies at any temperature T may readily be deduced provided the gaseous involved may be considered to behave ideally.

Factors affect on the K_c

1- Temperature:

According to mass action law, the value of equilibrium constant K_c as long as the temperature is constant. If the temperature rises, then its value increases if the rate K_1 more than K_2. This is the case in endothermic reactions where increasing the speed of the reaction by increasing the temperature. In the case of exothermic reactions the contrary is occurring, since the concentration of products decreases with temperature rise.

2- Effect of concentration:

The equilibrium defined the ratio between the concentrations of products to concentrations of reactants when approached the equilibrium state. If K_c or K_p had a great value, this indicates that the numerator of the biggest than demeanor. This means that the concentration of the products of the largest concentration of the reactants and this indicates that the interaction is going in the direction of forward direction. No change in the value of equilibrium constant with temperature value varies according to the degree of concentration or pressure as long as the balance had happened, but that change is the position of equilibrium.

For example, the following reaction

H_2 (gas) + Cl_2 (gas) $\rightleftharpoons$ 2HCl

If we assume that the amount of hydrogen has been added to the mix of gases after equilibrium, it leads to increase partial pressure of the hydrogen in the mixture and it follows that the relationship between the partial pressures represented in the equation may be disrupted. But, because the chemical equilibrium constant value must be fixed as long as the temperature is constant. Partial pressure of the molecule of hydrogen chloride must increase. This occurs through that the hydrogen reacts with chlorine gas. Mixture adjust itself meet the new partial pressure that the value of partial pressure values fulfill K_p still constant. The opposite occurs if added amount of hydrogen chloride gas.

Relation between K_c K_P ;

Since for an ideal gas

$P = (n/V)\,RT = [C]\,RT$

$P_A V = n_A RT$ or $P_A = (n_A/V) RT = [A] RT$

$p^{\alpha}_{A} = [A]^{\alpha} (RT)^{\alpha}$ and for other constituents with the same manner, we may write, on substitution of this relation in equation of equilibrium:

$$\frac{[C]^{c} (RT)^{c} [D]^{d} (RT)^{d}}{[A]^{\alpha} (RT)^{\alpha} [B]^{\text{ß}} (RT)^{\text{ß}}} = K_P \;..$$

$$\frac{[C]^{c} [D]^{d} (RT)^{c+d}}{[A]^{\alpha} [B]^{\text{ß}} (RT)^{\alpha+\text{ß}}} = K_P \;.$$

Or $K_P = K_c \, (RT)^{(c+d)-(\alpha+\text{ß})}$

But, $[\,(c+d) - (\alpha+\text{ß})]$ represents the changes in the total number of moles of gaseous products and reactants during the reaction letting this differences be Δn we obtain for the relation between the two constants:

$$K_P = K_c (RT)^{\Delta n} \qquad .\;.\;.\;.\;.\;.\;.$$

For the following reaction:

$$H_2 + I_2 \rightleftharpoons 2HI$$

$\Delta n =$ zero

$K_p = K_c$

The following reaction:

$$N_2O_4 \rightleftharpoons 2NO_2$$

$\Delta n = 1$

$K_p = K_c (RT)$, or $K_p = K_c$

Applications on mass action law

1- Reactions occur without change of molecules number:

Suppose that we have a gram mole of iodine, b gram mole of hydrogen, after approach the equilibrium, the amount of HI is 2x. P and V the pressure and volume of the mixture respectively.

$$H_2 + I_2 \rightleftharpoons 2HI$$

The number of gram moles of individual substance

a-x b-x 2x

The partial concentrations of mixture constituents are,

a-x/v b-x/v 2x/v

The total number of gram moles in the mixture is

a-x + b-x + 2x =a +b

The partial pressure for each constituent in the mixture is

$P_{H2} = (a-x/ a +b)P$

$P_{I2} = (b-x/ a +b)P$

$P_{HI} = (2x/ a +b)P$

$K_C = [HI]^2 / [H_2] . [I_2]$

$(2x/v)^2 / (a-x/v) (b-x/v) = 4x^2 / (a-x) (b-x)$

$K_p = P^2\,HI / PH_2 \,.\, P\,I_2$

$$K_p = \frac{\{(2x/\,a+b)p\}^2}{(a-x/a+b)p\ \ (b-x/\,a+b)\,p} = 4x^2 / (a-x)\ (b-x)$$

It is clear that

$K_P = K_C$

2- Reactions accompanied with change number of molecules

Suppose that we have a gram mole of N_2O_4, with approach to equilibrium the amount of N_2O_4 dissociated x, thus the amount of NO_2 is 2x, If p and V the pressure and volume of the mixture respectively at equilibrium.

$$N_2O_4 \rightleftharpoons 2NO_2$$

The number of gram moles of individual substance

a-x 2x

The partial concentrations of mixture constituents are,

a-x/ v 2x/v

The total numbers of gram moles in the mixture are

$$a-x + 2x = a + x$$

The partial pressure for each constituent in the mixture is

$P_{N2O4} = (a-x/\,a+x)P$

$P_{NO2} = (2x/\,a+x)P$

$K_C = [NO_2]^2 / [N_2O_4]$

$= (2x/v)^2/(a-x/v)= 4x^2/ (a-x) v$

$K_p = \{(2x/ a+x) p\}^2/ (a-x/ a +x)P$

$= 4x^2 P / (a-x/ a +x)$

It's clear that, K_p not equal K_C

and on the other hand, effect of pressure on the equilibrium. Furthermore of apperance of p & v

Degree of dissociation:

In the previous two examples if a= 1 the quantity of dissociated substance called the degree of dissociation α and the last equation becomes

$K_C =4 \boldsymbol{\alpha}^2/ (1- \boldsymbol{\alpha}) v$

$\mathbf{K_p =} 4 \boldsymbol{\alpha}^2 P / (1- \boldsymbol{\alpha} / 1 + \boldsymbol{\alpha})$

You can calculate the degree of dissociation of gas also from knowing its density before and after the dissociation

$$\alpha= d – d^/ / d^/(n -1)$$

You can also replace the molecular weights instead of density

$$\alpha= M – M^/ / M^/ (n -1)$$

Since d, $d^/$ are densities of gas before and after dissociation

M , $M^/$ are the molecular weights before and the average of molecular weights after dissociation respectively. n the number of molecules products.

