

## PREFACE

In most developing countries chemistry (or any science) poses as a very difficult and fearful subject to most students who enter the university for the first time. For some students, it a "natural" fear for the subject. Consequently, many students have little understanding of even the simple ideas, they are supposed to have, as they enter the university. It seems plausible to say that the lack of basic principles in chemistry in these students dates from their secondary education, where the deficiency of texts and laboratory equipment make teaching and learning difficult. At the university level, the problem is compounded by the unavailability of texts to the extent that students rely mostly on the lecturer's notes. In Agriculture and Nursing University libraries, it has also been observed that the focus is mainly in those areas and not in pure sciences that are also taught. As a result, they do not purchase books in the sciences. Many Agriculture and Nursing students also think that there is no Chemistry or Mathematics in those fields. Consequently, when they enter the university, they get frustrated at the sight of these subjects. It was against this background that I thought I should put down some useful principles in chemistry in form of a book, which should serve as a guide to the teaching of Chemistry on the one hand, and to the student's own understanding of the principles in the areas they feel deficient. I have tried to present the material in very simple English, and many worked out problems have been included. It is hoped that students will have no problems in understanding the material and the examples given will bring them closer to liking the subject.

The layout of the topics in this book is based on the syllabus used at the University of Malawi, Bunda College of Agriculture. The material is intended for university students. However, upper high school students may also use it as they prepare to enter the university.

The first issue of this book was produced in 1994 and that was updated in 1997. This issue is an update of the previous one which was reproduced in 2001. Initially, only two copies were produced for use by students at Bunda College of Agriculture. The great scramble for those issues and the request by students to include more problem examples in the book prompted me to rewrite and upgrade the book. In order to attain international standards, the last issue was sent for review at Makerere University in Uganda. As a result of the review, this new issue has been rewritten taking into account the reviewers' suggestions and the students' requests. Firstly, each chapter has learning objectives to assist students know what they are supposed to grasp in that chapter. Secondly, some chapters have been expanded with inclusion of new sections. For example, Chapter 1 has seen the addition of sub-sections 1.12.3 and 1.12.4; to Chapter 7, has been added a section on conductimetric titrations. Thirdly, I have used a mechanistic approach to equation writing for most equations in the

organic chapters. It is hoped that this will help the student to better grasp the reaction sequences. I'm greatly indebted to the reviewers: Professor H. Ssekaalo (Chapters 1, 2 and 8), Dr. J. Mbabazi (Chapters 3-10) and Dr. J.E.S. Murumu (Chapters 11-14). I'm also thankful to the Research and Publications Committee (RPC) of the University of Malawi for the provision of funds to write this manuscript. Funds for the original version were provided by the Committee on University Teaching and Learning (CUTL) of the University of Malawi. Many thanks go to the students at the University of Malawi and especially, Bunda College of Agriculture who were and continue to be a source of inspiration in writing the book. I also thank those students (at Bunda) who provided several suggestions for this revised issue. I hope the inclusion of those suggestions has perfected this issue to an extent that will remove fears for chemistry in the forthcoming students. I will greatly appreciate receiving more constructive suggestions from future students for the improvement of this new edition.

**Peter P. Mumba**  
*August 2007*

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## ATOMIC THEORY AND THE STRUCTURE OF THE ATOM

### Learning Objectives

By the end of this Chapter, students should be able to describe the electronic structures and properties of atoms.

#### 1.1 WHAT IS A THEORY?

Scientific problems are always checked by experimental work. If a large number of experiments all give similar results, the latter are then summarized into a single statement known as a **law**. Thus, a law is a summary of the results of a large number of separate experiments all giving the same conclusion. Further experiments are carried out to account for the law. This is done by proposing a **hypothesis**. If the results of the experiments agree with the hypothesis, those results are stated into what is called a **theory**.

#### 1.2 ATOMIC THEORY

The most important chemical theory was given by John Dalton (1766-1844). Initially, Dalton stated the hypothesis that all substances consist of small particles of matter of several different

kinds corresponding to the different elements.

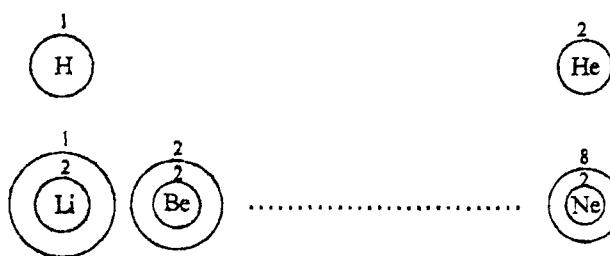
He called these particles **atoms** (from Greek: 'atomos' which means indivisible). Dalton also said that elements consist of atoms and that atoms of one element are identical and compounds result from the combination of atoms of two or more elements each in a definite number. He assigned a weight of 1 (one) to a hydrogen atom and built a table of relative weights of elements and compounds (but see Section 1.4).

This hypothesis was verified by further experimental work and so it became a theory. Thus Dalton's atomic theory can be summarized into the following statements:

- (a) All matter is made up of atoms that cannot be created or destroyed; that is, atoms are indivisible by ordinary chemical means
- (b) Atoms of a particular element are identical in size, shape, mass<sup>1</sup> and all other properties and differ from other atoms in these properties.

### **1.3 STRUCTURE OF THE ATOM**

From various studies such as radioactivity and field emission, it was found that the atom consists of a positively charged nucleus surrounded by negatively charged particles called **electrons**. In 1909, Ernest Rutherford studied the deflection patterns of alpha particles ( $\text{He}^{2+}$  ions) by thin metal foils and an analysis of the results led him to the conclusion that an atom has a tiny central nucleus that carries practically all the mass of the atom and that the electrons are around this nucleus. *The number of positive charges on the nucleus is called the atomic number (abbrev. Z).* Since the atom is neutral, the number of positively charged particles must equal the number of negatively charged particles (electrons). Therefore, the number of electrons surrounding the nucleus in a neutral atom, must also be equal to the atomic number. The positively charged particles are called **protons**. The hydrogen atom for example, has one proton in its nucleus and carries one proton. The electrons are arranged around the nucleus in "shells". Here, we imagine the first group of electrons to be on a small "circle" with the nucleus inside. The second group of electrons would be on a bigger circle with the smaller one inside it and so on. Figure 1.1 illustrates this pattern.



**Figure 1.1:** Electron arrangements in the shells of atoms

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<sup>1</sup>It was later found that atoms of one element may have different masses depending on the number of neutrons present. Atoms of one element having different masses are called isotopes (see Section 1.5). Statement (b) therefore, does not hold for mass.

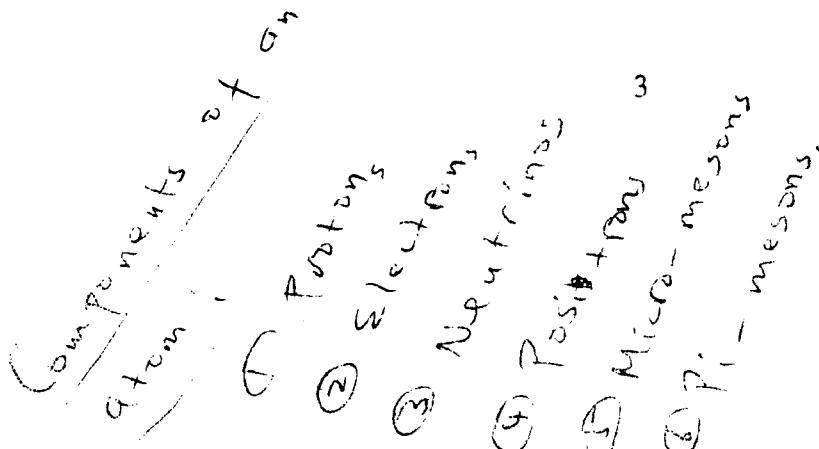
Thus the successively added electrons first fill the innermost shell, then the next shell to it and so on. The innermost shell is called the **K** shell, the other shells in order of increasing size are called **L**, **M**, **N**, and so on. We shall see later that the K shell is the lowest in energy, the L shell is higher in energy than the K shell, the M shell is higher in energy than the L shell and so on.

#### 1.4 RELATIVE ATOMIC MASS (RAM)

We have stated that an atom has some components. The electrons are negatively charged and each has a charge of  $-1.60206 \times 10^{-19}$  coulombs and a mass of  $9.109 \times 10^{-28}$  g. The electron charge is abbreviated 'e' ( $-1.60206 \times 10^{-19} = e$ ) so that one electron has a charge of -e or just -1. It should be noted here that the minus (-) sign does not mean that the electron is short of electric charge but that its electrical charge is of the type called negative. The protons are positively charged and each has a charge of  $+1.60206 \times 10^{-19}$  coulombs and a mass of  $1.672 \times 10^{-24}$  g. As for the electron, the charge on a proton is simplified to +1. All the atoms except hydrogen also have neutrons which are neutral (have a charge of zero) but have a mass of  $1.675 \times 10^{-24}$  g. The other components of an atom include neutrinos, positrons,  $\mu$ -mesons and pi-mesons among others but the detailed nature of these is beyond the scope of this book.

The absolute masses of atoms cannot be determined as the atoms are too light. Only the relative masses can be obtained. To get these relative masses, we need to assign a weight to one atom (the standard) and relate the masses of the others to it. Initially, hydrogen which had been assigned a mass of one, was chosen as the standard. However, for some practical reasons a carbon atom with six protons and six neutrons (carbon-12) was later chosen as the new standard. The carbon-12 has a mass of exactly 12. The atomic masses of all the atoms were obtained with reference to a carbon-12 as the standard. However, with technological revolution in modern times, mass spectrometers are used to determine the relative masses of atoms directly. Note that the relative atomic masses are ratios hence have no units.

Since there are more than one atom for a particular element (isotopes, Section 1.5) with differing relative masses we need to calculate a weighted mean of their masses taking into account their



relative abundances. This weighted mean for the mass of a particular element is called the *atomic weight* of that element. Therefore, we define the atomic weight of an element as the weighted mean of the relative masses of the isotopes of that particular element. For example, chlorine has two isotopes with the relative masses and abundances of 35 (75.5%) and 37 (24.5%). Thus the atomic weight (the relative atomic mass) of chlorine is:

$$\left[ \frac{35 \times 75.5}{100} \right] + \left[ \frac{37 \times 24.5}{100} \right] = 35.49$$

It must be noted here that there is no chlorine in nature with a mass of 35.49. The atomic unit is called the **Atomic mass unit** (amu, given the SI unit,  $\mu$ ). One atomic mass unit is equivalent to  $1.66 \times 10^{-24}$  g. Using this basis of measurement, the mass of an electron is  $9.109 \times 10^{-28}$  g  $\div 1.66 \times 10^{-24}$  g/amu = 0.000548 amu and that of a proton is  $1.672 \times 10^{-24}$  g  $\div 1.66 \times 10^{-24}$  g/amu = 1.00725 amu and that of a neutron is  $1.675 \times 10^{-24}$  g  $\div 1.66 \times 10^{-24}$  g/amu = 1.00861 amu. Atomic mass units are usually rounded off to whole numbers called *Mass Numbers* (abbrev. A). This means that the mass of an electron is 0 while that a proton and a neutron each has a mass of 1. The mass number (A) of an atom is the sum total of the number of protons and neutrons (since electrons are so light their contribution to the total mass is ignored). If we abbreviate the mass of neutrons N, then we have:

$$A = Z + N$$

where A, is the mass number, Z is the number (= mass) of protons and N is the number (= mass) of neutrons.

Atomic weights are recorded on various periodic tables (see Section 1.11) such as the one shown in the inside cover of this book. It is possible to calculate the weight of an atom in grams or kilograms. Suppose, for example that  $6 \times 10^{23}$  hydrogen atoms weigh 1g, what is the weight of one hydrogen atom?. Simple proportion shows that one hydrogen atom weighs  $1g \div 6 \times 10^{23} = 1.66 \times 10^{-24}$  g. Note that the value obtained equals the weight of a single proton as given earlier. Since one hydrogen atom also weighs 1 amu, this confirms the fact that 1 amu equals  $1.66 \times 10^{-24}$  g. However, atomic weights are not usually expressed in grams or kilograms as the values become cumbersome in metric units.

Since  $6 \times 10^{23}$  hydrogen atoms weigh 1g and one hydrogen atom weighs 1 amu, it follows that 1g =  $6 \times 10^{23}$  amu. The figure  $6 \times 10^{23}$  (or more correctly  $6.0226 \times 10^{23}$ ) can be used to convert grams to atomic mass units. It is called the **Avogadro's Number** and its importance will be appreciated in Chapter 3.

### 1.5 ISOTOPES

Atoms of a particular element all have the same atomic number and therefore, the same number of protons. However, most of the elements do not have all their atoms with the same number of neutrons. *Such atoms belonging to the same element but having different numbers of neutrons in their nuclei are called isotopes.* It is to be expected therefore that isotopes should have different masses (note the contrast with Dalton's postulate discussed earlier). This is indeed the case as shown by the example below for the isotopes of hydrogen.

Name	Z	N	Mass Number (Z+N)
Hydrogen	1	0	1
Deuterium	1	1	2
Tritium	1	2	3

### 1.6 ELEMENTS AND COMPOUNDS

In the last section, we saw that elements consist of atoms. An element is a substance which contains only one kind of atom. Table 1.1 shows the names of some elements and their symbols.

Table 1.1: Some elements and their symbols

Name of element	Hydrogen	Nitrogen	Fluorine	Chlorine
Symbol	H	N	F	Cl

Note that the first letter in the name of some few elements is taken as a symbol of that particular element. For example, hydrogen is H, carbon is C, nitrogen is N and so on. However, because there are many more elements than the number of letters in the alphabet, some elements have two letters

in their symbols. For these, the first letter is always in capitalized and the second one is written in small letter. For example, chlorine is Cl, magnesium is Mg, neon is Ne and so on. In the foregoing examples, the first letter is derived from the English name. In other cases, the symbols of the elements are derived from Latin or German names. For example, Antimony is Sb (from Latin, Stibnium), Copper is Cu (from Latin, Cuprum), Iron is Fe (from Latin, Ferrum), Sodium is Na (from German, Natrium), and potassium is K (from German, Kalium), sodium is Na (from German, Natrium) and potassium is K (from German, Kalium).

A compound is formed when atoms of two or more different elements combine. Examples of some compounds include water ( $H_2O$ ), methane ( $CH_4$ ), glucose ( $C_6H_{12}O_6$ ) and so on. The kind and number of atoms in a compound are described by a formula as shown in brackets after the names of those compounds. The usage of a formula can also be extended to an element if it naturally exists as a molecule. An example is dichloride ( $Cl_2$ ).

A formula indicates the relative numbers of atoms in a substance. There are three types of formulae; empirical formula is the simplest and gives a bare minimum information about a compound. Diamond for example, consists of an array of carbon atoms each covalently bonded to four other carbon atoms but the formula of diamond, C, does not indicate this. The other empirical formulae include, among others, NaCl (sodium chloride) and SiC (silicon carbide). In the general empirical formula of a compound,  $A_xB_y$  (where A and B are the atoms combined), the subscripts x and y are usually unity. The second is a molecular formula, which has more information about a compound than an empirical formula. In the general formula  $A_xD_y$ , (where A and D are the atoms combined), the subscripts x and y in a molecular formula, are the actual numbers of atoms in the compound. For example, water has two hydrogen atoms and one oxygen atom; its molecular formula is therefore  $H_2O$ . The third type is a structural formula which shows how the atoms are joined to each other. In this case, the dashes are used to represent bonds and the atomic symbols represent atoms. For example, the structural formula of water is H-O-H. We will encounter more structural formulae when we come to organic compounds later.

(1) Empirical formula (minimum information about compound)  
(2) More information about compound  
Due to empirical formula  
Molecular formula  
Structural formula

## 1.7 RELATIVE MOLECULAR AND FORMULA MASS

In the last section, it was mentioned that compounds that exist as discrete entities, are described by a molecular formula. Such compounds are called molecules. Since the masses of atoms are relative, the masses of molecules are also relative. Each molecule has its own relative mass which is the sum of the relative atomic masses of the atoms in that molecule. We therefore define the *Relative Molecular Mass (RMM)* as the sum of the relative masses of the atoms in a molecular formula.

For example:

(a)  $\text{H}_2\text{O}$  has two hydrogens and one oxygen

$$\begin{aligned}\therefore \text{Relative molecular mass of water} &= (2 \times \text{relative atomic mass of hydrogen}) + \\ &\quad (\text{relative atomic mass of oxygen}) \\ &= (2 \times 1) + 16 \\ &= 18\end{aligned}$$

(b)  $\text{N}_2$  has two Nitrogen atoms

$$\begin{aligned}\therefore \text{Relative molecular mass of nitrogen molecule} &= (2 \times \text{relative atomic mass of} \\ &\quad \text{nitrogen}) \\ &= 2 \times 14 \\ &= 28\end{aligned}$$

(c)  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose) has six carbon, 12 hydrogen and 6 oxygen atoms

$$\begin{aligned}\therefore \text{Relative molecular mass of glucose} &= (6 \times \text{relative atomic mass of carbon}) \\ &+ (12 \times \text{relative atomic mass of hydrogen}) \\ &+ (6 \times \text{relative atomic mass of oxygen}) \\ &= 72 + 12 + 96 \\ &= 180\end{aligned}$$

Compounds that do not exist as discrete entities however, do not form molecules and are represented by empirical formula. For these we do not assign a Relative Molecular Mass; instead a Relative Formula Mass (RFM) is used. *The relative formula mass is defined as the sum of the relative masses of the atoms in an empirical formula*. For example:

$\text{NaCl}$  has one sodium atom and one chlorine atom

$$\begin{aligned}\therefore \text{Relative formula mass of NaCl} &= (1 \times \text{relative atomic mass of sodium}) + (1 \times \text{relative} \\ &\quad \text{atomic mass of chlorine}) \\ &= (1 \times 23) + (1 \times 35.5) \\ &= 58.5\end{aligned}$$

Fe - Iron  
 $\text{Na} - \text{Sodium}$   
 $\text{K} - \text{Potassium}$

7  
 $\text{H}_2 - \text{Dihydrogen (molecule)}$   
 $\text{H}_2 - \text{Dihydrogen (molecule)}$   
 20  
 When combining atoms  $\rightarrow$  a compound

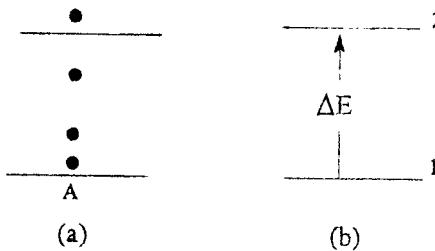
## **1.8 PURE SUBSTANCES AND MIXTURES**

A substance that contains only one kind of compound or element is said to be a pure substance. A bag of sugar, for example, contains only sugar molecules; therefore sugar is a pure substance. *Pure substances have got the same, definite composition. This means that the concentration of the substance in a pure compound is constant.*

When two or more different compounds (or elements) are put together and cannot react with each other, then we have a mixture. Air for example, which contains oxygen, nitrogen, water, carbon dioxide among others, is a mixture of gases. Unlike pure substances, *mixtures do not have definite compositions*. The composition of substances in air, for example, may vary depending on weather conditions. There are two types of mixtures; those in which the particles of each component are visibly present are called **heterogeneous mixtures**. An example is a mixture of say, salt and black pepper. The second type of mixture is where the particles of one component are evenly dispersed amongst those of the other. These are called **homogeneous mixtures**. They are also called **solutions** (see Chapter 3). Sugar or salt dissolved in water; methanol mixed with water; air on its own, are some examples of solutions.