Dissociation of PCl_5:

Suppose that we start with one gram mole of PCl_5 and α, its degree of dissociation, p and V are pressure and volume of the mixture respectively at equilibrium.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The number of gram moles of individual substance

$$1-\alpha \qquad \alpha \qquad \alpha$$

The partial concentrations of mixture constituents are,

$$1-\alpha/v \qquad \alpha/v \qquad \alpha/v$$

The total numbers of gram moles in the mixture are

$$1-\alpha+\alpha+\alpha = 1+\alpha$$

The partial pressure for each constituent in the mixture is

$P_{(PCl5)} = (1-\alpha/ 1 + \alpha)P$

$P_{(PCl3)} = (\alpha/ 1 + \alpha)P$

$P_{(Cl2)} = (\alpha/ 1 + \alpha)P$

$K_C = [PCl_3][Cl_2] / [PCl_5]$

$$K_C = (\alpha/v)(\alpha/v)/(1-\alpha/v) = \frac{\alpha^2}{(1-\alpha)\,v}$$

$$K_P = \frac{\{\alpha/(1+\alpha)\}P \,.\, \{\alpha/(1+\alpha)\}P}{(1-\alpha)^2} = \alpha^2 p/(1-\alpha)^2$$

It's clear that, K_p not equal K_C and on the other hand, effect of pressure on the equilibrium. Furthermore apperance of p & v.

<u>Effect addition of the products of reaction on the equilibrium position</u>:

Since the installation of the system depends on the equilibrium constant, the presence of one reaction products in the reaction mixture before it occurs reduces the extent of occurrence for example, if the dissociation of the PCl_5 in space contains some chlorine, the degree of dissociation are lower than in the absence of chlorine.

Suppose that α the degree of dissociation of PCl_5 in the absence of Cl_2, $\alpha^{/}$ is the degree of dissociation of PCl_5 in case of the presence of Cl_2

In the absence of Cl_2, we have

$K_C = (\alpha/v)(\alpha/v)/(1-\alpha/v) = \alpha^2/(1-\alpha)v$

In the presence of Cl_2

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The number of gram moles of individual substance

$$1-\alpha^{/} \qquad \alpha^{/} \qquad \alpha^{/}+y$$

The partial concentrations of mixture constituents are,

$$1-\alpha^{/}/v \qquad \alpha^{/}/v \qquad \alpha^{/}+y/v$$

$K_C = (\alpha^{/}/v)(\alpha^{/}+y/v)/(1-\alpha^{/}//v) = \alpha^{/2(1+y)}/(1-\alpha^{/})v$

i.e $\alpha >> \alpha^{/}$

Ionic Equilibrium

The purpose of this study is to learn how to apply the law of mass action on the electrolytic solutions with directing attention to the ionization of the weak electrolytes and that brings us to the subject of the hydrogen ion concentration in the electrolytic solution and the use of the pH scale. It is worth mentioning that the ion concentration problem, especially hydronium ion (HO_3^+) concentration appears constantly in biological studies. Blood, for example, can lead all vital functions, only when the pH number approximately constant. In addition, all fluids in the body have a certain hydrogen figures to lead these fluids their functions in the best case.

There are also enzymes and bacteria and microorganisms are active only under certain favorable conditions of acidity and less active if has become more acidic or more alkaline than the appropriate values.

1- Applications of mass action law on the electrolytic solutions

Equilibrium constant of acid ionization:

There is a weak electrolyte solution in equilibrium between the molecular state and the ionized form of the material. Mass action law can be applied on such systems. The following equation presents the ionization of weak acid (HA):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (1)$$

Since, A^- represents the anion of acid produced, and from the general mathematical formula for equilibrium constant K is,

$$K= a_{H3O}{}^{+}\times{}^{a}A^{-}/a_{HA}\times a_{H2O} \qquad (2)$$

and since the effectively of water to be in dilute solutions often fixed and it can be replace by k, thus the equation becomes:

$K= a_{H3O^+} \times a_{A^-} / a_{HA} \times k$ (3)

and K becomes K_a (called acid ionization constant)

$K \times k = K_a$

$K_a = a_{H3O}+ \times a_{A}- / a_{HA}$ (4)

Whereas the numerical values of the effectiveness of the different components in the dilute solutions of weak acids differ slightly from their concentrations, the equation (4) can be written as follows

$K_a = [H_3O^+] [A-] / [HA]$

As the concentration of each substance is expressed in the grams per liter (M), we must always remember that from the method of deriving equation (4) from equation (1), water activity is included in this equation (4) as part of the value of the ionization constant (Ka). And that the activity of the various components was replaced by the grams partial concentration in liters to express the concentration of the other components present in equation (4). Also, for the sake of ease, the H_3O^+ code is usually replaced with the H^+ hydrogen ion code, and on this the equation (4) can be written as:

$K_a = [H^+] [A^-]/[HA]$ (5)

It is worth emphasizing once again that the hydrogen ion H^+ is actually bound to a water molecule, so if confirmation of the solvent’s role in the ionization process is not required, then the use of the symbol H^+ instead of the symbol H_3O^+ simplifies circulation and writing the mathematical convention related to ionic balance.

Equation (5) means that the weak acid is ionized regardless of its concentration to the extent that it always leads to the stability of its value (K_a). That is, the value of (k_a) equals a fixed amount of weak acid and is not affected by dilution. This fixed amount regardless of the hydrogen ion source and the acid anion is characteristic of the acid.

And practical experiments have supported that this is fundamentally true, but it must be remembered that (k_a), like all equilibrium constants, changes with the temperature change, and it is constant as long as it is the temperature is constant. Normally, the values of the ionization constants for acids have been set at Cº25 so that their relative values can easily be compared.

Dealing with the equation (5) that the weak acid ionized regardless of the concentration to the limit, which always leads to a stable value (K_a) for it. This means that the value of (k_a) is equal to a constant amount of acid is not affected by dilution. This fixed amount regardless of the source of the hydrogen ion and anion acid is specific for acid. The practical experiments confirmed that this is true in essence, but it must be remembered that (k_a) like all equilibrium constants vary with temperature and that it be fixed as long as they the temperature be constant. It has traditionally been set ionization constants values of acids when 25°C so you can easily compare the relative values.

Ostwald dilution law:

Another expression for a weak acid ionization constant can be obtained by knowing the degree of α acid ionization and the total acid concentration in solution (C) in grams per liter. Whereas, the concentration of both the hydrogen ion H^+ and the A^- is equal to the acid concentration multiplied by the degree of ionization, then:

The concentration of: $[H^+] = \alpha C$, $A^- = \alpha C$ and unionized acid,

$$HA = (1- \alpha) C.$$

The compensation for these values in the equation (5) we get:

$K_a = \alpha C \times \alpha C / (1- \alpha) C$,

$K_a = \alpha^2 C / (1- \alpha)$

$$K_a = \alpha^2 C / (1- \alpha) \qquad (6)$$

Since the concentration is the opposite of dilution, i.e. ($C = 1 / V$), where V is the volume of the solution in liters, the relationship (6) can be placed in one of the following two ways:

$K_a = \alpha^2 / (1- \alpha)$ or

$$K_a = \alpha^2 / (1- \alpha) V \qquad (7)$$

This law is known as the Ostwald Dilution Law. This law can be used by knowing the degree of ionization (α) for a weak acid calculating K_a. Conversely, if the value of K_a is known for a weak acid, the degree of ionization can be known at any concentration and the degree of ionization (α) for a weak acid can be calculated from the equivalent conduction measurement at Infinite dilution where:

$$\alpha = \Lambda / \Lambda\infty$$

Where the numerator is the equivalent conduction, and the denominator is the equivalent conduction, when infinite dilution. Ostwald’s law applies only to solutions of weak electrolytes where there is a state of equilibrium between the ionized part and the non-ionized part of the weak electrolytes, as it was found that the value of k_a is equal to a fixed amount of the specific electrolytes and does not depend on the dilution (or concentration) because the dilution will lead to an increase in the value of the degree of ionization and that as long as the temperature is constant. But if in the case of strong electrolytes, due to their complete ionization, then the law of mass action cannot be applied to them, and thus the Ostwald Law to mitigate the lack of equilibrium, so the value of ka is not constant, but changes as shown in the results listed in the following table:

Ionization of acetic acid at 25 °C

k_a	α	C (M)
$^{5-}10 \times 1.821$	0.0095	0.2000
$^{5-}10 \times 1.846$	0.0135	0.1000
$^{5-}10 \times 1.849$	0.0190	0.0500
$^{5-}10 \times 1.840$	0.0299	0.0200
$^{5-}10 \times 1.832$	0.0422	0.0098
$^{5-}10 \times 1.823$	0.0540	0.0059

It is noted from this table that the value of k_a is almost constant, and if it increases slightly, the greater the ionic strength of the solution.

Ionization of sodium chloride at 18 °C

C(M)	α	k_a
2	0.777	$1.353\ 10^{-1}$
10	0.852	0.491×10^{-1}
50	0.916	0.200×10^{-1}
200	0.953	0.0967×10^{-1}

From this table it is clear that the value of k_a is not constant and varies with the change in the concentration of the solution. It is worth noting that we confirm once again that the expression of the ionization constant has no significance except in the case of weak electrolytes whether they are weak acids or weak bases where the degree of ionization is always small under normal conditions of mitigation and in this case it can be neglected from the denominator in equation (6) where its value It is small when compared to the correct one, which means that:

$(1-\alpha) = 1$

This follows usually in weak electrolytes that have $k_a = 10^{-4}$ or less and then reduced to the equation (6) to:

$K_a = \alpha^2 C$ or α^2/V (8)

From these two relationships it can calculate the value of the degree of ionization as follows:

$\alpha = (k_a/C)^{1/2}$ (9)

or $\alpha = (k_a V)^{1/2}$ (10)

It has been found that these two equations are to some extent consistent with the simplified law of Debye and Huckel (Debye and Huckel), but in this equation it is necessary to use the effectiveness of materials instead of degrees of concentration.

Ionization of weak base:

It is common to use the formula BOH to represent the general formula for a weak base, but given that the hydroxyl bases are strong electrolytes and organic derivatives are the most weak bases, it makes sense that we use the formula RNH_2 to represent the general formula for a weak base where R stands for hydrogen atom as in the case of ammonia or symbolizes. For an organic radical, a weak base ionization can be represented by the following equation:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \qquad (11)$$

If we start with the general equation and using the same steps that were followed to obtain the ionization constant for a weak acid, we can see that the equilibrium expression for a weak base is:

$$K_b = {}^{a}{}_{RNH3}{}^{+} \times {}^{a}{}_{OH-} / {}^{a}{}_{RNH2} \qquad (12)$$

If we substitute for effectiveness by concentration, then the previous expression becomes as follows:

$$K_b = [RNH_3^+] \times [OH^-] / [RNH_2] \qquad (13)$$

If we use the previous conventions mentioned in the case of a weak acid, a degree of ionization α and C, concentration, on following relationships:

$$K_b = \alpha C \times \alpha C / (1- \alpha) C$$

$$K_b = (\alpha C)^2 / (1-\alpha) C$$

$$K_b = \alpha^2 C / (1- \alpha) \qquad (14)$$

Given that the degree of ionization is small when compared to the correct one, it may be neglected from the denominator and reduce equation (14) to:

$K_b = \alpha^2 C$ (15)

Account ionization constant:

If you knew how much ionization of a weak acid or weak base (α) expressed as a percentage or degree of ionization, it can calculate ionization constant using the previous relationships mentioned.