## **1.9 QUANTUM THEORY**

It is common experience that when you hit a football, it will move to any distance depending on the amount of energy you give it. Consider Figure 1.2a as an example. The ball which is hit from position **A**, can stop at any of the dark points indicated. In this case, we say that the **energy of the ball** is continuous; That is, the ball can have any amount of energy. The motion of the ball here, is a part of the physics called **classical physics**. Newton's Laws of motion are part of this physics. In reality, laws of classical physics apply to large particles such as the ball, automobiles, etc.



**Figure 1.2:** Comparison of a football having any amount of energy (a)(classical physics) and another one having only enough energy to take it from one point to the next (b)(quantum physics)

When classical physics was applied to atoms and other smaller particles, the results obtained were contrary to those expected. In 1900, Max Planck solved this mystery by stating that the energy of an object is not continuous; and that the object will only acquire enough energy to take it from one energy level to another. Figure 1.2b illustrates this. If we give energy to an object in state 1, the object will only move to state 2 if it has acquired enough energy equal to  $\Delta E = E_2 - E_1$  (where  $E_2$  is the energy of state 2 and  $E_1$  that of state 1). The energy in this case is in form of a packet or bundle and so, we speak of the energy being quantized. *Thus the object can only have a certain definite energy value.* Planck called this packet of energy ( $=\Delta E$ ) a **quantum of energy**. If the energy of the object in energy level 1 is less than  $\Delta E$ , the object will not move. This started a new branch of physics called **quantum physics** whose laws apply to tiny particles like atoms, electrons, etc.

On the basis of this quantum theory, Bohr in 1913 said that electrons move around the nucleus in circular orbits and as they do so, they emit or absorb energy that is quantized (it is now known that electrons do not actually behave this way). *Centrifugal or centripetal force*

The energy of an electron is governed by an integer called the **Principal Quantum Number (n)**. The principal quantum numbers are just arbitrary numbers which are introduced in order to make predictions match experiment. They are given numbers 1,2,3,4, etc, increasing as an electron moves further away from the nucleus. In simple terms, the principal quantum numbers are the shell numbers; thus the K shell is principal quantum number 1, L shell is principal quantum number 2 and so on.

The modern quantum theory says that electrons move around the nucleus in a definite region of space. *The region of space in which the electron spends at least 95% of its time is called an orbital.* The orbitals are arranged in **shells** around the nucleus. For each principal quantum number ( $n$ ), there are  $n^2$  orbitals. These are shown in Table 1.2. Note that numbering starts from the innermost shell since the K shell is shell number 1 (that is principal quantum number 1).

**Table 1.2:** Shell symbols, orbitals and the maximum number of electrons in them for each principal quantum number

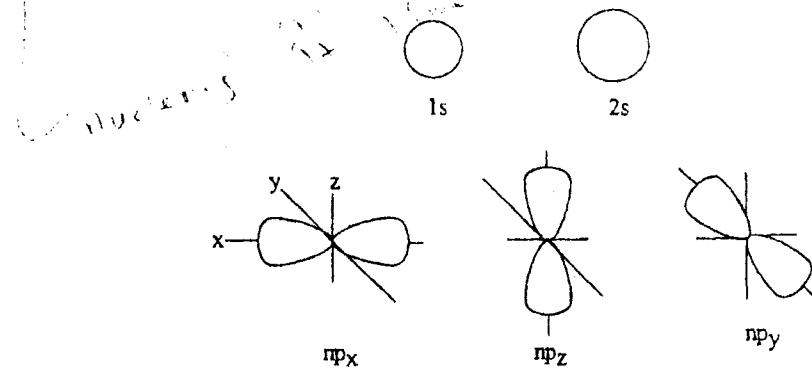
Shell Number ( $n$ )	Symbol	Number of orbitals ( $n^2$ )	Maximum number of electrons <sup>2</sup>
1	K	1	2
2	L	4	8
3	M	9	18
4	N	16	32
5	O	25	50
6	P	36	72

Apart from the K shell which has one orbital (the s orbital), both theory and experiments have shown that the group of orbitals in each of the L, M, N, etc., shells do not have the same energies especially in a many-electron atom. In a hydrogen atom, which has only one electron, the orbitals in each group have the same energy. Such orbitals having the same energy are said to be **degenerate**. In a many-electron atom, the L shell has two energy levels; the lower one has one orbital which is called an **s orbital**, the higher one has three identical orbitals which are degenerate and these are called **p orbitals**. The s orbital is spherical whereas the p orbitals are dumb-bell shaped situated at right angles to each other and in three dimensions along the x-, y- and z-axes; hence designated  $np_x$ ,  $np_y$  and  $np_z$ , respectively, (where  $n$  is the principal quantum number) as shown in Figure 1.3.

The M shell has three energy levels; the lowest one consists of one orbital (also an s orbital), the second one has three orbitals which are identical and degenerate (also called p orbitals); and the third level consists of five degenerate orbitals called **d orbitals**. The N shell has four energy levels, s, p and d just like the M shell, but in addition, the highest one has seven degenerate orbitals called **f orbitals**.

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<sup>2</sup>The maximum number of electrons allowed for each n-value is  $2n^2$  (see Section 1.10).



**Figure 1.3:** s and p orbitals of an atom

Therefore, within a given shell, the energies increase in the order  $s < p < d < f^3$ , etc. It was stated earlier that the energy of the electron is governed by the principal quantum number  $n$ ; this number also governs the size of the orbitals. As shown in Figure 1.3, an s orbital of principal quantum number one (denoted 1s) is smaller than an s orbital of principal quantum number two (denoted 2s). As we shall see in the next section, the orbitals can be specified by the "n" values in which they appear; thus we would talk of a 1s orbital to mean an s orbital of principal quantum number one. Similarly, a 2s or 3s orbital would mean an s orbital in principal quantum numbers two and three respectively. Analogously, 2p orbitals are those of principal quantum number two ( $2p_x$ ,  $2p_y$ , or  $2p_z$ ). In the same way, we can also specify an electron in a particular orbital. Thus a 1s electron or a 3d electron means an electron in the s orbital of principal quantum number one or an electron in the d orbital of principal quantum number three, and so on.

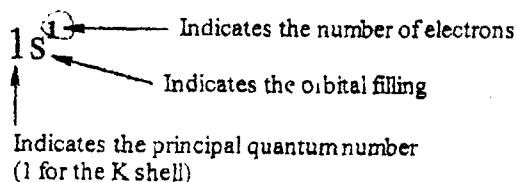
### **1.10 ELECTRONIC STRUCTURES**

Electrons are added to each atom, one at a time across a period. The lowest energy orbitals fill first and once those are full, the next lower energy ones fill and so on. Structures which show the  $n$ -values and their orbitals that are occupied, together with the number of electrons in them are called **electronic structures**. The question one can ask at this point is: "how many electrons can a single

<sup>3</sup>The symbols s, p, d and f arise from electronic transitions in spectroscopy; s for Sharp, p for Principal, d for Diffuse and f for Fundamental (see for example, the more advanced references 1 and 4).

orbital accommodate?". The answer to this question was arrived at by Wolfgang Pauli, who introduced a restriction on the number of electrons which can go into a single orbital. The restriction called the *Pauli Exclusion Principle* states that "any orbital will not hold more than two electrons". This means that any orbital can hold 0, 1 or 2 electrons but not more than 2. Therefore, *the maximum number of electron allowed for each n value will be equal to  $2n^2$*  (see Table 1.2)..

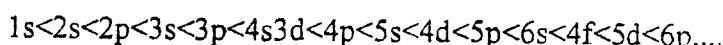
In any atom the K shell is the lowest in energy followed by the L and then the M and so on. Within a shell, the s orbital is the lowest in energy followed by the p orbitals and then the d orbitals and so on. *The lowest energy shell and the lowest energy orbital in that shell fills first.* With this and the Pauli Exclusion Principle in mind, we can now write the electronic structures for some of the atoms. We begin with the simplest atom, hydrogen. This atom has got only one electron, and this will therefore, go into the s orbital of the K shell. The electronic structure we can write for hydrogen is therefore,  $1s^1$ .



The lowest energy level of an atom is called the *ground state* of that atom. For example, we have seen above that in hydrogen the electron normally resides in the  $1s$  orbital. The electronic state  $1s^1$  is the lowest energy state for hydrogen and it is therefore the ground state. However, the electron in hydrogen can also move to higher levels, say to a  $2s$  orbital. Such states of higher energy are called excited states of the atom.

Note that the s orbital of the K shell of hydrogen is half-full so that in the next atom, helium, an added electron will go into the same orbital and the electronic structure for helium is therefore  $1s^2$ . At this point, the s orbital of the K shell is full in accord with Pauli Exclusion Principle. In the next atom, lithium (Li), the L shell starts filling and the electron will go into the s orbital of this shell ( $n = 2$ ). The electronic structure of lithium is therefore,  $1s^2 2s^1$  and that of beryllium (Be) is  $1s^2 2s^2$ . The s orbital of the L shell is now filled up, and in the next atom boron (B), the p orbitals of the L shell

start filling so that the electronic structure of boron is  $1s^2 2s^2 2p^1$ . Since there are three p orbitals, six electrons are required to fill them completely and the atoms B, C, O, F and Ne all fill up the 2p orbitals with Ne having the electronic structure  $1s^2 2s^2 2p^6$ . The trend is the same in the third row of the periodic table. The s orbital fills first for this row (note: this is the s orbital of the M shell) in Na and Mg, followed by the p orbitals. The d orbitals are not filled. In the fourth row, the s orbital of the N shell fills first (in K and Ca). In the next atom scandium (Sc), the d orbitals of row three become lower in energy than the p orbitals of row four, and so they start filling. The electronic structure we can write for scandium is therefore,  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ . The d orbitals require ten electrons (for the five of them) and the ten atoms Sc to Zn fill these orbitals. After the 3d orbitals are filled, the p orbitals of the fourth row start filling. Again, note that the d and f orbitals of the fourth row are not filled at this point. The d orbitals for row four are filled in the fifth row after the s orbital of that row is filled. In the sixth row, the s orbital of that row fills first and then the next electron in La (atom 57) enters the 5d orbital after which, the f orbitals of row four (elements Ce-Lu) start filling. These require fourteen electrons (for the seven of them) and so we see a group of fourteen atoms normally written at the bottom of the table. After the 4f orbitals are filled, the 5d orbitals continue filling in the remaining nine atoms (Hf-Hg; note that one 5d electron went into La) followed by the 6p orbitals. The filling up of electrons into orbitals becomes complicated as we go down the table so that we will not continue any further. From the foregoing discussion, we note that the orbitals are filled in the order:



The electronic structures are also written in the same order. There are three points to be noted in these structures. The first is that the sum of the superscripts in the electronic structure gives the atomic number of the atom. For example, in the electronic structure of oxygen,  $1s^2 2s^2 2p^4$ , the sum of the superscripts is 8 ( $2+2+4$ ), so the atomic number of oxygen is 8. This means that once we know the atomic number of an atom, we can easily write its electronic structure and vice versa. The second is that the sum of the electrons in the highest principal quantum number, especially for the main group atoms, gives the group number of that atom. For example, in the electronic structure of oxygen, the highest principal quantum number is 2, and there are 6 electrons there ( $2+4$ ). So

oxygen is a group 6A element. Finally, *the highest principal quantum number in the electronic structure gives the period in which that atom appears*. In the example of oxygen, the highest principal quantum number in its electronic structure is 2, so oxygen is in period 2.

**1.10.1 Hund's rule:** The Pauli Exclusion principle stated earlier tells us exactly how many electrons can go into a particular orbital; *an orbital will not have more than two electrons*. With this principle, we can straight away write the electronic structure of for example, carbon as,  $1s^2 2s^2 2p^2$ . In Section 1.9, we saw that there are three degenerate p orbitals designated  $np_x$ ,  $np_y$ ,  $np_z$ . The question now arises: "how do the two 2p electrons of carbon enter the three p orbitals?". There are two possibilities; either both can go into the  $2p_x$  orbital (i.e.,  $1s^2 2s^2 2p_x^2$ , with the  $2p_y$  and  $2p_z$  orbitals empty) or one can go into the  $2p_x$  and the other one into the  $2p_y$  (i.e.,  $1s^2 2s^2 2p_x^1 2p_y^1$  with the  $2p_z$  orbital empty). **Friedrich Hund** came up with a rule that is used to decide which electronic structure will be the most stable. The rule, called Hund's rule states that "**electrons will occupy degenerate orbitals singly if those orbitals are empty**". This means that as long as there is a set of orbitals with the same energy, the electrons will go in separate orbitals until each such orbital has one electron. After that, additional electrons will start pairing up in accord with the Pauli Principle. With this, we can write the most stable electronic structure of carbon as:  $1s^2 2s^2 2p_x^1 2p_y^1$  (note: the choice of which orbital is occupied i.e., whether the  $2p_x$ ,  $2p_y$  or  $2p_z$ , is pure arbitrary). The electronic structure of nitrogen, oxygen, fluorine and neon are: N:  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ , O:  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ , F:  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ , Ne:  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$ . Note that nitrogen has one electron in each of the p orbitals in accord with Hund's rule and that pairing starts in oxygen. The same trend applies to the d orbitals and also, the f orbitals.

- \* **1.10.2 Paramagnetism and diamagnetism:** The electronic structure of carbon given above has two unpaired electrons in the p orbitals while nitrogen has three such electrons. Oxygen and fluorine have two and one unpaired electrons respectively, while neon has no unpaired electrons. Elements such as carbon, with unpaired electrons, tend to be attracted by a magnet and are said to be **paramagnetic**. Elements such as neon with all the electrons paired, tend to be repelled by a magnet and are said to be **diamagnetic**.

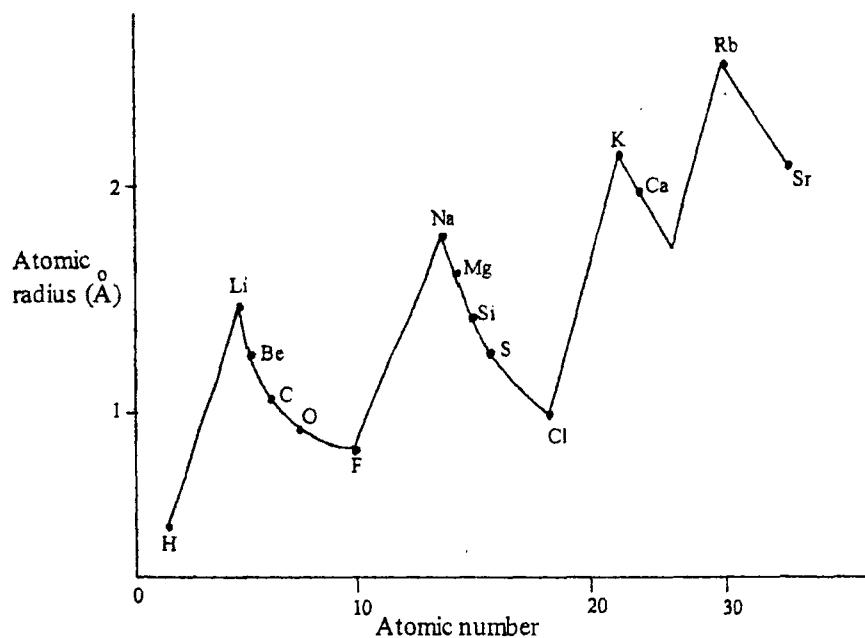
## 1.11 PERIODIC TABLE

The periodic table groups elements with similar chemical and physical properties together. Initially, the Russian chemist, Dmitri Mendeleev grouped elements in order of increasing atomic weights but this arrangement was later changed to one which grouped the elements in order of increasing atomic numbers. It was observed that if elements were arranged in order of increasing atomic numbers, elements with similar chemical properties recurred periodically and at regular intervals. This so called *periodic law* was used in the construction of the periodic table whose widely used version is shown on the inside of the back cover. In that table, there are eighteen (18) vertical columns which are called **groups** and about seven (7) rows, called **periods**. *All the members of a group have the same outer shell electron configuration, apart from the "n" value which is different.* For example, the lithium group elements all have the  $ns^1$  outer shell configuration. Members of a group also have similar chemical properties (see Section 1.12). *Group 1a elements are called alkali elements* (hydrogen is not included in this group). *Group 2a elements are called alkaline earth elements*, and these have the  $ns^2$  outer shell structure. *Group 7a elements are called halogens* with an outer shell configuration of  $ns^2np^5$ . *Group 8a elements are called rare gases or noble gases.* Another way of naming the different groups of elements depends on the outer shell orbital which the different groups fill. *Thus, groups 1a and 2a elements are called s-block elements. Groups 3a-8a elements are called p-block elements.* Groups 1a to 7a which have incompletely filled s and p orbitals of the highest n-value are also referred to as **representative (or main group) elements** while the noble gases have a completely filled p orbital of highest n-value. *Groups 1b-8b in which the d orbitals are filled are called d-block elements. Groups 1b, 3b-8b have incompletely filled d orbitals* and these are referred to as **transition elements**. Group 2b, with a completely filled d orbital is not normally included in the group of transition elements. *The elements Ce-Lu, in which the 4f orbitals are filled are called rare earth elements or lanthanides. The elements Th-Lr, in which the 5f orbitals are filled are called actinides* (another group of rare earth elements). The lanthanides and actinides together are called the **inner-transition elements or f-block elements**.

**1.11.1 Periodicity:** As it has been mentioned in the previous section, the periodic table groups elements with similar outer shell electronic configurations together. This periodicity leads to

elements with similar chemical properties falling in the same group. A few examples will illustrate this periodicity.