Example:

It was found that the ionization of acetic acid in 0.1 G solution per liter is 1.43% at 25 ° C. Calculate the ionization constant at this temperature.

solution:

By neglecting the solvent's role in the ionization process, acid ionization can be represented by the following equation:

$HAc \rightleftharpoons H^+ + A^-$

According to equation (5) the term fixed ionization is expressed by the equation:

$K_a = [H^+] [Ac^-]/[HAc]$

It found that the ionization degree of acetic acid in a 0.1 gram mole/l solution is 1.43% at 25 °C. Calculate the ionization constant at this temperature.

The solution:

Neglecting the role of the solvent in the ionization process, it can be represented ionization of HAc as follows:

According to equation (5) expresses the ionization constant

$[H^+]$ = 0.0134 × 0.100 = 0.00134 M/L

l$[Ac^-]$ = 0.0134 × 0.100 = 0.00134 M/L

And the concentration of the acid is ionized 98.66% of the total concentration

[HAc]= 98.66×0.1000 = 0.09866 M/L

Substitution for former concentrations in the special relationship of the equilibrium constant, we get the following value at 25 °C:

$K_a = 0.00134 \times 0.00134 / 0.09866 = 1.82 \times 10^{-5}$

Another way to solve:

According to equation (6) can k_a account by the expression:

$Ka = \alpha^2 C /1- \alpha$

If the degree of ionization of the acid 1.34%, degree of ionization α be equal to 0.0134. Thus, at 25 °C k_a will be equal to the value:

$K_a = \alpha^2 C/1- \alpha$

$k_a= (0.0134)^2 \times (0.100)/(1- 0.0134)=1.82 \times 10^{-5}$.

Since the value of the degree of ionization is very small when compared to the correct one in the denominator of the fraction, it is possible to use dependency (7) without this leading to a slight error.

Common ion effect;

The addition of acetate ions to the solution of acetic acid will lead, according to the law of the action of the mass to reduce the degree of ionization of acetic acid and the visible result on this is to reduce the concentration of hydrogen ion to a large degree (that is, the hydronium ion (H_3O^+) because the reaction will go under these conditions in the opposite direction:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Acetate ions can be obtained by adding strong electrolytes such as sodium acetate. The process of reducing electrolyte ionization is called weak as a result of adding one of its ions to the term “common ion effect”. The added ion is called the common ion. By adding this common ion.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Acetate ions can be obtained by addition of strong electrolytes such as sodium acetate. The process of reducing the ionization of weak electrolytes as a result of the addition of one of own ion is called (Common ion effect) and called on the ion additive (Common ion). It should be noted here that the ionization constant does not change as a results of addition of this common ion.

The extent of the decrease in the hydrogen concentration can be illustrated when adding the acetate ion from the following example.
The expression for the ionization constant of acetic acid can be calculated:
Example: Calculate the hydronium ion concentration at 25°C in a solution consisting of 500ml of 0.300M/ l of acetic acid and 500ml of 0.300 M/l of sodium acetate assuming that the sodium acetate is fully ionized

The solution:

We have already explained that it is in a solution of pure acetic acid

$$[Ac^{-}] = [H^{+}]$$

However, in the presence of fully ionized sodium acetate, the ac-ions in the number greatly exceed H^{+} ions and for the HAc equilibrium constant to remain unchanged when $Na^{+}\ Ac^{-}$ is added, the hydronium ions must combine with the acetate ions in order for the ionic concentrations to achieve the k-equilibrium value and build on this the issue can be resolved. The final volume of the solution after mixing the solutions equals 1000ml. If we assume that

$\alpha^{/} = H^{+.}$ the total concentration of the acetate ions, that is, Ac^{-} is equal to the concentration of the acetate ion from salt in addition to the concentration of the acetate ion from the HAc as follows:

The total concentration of acetate ions Ac^{-} equals acetate ion concentration of salt in addition to the ion concentration of acetate acid of HAc as follows:

$$\alpha^{/} + 0.03x500/1000 = (\alpha^{/} + 0.15)$$

HAc concentration is equal to the total concentration, minus the amount which is ionized to H^{+} and Ac^{-} and can be calculated as follows:

$$[HAc] = \{0.200 \times (500/1000)\} - \alpha^{/} = 0.100 - \alpha^{/}$$

The substitution for these values in ionization equilibrium constant of acetic acid expression we get:

$$K_a = \quad (\alpha^{/} + 0.15) \times \alpha^{/} \quad = 1.8 \times 10^{-5}$$

$$(0.100 - \alpha^{/})$$

Since $\alpha^{/}$ is very small compared to the values of 0.150 and 0.100, it can be neglected in the limits mentioned in the previous expression. Then it can write as follows:

$$\frac{(0.15) \times \alpha^{/}}{(0.100)} = 1.8 \times 10^{-5}$$

and it can be calculated $\alpha^{/}$ as follows:

$\alpha^{/} = 1.2 \times 10^{-5}$ M/l

The great effect of the combined ion as evidenced by the above example can be known from the hydronium ion concentration that arises when adding 500 ml of water instead of adding 500 ml 0.300 grams of NaAc, then the concentration of the hydronium ion will be equal to 1.3×10^{-3} grams per liter instead of 1.2×10^{-5} grams per liter. On this basis it is clear that the H_3O^+ ion concentration has been reduced to the approximately 1/110 of their value as a results of add the common ion.