Atomic sizes of atoms can be used to show the variation of chemical properties. The atomic radius is a good indication of the size of an atom. In both the diatomic molecules such as chlorine and the metals, the atomic radius is obtained by taking half the distance between the two nuclei of the atoms that are "touching". Now if atomic radii of various atoms are plotted against their respective atomic numbers, then Figure 1.4 results

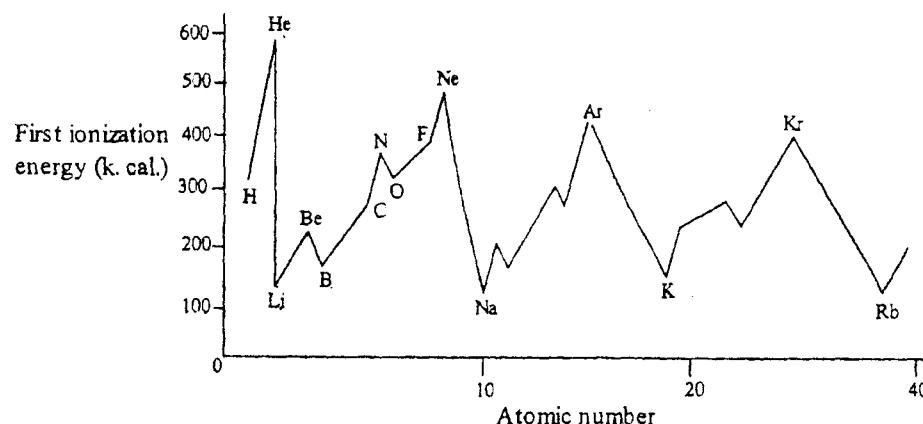


**Figure 1.4: Variation of atomic radii of the elements with atomic number**

Although the atomic radius is a physical property, it has a profound effect on chemical properties. In Figure 1.4, note that the alkali elements have large atomic radii. This is because these elements always "see" the beginning of a new shell, i.e., an additional electron starts filling a new shell as we move from one period to the next. The periodicity here is shown by the fact that the group 1 elements have the largest radii (hence sizes), the elements in the middle of the table have smaller sizes and so

a repeating pattern is obtained with successive periods. In Figure 1.4, the elements Lithium (Li) to Fluorine (F), are in the same period (have the same number of shells) as are sodium (Na) to chlorine (Cl). Taking period two (with atoms Li to F) as an example, we notice that the atomic radius decreases as we move from Li to F, i.e., from left to right in that row. *Why is this so?*. In answering this question, let's first consider the force of attraction between the outer shell electron and the nucleus. We will take lithium as our example. This atom has two electrons in the inner (K) shell and one electron in the outer (L) shell. Its nuclear charge is +3. The electron(s) in the K shell prevent the outer electron from experiencing the full attractive force of the nucleus. We say that the outer shell electron in lithium is shielded from the nucleus by the two inner shell electrons. The consequence of this is that the net force of attraction experienced by the outer shell electron from the nucleus, is as if the two inner electrons were placed at the nucleus where there is also a +3 positive charge. The net force of attraction of the outer shell electron to the nucleus is therefore +1 (i.e., +3 - 2). *We say therefore that the effective nuclear charge of lithium is +1*. If we make similar calculations for all the atoms in a period, we find that the effective nuclear charge increases from +1 to +8 across a period. Since the number of shells is the same in a period, the effect of increased effective nuclear charge as we move from left to right is that the radii become smaller and smaller.

Another example to illustrate the periodicity is to look at the first ionization energy (see Section 1.13). A plot of these energies against atomic number is given in Figure 1.5.



**Figure 1.5: Variation of the first ionization energy with atomic number**

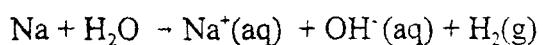
The above graph resembles that of Figure 1.4 in shape. A few things should be noted from graph. As we move along a period of the periodic table (e.g., from Li to Ne), there is a rise in the first ionization energy. This rise is due to increasing effective nuclear charge in the atoms; +1 in Li to +8 in Ne, so that less energy is required to remove an electron from an atom with a smaller effective nuclear charge (e.g., of +1) than from an atom with a larger effective nuclear charge (e.g., of +8). Note that the atoms in the same period have the same number of shells. From one period to the next one below (e.g., from He to Li), there is a general drop in the ionization energy. This is because as a new period starts, a new shell begins to fill (see Figure 1.1) and this results in an instant increase in the radius of the first atom. Since alkali elements always "see" the beginning of a new shell, these elements have the lowest first ionization energies. Note that these elements are at the bottom of the curve in Figure 1.5.

Within a group, there is also a general drop of the first ionization energy. This is due to increasing atomic radius from top to bottom (e.g., He to Kr). The periodic recurrence of atoms with similar electronic configurations has been illustrated with the two examples above. We shall see later that this periodic recurrence of similar configurations leads to periodic recurrence of chemical and physical properties as well.

## **1.12 SOME REPRESENTATIVE ELEMENTS OF IMPORTANCE**

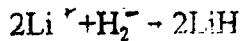
**1.12.1 Group 1a Elements:** **Li, Na, K, Rb, Cs, Fr.** These elements have one outer shell electron, with the  $ns^1$  structure. Group 1a elements are called **alkali elements**. These elements are so reactive that they are rarely found in elemental. They are soft, malleable and have a silver luster and being metals, they are good conductors of heat and electricity. They have low melting points which decrease down the group from 180 °C in lithium to 28.7 °C in cesium. Francium (Fr) occurs only in small amounts and most of its isotopes are radioactive( see footnote on page 21).

Alkali elements all have similar chemical properties. They are strong reducing agents as shown by their violent reaction with water, exemplified by sodium:



The hydroxides produced are high melting solids which are soluble in water. The great reactivity of

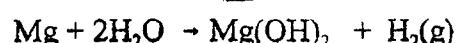
these elements is reflected in their atomic structure and their large atomic radius. The atoms lose the outer electron to acquire the electronic configuration of the nearest inert gas. Since the radii increase down the group, the outer electron in the heavier elements, such as cesium, is loosely held by the nuclear charge compared to the outer electron in the lighter elements such as lithium. Consequently, reactivity of the alkali elements increase as we go down the group. The reaction of potassium with water is more vigorous than that of sodium with water, for this reason. Alkali elements also react with hydrogen to give hydrides, e.g.,



Alkali elements also react with oxygen to form oxides. Simple monoxides of the form  $\text{M}_2\text{O}$  are only formed with lithium. Sodium gives  $\text{Na}_2\text{O}_2$ , a peroxide on direct reaction with oxygen. The other metals give superoxides of the form  $\text{MO}_2$ .

**1.12.2 Group 2a Elements:** Be, Mg, Ca, Sr, Ba, Ra. These elements have two outer shell electrons, with the  $ns^2$  structure, with the exception of helium which belongs to group 8a. Group 2a elements are called **alkaline earth elements**. These elements are also rarely found in the elemental state. They are hard, dense, with high melting and boiling points and being metals, are good conductors of heat and electricity. Radium is radioactive (see footnote on page 21). Compared with group 1a elements, group 2a elements have larger nuclear charges hence, their atomic sizes are smaller than those of group 1a elements.

Alkaline earths react with water only at high temperatures (compare, group 1a) to form hydroxides:



These elements are, like group 1a elements, very reactive. Their reactivities also increase down the group for the same reason as the alkali elements. Unfortunately, *elements like magnesium, readily react with oxygen in the air and form a thin layer of metal oxide on the surface of the metal. This greatly reduces their reactivity. Magnesium is therefore, much less reactive with say, cold water than calcium is, unless the water is heated up.*

At high temperatures, the elements in their metallic form can reduce other compounds as in the

following example:



The resulting oxides are strong bases which react with acids and to some extent, water. In the latter solvent, the oxides form hydroxides (e.g., magnesium hydroxide, also known as *milk of magnesia*  $\text{Mg}(\text{OH})_2$ ). The solubilities of the hydroxides in water increase in the order:  $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{Be}$ .

**1.12.4 Group 4a Elements: C, Si, Ge, Sn, Pb.** Group 4a elements have four outer shell electrons with the  $ns_2np^2$  structure. Carbon is a non-metal, silicon and germanium are metalloids (such elements with properties between non-metals and metals are also termed *semi-metals*) and tin and lead are metals. Large amounts of carbon are found in living systems (plants and animals). There are two forms (different forms of the same element are also called *allotropes*) of carbon: graphite, which is widely used for making pencil leads is an extended multilayered structure. In this structure, carbon atoms form six-membered rings which in turn, are joined to each other to form a planar structure. Several of these layers are then stuck together by Van der Waals forces (see Chapter 2). Graphite conducts electricity in plane parallel to the plane but not perpendicular to it. The other allotrope of carbon is diamond in which each carbon is covalently bonded to four other carbons to form a three dimensional network which is hard. Carbon is somehow unique in group 4a in that it is able to form compounds in which several carbon atoms are bonded to each other to form chains or rings. This property of carbon is called catenation and is responsible for the variety of organic compounds. Organic compounds are discussed in Chapters 11-14.

Silicon occurs in silica ( $\text{SiO}_2$ ) and silicate minerals. Silicon is widely used in the manufacture of computer chips and transistors. Lead occurs mostly in the metallic form. It is used for making electrodes in car batteries and also as an oil additive in the form of tetraethyllead ( $(\text{CH}_3\text{CH}_2)\text{Pb}$ ). Group 4a elements can form are able to form four covalent bonds in their compounds. Examples include the hydrides (e.g.,  $\text{CH}_4$ ,  $\text{SiH}_4$ ,  $\text{PbH}_4$ ), chlorides (e.g.,  $\text{CCl}_4$ ,  $\text{SnCl}_4$ ) and oxides (e.g.,  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{GeO}_2$ ). However, from silicon downwards, the elements can also form six covalent bonds. For example,  $\text{SiF}_6^{2-}$ ,  $\text{Pb}(\text{OH})_6^{2-}$ .

## Elements

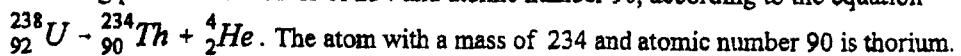
**1.12.4 Group 5a Elements:** N, P, As, Sb, Bi. Elements in this group have five outer shell electrons. The outer shell configuration is  $ns^2np^3$ . Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while bismuth is a metal. Nitrogen occurs in abundance in the atmosphere as a diatomic molecule,  $N_2$ . Phosphorus exists in rock phosphates ( $Ca_3(PO_4)_2$ ). Arsenic and antimony occur mostly as sulphite minerals while bismuth exists in pure form as a metal.

There are three allotropes of phosphorus: the reactive white phosphorus has a tetrahedral structure ( $P_4$ ), red phosphorus exists as a polymer and the third form, black phosphorus is a layer structure much like graphite. Arsenic and antimony also have tetrahedral structure  $As_4$  and  $Sb_4$  respectively.

Group 5a elements form various compounds including hydrides (e.g.,  $NH_3$ ,  $PH_3$ ,  $AsH_3$ ,  $SbH_3$ ,  $BiH_3$ ), oxides (e.g.,  $NO$ ,  $NO_2$ ,  $P_2O_5$ ,  $As_4O_6$ ,  $Bi_2O_3$ ) and halides (e.g.,  $NF_3$ ,  $PCl_3$ ). The hydrides are basic compounds and this basicity decreases as we go down the group.

**1.12.5 Group 7a Elements:** F, Cl, Br, I and At. These elements have seven outer shell electrons, i.e., the  $ns^2np^5$  structure. Group 7a elements are called the halogens and unlike groups 1a and 2a elements which are metals, these are non-metals. Astatine (At) is a radioactive<sup>4</sup> element. Fluorine is the most electronegative (see Section 1.13.3) of the elements and usually has an oxidation number of -1 (see Chapter 8). The other elements are also electronegative but unlike fluorine, they exhibit both negative as well as positive oxidation numbers. Halogens are very reactive and they act as oxidants in most of their reactions. Their strength as oxidants decreases as the atomic number increases. Unlike group 1a and 2a elements, halogens gain electrons when they react. This means that the smaller the volume of the element, the easier it will grab the electrons. Consequently, reactivity in the halogens increases as we go up the group, with fluorine being more the most reactive. The reaction of potassium with fluorine is more vigorous than that of potassium with chlorine. Halogens are colored, poisonous molecules with unpleasant smell; fluorine is a yellow gas,

<sup>4</sup>Radioactivity is a spontaneous emission of radiation and particles from an unstable nucleus of an atom. For example, uranium-238 is an unstable element which emits  $\alpha$ -radiation ( $He^{2+}$  ions with a mass of 4) and the remaining particle has a mass of 234 and atomic number 90, according to the equation



chlorine is green/yellow gas, bromine is red and iodine is a purple solid.

Group 7a elements react with metals to form metal halides. Large metals, with low oxidation numbers (e.g., +1 or +2), form ionic halides whereas small metals with high oxidation numbers result in semi metallic halides. Halogens also react with each other as shown by the oxidation of bromide ( $\text{Br}^-$ ) by chlorine- a reaction that is used to recover bromine from sea water.



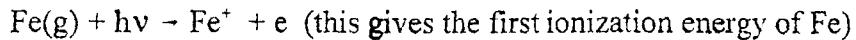
**1.12.6 Group 8a Elements:** He, Ne, Ar, Kr, Xe, Rn. Group 8a elements have eight outer shell electrons with the  $\text{ns}^2\text{np}^6$  structure except helium which has the  $\text{s}^2$  structure. Group 8a elements are called **rare, inert or noble gases**. Since they have a complete octet, their structures are very stable, hence the name **inert**. The word **inert** is however, a misnomer since compounds of some of these elements have been detected such as xenon difluoride ( $\text{XeF}_2$ ) and xenon oxyfluoride ( $\text{XeOF}_2$ ), among others. *It is perhaps important to note that it is only this group of elements that has atoms which exist in nature as single-atomed molecules.* This property is a reflection of the stable electronic configurations of these elements.

### **1.13 SOME ATOMIC PROPERTIES OF THE ELEMENTS OF THE PERIODIC TABLE**

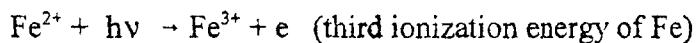
In the preceding section, we have looked at only four of the groups of concern at this stage. In order to increase depth on the other groups, the student is advised to consult the reference books given in this chapter. For the mean time, we turn our discussion to some properties of elements of the periodic table.

**1.13.1 Ionization energy:** Ionization energy is defined as *the minimum energy required to remove an electron from a gaseous atom to form a gaseous ion*. There can be the first ionization energy corresponding to the removal of the first electron from the atom. Similarly, the second, third and so on, ionization energies can be obtained corresponding to the removal of the second, third, etc., electrons respectively. For example, when iron is exposed to a high energy radiation  $h\nu$  (where  $h$ , is Planck's constant equal to  $6.63 \times 10^{-34}$  Joules second per molecule and  $\nu$ , is the frequency of radiation), it is possible for an electron to be removed from the gaseous iron atom to form  $\text{Fe}^+(g)$  (a

gaseous iron ion), viz:



and subsequently, we can have:



and so on.

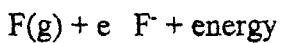
We have already discussed the periodicity in the values of the first ionization energies in Sub-section 1.11.1. We saw that within a period, the first ionization energy increases across a row due to increasing effective nuclear charge. This trend starts again in the next period and so on.

There is one striking observation in Figure 1.5 however, which needs some clarification. While we say that ionization energies increase from left to right within a period, we note that there are some breaks or drops somewhere in the rows. In other words, the trend is not smooth. For example, in the second period, (Li to Ne), boron (B) has lower first ionization energy than beryllium (Be). Similarly, we notice that oxygen (O) has lower first ionization energy than the preceding atom, nitrogen (N). Taking the first pair of atoms (B and Be) first, the electronic structures of these elements are Be:  $1s^2 2s^2$  and B:  $1s^2 2s^2 2p^1$ . The lower first ionization energy of boron is a result of the fact that the p orbital in this element is higher in energy than the s orbital of the same principal quantum number. This means then that less energy is required to remove the "2p" electron in boron than the "2s" electron in beryllium.

Electrons are negatively charged and so they repel each other. When the electrons occupy orbitals, the **Pauli exclusion principle and Hund's rule** (Section 1.10) will apply. With these two rules in mind, (i.e., Hund's and Pauli's principle), the electronic structure of nitrogen (see also Sub-section 1.10.1) is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  (note that there are three of the p orbitals all degenerate and situated at right angles to each other along the x-, y- and z-axes). When another electron goes into oxygen, it will go into one of the p orbitals already containing an electron (recall that a maximum of six

electrons are required for the p orbitals each one taking two electrons in accord with Pauli exclusion principle). The two electrons will thus repel each other; this repulsion is in fact, far more than the increased nuclear charge from nitrogen to oxygen. As a result, it is easier to remove the first electron in oxygen than that in nitrogen. This explains the lower first ionization energy of oxygen than that of nitrogen.

**1.13.2 Electron Affinity:** The electron affinity is the energy released when an electron is added to a gaseous atom. For example, when an electron is added to a gaseous fluorine atom, energy is given out, viz.:



The resulting ion in the above equation (an anion) is called a fluoride ion. There can be the first, second, third, etc., electron affinities corresponding to the addition of the first and so on, electrons. Energy will be given off when an electron is added to an atom as in the example above, so that the electron affinity for say, fluorine will be a negative quantity. *The more negative the electron affinity, the more stable the resulting ion formed. In other words, the more negative the values, the greater the tendency of the gaseous atom to grab an electron. Positive values then mean that the gaseous atom involved, does not readily grab electrons.* In this case the ion formed would be unstable. When a second electron is added to the fluoride ion ( $F^-$ ), there will be repulsion between the first added electron and the second one, so that the second electron affinity will be positive. Some selected electron affinities are given in Table 1.3.

**Table 1.3:** Some selected electron affinities (kJ/mole)

H						
-72						
Li	B	C	N	O	F	
-52	-29	-120	-3	-141	-333	
Na		Si	P	S	Cl	
-71		-180	-70	-201	-343	
			I			
			-295			

A Few things need to be noted here. The electron affinity of an atom will equal to the first ionization energy of the corresponding anion. In the case of fluorine, for example, the electron affinity of F(g) will be equal to the first ionization energy of F<sup>-</sup>(g). This is an example of the law of conservation of energy. In Table 1.3, it can be seen that halogens have the highest electron affinities compared to the other elements, implying that the ions (halides) formed from these elements are quite stable. Although the trends in the values of the electron affinities are not distinct, in general non-metals have higher values than metals. Also, the values tend to increase across a period as atomic number increases but they tend to decrease down a group.

✓ **1.13.3 Electronegativity:** Electronegativity is the power with which an atom will attract electrons to itself in a molecule. Electronegativity values are obtained by considering the energy released when a bond breaks. The values have been adjusted so that fluorine, the most electronegative element, has a value of 4.0. As such, electronegativities are relative numbers rather than measurable quantities like electron affinities. An atom that tends to acquire rather than lose electrons is said to be electronegative. It will be seen in Chapter 2 that electronegativity plays an important role in determining the polarity of bonds, i.e., whether the bond between two atoms is covalent, ionic or metallic. Electronegativity values for some elements are given in Table 1.4.

**Table 1.4:** Electronegativity values of selected elements

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca					
0.8	1.0					

As Table 1.4 shows, electronegativity values tend to increase across a period and decrease down the group. The halogens have the highest values and so they are the most electronegative of all the elements in the periodic table. In contrast, the metals have the lowest values. Also, note that electronegativity values show more periodicity.

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## MORE ADVANCE TEXTS

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## 2

# CHEMICAL BONDING

### Learning Objectives

By the end of this Chapter students should be able to describe the types of bonds and how they are formed.

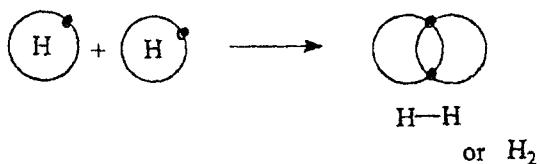
**2.0** It was mentioned in Sub-section 1.12.6 that only the rare gases exist as single atoms in nature. The atoms of most elements are linked together by chemical bonds to other atoms to yield molecules, e.g., H-H ( $H_2$ ) or I-I ( $I_2$ ). They may also unite with other elements to form compounds, e.g.,  $CH_4$ . *The link holding the atoms together is called a bond.* Bonding occurs in an attempt by an atom to acquire the inert gas configuration, either by removing, gaining or sharing of electrons. The inert gas configurations, are so called, because they are stable and so most atoms strive to acquire them. Bonding, therefore, involves shells that are not completely filled with electrons, the outermost shells. Electrons in the outermost shells are termed **valence electrons**. Since noble gases have outer shells that are filled,

they are not usually involved in bonding to other atoms. The electrons that are involved in bonding are called *bonding electrons* as opposed to *non-bonding electrons* or *lone pair electrons* that are not involved in bonding.

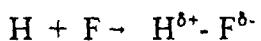
### 2.1 ELECTRONEGATIVITY AND BONDING

Bonding can involve either the same atoms, as in hydrogen molecule (H-H) or it can involve two different atoms, as in hydrogen fluoride (H-F). Molecules of the former type are called homonuclear diatomic molecules and those of the latter type are called heteronuclear diatomic molecules. The nature of the chemical bond is determined by the electronegativity values of the two uniting atoms.

If the two atoms have got the same electronegativity values, they will attract each other's electrons equally, and the compromise is reached by them sharing the electrons. An example with hydrogen ( shown below ) will make this clear:



The shared pair of electrons will be in the middle of the two nuclei. Note that each hydrogen atom gets a share of the other's electron and so acquires the helium (He) configuration. On the other hand, if the two uniting atoms have got different electronegativity values, one will attract the electrons more than the other and an example with hydrogen fluoride is shown below:

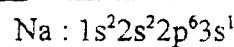
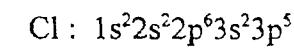


Since fluorine is more electronegative than hydrogen, the electrons spend more time closer to it than to hydrogen. This makes fluorine acquire a partial negative charge ( $\delta^-$ ) and hydrogen has acquired a partial positive charge ( $\delta^+$ ). *Such a molecule with partial charges is said to be polarized.* In a polarized molecule such as HF, the electrons are still shared as in  $\text{H}_2$ , but unequally. Some molecules however, exhibit extreme polarization in which the electrons are completely transferred from one atom to the other. This situation exists mostly where one atom is a metal and the other is a nonmetal. Different types of bonds are formed depending on the electronegativity of the uniting atoms. We look at some of these in the next section.

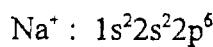
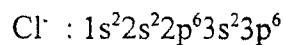
## 2.2 TYPES OF CHEMICALS BONDS

**2.2.1 Ionic Bond:** The ionic bond involves atoms that have different electronegativities. This is where extreme polarization is exhibited. One atom (usually a metal) transfers its electron(s) completely to another atom (usually a nonmetal). The former becomes positively charged and is called a *cation*, while the latter becomes negatively charged and is called an *anion*.

Consider sodium chloride (NaCl). The electronic structures of sodium and chlorine are:

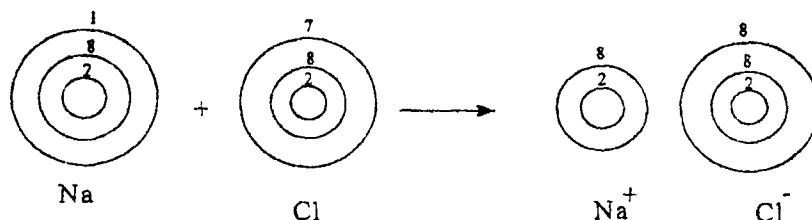


If the 3s electron of sodium is transferred to chlorine, the electronic configurations of the resulting ions become:

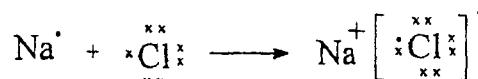


Sodium acquires the neon configuration while chlorine acquires the argon configuration. Unlike charges of the ions are then held together by electrostatic attraction. The type of bond that holds the ions together is called an **ionic bond**. Compounds that contain ionic bonds are called *ionic compounds*. Sodium chloride is an example where only one electron is transferred. However, there are cases where more than one electron is transferred. These include calcium (Ca) which loses two electrons and becomes  $\text{Ca}^{2+}$ , aluminum (Al), which loses three electrons and becomes  $\text{Al}^{3+}$ , etc.

It should be noted however that although the ions acquire the electronic configuration of the inert gases, with consequent stability, the resulting ionic compounds are not gases. This is because the ions are charged and they attract each other so strongly that the compounds are solids even at high temperatures. The reaction of sodium and chlorine can be represented pictorially like this:



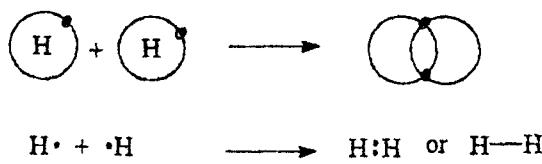
Sometimes the inner shells are ignored, since they do not take part in the reaction, and the valence (or outer shell) electrons are represented by dots and crosses as in the following example:



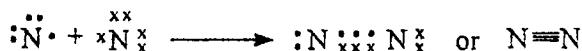
The symbols of elements with dots or crosses representing the valence electrons are also known as **Lewis electron-dot symbols**. For example, the Lewis electron-dot symbol for sodium is  $\text{Na}^+$ .

Remember that the number of electrons in the valence shell of an element is the same as the group number for that element.

**2.2.2 Covalent Bond:** A covalent bond is formed by the sharing of two electrons between two atoms. *In sharing of the electrons, an orbital of one atom overlaps with another from a different atom.* Each orbital contains one electron and so, each atom contributes one electron to the bond. The greater the overlap, the stronger the bond formed. This implies of course that the two atoms have equal or nearly equal electronegativities. For example, consider a hydrogen molecule, H<sub>2</sub>; when the two hydrogen atoms come together, the positive nucleus of each will attract both electrons (that is, its own and that of the other atom). Since the attraction power for the electrons is the same in both atoms, they end up sharing the electrons. This can be presented pictorially as in the diagram below:



The shared pair of electrons is in the region of space between the two nuclei. Such a shared pair of electrons is usually represented as a single solid line as in H - H. A covalently bonded structure with the bonding electron pairs are represented as dots (as in H:H) is also known as a **Lewis structure**. Sometimes multiple covalent bonds can be formed as in nitrogen, which has three pairs of electrons between the two nitrogen nuclei. Using the Lewis electron-dot symbol for nitrogen, the nitrogen molecule can be represented as a Lewis structure in the form:



The electrons are shown here as dots and crosses to show that they are from different atoms. This does not mean, however that the electrons in different atoms are different; they are the same. Also note that, in the formation of the nitrogen molecule, three electrons are used on each nitrogen and there are two others (lone pair) left. *The importance of Lewis structures lies in the*

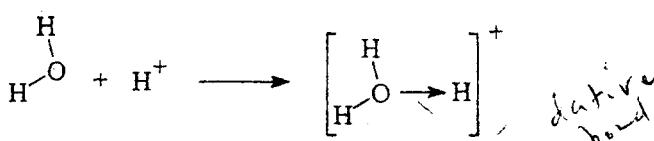
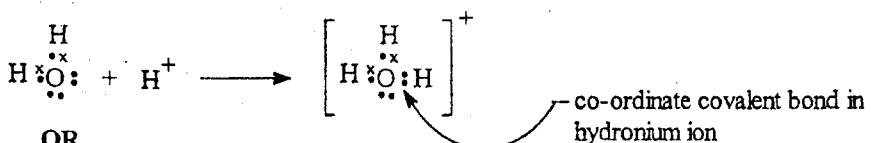
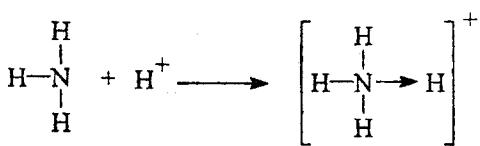
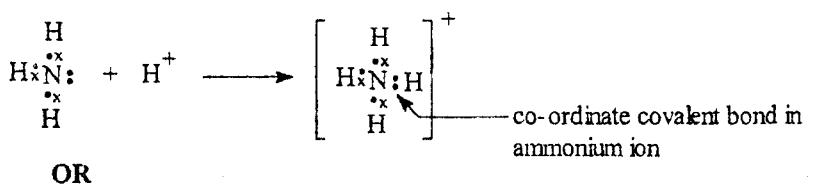
fact that we can easily keep track of the electrons in the outer shell. As in ionic compounds, the formation of a covalent bond leads to each atom acquiring the inert gas configuration. In the hydrogen molecule, each atom has got two electrons in its outer shell, thus acquiring the helium configuration. In nitrogen molecule, each atom has eight electrons in its outer shell and so it acquires the neon arrangements. Table 2.1 gives a comparison of the covalent and ionic compounds.

**Table 2.1:** Comparison of covalent and ionic compounds

	<i>Ionic compounds</i>	<i>Covalent compounds</i>
Electronegativity difference	Large between atoms	Very small or none between atoms
Molecules	No molecules formed	molecules formed
Solubility	Soluble in polar solvents but insoluble in non-polar solvents	Insoluble in polar solvents but soluble in non-polar solvents
Boiling and melting points	Often high boiling and melting points	Usually low boiling and melting points ✓
Conductivity in aqueous solutions or in molten state	Very high in polar solvents and in molten state	None

**2.2.3 Coordinate Covalent or Dative Bond:** This bond is usually found in coordination compounds or complexes. It is similar to the covalent bond described above in that it involves sharing of electrons. However, in dative bonds, *both shared electrons come from the same atom termed the donor*; the other atom with which they share the electrons is termed the *acceptor*. In other words, a coordinate covalent bond is formed by overlap of two atomic orbitals but the shared electrons are contained in only one orbital and the other overlapping orbital is empty. It is not surprising then that this bond is sometimes called the *donor-acceptor bond*. Usually the donor atom is a very electronegative atom such as oxygen or nitrogen. To distinguish a dative bond from a normal covalent bond, the former is usually represented by an arrow in the direction

of the acceptor atom. Thus a dative bond between the atoms A and B in which A is the donor and B, the acceptor would be represented as A→B. Some examples of this bond type are given below for the ammonium and hydronium ions.



It should be emphasized that the coordinate bond so formed is not different from the other covalent bonds in the molecules; for example, all the four bonds in ammonium are the same.

### 2.3 INTERMOLECULAR FORCES

The two bond types we have discussed above are both interatomic. They occur between atoms. Intermolecular bonds are common as well and these markedly affect the state of the molecules, that is to say whether, liquid, gaseous or solid state. In Section 2.2, we mentioned that molecules can be formed either from two or more different atoms (heteronuclear) or two similar atoms (homonuclear). In both cases, strong covalent bonds are involved in holding the atoms together. Heteronuclear molecules are either gas, liquid or solid at room temperature but almost all homonuclear molecules are gases under the same conditions. The nature of the intermolecular forces is therefore different in different molecules. What then makes the difference in the sizes

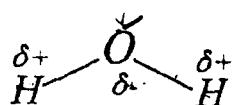
of the intermolecular forces? One determining factor here, is the electronegativity of the atoms that are joined together.

It was also explained in Section 2.2 that molecules like HF are polarized. Such molecules are called **dipoles**. The dipole moment in a molecule like HF is along the direction of the most electronegative atom, fluorine and is represented by a crossed arrow, as follows:

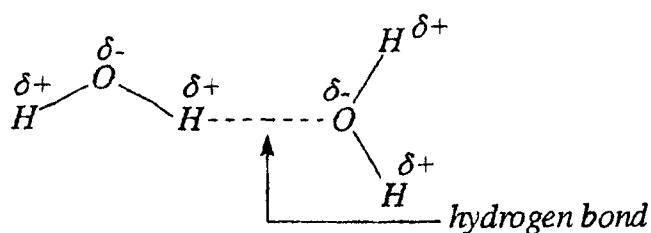


Since the molecules are charged, they attract each other. *These forces of attraction are called dipole-dipole attractions* since they are between two dipoles. The existence of these dipoles in polar molecules markedly affects the state of those substances. The liquid state of such substances as chloroform ( $\text{CH}_3\text{Cl}$ ) and 1,2-dichloroethane ( $\text{CH}_2\text{ClCH}_2\text{Cl}$ ), may be explained by the presence of these dipole-dipole attractions. While some molecules have permanent dipoles, in others, especially in homonuclear molecules, the dipoles can be induced. In view of the differences in the type of dipoles that can be formed i.e., whether permanent or induced, it is proper to discuss the most common intermolecular forces under separate subheadings. These are hydrogen bonds and Van der Waals forces.

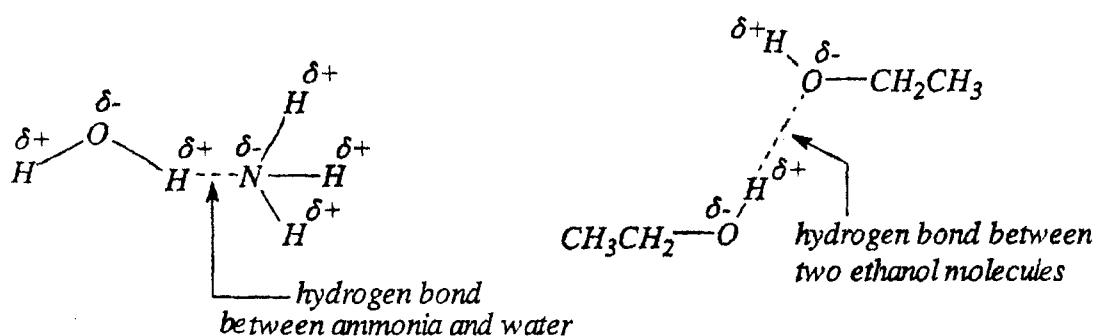
2.3.1 **Hydrogen Bonds:** Permanent dipoles exist in all polar molecules and so dipole-dipole attractions are always present in those substances. An exceptional type of bond exists where a hydrogen atom is attached to a very electronegative atom such as oxygen, nitrogen or fluorine (i.e., O - H, N - H or F - H) and the resulting molecules are highly polarized. Examples are found as in ammonia ( $\text{NH}_3$ ), water ( $\text{H}_2\text{O}$ ) or HF among others. In these and many other molecules, the electronegative atom has a partial negative charge while the hydrogen atom has a partial positive charge. The example is given for water below.



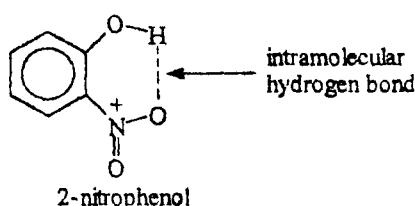
A water molecule is like a dipole; the partially positively charged hydrogen of one water molecule can therefore be attracted to the partially negatively charged oxygen in another water molecule. This dipole-dipole attraction can be represented thus:



The bridge between the two water molecules is called a hydrogen bond; it is indicated by a dotted line to distinguish it from other types of bonds. The diagrams below show hydrogen bonds between ammonia and water molecules and also between two ethanol molecules.



The examples given above illustrate intermolecular hydrogen bonding. Intramolecular hydrogen bonding is also prevalent in many molecules such as 2-nitrophenol given below:

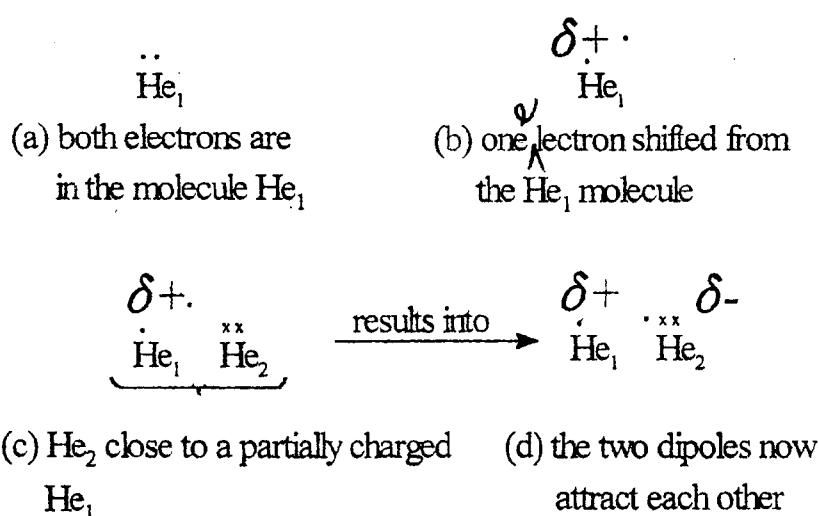


Many molecules of biological importance also exhibit internal hydrogen bonds. The  $\alpha$ -helix structure of a protein molecule is an example of a biological molecule with internal hydrogen bonds. Hydrogen bonding always increases the boiling points and melting points of compounds.

For example the boiling point of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is  $78^\circ\text{C}$  whereas ethane ( $\text{CH}_3\text{CH}_3$ ) with the same number of carbon atoms has a boiling point of  $88.6^\circ\text{C}$  which is much lower.

~~outward dipole and dispersion forces~~

**2.3.2 Van der Waals Forces:** Homonuclear molecules such as oxygen ( $\text{O}_2$ ), nitrogen ( $\text{N}_2$ ) among others and the inert gases are all non-polar. Some heteronuclear molecules such as the alkane series (see Chapter 11) are also non-polar. In the alkanes, we find that boiling points increase with increasing molecular weight of the compounds such that the lower molecule ones are gases, the medium ones are liquids and the higher ones are solids at room temperature (see Table 11.2). The non-polar diatomic molecules and even the inert gases can be liquefied. This change in state from gas to liquid, as also observed in the alkane series is brought about by some intermolecular attractions. The explanation for this is as follows. Since the electrons are continuously moving around the nucleus of an atom, we can imagine that at some instant of time, they will be shifted away from the nucleus. This will induce a partial charge in the molecule which then becomes a temporary dipole. This charge can induce an instantaneous charge in a neighbouring molecule. For example, imagine two helium molecules in a container, at a very low temperature. For convenience, we will label the two molecules as 1 and 2, but it should be understood that they are the same.