Ionization of polybasic acids;

Acids that contain more than one ionized hydrogen atom are called polyunsaturated acids or protons. Such acids are always ionized on steps, i.e. the first ionization has an equation of equilibrium and an equilibrium constant characteristic of this step of equilibrium. This can be illustrated by examining the equilibrium states that carbonic acid ionization involves as a typical example of bi proton (polybasic acid):

$H_2CO_3+H_2O \rightleftharpoons H_3O^++HCO_3^-$ (Primary ionization)

$HCO_3^- + H_2O \rightleftharpoons H_3O^++CO_3^{--}$ (Secondary ionization)

The corresponding ionization constant for each equilibrium equation is deduced in the same way as in the case of ordinary mono-proton acids. If we use the symbol H^+ to represent the H_3O^+ ion formula for ease, we obtain the following equations:

$K_1 = [H^+][HCO_3^-] / [H_2CO_3] = 4.3\times10^{-7}$(at 25ºC) (16)

$K_2 = [H^+][CO_3^{--}] = 5.6\times 10^{-11} / [HCO_3^-]$ (at 25ºC) (17)

Both processes of ionization occur at the same time, but the second ionization is much smaller than the first ionization, and the explanation for this is due to the fact that the neutral molecule can give H^+ or proton to water more easily than negative ion HCO_3^-, so the negative charge on this ion delays or hinders proton transport from it. To the water molecule. It is noted from the values of the ionization constant mentioned that k_1 for the first ionization is greater and reaches 10,000 times k_2 for the second reaction. It is usually useful to combine the ionization equations into one equation as follows:

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{--}$$

The equilibrium constant is given as

$K\ [H^+]^2\ [CO_3^{--}] / [H_2CO_3]$ (18)

Then expression of ionization read as follows:

$K = K_1K_2 = [HCO_3^-] \times [H^+][H^+] x [CO_3^{--}] / [HCO_3^-][H_2CO_3]$ (19)

Since $[HCO_3^-]$ found in the numerator deleted with its counterpart in numerator, the equation (19) will be similar to the equation (18) and is stable full ionization numerically equal to the product of

$K_1 \times K_2$ i.e, 2.4×10^{-17}

Ionization constants of some weak acids

K_3	K_2	K_1	acid
	6.1×10^{-5}	6.5×10^{-2}	Oxalic acid
	5.6×10^{-11}	4.3×10^{-7}	Carbonic acid
	1.2×10^{-15}	5.7×10^{-8}	Hydrogen sulphide
4.5×10^{-6}	1.2×10^{-5}	8.7×10^{-4}	Citric acid
4.8×10^{-13}	6.2×10^{-8}	7.5×10^{-3}	Phosphoric

Ionization constants of some weak bases

K_b	base	K_b	base
3.8×10^{-7}	Aniline	1.8×10^{-5}	Ammonia
1.4×10^{-9}	Pyridine	4.4×10^{-4}	Methyl amine
		5.3×10^{-5}	Tri- methyl amine

The ion product of water

Water can be classified as amphoteric, because the water molecule can donate protons when interaction with the base (such as ammonia)

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

or accept protons when interaction with acid

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

and thus it is not surprising that there are a small number of even in pure as ions. Some small molecules of water, including protons, move to an equal number of water molecules to give the following equilibrium state:

$$H_2O + H_2O \rightleftharpoons H_3O^{+} + OH^{-}$$

What indicates that the water actually contains ions, even in its purest form, that pure water is a weak conductor of the electric current. However, given that H_3O^+ and OH^- are as strong as acid and as a base, respectively, they are never present together with high concentrations and the equilibrium constant for water ionization is represented by the following expression:

$$K = {}^{\mathbf{a}}H_3O^{+} \times {}^{\mathbf{a}}OH^{-} / \; {}^{\mathbf{a2}}H_2O \qquad (20)$$

As the degree of ionization very low for water in all conditions, it can be considered non-ionized water effectively constant can then be compensated for $k^{2.}$ then equation (21) becomes as follows:

$$K \times K^2 = {}^{a}H_3O^{+} \times {}^{a}OH^{-} \qquad (21)$$

The product of the three times $K\times K^2$ gives a fixed location called the water ionization constant and is characterized by the symbol K_w. In this case, the effectiveness can be replaced by concentrations using H^+ none from H_3O^+ we get:

$$K_w = [H^+]\,[OH^-] \qquad (22)$$

The estimated value of the K_w by several independent ways were found that most of these values of such equilibrium constants vary with temperature and at 25ºC it is approximately equal 1×10^{-14}

In purified water, the hydrogen ion concentration should be equal to the concentration of the hydroxyl group equal to 1×10^{-7} grams per liter until the value of K_w becomes equal to the value of 1×10^{-14}. However equation (22) only requires that the product of hydrogen and hydroxide ion concentrations be equal to K_w. Regardless of their source and acidity of the solution, if a little HCl acid is added to the water, this will lead to an increase in the concentration of H^+ ions, followed by a corresponding decrease in the concentration of OH^- ions so that their product is equal to the value of K_w. If a base is added to the water, then the concentration of hydroxyl ions will be large, followed by a decrease in hydrogen ions H^+, so if the value of any of the H^+ or OH^- is known in any aqueous solution, then the concentration of the other ion can be calculated from the equation (22).