In (a) both electrons in  $\text{He}_1$  are close to the nucleus but in (b) one electron has moved away from the nucleus, and so the  $\text{He}_1$  molecule acquires a partial positive charge. If the  $\text{He}_2$  molecule is close to the  $\text{He}_1$  (c), the latter induces a partial negative charge in  $\text{He}_2$  since the shifted electron in  $\text{He}_1$  is now closer to the  $\text{He}_2$  nucleus. The two dipoles now attract each other (d). The existence of these attractive forces was proposed by Van der Waals who modified the ideal gas equation (see Chapter 4) in 1873. These forces have since been called *Van der Waals forces*. Van der Waals forces are much weaker than covalent or ionic bonds and they only operate at short distances, at high pressures and low temperatures when the molecules are moving slowly.

## 2.4 METALLIC BONDS

Metals are characterized by having good conductivity of both heat and electricity. The other properties are malleability and ductility. In a metal structure, the atoms are packed. Each atom loses one or two electrons which become part of the whole structure. There is thus a "sea" of electrons that are free to move in the structure and are attracted not only to one cation but to all cations in the structure. The strong attraction between the electrons and the cations imbedded in them cements the cations together. The free movement of the electrons in the structure explains why metallic structures are good conductors of heat and electricity.

## SUGGESTED READING TEXTS

1. Chang R., 2005. *Chemistry, 8th edn. International edn.* McGraw-Hill, Boston.
2. Ebbing D.D. and Gammon S.D., 1990. *General Chemistry, 6rd ed., International Student Edition*, Houghton Mifflin Co., New York, USA.
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## CONCENTRATION OF SOLUTIONS

### Learning Objectives

By the end of this Chapter, students should be able to define the various concentration terms and to calculate concentrations of various solutions.

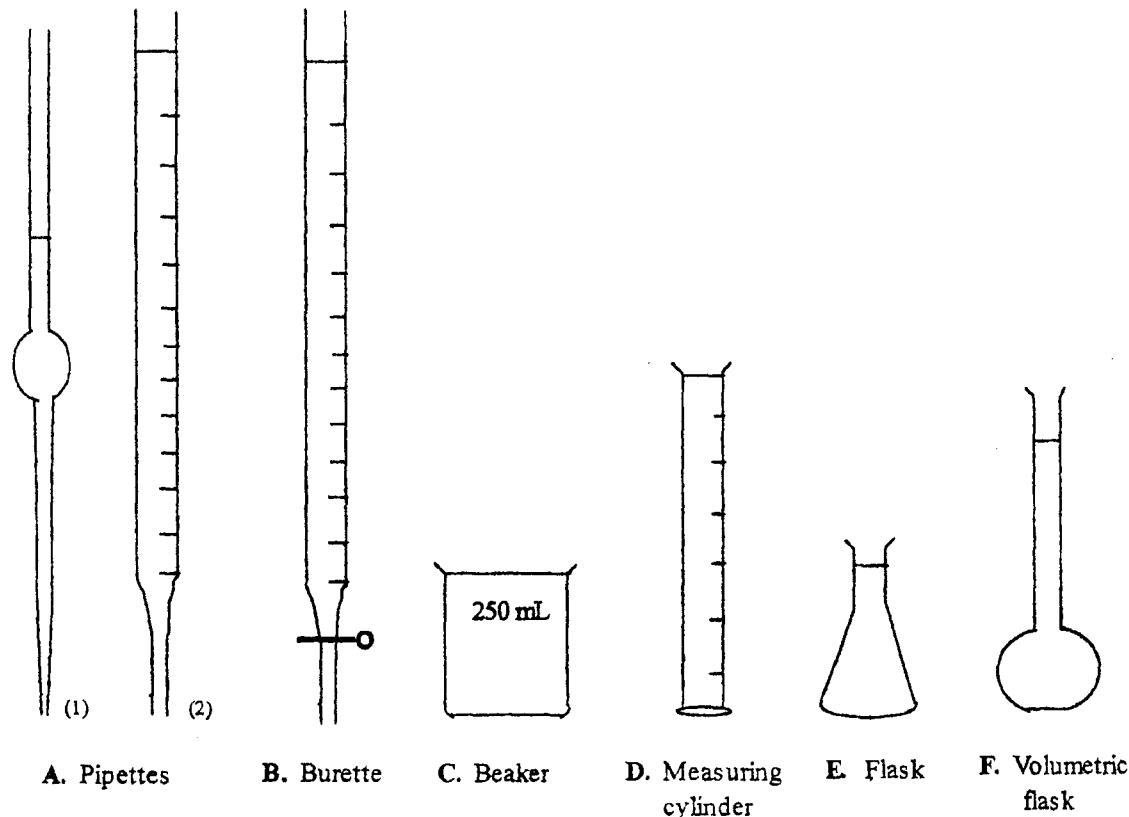
#### **3.1 SOLUTIONS**

When a solid is dissolved in a liquid, we get a homogeneous mixture, in which the molecules/ions of the substance are evenly distributed among those of the liquid. Such a mixture is called a solution. The liquid, which retains its physical state, is called the solvent. Quite often, (though not always) the solvent is the component of the solution which is in larger quantity. The dissolved solid (the minor component) is called the solute. A *solution is a mixture in which the molecules/ions of one component are uniformly distributed among molecules of the other*. For example, if we add common salt to water, the salt ions become evenly dispersed in water molecules and we have a salt solution. The proportion of the dissolved solute to the quantity of the solvent, is called

the concentration of the solution. There can be gaseous solutions (e.g., air is a mixture of oxygen, carbon dioxide, nitrogen and water vapor, among others, all evenly dispersed into each other) or liquid solutions in which two or more different miscible liquids are mixed (e.g., methanol in water). Solid solutions are also encountered. An example is brass which consists of zinc dissolved in copper. Liquid solutions are, however, the most common and we shall concentrate on them in this chapter. Before the various concentration measurements are discussed, it is perhaps important to look at some apparatus (*the chemist's instruments*) used in measuring volumes of solutions and their concentrations. This is important as most students, at the first encounter of a chemistry practical, do not know what a burette, for example, looks like and what it is used for.

### **3.2 LABORATORY APPARATUS**

The most frequently used apparatuses in a chemistry laboratory are shown diagrammatically in Figure 3.1.



**Figure 3.1:** Some common apparatus used in a chemistry laboratory.

(a) **Pipettes (A):** Various types of these exist, those with a bulb (type 1), range from those that deliver  $1 \text{ cm}^3$  to those that deliver  $250 \text{ cm}^3$  of solution<sup>5</sup>. The graduated ones (type 2) range from those that transfer  $1\text{cm}^3$  to those that transfer  $50 \text{ cm}^3$  of solution. There are also micropipettes (not shown in Figure 3.1) which transfer volumes less than  $1 \text{ cm}^3$ . Pipettes are used to transfer solutions with great accuracy. Type 1 pipettes have a mark above the bulb that shows the volume to be

<sup>5</sup>Note that  $1 \text{ cm}^3 = 1 \text{ millilitre (1ml)}$  and  $1\text{dm}^3 = 1 \text{ litre (1L)}$ . We will use the SI units of  $\text{cm}^3$  and  $\text{dm}^3$  in this book rather than the non-SI units (millilitre or the litre).

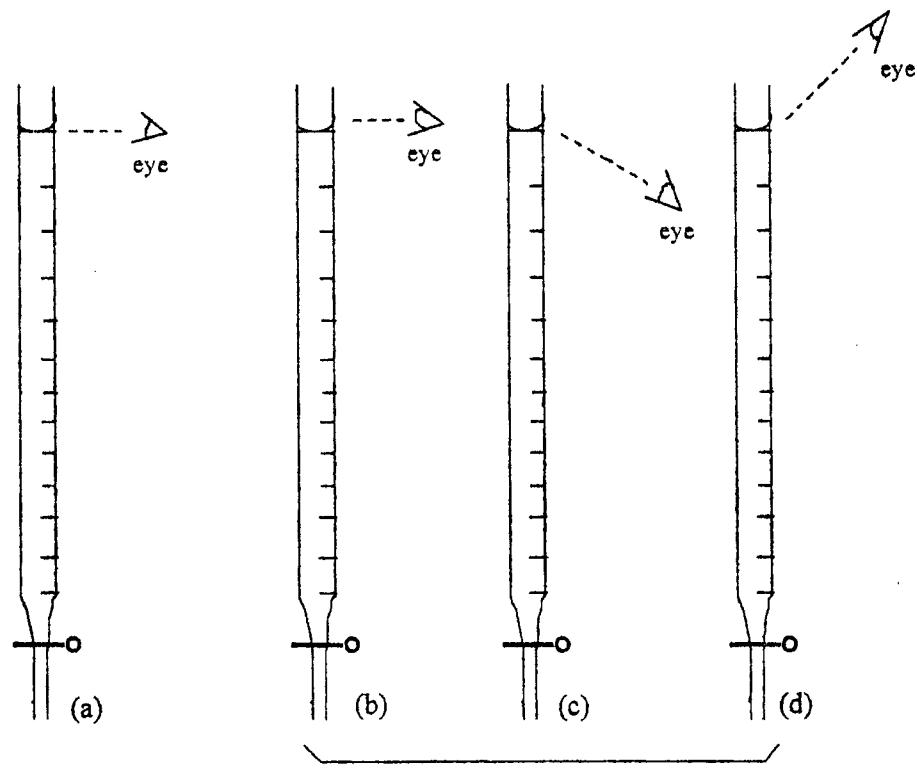
delivered and this volume is up to the tip of the pipette. Type 2 pipettes are of two makes; one is made in such a way that a certain amount of solution remains at the tip of the pipette, i.e., the graduations start about 2.5 cm from the tip and run up to the top volume mark. If the whole volume is to be transferred from such pipettes, care should be taken not to go beyond the last mark at the bottom or else more solution than required will be obtained. The second make of type 2 has graduations running from the tip of the pipette to the volume mark (compare type 1). For whole volume transfers, the solution in this pipette (and type 1) runs out up to the tip. It is recommended that when transferring solutions from any pipette, the tip of the pipette should touch the side of the container in which the solution is being transferred. This ensures whole solution transfer in the case of type 1 and type 2 pipettes with graduations to the tip. Also with the tip touching the side of the container, splashing (which can cause loss of some solution) is avoided.

(b) **Burettes (B):** These are also of various types but the simplest is the one shown in the diagram. They are mostly used in titration (see Chapter 7), when accuracy is required to determine the concentration of an unknown solution. They may also be used to transfer solutions when larger volumes are needed.

(c) **Beakers (C), Cylinders (D), and Flasks (E):** These three pieces of apparatus are of various types. All of them are used for transferring solutions of known volumes but with moderate accuracy. They have numbers inscribed on them (the cylinders are also graduated) which indicate the volumes which they contain and not those volumes that are delivered. This is because when a solution is poured from them, some liquid remains inside due to adhesion. Both plastic and glass type exist.

(d) **Volumetric Flasks(F):** A variety of sizes are available for volumetric flasks ranging from capacities of  $1 \text{ cm}^3$  through to  $2 \text{ dm}^3$ . Volumetric flasks are used for diluting solutions to some desired volume (diluting concentrations) or preparing a required volume of solution of known and accurate concentration. It should be emphasized that the apparatus described above are just some of the many that are found in any chemistry laboratory. *When reading volumes of solutions on these pieces of apparatus, the eye should be in line with the bottom of the meniscus of the solution, at the*

*mark you are reading.* If the eye is set above or below the mark, incorrect readings will be obtained. Figure 3.2 shows the correct and wrong reading styles on a burette. In that figure, style (a) is correct in both eye position and reading mark. In (b) the eye is reading the top of the meniscus and will automatically give a wrong volume mark. Positions (c) and (d), are also wrong in that they give wrong indications of the mark. Care should therefore, be taken in reading volumes on the apparatus or else, wrong results will be obtained.



Correct position of the eye;  
reading from the bottom  
of the meniscus (i.e., eye  
in level with the bottom of  
the meniscus).

Wrong positions of the eye: reading  
from the top of the meniscus (b); eye  
below the level (c) and above level (d) of  
the buret.

**Figure 3.2:** Diagrammatic representation of the correct (a) and wrong (b)  
(c) and (d) styles of reading volume marks on a burette.

### 3.3 THE MOLE

The counting system has been made easy for the world population by introducing figures that all reduce to one. For example, twelve eggs are said to be one dozen eggs (1 dozen), one hundred and

forty-four (144) nails are said to be one-gross of nails (1 gross) and so on. It seems conceivable that the figures 12 and 144, were chosen for convenience.

In the laboratory, we do not work with fewer molecules as 12 or 144; a drop of liquid (e.g., water) contains trillions of molecules which cannot easily be counted. It is still necessary, however, that the number of molecules in that drop should be counted. Since there are many molecules even in a volume as small as  $0.05 \text{ cm}^3$ , scientists thought it necessary to introduce a figure that will simplify the counting. The figure "chosen" is  $6 \times 10^{23}$ . *This number equals one mole*, i.e.,  $6 \times 10^{23} = 1 \text{ mole}$ . The abbreviation for the mole, is *mol*. Therefore,  $6 \times 10^{23}$  molecules are one mole of molecules. Similarly,  $6 \times 10^{23}$  atoms are one mole of atoms. In the same way there can be a dozen of anything, so too there can be a mole of anything. So we can have a mole of molecules, atoms, electrons, people, eggs etc. The figure  $6 \times 10^{23}$  is called **Avogadro's number** (abbrev. N, see Section 1.4). One mole of "anything" contains Avogadro's number of "anything" (note that *the mole is the amount of substance* not just the number). By convention, when we say a mole of hydrogen, we mean  $6 \times 10^{23}$  hydrogen molecules since the most common form of hydrogen is the diatomic molecule  $\text{H}_2$ . Therefore, a mole of hydrogen contains  $6 \times 10^{23} \times 2 = 1.2 \times 10^{24}$  hydrogen atoms.

A question that might immediately arise is "why was this figure chosen?". Well, in section 1.4, we mentioned that there is a relationship between the weight of a mole of hydrogen atoms and Avogadro's number; we showed that  $6 \times 10^{23}$  hydrogen atoms weigh 1 g. From several different weight measurements of different substances, it is found that  $6 \times 10^{23}$  atoms of an element weigh exactly  $A_e$  g, where  $A_e$  is the relative atomic mass of the element. Similarly, it is found that  $6 \times 10^{23}$  molecules weigh exactly  $A_m$  g, where  $A_m$  is the relative molecular mass of the molecule. These findings are summarized in the Table 3.1.

Table 3.1: Relationship between a mole and Relative molecular or atomic masses.

Atom or molecule.	Mass of one of them.	Mass of $6 \times 10^{23}$ ( 1 mole) of them.
H	1 amu.	1 g
C	12 amu.	12 g
O	16 amu.	16 g
CH <sub>4</sub>	16 amu.	16 g
H <sub>2</sub> O	18 amu.	18 g
CH <sub>3</sub> CH <sub>3</sub>	30 amu.	30 g
NaOH	40 amu.	40 g

From the table above we see that one mole ( $6 \times 10^{23}$ ) of hydrogen atoms weigh 1 g and since one hydrogen atom weighs 1 amu, it follows that  $1 \text{ g} = 6 \times 10^{23} \text{ amu}$ . Thus,  $6 \times 10^{23}$  is a conversion factor; it converts atomic mass units to grams and vice versa.

It is easy enough to find the number of moles of a substance once we know the weight of the sample and the relative molecular or atomic mass of the substance.

**Example 1:** How many moles are there in 6 g of hydrogen?

**Solution :** Since hydrogen exists as H<sub>2</sub>, its relative molecular mass is

$$1 \text{ amu} \times 2 \text{ H atoms} = 2 \text{ amu}$$

$\therefore$  1 mole of H<sub>2</sub> weighs 2 g

$$\text{No. of moles in } 6 \text{ g H}_2 = \frac{6}{2} = 3 \text{ moles.}$$

**Example 2:** How many moles are there in 4 g of sodium (Na)?

**Solution :** The relative atomic mass of Na = 23 amu

$\therefore$  1 mole Na weighs 23 g.

$$\text{No. of mole in } 4 \text{ g} = \frac{4}{23} = 0.174 \text{ moles.}$$

**Example 3:** Calculate the number of moles in 4 g of sodium hydroxide (NaOH)

**Solution :** Relative formula mass of NaOH = 40 amu.  $\therefore 40$  g

$\therefore$  1 mole NaOH weighs 40 g.

$$\text{No. of mole in } 4 \text{ g} = \frac{4}{40} = 0.1 \text{ mole.}$$

We see from the three examples above that to get the number of moles of a substance, we simply divide the weight of the sample given by the relative molecular/atomic mass of that substance, i.e.,

$$\text{No. moles} = \left[ \frac{\text{Wt. (grams) given}}{\text{Relativemolecular(formula/atomic)mass of the substance}} \right]$$

We have already said that concentration of a solution is a ratio of the quantity of solute to the quantity of solvent in solution. There are many ways of expressing this ratio. In the next sections, we look at some various ways of expressing concentrations of solutions.

### **3.4 MOLARITY (M).**

Concentrations of solutions are usually expressed in *molarity*, which is an abbreviation for *the number of moles of solute contained in 1 dm<sup>3</sup> of solution*. The symbol for molarity is M (capital M).

**Example 1:** What is the molarity of a solution prepared by dissolving 40 g NaOH and making it up to 1 dm<sup>3</sup> (1000 cm<sup>3</sup>) with water?

**Solution:** Mol. wt. of NaOH = 23 + 16 + 1 = 40 amu.

$\therefore$  1 mole of NaOH weighs 40 g.

No. of moles in 40 g NaOH dissolved is  $40/40 = 1$  mole.

So we have 1 mole NaOH in 1 dm<sup>3</sup>, ∴ Concentration of the solution is 1 mole/dm<sup>3</sup> or 1M.

**Example 2:** Suppose you had 1dm<sup>3</sup> of 0.2M solution of NaOH,

- (a) How many moles of NaOH were there?
- (b) What weight of NaOH was dissolved?

**Solution :** (a) 0.2 M means 0.2 moles in 1dm<sup>3</sup>

Since we have a 1dm<sup>3</sup> solution, No. of moles  
is 0.2 mole.

(b) From example 1, 1 mole NaOH weighs 40 g

∴ wt. of NaOH dissolved in 1dm<sup>3</sup>

$$= \frac{0.2 \text{ mole}}{1 \text{ mole}} \times 40 \text{ g}$$

✓  
= 8 g.

**Example 3:** What weight of NaOH is dissolved to make 250 cm<sup>3</sup> of 0.2 M solution?

**Solution :** 0.2 M means 0.2 mole in 1dm<sup>3</sup> (1000 cm<sup>3</sup>)

$$\therefore 250 \text{ cm}^3 \text{ contain } \frac{250}{1000} \times 0.2 = 0.05 \text{ mole}$$

1 mole NaOH weighs 40 g

$$\therefore 0.05 \text{ mole weighs } \frac{0.05}{1} \times 40 = 2 \text{ g.}$$

So wt. dissolved = 2 g., i.e., 2 g NaOH dissolved in 250 cm<sup>3</sup>,

gives 0.2 M solution of NaOH.

**Example 4:** Suppose you are given 50 cm<sup>3</sup> of 0.1 M solution of NaOH, how would you prepare 10 cm<sup>3</sup> of

- (a) 0.05 M NaOH solution?

(b) A solution that contains 0.1 g NaOH per dm<sup>3</sup>?

**Solution :** (a) The question is asking "what volume should we take from the 50 cm<sup>3</sup> of 0.1 M solution which when diluted to 10 cm<sup>3</sup>, will give us 10 cm<sup>3</sup> of 0.05 M solution?".

O.K. let's take this volume to be  $V \text{ cm}^3$  (note that this is  $V \text{ cm}^3$  taken away from 50 cm<sup>3</sup> of 0.1 M solution).

Since it's  $V \text{ cm}^3$  of 0.1 M solution and,

$$0.1 \text{ M} \Leftrightarrow 0.1 \text{ mole/dm}^3 \text{ or } 0.1 \text{ mole}/1000 \text{ cm}^3,$$

$\therefore$  No. of mole in  $V \text{ cm}^3$

$$= \left( \frac{V}{1000} \times 0.1 \right) = \mathbf{A} \text{ mole.}$$

Now we want 10 cm<sup>3</sup> of 0.05 M solution and,

$$0.05 \text{ M} \Leftrightarrow 0.05 \text{ mole/dm}^3$$

$\therefore$  No. of mole in 10 cm<sup>3</sup>

$$= \left( \frac{10}{1000} \times 0.05 \right) = \mathbf{B} \text{ mole.}$$

When  $V \text{ cm}^3$  is diluted to 10 cm<sup>3</sup>, we shall have 10 cm<sup>3</sup> of 0.05 M solution

$$\therefore \mathbf{A} = \mathbf{B}$$

$$\text{i.e., } \left( \frac{V}{1000} \times 0.1 \right) = \left( \frac{10}{1000} \times 0.05 \right) \dots\dots\dots\dots \mathbf{C}$$

$$\text{So } V = \frac{10 \times 0.05}{1000} \times \frac{1000}{0.1}$$

$$= 5 \text{ cm}^3.$$

Therefore by taking 5 cm<sup>3</sup> from the 50 cm<sup>3</sup> of 0.1 M solution of NaOH and adding 5 cm<sup>3</sup> of water, you have 10 cm<sup>3</sup> of 0.05 M solution

(b) We want 10 cm<sup>3</sup> of 0.1 g NaOH/dm<sup>3</sup>. Note that 0.1 g NaOH/dm<sup>3</sup>

$$= \frac{0.1}{40} \text{ moles/dm}^3$$

$$= 2.5 \times 10^{-3} \text{ mole/dm}^3$$

or  $2.5 \times 10^{-3} \text{ M.}$

So  $10 \text{ cm}^3$  of  $2.5 \times 10^{-3} \text{ M}$  solution is required. Following the same method as in (a), we have:

$$\left( \frac{V}{1000} \times 0.1 \right) = \left( \frac{10}{1000} \times 2.5 \times 10^{-3} \right)$$

and so  $V = \frac{10}{1000} \times 2.5 \times 10^{-3} \times \frac{1000}{0.1}$

$$= 0.25 \text{ cm}^3.$$

Therefore, take  $0.25 \text{ cm}^3$  from the  $50 \text{ cm}^3$  of  $0.1 \text{ M}$  solution and dilute to  $10 \text{ cm}^3$  with water. Note from example 4 (a) that in the equality (C), denominators cancel each other and we are left with a volume and its concentration on either side. Therefore, we can derive a general equation for preparing a solution of known volume and concentration from another of known concentration, as follows :

Suppose we want to prepare  $V_2 \text{ cm}^3$  of solution of concentration  $M_2$  from another of concentration  $M_1$ . If the volume to be taken out of the solution of concentration  $M_1$  is  $V_1$ , then,

$$V_1 \times M_1 = V_2 \times M_2$$

Where  $V_1$  is the volume to be diluted

$M_1$  is the concentration of the original solution

$V_2$  is the volume to be prepared

$M_2$  is the concentration of the volume to be prepared.

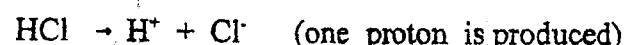
### 3.5 NORMALITY (N).

Another way of expressing concentration is the normality (symbol, N), which is the number of equivalents of solute dissolved in 1 dm<sup>3</sup> (1000 cm<sup>3</sup>) of solution. A one normal (1 N) solution contains one equivalent of solute dissolved in one dm<sup>3</sup> of solution.

To calculate the number of equivalents of a substance, we need to know a quantity called the **equivalent weight** of that substance first. The definition of the equivalent weight of a substance depends on the type of reaction the substance is participating in; whether the reaction is acid -base, oxidation-reduction, complex formation reaction, etc.

For acids, the equivalent weight is the relative molecular mass of the acid divided by the number of ionizable protons (H<sup>+</sup>) the acid produces (or, the number of protons that can react with the base); and for a base, it is the relative molecular/formula mass of the base divided by the number of hydroxide ions the base will produce in its reaction. The examples below show how to obtain the equivalent weights of some acids and bases.

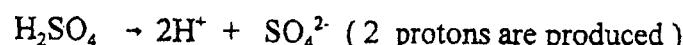
**Example 1:** HCl ionizes according to the equation:



$$\therefore \text{equivalent weight of HCl} = \frac{\text{RelativemolecularmassofHCl}}{1}$$

$$= \frac{36.5}{1} = 36.5 \text{ g}$$

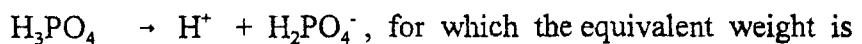
**Example 2:** H<sub>2</sub>SO<sub>4</sub> ionizes as follows :



$$\therefore \text{equivalent weight of } H_2SO_4 = \frac{\text{Relative molecular mass of } H_2SO_4}{2}$$

$$= \frac{98.08}{2} = 49.04 \text{ g}$$

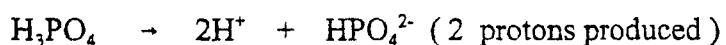
**Example 3:** Phosphoric acid ( $H_3PO_4$ ), however, can ionize either according to the equation:



$$\frac{\text{Relative molecular mass of } H_3PO_4}{1}$$

$$= \frac{98}{1} = 98 \text{ g} \quad \checkmark$$

or according to:



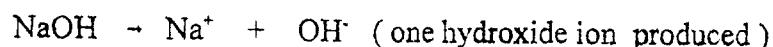
for which the equivalent weight is

$$\frac{\text{Relative molecular mass of } H_3PO_4}{2}$$

$$= \frac{98}{2} = 49 \text{ g} \quad \checkmark$$

However, phosphoric acid does not ionize completely, i.e., the reaction  $H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$  does not readily occur. This means that one cannot obtain the equivalent weight of  $H_3PO_4$  that is one-third its relative molecular mass.

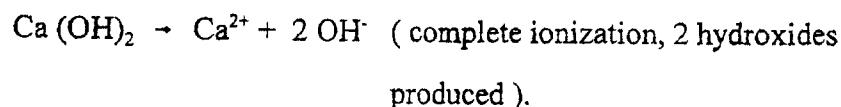
**Example 4:** NaOH ionizes as follows :



$$\therefore \text{equivalent weight of NaOH} = \frac{\text{Relative formula mass of NaOH}}{1}$$

$$= \frac{40}{1} = 40 \text{ g} \quad / N$$

**Example 5:** Ca(OH)<sub>2</sub> ionizes according to the equation:



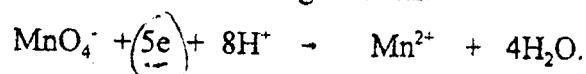
$$\therefore \text{equivalent weight of Ca(OH)}_2 = \frac{\text{Relative formula mass of Ca(OH)}_2}{2}$$

$$= \frac{74}{2} = 37 \text{ g}$$

The example of phosphoric acid given in (3) above indicates that in order to get the equivalent weight of a substance, one has to know the way the substance is reacting in a system. Wrong results may be obtained if this information is not known.

For oxidation-reduction reaction, the equivalent weight is the relative formula/atomic mass of the substance involved in the reaction divided by the number of electrons the substance loses (in case of a reducing agent, see Chapter 8) or gains (in case of an oxidizing agent), as shown the examples below:

**Example 1:** Consider the following reaction:

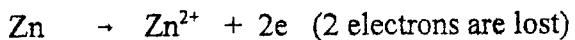


Now What is the equivalent weight of MnO<sub>4</sub><sup>-</sup>?

**Solution :** We see that in the reaction above,  $\text{MnO}_4^-$  is gaining 5 electrons. Thus,

$$\text{the equivalent wt. of } \text{MnO}_4^- = \frac{\text{Relative formula mass of } \text{MnO}_4^-}{5}$$

**Example 2:** Zinc (Zn) ionizes as follows:



$$\therefore \text{equivalent wt. of Zn} = \frac{\text{Relative atomic mass of Zn}}{2}$$

These two examples should suffice our explanation of what an equivalent weight is for compounds involved in oxidation-reduction reaction. The definition of an equivalent weight for compounds taking part in complex formation reactions, is somehow complicated and so will not be dealt with at this stage.

As for moles and molarities, it is easy to calculate the number of equivalents and hence normalities, once we know the equivalent weight of the substance in a given volume of solution.

**Example 1:** Suppose you dissolved 36.5 g HCl in 1dm<sup>3</sup> of solution,  
What is the normality of the solution?

**Solution :** First, we calculate the number of equivalents dissolved.

Equivalent wt. of HCl is 36.5 g.

$$\therefore \text{No. of equivalents dissolved} = \frac{36.5}{36.5}$$

$$= 1 \text{ eq. } 1N$$

So we have 1 equivalent of HCl dissolved in 1 dm<sup>3</sup>.

we have 1 eq./dm<sup>3</sup> or 1 N solution.

**NOTE** that the number of equivalents is obtained by dividing the weight of the substance given by its equivalent weight. i.e.,

$$\text{No. of Equivalents} = \frac{\text{Wwt. (grams) given}}{\text{Eq. wt. of the substance}}$$

**Example 2:** Suppose you dissolved 98 g H<sub>2</sub>SO<sub>4</sub> in 1dm<sup>3</sup> of solution, what would be the normality of the solution?

**Solution :** For H<sub>2</sub>SO<sub>4</sub>, if we assume complete ionization, then 2 protons are

$$\text{furnished; so its equivalent wt.} = \frac{\text{Relative molecular mass}}{2}$$

$$= \frac{98}{2} = 49 \text{ g}$$

$$\therefore \text{No. of equivalents dissolved} = \frac{98}{49} = 2 \text{ eq.}$$

So, we have 2 eq/dm<sup>3</sup> or 2 N solution.

Note that a 1M solution of H<sub>2</sub>SO<sub>4</sub> is equivalent to a 2N solution of H<sub>2</sub>SO<sub>4</sub>, if ionization is complete. It is now left to the reader to verify that for Ca(OH)<sub>2</sub>, 74 g dissolved in 1dm<sup>3</sup> will give a 2N solution. Other calculations for normalities are similar to those of molarities. For example we would use the equation, V<sub>1</sub> × N<sub>1</sub> = V<sub>2</sub> × N<sub>2</sub> to find the N<sub>2</sub> once we know the other three variables and vice versa.

### 3.6 MOLALITY (m)

This is the number of moles of a solute dissolved in one kilogram of solvent. It is designated by a

small letter "m". Molality is important in a number of aspects such as in calculating boiling point elevation, freezing point depression, osmotic pressure calculations and molar mass determinations. All these properties depend on the number of solute particles dissolved rather than the nature of the solute. Such properties are called **colligative properties**. As an example, we know that pure water freezes at  $0^{\circ}\text{C}$ . Now when common salt is added to water, the freezing point of the solution lowered to below  $0^{\circ}\text{C}$  but the actual temperature at which the solution freezes will depend on the number of salt "molecules" dissolved (the molal concentration of the salt). For example, if 2g of salt was added to 1kg of water, the freezing temperature will be much lower than if 0.5g of the salt was added to the same amount of water. In countries which get snow in winter, common salt is usually poured on the ice to lower its melting temperature and so, the ice melts.

We also make use of molality to determine whether water has been added to pure milk or not. In this case, we determine the freezing point depression of pure milk and compare values to the freezing points of samples we suspect water has been added. From this, we can determine not only whether water was added to the milk but also how much was added.

Let's now look at one calculation involving molality. An unknown substance weighing 0.182g was dissolved in 2.135g benzene. The concentration of the solution was found to be 0.698m. Calculate the Relative Molecular Mass (RMM) of the substance.

**Solution:** First we must find the number of moles of the substance in 2.135g benzene.

0.698 moles are in 1000g

$$\therefore \text{No. of moles in } 2.135\text{g} = \frac{2.135 \times 0.698}{1000}$$
$$= 1.49 \times 10^{-3} \text{ mole}$$

So  $1.49 \times 10^{-3}$  moles weigh 0.182g

$$\therefore 1 \text{ mole weighs } \frac{1 \times 0.182}{1.49 \times 10^{-3}} = 122.13\text{g}$$

And so, the RMM of the substance = 122.13g

### 3.7 MOLE FRACTION

The mole fraction is the ratio of the number of moles of one component to the total number of moles in the solution. The sum of the mole fractions of all components in a solution add up to one. For example, if we have  $x$  moles of A and  $y$  moles of B in a solution mixture, then the mole fraction of A equals  $\frac{x}{x+y}$ , and that of B is  $\frac{y}{x+y}$  and

$$\frac{x}{x+y} + \frac{y}{x+y} = 1. \text{ ( note that this is always true )}$$

**Example:** Suppose we want to prepare 200g of an aqueous solution in which the mole fraction of NaCl ( $X_{\text{NaCl}}$ ), is 0.2, how much salt would we need to dissolve?

**Solution:** Note that the salt is to be dissolved in water

$$\text{So, wt of salt} + \text{wt of water} = 200\text{g}$$

Relative formula mass of NaCl = 58.5g and relative molecular mass of H<sub>2</sub>O = 18g

Let the number of moles of NaCl be  $x$ , and that of water be  $y$ .

$$\therefore 18y + 58.5x = 200$$

$$\text{and } = 0.2$$

Solving the simultaneous equations above gives  $x = 1.53$  and  $y = 6.13$ . So the weight of NaCl required is  $1.53 \times 58.5 = 89.5\text{g}$  and that of water is  $6.13 \times 18 = 110.34$

### 3.8 PERCENT OF SOLUTE

Percent of solute, in absolute terms, means *Part per one hundred* (see Section 3.9 below). This can either be *percent by mass* (designated w/w) or *percent by volume* (designated v/v). The former means the percentage of the total solution mass contributed by the solute. Mathematically, this is expressed as  $\{( \text{weight of solute} / \text{weight of solution} ) \times 100\}$ . Thus a 20% w/w solution of sodium chloride (NaCl) contains 20 g of NaCl in each 100 g of solution (i.e.,  $(20/100) \times 100 =$

20%, in other words, we take 20 g of NaCl and add it to 80 g of solvent). Percent by volume means the percentage of the total volume that is contributed by the volume of the solute. It is given by  $\{(volume\ of\ solute / volume\ of\ solution) \times 100\}$ . Thus a 20 % v/v solution of ethanol means 20 cm<sup>3</sup> ethanol diluted to 100 cm<sup>3</sup> with some solvent such as water (or,  $20\text{ cm}^3/100\text{ cm}^3 \times 100 = 20\%$ , in other words, we take 20 cm<sup>3</sup> of ethanol and add it to 80 cm<sup>3</sup> of solvent). *Weight - volume percentage (w/v)* is also commonly used. This is given by  $\{(weight\ of\ solute / volume\ of\ solution) \times 100\}$ . Thus a 5 % w/v solution of potassium nitrate (KNO<sub>3</sub>) contains 5 g of KNO<sub>3</sub> dissolved (say, in water) and the solution diluted to 100 cm<sup>3</sup> volume.

The statement of percent by volume (v/v) given above, implies that the 20 cm<sup>3</sup> of ethanol was taken from an ethanol batch that was 100% pure. Most of the marketed solutions are not, however 100% pure. For example, ethanol itself may be obtained either in 95%, 99% or 100% (absolute) pure state. It would be wrong to prepare a 20% ethanol solution from say, 95% ethanol by diluting 20 cm<sup>3</sup> of the ethanol to 100 cm<sup>3</sup>. To prepare such a solution, we use a dilution equation which is similar to one we derived for molarities. For the latter, we derived the equation;  $V_1 \times M_1 = V_2 \times M_2$  and in this case, we use the equation  $V_1 \times \%_1 = V_2 \times \%_2$ , Where  $V_1$  is the volume of the original solution to be diluted,  $\%_1$  is the percentage of the original solution  $V_2$  is the volume to be prepared,  $\%_2$  is the percentage of the final solution to be prepared.

**Example :** How would you prepare 100 cm<sup>3</sup> of 20 % ethanol from a 95% ethanol solution?

**Solution:** Let the volume to be diluted be  $V_1$ .

$$\text{So, } V_1 \times \%_1 = 100 \times 20\%$$

$$V_1 \times 95\% = 100 \times 20$$

$$V_1 = \frac{100 \times 20}{95} = 21.05 \text{ cm}^3$$

∴ Dilute 21.05 cm<sup>3</sup> of 95% ethanol to 100 cm<sup>3</sup> with water. Note that the volume required here is larger (21.05cm<sup>3</sup>) than if we had used 100% ethanol.