This table shows the values of K_w at different temperature

50	40	30	25	10	zero	Temperature 25°C
5.474×10^{-14}	2.917×10^{-14}	1.468×10^{-14}	1.008×10^{-14}	10^{-} 0.292×10^{-14}	0.113×10^{-14}	K_W

It must be remembered that the hydronium ion (**H_3O^+**) concentration and hydroxyl ion (OH^-) are equally when only at equivalent point. But if added any material change of this equality, this will not affect the value of K_w at that degree of temperature.

Hydrogen ion exponent (pH)

In 1909 used the assurance that the term pH, for ease of expression of the hydrogen ion concentration in the solution where it would be easy to express all acidity degrees or alkaline limited numbers between zero and 14. While in neutral solutions, for example, it contains 10^{-7} gram ion per liter and, the pH value expressed as follows:

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

$pH = - \log 10^{-7} = 7$

The solution containing the gram ion of hydrogen per liter be, the concentration of hydrogen ion = one.

The value of pH is 0:

Example:

You have a solution of HCl acid of 1 gm mole/L, calculate the pH value?

Solution:

Since HCl is a strong electrolyte. It means that it wile be completely ionized

$$\underset{\text{1 gm mole}}{HCl} \rightarrow \underset{\text{1gm ion}}{H^+} + \underset{\text{1gm ion}}{Cl^-}$$

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

$pH = -\log 1 =$ Zero

While the solution containing gram-ion of OH^- will be 14:

Example:

You have a solution of NaOH base of 1 gm mole/L, calculate the pH value?

Solution: The solution containing the gram ion of hydrogen per liter be, the concentration of hydrogen ion = one.

The value of pH is 0:

Since NaOH is a strong electrolyte. It means that it will be completely ionized

$$\underset{\text{1 gm mole}}{NaOH} \rightarrow \underset{\text{1gm ion}}{OH^-} + \underset{\text{1gm ion}}{Na^+}$$

$[OH^-] = K_w / [H^+] = 10^{-14} / 1 = 10^{-14}$

The value of pOH equal as follows:

$pOH = - \text{Log } 10^{-14} = 14$

From this we see that if we move from the maximum acidity to the maximum alkalinity, we find that we have moved from the values of pH=Zero to the value of pH=14. Acidity decreases from zero to seven (neutral) and alkalinity increases from pH equal to seven to pH equal to fourteen. POH can be used in place of pH as:

$p_{OH} = -\log [OH^-]$

And it can be concluded the relationship between pH and pOH as follows:

$[H^+] [OH^-] = 10^{-14} = K_w$

Taking logarithms, we find that:

$\log [H^+] + \log [OH^-] = \log 10^{-14}$

$-\text{Log } [H^+] + (-\log [OH^-]) = - \log 10^{-14}$

$p^H + p^{OH} = 14$

The solubility product

If suspended in water sparingly soluble, such as silver chloride salt, the salt in water dissolves to a small extent, and when they reach the dynamic equilibrium between the salt and salt dissolved (ions). There is no other change in the concentration of dissolved material, provided that the temperature remains constant. This situation can be represented as follows:

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$K = {}^aAg^+ \times {}^aCl^- / {}^aAgCl$ (23)

Since the effectiveness of the solid body equals unity, the equation (23) becomes the following image:

$K = {}^aAg^+ \times {}^aCl^-$ (24)

In dilute solutions can replace the effectiveness by concentrations and we get:

$[Ag^+] \times [Cl^-] = K_{sp}$ (25)

Buffer solutions

In practice it was found that the pH of NaCl and ammonium acetate solution was approximately 7.5, that is, both of them are neutral. If one liter of $1cm^3$ of each 0.1N of HCl were added to each liter, we would find that the pH value of NaCl solution was 4, while the ammonium acetate solution was not affected. Likewise, when adding $1cm^3$ of 0.1N solution of NaOH to liters of each of them, the pH value of NaCl solution becomes 10, while the ammonium acetate solution is negatively affected.

Therefore it is said that the solution of ammonium acetate can resist change in pH value when adding an acid or base to it. This property is known as buffering action and buffer solutions are solutions in which the hydrogen ion concentration is not affected to a significant extent when adding amounts of acid or alkali to it and it usually consists of weak acid with one of its salts from a strong base or from a weak base with one of its salts from Strong acid Below are some examples and how much pH is for each.

Some examples recorded in the following table and the pH of each.

Buffer solution	**pH**
Acetic acid, sodium acetate	3.7 ---- 5.6
Di sodium citrate tri sodium citrate	5 ------ 6.3
Phosphate monobasic sodium phosphate bisodium phosphate	5.8 ------8
Boric acid and sodium borate	6.8 ----- 9.2
Borax and sodium hydroxide	9.2 ---- 11
Disodium phosphate and tri sodium phosphate	11------12

Mechanism of buffer action

It can explain the mechanism of buffer action (how the buffer solution work) as follows:

First: When adding an amount of HCl to a buffer solution of acetic acid and sodium acetate, as it is completely ionized, it interacts with the acetate, forming sodium chloride and weakly ionized acetic acid. That is, the hydrogen ions that were produced from the acid were converted from effective acid ions into the non-ionic acetic acid molecules, and accordingly there is no significant change in the value of pH and what can happen is explained thus:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$HCl \rightarrow H^+ + Cl^-$

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

Secondly, when adding a quantity of NaOH to the aforementioned buffer solution, the added hydroxyl ions were converted into neutral water by the action of the hydrogen ions resulting from the ionization of the acetic acid, and then a portion of the acetic acid disintegrates to compensate for the lost hydrogen ions and restore the equilibrium to its first state:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$NaOH \rightarrow Na^+ + OH^-$

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

From this it can be said that these solutions contain an acid reserve and an alkali reserve because they have the effect of adding acid or frying from the outside.The ability of the regulating solution to resist changes in the pH value is evident from the calibration of the weak acid by strong bases as we will see later. It was found that the regulating ability of the solution, which is the ability of the solution to resist the changes that occur as a result of adding a base or acid to it, depends on the ratio of the concentration of the acid or base to its salt. It reaches its maximum when the ratio is the correct one, that is, when the acidity ratio is 50%. It has also been found that the regulating capacity increases with the increase in the concentration of the solution.