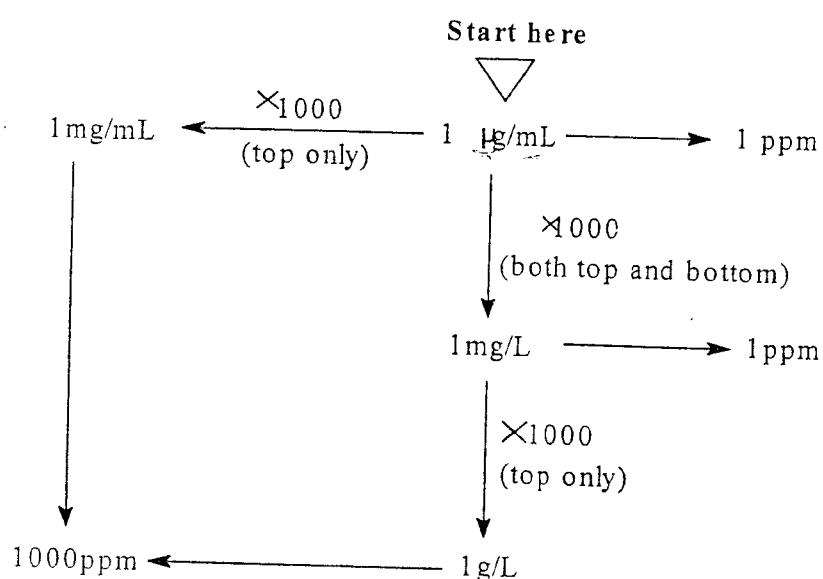
### 3.9 PARTS PER MILLION (ppm)

This concentration term, or others similar to it, is used when dealing with dilute solutions or trace concentrations of solutions and is similar to percent of solute discussed above. It is used quite often in soil science. Parts per million can either be on weight-weight (w/w), weight-volume (w/v) or volume-volume (v/v) basis. Just as percent by mass is  $\{(weight\ of\ solute / weight\ of\ solution) \times 100\}$ , parts per million, on w/w basis is  $\{(weight\ of\ solute / weight\ of\ solution) \times 10^6\}$  and the others follow a similar pattern. In section 3.8, we said that 20 g of NaCl in 100 g of solution, gives a 20% w/w solution (i.e., 20 parts per 100), so too, 20 g of a compound in  $10^6$  g of solution will give a 20 ppm solution (or, 20 parts per million). The designations w/w, w/v and v/v for parts per million are as follows:

w/w	w/v	v/v*
mg/Kg	mg/dm <sup>3</sup>	$\mu$ L/L
or $\mu$ g/g	or $\mu$ g/cm <sup>3</sup>	or nL/mL

\* Note we have used the non-SI unit (L) here

The chart below may be useful in calculations involving parts per million.



How do we use the chart? From the "start here" position, you can go either direction round the square to end up at the 1000 ppm position. As an example, let us go left; if we multiply 1 $\mu\text{g}$  by 1000 (note we multiply the top only, and we leave the bottom part), then we have 1000  $\mu\text{g/mL}$ . This is equivalent to 1mg/mL. 1 mg/cm<sup>3</sup> is the same as 1000 ppm. Note that we can also go in the reverse direction. Here, we would have to divide the 1 mg (=1000 $\mu\text{g}$ ) by a 1000. The readers should familiarize themselves with the units such as microgram ( $1 \mu\text{g} = 10^{-6} \text{ g}$ ), etc. Since 1 g/dm<sup>3</sup> is 1000 ppm, if we dissolve 1 g sodium in one liter, we have 1000 ppm Na. Quite often in trace element analyses, stock (or sometimes called standard) solutions are prepared. Stock solutions are prepared from compounds of known composition. For example, we would easily prepare a solution that is 1000 ppm Na from a sample of NaCl.

**Example 1:** How would prepare 1dm<sup>3</sup> of 1000 ppm Na, from NaCl?

**Solution :** We need 1 g Na in 1dm<sup>3</sup> of solution

$$\text{Relative formula mass of NaCl} = 23 + 35.5 = 58.5 \text{ g}$$

$\therefore$  58.5 g NaCl contains 23 g of Na.

$$\text{So the wt. of NaCl that contains 1 g Na, is } \frac{58.5}{23} = 2.54 \text{ g NaCl.}$$

So if we dissolve 2.54 g NaCl and dilute the solution to 1dm<sup>3</sup> with water, we shall have 1 g Na in 1dm<sup>3</sup> of solution or 1000 ppm Na.

**Example 2:** What weight of potassium nitrate (KNO<sub>3</sub>) is dissolved in 500 cm<sup>3</sup> that will give 0.2 ppm K?

**Solution :** 0.2 ppm  $\Rightarrow$  0.2 mg / dm<sup>3</sup>

$$\therefore \text{in } 500 \text{ cm}^3, \text{ we have } \frac{500 \text{ cm}^3}{1000 \text{ cm}^3 L} \times 0.2 = 0.1 \text{ mg} = 10^{-4} \text{ g}$$

So we need 0.1 mg (or  $10^{-4}$  g) K in 500 cm<sup>3</sup>. The question is

"what weight of  $\text{KNO}_3$  will give  $10^{-4}$  g K?"

O.K., Relative mass of 1 mole  $\text{KNO}_3 = 39.1 + 14 + 48 = 101.1$  g

So 101.1 g  $\text{KNO}_3$  has 39.1 g K

$\therefore$  The wt. of  $\text{KNO}_3$  that contains  $10^{-4}$  g K is

$$\frac{10^{-4}}{39.1} \times 101.1 = 2.59 \times 10^{-4}$$

$2.59 \times 10^{-4}$  g  $\text{KNO}_3$  dissolved and diluted to  $500 \text{ cm}^3$  with water gives 0.2 ppm K.

**Example 3:** If one microgram per gram ( $1 \mu\text{g/g}$ ) is equivalent to 1 ppm,  
what would one microgram per kilogram ( $1 \mu\text{g/Kg}$ ) be equivalent  
to?

**Solution :**  $1 \mu\text{g/g} \equiv 1 \text{ ppm}$ , i.e.,  $(10^{-6} \text{ g}/1\text{g}) \times 10^6 = 1$  (from definition of ppm)

So  $1 \mu\text{g/Kg} \equiv (10^{-6} \text{ g}/1000\text{g}) \times 10^6 = 10^{-3}$  ppm.

= 1 part per billion (1 ppb)

Note that 1 part per billion is  $1/1000$  of a part per million. Part per billion is a concentration term used for even more dilute solutions.

**Example 4:** How would you prepare  $10 \text{ cm}^3$  of 5 ppm Na from a solution  
that is 1000 ppm in Na?

**Solution :** Here we proceed as for molarities

i.e.,  $V_1 \times \text{ppm}_1 = V_2 \times \text{ppm}_2$  (where  $V_1$  is volume to be diluted)

$$V_1 \times 1000 = 10 \times 5$$

$$\text{So } V_1 = \frac{10 \times 5}{1000} = 0.05 \text{ cm}^3.$$

Therefore, if we take  $0.05 \text{ cm}^3$  from the solution that is 1000 ppm in Na and dilute it to  $10 \text{ cm}^3$ , we will have  $10 \text{ cm}^3$  of 5 ppm Na.

**Example 5:** What weight of  $\text{AgNO}_3$  is required to prepare  $300 \text{ cm}^3$  of 0.1 ppm  $\text{Ag}^+$ ?

**Solution:** Relative formula mass of  $\text{AgNO}_3 = 169.9\text{g}$

Now, 0.1 ppm means  $0.1 \text{ mg/dm}^3$

$$300 \text{ cm}^3 \text{ contain } \frac{300 \times 0.1}{1000} = 0.03 \text{ mg } \text{Ag}^+ \text{ or } 3 \times 10^{-5} \text{ g } \text{Ag}^+$$

Now  $169.9\text{g AgNO}_3$  contains  $107.9\text{g Ag}$

$$\begin{aligned} \text{wt. of } \text{AgNO}_3 \text{ containing } 3 \times 10^{-5} \text{ g } \text{Ag}^+ &= \frac{3 \times 10^{-5} \times 169.9}{107.9} \\ &= 4.72 \times 10^{-5} \text{ g } \text{AgNO}_3 \end{aligned}$$

#### SUGGESTED READING TEXTS

1. Ebbing D.D. and Gannon S.D. 1999. *General Chemistry, 6rd. ed., International Student Edition*, Houghton Mifflin Co.
2. Chang R., 2005. *Chemistry, 8th ed. International edn.* McGraw-Hill. New York, USA.
3. Christian G.D., 1977. *Analytical Chemistry, 2nd ed.*, John Wiley and Sons.
4. Skoog D.A. and West D.M., 1976. *Fundamentals of Analytical Chemistry, 3rd ed.*, Holt, Rinehart and Winston.

## THE GASEOUS STATE

### Learning Objectives

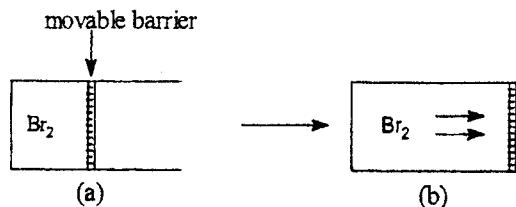
By the end of this Chapter, students should be able to discuss the properties and theories of gases

**4.0** The three states of matter are gaseous, liquid, and solid. Because of interaction between the molecules, the latter two states are more complex. The gaseous state is a simple one because the molecules do not interact so strongly. Apart from its simplicity, understanding gas behaviour is important in many concepts. For example, by studying the properties of gases, one can get an insight into the concept of temperature. This chapter looks at some properties of gases and gas laws. The concept of temperature is introduced at the end.

### 4.1 PROPERTIES OF GASES

There are many properties of gases, and we shall cite only a few here. Bromine gas is

brown in colour; if it is placed in a container, the whole container turns brown. Other gases though not visible, behave in the same way. It can be concluded from this that *gases are very mobile* and will fill any container unless a barrier prevents them to do so. The bromine gas can be put in a glass tube so that it is constrained by a movable barrier in one-half of the tube as



shown in the diagram (a) below.

Now if the barrier is moved to the end as in (b), it is found that the bromine gas fills the whole tube, mixing with the air in the other half evenly. If the barrier is drawn back, the gas is pushed to position (a) again. Two conclusions can be drawn from this experiment; first, *gases can easily be compressed*. An equal volume of liquid or solid would not be so easily compressed. The second conclusion is that *gases can mix with each other quite easily*. The molecules of one gas move in the spaces between the molecules of the other gas in a process called diffusion. It is found that for two gases A and B, under the same conditions of temperature and pressure, the rate of diffusion is inversely proportional to the square root of their relative molecular masses. This is called *Graham's Law of gaseous diffusion*. The rate of diffusion is the speed, which is defined in terms of the average kinetic energy ( $\bar{KE}$ ) of the molecules given by  $\bar{KE} = \frac{1}{2} MV^2$  (where  $M$  = relative molecular mass

and  $V$  = speed). Therefore, for gas A, we have  $\bar{KE}_A = \frac{1}{2} M_A V_A^2$  and for B, we have

$\bar{KE}_B = \frac{1}{2} M_B vV_B^2$ . Now at the same temperature and pressure, gases have the same average kinetic

energy, i.e.  $\bar{KE}_A = \bar{KE}_B$ , which then gives:

$$\frac{V_A}{V_B} = \left( \frac{M_B}{M_{AB}} \right)^{\frac{1}{2}}$$

So, Graham's law of gaseous diffusion can be summarized into the following equation:

$$\frac{\text{Rate of diffusion of } A}{\text{Rate of diffusion of } B} = \sqrt{\frac{\text{Relative Molecular Mass of } B}{\text{Relative Molecular Mass of } A}}$$

Gas molecules also *move at very high speeds*, which approximate the speed of sound, i.e., 740 m.p.h.. The result of these high speeds is that gas molecules placed in a container will exert pressure on the walls of that vessel. A detailed discussion of gas pressure is given later.

## 4.2 KINETIC THEORY OF GASES

The properties of gases that we have discussed above, led to the idea that gas molecules are composed of many molecules that move at high speeds in straight lines and collide with each other and with the walls of the container as they move. Ideas based on this statement formed the basis of the kinetic theory of gases. This theory postulates that:

1. A gas consists of a large number of molecules whose sizes are negligible compared to the volume of space between them.
2. There are no attractive forces between the molecules, and so they behave independently of one another.
3. As the molecules move randomly at high speed, they can collide with each other and with the walls of the containing vessel, but the collisions are elastic. An elastic collision is one in which there is no loss of energy; in other words, the energies of the molecules (kinetic energy) are the same before and after the collision.
4. The average kinetic energy of the molecules is proportional to the temperature.

## 4.3 GAS PRESSURE

As noted in the previous two sections, gas molecules are always moving at high speeds. If such a gas is placed in a container, the molecules will collide with the walls of the container and exert a force on it. If the temperature of the gas is raised, the molecules will move at higher speed and consequently, the force exerted will also increase. Similarly, if the number of gas molecules is increased at constant temperature, the force will increase proportionally. The *force exerted per unit area of the wall* is called **Pressure**. We therefore define:

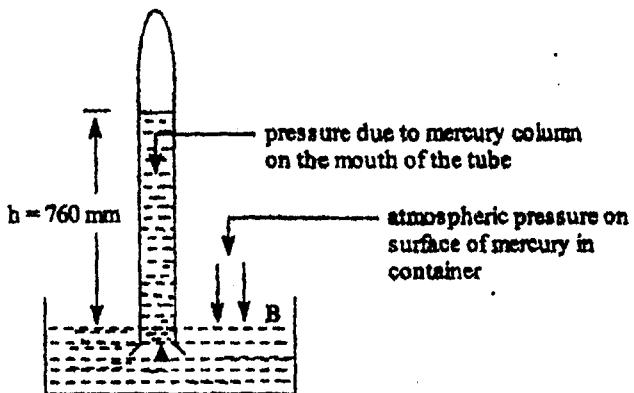
$$\begin{aligned} \text{Pressure} &= \frac{\text{Force}}{\text{Area}} \\ &= \frac{F}{A} \end{aligned} \tag{4.1}$$

$$= \frac{Kg m/s^2}{m^2}$$

= Newton/m<sup>2</sup> (note that 1 Kg m s<sup>-2</sup> is equivalent to 1 newton).

or = N/m<sup>2</sup>

The unit, newton per meter square (N/m<sup>2</sup>), is sometimes given the name **Pascal** (abbrev. Pa), i.e., 1 N/m<sup>2</sup> = 1 Pa. The air in the atmosphere is pulled downwards by gravity. Therefore, the air exerts a force on the earth's surface. The force exerted per unit area of the earth's surface is called the **atmospheric pressure**. This pressure is normally measured by an instrument called a barometer (invented by Evangelista Torricelli, 1608-1647). Figure 4.1 shows a simplified form of the device.



**Figure 4.1:** A simple barometer for measuring atmospheric pressure

In the figure above, a long column of mercury is inverted in a dish containing mercury. At first, the mercury flows out of the column due to gravity but this flow stops when the pressure due to the mercury in the column (at A) just balances that of the atmospheric on the surface of the mercury in the dish at (B). At sea level, the height of the mercury in the tube (when A = B), is 760 mm. Therefore, by definition, *one standard atmosphere* is taken to be equal to 760 mm Hg at 0 °C. The atmospheric pressure is defined here in terms of millimeters of mercury and yet equation 4.1 shows that pressure should have the units of Newton per square meter (N/m<sup>2</sup>). How are the two (i.e., mmHg and N/m<sup>2</sup>) related? Using first principles in physics, we can easily derive the relationship. Let us consider a column of mercury that has a cross sectional area of 1 cm<sup>2</sup>. From Newton's second

law of motion, we have:

$$\begin{aligned} \text{Force} &= \text{mass} \times \text{acceleration due to gravity.} \\ &= m \times a \end{aligned} \tag{4.2}$$

The acceleration to gravity is  $980.7 \text{ cm/sec}^2$

From equation 4.1, we have

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{F}{A}$$

or  $\text{Pressure} = F \times A^{-1}$

Substituting equation 4.2 into 4.1 gives

$$\text{Pressure} = m \times a \times A^{-1} \tag{4.3}$$

and mass ( $m$ ) = density  $\times$  volume  $\tag{4.4}$

For mercury, at  $0^\circ\text{C}$ , density =  $13.59 \text{ g/cm}^3$

Substituting equation 4.4 into 4.3, gives:

$$\begin{aligned} \text{Pressure} (P) &= \frac{13.59 \text{ g/cm}^3 \times 76 \text{ cm} \times 1 \text{ cm}^2 \times 980.7 \text{ cm/sec}^2}{1 \text{ cm}^2} \\ &= 1013278.85 \text{ g cm sec}^{-2} / \text{cm}^2 \end{aligned} \tag{4.5}$$

In equation 4.5, converting grams to kilograms and centimeters to meters, we get:

$$P = 101327.9 \text{ Kg m sec}^{-2}/\text{m}^2$$

$$= 101327.9 \text{ N/m}^2$$

or  $101327.9 \text{ Pa.}$

Therefore, one standard atmosphere is equal to  $101327.9 \text{ N/m}^2$ . The unit, mm Hg is sometimes given the name **torr** (after Torricelli) and since  $1 \text{ atm} = 760 \text{ mm Hg}$ , it means that:

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mm Hg} \\ &= 760 \text{ torr.} \end{aligned}$$

In other words,  $1 \text{ torr} = \frac{1}{760} \text{ atm}$ . Now 1 atmosphere equals  $101327.9 \text{ N/m}^2$  and so:

$$\begin{aligned} 760 \text{ torr} &= 101327.9 \text{ N/m}^2 \\ \therefore 1 \text{ torr} &= \frac{101327.9 \text{ N/m}^2}{760} \\ &= 133.3 \text{ N/m}^2 \\ &= 133.3 \text{ Pa.} \end{aligned}$$

#### 4.4 GAS LAWS

The ideas formulated in the kinetic theory of gases led to the development of a series of experiments in which scientists wanted to find the relationship between pressure, volume and the temperature of a given amount of gas. These experiments resulted in several gas laws which we now discuss.

**4.4.1 Boyle's Law:** Robert Boyle (1661) discovered the relationship between the pressure (P) of and the volume (V) of a fixed amount of gas (n, the number of mole) at a constant temperature(T). He found that "*At a fixed temperature the volume of a fixed amount of gas was inversely proportional to the pressure*". This can be expressed mathematically in the form:

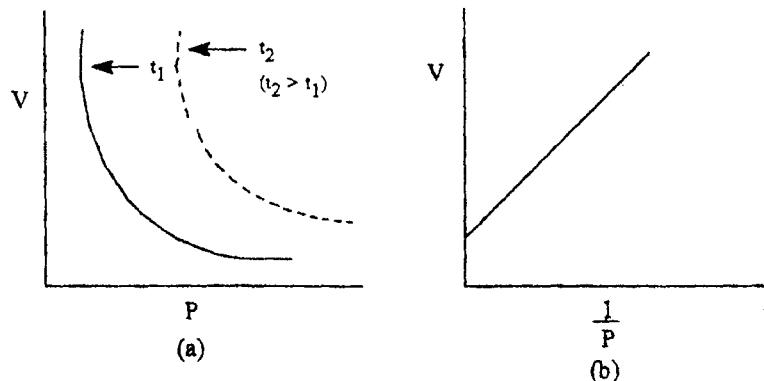
$$\text{Boyle's Law: } V \propto \frac{1}{P} \quad (\text{at constant T and n}) \quad (4.6)$$

If we introduce a proportionality constant (let us call it  $k_1$ ), then the equation above becomes:

$$V = k_1 \left( \frac{1}{P} \right)$$

$$\text{or } PV = k_1$$

This inverse relationship can be confirmed from a plot of  $V$  against  $P$ , which gives a hyperbolic curve as shown in Figure 4.2 (a). However, if  $V$  is plotted against  $1/P$  (Figure 4.2(b) ), a straight line is obtained having a gradient of  $k_1$ .



**Figure 4.2:** Pressure-volume curves (isotherms) for a gas (a). Volume of a gas as function of the reciprocal of pressure

The pressure-volume relation in Figure 4.2 (a), is only obtained at a given temperature (say  $t_1$ ). If the temperature is changed (say, to  $t_2$ , here  $t_2 > t_1$ ), a curve similar to the first one is obtained but runs parallel to it as shown by the dotted line in the figure. Since each curve has got a constant temperature all along, it is called an **isotherm**. The proportionality constant will be different at different temperatures, but at the same fixed temperature, it will have the same value. Therefore, at a fixed temperature, if the volume of a fixed amount of gas changes, it is easy enough to predict the corresponding pressure change at that temperature. For example, a given amount of gas at a certain temperature, may be contained in a volume  $V_1$ , and exert a pressure  $P_1$ . Now if the volume is changed to  $V_2$ , we can use Boyle's law to predict how much the pressure has changed, i.e., the new pressure,  $P_2$ , exerted. Since the amount of gas is the same and the temperature is also unchanged, we can write:

$$P_1 V_1 = k_1 \quad \text{and} \quad P_2 V_2 = k_1$$

$$\therefore P_2 V_2 = P_1 V_1$$

$$So \quad P_2 = \frac{P_1 V_1}{V_2} \quad \text{Final pressure is therefore predicted.}$$

Similarly, a gas might be in a volume  $V_1$  and exerting a pressure  $P_1$ . If the pressure changes to  $P_2$  at that fixed temperature, we can predict the corresponding volume change; we would have:

$$P_1 V_1 = k_1 \text{ and } P_2 V_2 = k_1$$

$$\therefore P_2 V_2 = P_1 V_1$$

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

**4.4.2 Law of Gay-Lussac and Charles:** The effect of temperature on the volume of a fixed amount of gas at constant pressure was initially studied by Jacques Charles (1787) and later confirmed by Joseph Gay-Lussac(1802). From various experimental work, Gay-Lussac formulated a law which is now called the law of Gay-Lussac and Charles. The law states that "*At constant pressure, the volume of a fixed amount of gas increases linearly with increasing temperature*". We can express this mathematically in the form:

$$V \propto T \quad (\text{at constant } P \text{ and } n) \quad (4.7a)$$

If we put in a proportionality constant ( let us call it  $k_2$  ) then the equation becomes:

$$V = k_2 T \quad (\text{at constant } P \text{ and } n). \quad (4.7b)$$

The law of Gay-Lussac and Charles may be stated in a different form, and that is "*The pressure of a fixed amount of gas increases linearly with increasing temperature at constant volume*", i.e.,

$$P \propto T \quad (\text{at constant } V \text{ and } n). \quad (4.8a)$$

This statement may be seen as a corollary of the first one. Since the law gives a linear relation, the proportionality constant will be the same and so we can write:

$$P = k_2 T \quad (\text{at constant } V \text{ and } n). \quad (4.8b)$$

Equation 4.7b can be used to predict the volume change when the temperature of a fixed amount of gas is changed at constant pressure. If the initial volume was  $V_1$  and its temperature changed from  $T_1$  to  $T_2$  at the same pressure, then the corresponding volume change,  $V_2$ , can be calculated. Here, we have:

$$V_1 = k_2 T_1 \quad \text{and} \quad V_2 = k_2 T_2 \quad (\text{at constant } P \text{ and } n).$$

$$\text{or} \quad \frac{V_1}{T_1} = k_2 \quad \text{and} \quad \frac{V_2}{T_2} = k_2$$

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

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

Equation 4.8b can be used to predict the new pressure when the temperature of a fixed amount of gas is changed, at constant volume. If the initial pressure of a given amount of gas was  $P_1$  and if the temperature of the gas changed from  $T_1$  to  $T_2$  at constant volume, then the new pressure  $P_2$  can be calculated from:

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

$$\text{and so} \quad P_2 = \frac{P_1 T_2}{T_1}$$

**4.4.3 The ideal Gas Law:** It was mentioned in section 4.3 that if we increase the number of gas molecules at constant volume and temperature, the pressure also increases. For example, if the number of gas molecules, in a given volume and at constant temperature, is doubled, the number of collisions, the molecules make with the walls of the container also doubles. Therefore, the pressure also doubles. Similarly, the volume will double if we double the number of gas molecules

at constant pressure and temperature. Mathematically, these two facts can be presented in the form:

$$P \propto n \quad (\text{at constant } V \text{ and } T).$$

$$\text{and} \quad V \propto n \quad (\text{at constant } P \text{ and } T).$$

In the two relations above, "n" is the number of moles of gas since the mole is a measure of the amount of substance. Now Boyle's law, is  $PV = k_1$  and the law of Gay-Lussac and Charles is  $V = k_2 T$  (or  $P = k_2 T$ ). We can now combine these two laws with the relations above and obtain:

$$PV = n RT \quad (4.9)$$

Equation 4.9 is called the *ideal gas law*, and a gas that obeys this equation is said to be ideal (but see Section 4.4.6). The constant, R, is called the *universal gas constant* and it can be considered as a combination of the constants  $k_1$  and  $k_2$ . Its value depends on the units of pressure (P), and volume (V) chosen. If P is in N/m<sup>2</sup> and volume m<sup>3</sup>, then we have the units of R as:

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{N/m^2 \times m^3}{mole \times degree} \\ &= Nm \text{ mole}^{-1} \text{ deg}^{-1} \\ &= \text{Joules mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

and the value in this case is 8.31 J.mole<sup>-1</sup> deg<sup>-1</sup>. If the pressure is in atmosphere (atm), and the volume is in liters (L), the units of R then become:

$$\begin{aligned} R &= \frac{Atm. \times L}{mole \times degree} \\ &= \text{Liter-atm. mole}^{-1} \text{ deg}^{-1} \end{aligned}$$

and the value here is 0.0821 L-atm deg<sup>-1</sup> mole<sup>-1</sup>.

**4.4.4 Avogadro's Law:** In the previous section, we derived the ideal gas law. We saw that  $PV = nRT$ . Therefore, for any two gases, x and y, we can ably write:

$$P_x V_x = n_x RT_x \quad \text{and} \quad P_y V_y = n_y RT_y$$

Now, if the two gases are at the same temperature and pressure and contained in equal volumes, i.e., if

$$P_x = P_y, \quad V_x = V_y \quad \text{and} \quad T_x = T_y, \text{ then}$$

$$\frac{P_x V_x}{R T_x} = \frac{P_y V_y}{R T_y} = n_x = n_y$$

Therefore,  $n_x = n_y$ , that is, the number of moles of gas x equals those of y. This general relation holds for any two gases with the same conditions and it is called the **Avogadro's law**. This can be stated as follows : "Equal volumes of gases at the same temperature and pressure, contain equal numbers of molecules". The corollary of this statement, i.e., "Equal numbers of gas molecules at the same temperature and pressure occupy equal volumes", also applies.

Sometimes measurements in gases are carried out at *Standard Temperature and Pressure* (S.T.P.). This is a condition when the temperature equals  $0^\circ\text{C}$ , and the pressure equals one atmosphere (1 atm). For example, it is found that one mole of hydrogen gas weighs 2.016 g at STP and that 1 dm<sup>3</sup> of hydrogen gas weighs 0.09 g. From this we can calculate the volume that one mole of the gas occupies at STP.

We are given:

$$0.09 \text{ g of hydrogen occupies } 1 \text{ dm}^3$$

$$\text{So } 2.016 \text{ g of hydrogen occupy}$$

$$\frac{2.016 \times 1}{0.09}$$

$$= 22.4 \text{ dm}^3.$$

Since one mole of gas occupies the same volume as one mole of any gas at the same temperature and pressure (Avogadro's law), it follows then that one mole of any gas at STP will occupy  $22.4 \text{ dm}^3$ . This figure is called the **standard molar volume**. Let's look at some calculations that involve the standard molar volume.

**Example 1:**  $1.12 \text{ dm}^3$  of a gas weigh 1.5 g at S.T.P.

- (a) What is the molecular weight of the gas?
- (b) What volume will 10 g of the gas occupy at STP?

**Solution :** (a) At S.T.P., 1 mole of gas occupies  $22.4 \text{ dm}^3$

$$\therefore \text{No. of mole in } 1.12 \text{ dm}^3 = \frac{1.12}{22.4} = 0.05 \text{ mole.}$$

So 0.05 moles weigh 1.5 g

$$\therefore \text{wt. of 1 mole} = \frac{1}{0.05} \times 1.5 = 30 \text{ g.}$$

(b) From (a), 30 g of the gas occupy  $22.4 \text{ dm}^3$

$$\text{So } 10 \text{ g occupy, } \frac{10}{30} \times 22.4 = 7.47 \text{ dm}^3.$$

**Example 2:** A gas occupies  $2 \text{ dm}^3$ , at STP. What volume will it occupy at 2 atm pressure and at a temperature of 546 K?

**Solution :** At STP, 1 mole occupies  $22.4 \text{ dm}^3$ .

$$\therefore \text{No. of mole} = 2/22.4 = 0.089 \text{ mole.}$$

$$\text{Now } PV = nRT$$

$$2 \times V = 0.089 \times 0.0821 \times 546 \text{ (note P is in liters (dm}^3\text{))}, \text{ so we use}$$

0.0821 as R)

$$\begin{aligned}V &= (0.089 \times 0.0821 \times 546)/2 \\&= 1.99 \text{ dm}^3\end{aligned}$$

**4.4.5 The Law of Partial Pressures:** It was mentioned in Section 4.1 that any two (even more) gases, will readily mix. As long as the gases do not react in the mixture, then the total pressure (let's call it  $P_T$ ) of the mixture should be equal to the sum of the pressures of the individual gas components in that mixture. This is called *Dalton's Law of Partial Pressures*. The implication is that *the partial pressure of a gas in a mixture is the pressure that the gas will exert if it alone occupied the volume of the mixture*. This assumes of course that the gases behave ideally with no interaction between them. Thus if a mixture contained the gases a, b, c, and d then we have:

$$P_T = P_a + P_b + P_c + P_d \quad (\text{where } P_a \text{ is the pressure exerted by gas a in the mixture etc.})$$

Each of the pressures,  $P_a$ ,  $P_b$  etc., is called the *partial pressure* of that particular gas. For example  $P_a$  is the partial pressure of gas a. The law of partial pressures states that "*In a mixture of gases, the total pressure is equal to the sum of the partial pressures of the individual gases in the mixture*". At low pressures when a gas behaves ideally, the ideal gas equation can be applied to a mixture of gases. For each gas we can write:

$$P_a = \frac{n_a RT}{V}, \quad P_b = \frac{n_b RT}{V}, \quad P_c = \frac{n_c RT}{V}, \quad P_d = \frac{n_d RT}{V}$$

and combining all the equations, we get:

$$P_T = \frac{(n_a + n_b + n_c + n_d)RT}{V}$$

$$= \frac{n_{total} R T}{V}$$

**4.4.6 Deviation From the Ideal Gas Law:** The derivation of the ideal gas law equation is based on the assumptions formulated in the kinetic theory of gases (Section 4.2). As mentioned previously, any gas that will obey the ideal gas law is said to be an ideal gas. There are some limitations to this law so that real gases will deviate from it. Indeed to say that gases do not attract each other and that the molecules have zero volume is an over simplification in the kinetic theory. Real gases have masses which occupy a certain volume in space and, at high pressure and low temperatures, the molecules do attract each other (see Section 2.3.2). These two factors will make real gases deviate from the ideal gas law. If we are to allow for the effects of these factors, then a corrected equation is necessary. The ideal gas equation is only obeyed under conditions of low pressures and at high temperatures. Even real gases conform to the ideal gas behavior under these conditions. At high pressures however, the molecules are so close together that attractive forces are possible. A molecule approaching the wall of a container, will be attracted by molecules in the bulk. The effect is a reduction of the speed of the molecule, and since pressure is a result of the bombardment of the molecules on the wall of the container, these attractive forces also result in a reduction of the pressure. These forces of attraction are proportional to the number of those molecules moving towards the wall per unit volume and also to the number of molecules in the container as a whole. The pressure reduction is therefore proportional to the square of the concentration of the gas molecules.

Thus, for  $n$  moles of gas molecules in the container, the pressure reduction will be equal to:

$$\frac{an^2}{V^2} \quad (\text{where } a, \text{ is a constant characteristic for each}$$

gas and note that  $n/V$  gives the concentration).

The pressure that the gas molecules in the container exert, will therefore be less by this amount,

$an^2/V$ . Consequently, this amount should be added to the observed pressure to reach that of the ideal gas. This then gives:

$$(P + an^2 / V) \quad (\text{where } P \text{ is the actual gas pressure observed}).$$

Gas molecules also have some masses which take up some space in the containing vessel. This means that the space in which the molecules move in the vessel is actually less than that predicted by the ideal gas equation. This volume, which is occupied by the gas molecular masses and therefore not available for motion, is called the "*excluded volume*". It is a constant for a particular gas and is usually designated  $b$ . Therefore, for  $n$  moles of gas, the excluded volume will be equal to  $nb$  and this should be subtracted from the volume of the container to give  $(V-nb)$ . If we now combine the corrected terms for pressure and volume, the final equation becomes:

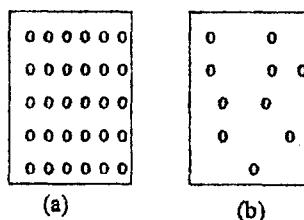
$$(P + \frac{an^2}{V^2})(V-nb) = nRT \quad (4.10)$$

or  $(P + \frac{a}{V^2})(V-b) = RT$  for one mole of gas.

This equation, derived in 1873, is called **Van der Waals equation**, named after the Dutch Physicist, Johannes Van der Waals who provided the interpretation. It should be noted from the equation above that when the pressures are low, the volume becomes large so that both  $an^2 / V^2$  and  $b$ , become almost zero. The equation then reduces to the ideal gas equation,  $PV = nRT$ .

**4.5 KINETIC THEORY OF GASES AND THE ABSOLUTE TEMPERATURE SCALE** The law of Gay-Lussac and Charles discussed in Sub-section 4.4.2 shows the variation of the volume, of a fixed amount of gas at constant pressure, with temperature (or the variation of the pressure of a fixed amount of gas at constant volume, with temperature). We saw in that section that  $V \propto T$  or  $P \propto T$ . We will now take a closer look at this relationship and see how it relates to kinetic theory.

Let's consider two equal size drums as shown in Figure 4.3; one contains 30 gaseous molecules (Figure 4.3a), and the second one (Figure 4.3b), contains 10 gaseous molecules of the same type as in (a).



**Figure 4.3:** Equal sized drums with 30 gas molecules (a)  
and 10 gas molecules (b).

If both drums are each given the same amount of heat (let's say, 20 Joules), they will receive the same amount of molecular kinetic energy but there will be *more kinetic energy per molecule* in drum (b) than in drum (a); (energy shared between fewer molecules in (b) than in (a) so that drum (b) will be at higher temperature than drum (a). In other words the molecules in (b) will have more translational energy and so will move at a faster speed than those of (a). The total kinetic energy of the molecules is called *heat*, and the average translational kinetic energy is called *temperature*. The symbols,  $\bar{KE}$  and  $KE$ , are usually used to mean average kinetic energy and total kinetic energy (see also Section 4.1) respectively. From this, we see that speed of the molecules,  $\bar{V^2}$ , will be proportional to the temperature, a postulate which is given in the kinetic theory of gases. This can be expressed mathematically in the form:

$$T \propto , \text{ where } , \text{ is the average kinetic energy, } M \text{ is the mass and } \bar{V^2}, \text{ is the mean of the squares of the speed.}$$

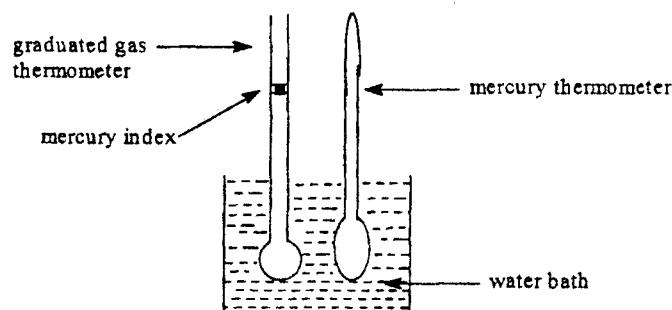
Now in Section 4.3.3, we saw that  $PV$  for gas molecules is proportional to the temperature ( $PV = nRT$ ), but  $PV$  also depends on the number and speed of the gas molecules. The equation that connects all these is given by:

$$PV = \frac{2}{3} N \left( \frac{1}{2} M \bar{V^2} \right)$$

or  $PV = \frac{2}{3} N \bar{KE}$  where N is Avogadro's number.

The equation above is derived from the kinetic theory of gases and no attempt will be made to rederive it here.<sup>6</sup> Temperature measurements are carried out using mercury in glass thermometers, which give readings in degrees Celsius ( $^{\circ}\text{C}$ ) or degrees Fahrenheit ( $^{\circ}\text{F}$ ), but we have defined temperature as the average of the molecules ( $\bar{KE}$ ). These two facts might appear confusing but it is easy enough to connect them. From the equation,  $PV = \frac{2}{3} N \bar{KE}$ , we see that measurements of

either P or V (even or PV) will give a direct measurement of the average kinetic energy ( $\bar{KE}$ ) since all are linearly related to  $\bar{KE}$ . For example we could investigate the variation of the volume of a fixed amount of gas at constant pressure with temperature. We could have a gas thermometer placed side by side with a mercury thermometer in a water bath which is slowly heated. At each step in the heating process, changes in the water temperature (measured with the mercury thermometer, reading in  $^{\circ}\text{C}$ ) and the gas volume (in the gas thermometer, reading in  $\text{cm}^3$ ), are noted. The setup for such an experiment would be as shown in Figure 4.4.



**Figure 4.4:** Gas thermometer placed side by side with a mercury thermometer in a water bath.

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<sup>6</sup> Any reader interested in its derivation may check in the suggested reading texts at the end of the chapter.