From the previous table, we see that each regulated solution has a limited range in which the regulating capacity reaches its maximum. It has been found that if two regulated solutions are mixed, the resulting mixture is suitable for use in the range of the two solutions together. For example, if citric acid is sutured with di-sodium citrate in different proportions, solutions can be obtained for pH values ranging between 2.2 - 8.

Bronsted Lowry Theory

Acid is defined according to this theory as each substance tends to lose a proton. As for the base, it is defined as every substance that tends to acquire a proton. In order for the substance to be able to show its acidic strength, there is a substance that can acquire the proton. In order for its base strength to appear, there must be a substance that can give the proton or in other words. The acid and base must both be present in the reaction that represents the equation:

Acid $\rightleftharpoons$ H^+ + base

The acid when dissolved in water due to its tendency to give the proton to the water molecule, which in this case acts as the base

HCl (acid) + H_2O (base) $\rightarrow$ H_3O^+ (acid) + Cl^- (base)

In the case of the base, the water acts as an acid:

NH_3 (base) + H_2O (acid) $\rightleftharpoons$ NH_4^+ (acid) + OH^- (base)

It has been found that when the acid is strong, the resulting base, which is called the Conjugate base, is weak. If the acid is weak, then the derived base is strong, then the water is a weak base, but the derived acid H_3O^+ is strong.

The solutions of nitric, hydrochloric and sulfuric acid are not considered acids but the real acid is the non-ionizing molecule which, when dissolved in water, is given a proton.

Likewise, strong alkalis such as sodium hydroxide, potassium and calcium are not considered bases. They are ionized in the solid state to the metal ion and the hydroxyl ion is the real base, while sodium hydroxide is salt.

Hydrolysis

Since the salt is formed by combining equal quantities of acid and the base, it must be neutral, but some salts when dissolved in water are not neutral, some are alkaline, some are acidic, and others are neutral. The reason for this is that the salt unites with water when dissolved in it, forming the acid and base that resulted from their union with this salt. This is usually called hydration or water dissociation, which is the opposite of neutralization. The effect of the final solution depends on the ratio between the degree of acidification and acidification of the base. If they were of equal strength or weakness, the salt solution was neutral, but if the acid ionization K_a was stronger than the base ionization K_b, the salt solution was acidic, and if the opposite was the salt solution was alkaline.

Hydration can be defined as a double exchange between salt and water ions to form an acid and a base, one of which is weak, and the salts are divided according to the strength of both the acid and the base they form into four sections.

A- Salts resulting from strong acid and strong base, and these salts are neutral in solution

B - Salts from a strong acid and a weak base, and their acid solutions

C- Salts resulting from weak acid, strong base and alkaline solutions

D- Salts resulting from strong acid and weak base, and their solutions depend on the ratio between the acid and base ionization constant, which are either neutral, weak acid, or weak alkaline.

A- In the case of a salt derived from a strong acid and a strong base, such as sodium chloride. Both acidic and alkaline radicals does not have any susceptibility union ions with OH^- (base full ionized) as well as the acidic radical not desire to union ions H^+ ion (acid ionized fully).

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

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

$$NaCl + H_2O \rightarrow Na^+ + OH^- + Cl^- + H^+$$

B- If the salt is derived from a strong acid and a weak base, such as ammonium chloride, and then the salt solution is acidic because the base resulting from the hydration is weakly ionized, while the acid is fully ionized. The resulting salt and ion (OH^-) produced from the water are more than necessary for the equilibrium event:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

The ions combine with each other to form non-ionizing molecules of ammonium hydroxide, and when the hydroxyl ions are depleted from the solution, other ions are formed instead of the dissociation of water molecules. The result is that the hydrogen ion concentration increases and the solution become acidic.

$$Cl^- + NH_4^+ + H_2O \rightleftharpoons Cl^- + H^+ + NH_4OH$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

It can be explained by what is occurring in some other way like this:

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$ (a)

$H_2O \rightleftharpoons OH^- + H^+$ (b)

and collect the above equations:

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$

C- If the salt is derived from a strong base and a weak acid, such as sodium acetate, then the salt solution is alkaline because the resulting base is strong, so the ionization is complete. As for the acid weakly ionized, in this case the acetate ions interact with the hydrogen ion to form the non-ionic acetic acid because the concentration of these ions exceeds what is necessary for the following equilibrium event:

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$

Hydrogen consumption constantly breaks down water molecules in order to restore equilibrium between non-dissociation molecules and H^+ and OH^- ions, thereby increasing the concentration of OH^- in the solution and becoming alkaline. This incident reaction can be deformed like this:

Continuous hydrogen consumption from dissociation of water molecules in order to restore equilibrium between the unionized water molecules (H^+ and OH^-) and thus increasing the concentration of OH^- in the solution, i.e, the solution becomes alkaline. This can occur by other way, thus:

$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + OH^- + Na^+$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

Or in some other way:

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

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

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

D- In the case of salt derived from weak acid and a weak base, such as ammonium acetate, both acid and base are weak and when the salt is dissolved in water the OH^- and H^+ ions combine to give the weak acid and base. By constantly consuming these ions, the water molecules break apart to restore the following equilibrium:

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

Then the reaction takes place as:

$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

Or in some other way:

$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$

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

$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$

And the effect of the resulting solution will depend on the strength of each of the acid and the base is mostly neutral, but may be weak acidic or alkaline weak, depending on the strength of the acid and the base (K_a and K_b). $K_a > K_b$ (acidic) $K_a < K_b$ (basic) and $K_a = K_b$ (neutral).

Equivalent acids and bases

We knew from the hydration salts how the salt it contains equal amounts of each of the acid and the base. But it not always be neutral in any solution (pH= 7). If we look at this issue on the other hand, a salt formation reaction of equal amounts of acid and base, we can divide the composition of salts according to the equation:

$$HA + BOH \rightleftharpoons BA + H_2O$$

Into four sections:

1- **Strong acid with a strong base reaction**

There we find that the interaction is going according to the previous equation from right to left until the fullness there is no reverse reaction (hydration) and it is resulting solution neutral (pH = 7).

$$HA + BOH \rightarrow BA + H_2O$$

2- **Strong acid with a weak base reaction**

In this case the reaction is inversely. Since hydration of the resulting salt (when add an equal amounts of the acid and the base) are strong acid and weak base. The resulting solution is acidic.

Example, it was found that the pH of the solution of strength 0.1N ammonium chloride equal to 5.

3- **Weak acid with a strong base reaction.**

As in the previous case, we find that there is un-complete neutralization (as a result of re hydration). Since the base is strong, the resulting solution from add an equivalent amounts of acid is alkaline

For example, it was found that the pH of the solution of 0.1N sodium acetate equals 8.9.

4- Weak acid with a weak base reaction

In this case, we find that the reaction is reversible to a larger degree than in the previous reactions. Salt results hydrated to a large degree, and although the resulting solution is weak acidic, alkaline, or neutral depending on the strength of each of the acid and the base. From the above we see that there is no perfect equivalent sense of the word except in the case of strong and strong base. While in the last three cases the neutrality is not fulfilled. Despite Add equal amounts of the acid and the base and the resulting salt is acidic or basic depending on what was weak the base or the acid or both.

The importance of these reactions in the calibration operations (Titrations) which is intended to find out the amount of the acid or the base that equivalents quantity of the base or acid which is contained in the titrated solution.

If the strength of the first solution is known, its possible to determine the concentration of the second unknown solution. Its became important then is to identify the point at which, the amount of acid added equivalent to the amount of existing base in the solution, or vice versa.

Adopt this point (equivalent point) depends on the effect of the resulting salt solution (i.e, on the strength of each of the acid and base) and to determine the point used the so called indicators.

Indicators

Indicators used in an acidity and alkalinity calibration are weak organic acids or bases changes color depending on the changing pH of the solution in which it exit. Examples of these indicators are litmus dyes, in acidic solution red and in alkaline solution is blue. In the neutral solution is purple. Methyl orange, methyl red, phenolphaline and others.

Ostewald have interpreted the change in the color is due to ionized indicator differs in its color about the no ionized one, for example, according to this theory, a weak acid indicator and symbolized to it a symbol HA ionized as follows:

$$\text{HIn (Colorless)} \rightleftharpoons \text{H}^{+} + \text{In}^{-} \text{ (Pink)}$$

Non ionized indicator is colorless while others ionized with red color. Unless added ionized base to the indicator such as NaOH, the hydroxyl ions combine with hydrogen ions resulting from ionization of indicator and thus disturb the equilibrium (indicator molecules) and thus the concentration of colored ion increases and take the solution a violet color and vice versa. If you add acid, such as HCl to the above indicator, the existence of the common ion reduces the ionization of indicator and so increase the proportion of ionized indicator and the solution remains colorless.

The methyl orange indicator is weak base and symbolized by the symbol InOH and is ionized as the following equation:

$InOH$ (Yellow) $\rightleftharpoons$ In^{+} (Red) + OH^{-}

The presence of acid leads to increase the ionization and that due to the union of hydrogen of acid with hydroxyl ions resulting from the indicator, and so the color red. In the presence of the base leads to decrease the degree of ionization through the common ion effect. So the solution takes the color yellow (color of non ionized indicator).

Hantzsch have interpreted the change in the color is due to change of the molecular structure of indicator itself. Indicator is exit in two or more formula, each formula has its own color. The two formula in the solution are in equilibrium depends on the pH and the color indicator is no different from the color of the ion resulting from ionization.

Validity of indicator;

Since the indicator according to the Ostewald theory ionized as follows:

HIn (Color 1) $\rightleftharpoons$ $H^{+} + In^{-}$ (Color 2)

Application of the law of mass action, equilibrium constant of indicator know K_{In} as follows:

$K_{In} = [In^{-}] \times [H^{+}] / [HIn]$

From this equation, we find that: $[H^{+}] = [HIn] \times K_{In} / [In^{-}]$

and we can say that (the intensity of color 1 / color intensity 2) = K_{In}

This is because the intensity of the color depends on the concentration of each of the ionized and non-ionized indicator. In order for the two colors clearly shows (the color is not affected by the other) must be a concentration ten-fold the other color. To observe color (1) must be:

$[H^+] = 10\ K_{In}$

So the color (2) must be:

$[H^+] = 0.1\ K_{In}$

$pH = pK_{In} + 1$

From this we see that in order to change the indicator color should change the hydrogen ion concentration in a range between 10 K_{In} and $0.1K_{In.}$, then the extent of the validity sandwiched between pH over the

$pH == pK_{In} \pm 1$

In the following table some of the indicators and their colors and their suitability:

Indicator	acidic color	basic color	K_{in}	range of validity
Methyl orange	red	yellow	2×10^{-4}	3.1 - 4.4
Methyl Red	red	Yellow	8×10^{-6}	4.2 - 6.3
Sunflower	red	Blue	1×10^{-7}	6 - 8
Phenol red	yellow	red	1×10^{-8}	6.8 - 8.4
Phenolphthalein	colorless	red	4×10^{-10}	8.3 - 10

it was possible made by using a mixture of several indicators known as the universal indicator to determine the pH of the solution.