Chapter 5

STOICHIOMETRY

Objectives

After studying this chapter, you will be able to

- explain the characteristics of three states of matter;
- classify different substances into elements,compounds and mixtures;
- define SI base units and list some commonly used prefixes;
- use scientific notations and perform simple mathematical operations on numbers;
- determine significant figures;
- convert physical quantities from one system of units to another;
- explain various laws of chemical combination;
- describe the terms - molecular mass and formula mass,mole and molar mass;
- determine empirical formula and molecular formula for a compound from the given experimental data;
- perform the stoichiometric calculations.
- define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent) and redox reactions;
- explain mechanism of redox reactions by electron transfer process;
- identify oxidant and reductant in a reaction using concept of oxidation number
- classify redox reactions;
- suggest a comparative order among some reductants and oxidants;
- balance chemical equations using
  (i) oxidation number
  (ii) half reaction method;

> ***“Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them ...”***
>
> *Roald Hoffmann*

> ***“Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems.”***

Chemistry deals with the composition, structure and properties of matter. These aspects can be best described and understood in terms of basic constituents of matter i.e, **atoms** and **molecules**. That is why chemistry is called the science of atoms and molecules. Can we see, weigh and perceive these entities? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and number of these particles (atoms and molecules)? We will like to answer some of these questions in this Unit. We would further describe how physical properties of matter can be quantitatively described using numerical values with suitable units.

5.1 IMPORTANCE OF CHEMISTRY

Science can be viewed as a continuing human effort to systematize knowledge for describing and understanding nature. For the sake of convenience science is sub-divided into various disciplines: chemistry, physics, biology, geology etc. Chemistry is the branch of science that studies the composition, properties and interaction of matter. Chemists are interested in knowing how chemical transformations occur. Chemistry plays a central role in science and is often intertwined with other branches of science like physics, biology, geology etc. Chemistry also plays an important role in daily life.

Chemical principles are important in diverse areas, such as: weather patterns, functioning of brain and operation of a computer. Chemical industries manufacturing fertilizers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys and other inorganic and organic chemicals, including new materials, contribute in a big way to the national economy.

Chemistry plays an important role in meeting human needs for food, health care products and other materials aimed at improving the quality of life. This is exemplified by the large scale production of a variety of fertilizers, improved varieties of pesticides and insecticides. Similarly many life saving drugs such as **cisplatin** and **taxol**, are effective in cancer therapy and AZT (Azidothymidine) used for helping AIDS victims, have been isolated from plant and animal sources or prepared by synthetic methods.

With a better understanding of chemical principles it has now become possible to design and synthesize new materials having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres and large scale examination of solid state devices. In recent years chemistry has tackled, with a fair degree of success, some of the pressing aspects of environmental degradation. Safer alternatives to environmentally harmful refrigerants like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases like methane, carbon dioxide etc. Understanding of bio-chemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic materials are some of the intellectual challenges for the future generation of chemists. A developing country like India needs talented and creative chemists for accepting such challenges.

5.1.1 Properties of matter

You are already familiar with the term **matter** from your earlier classes. Anything which has mass and occupies space is called **matter**.

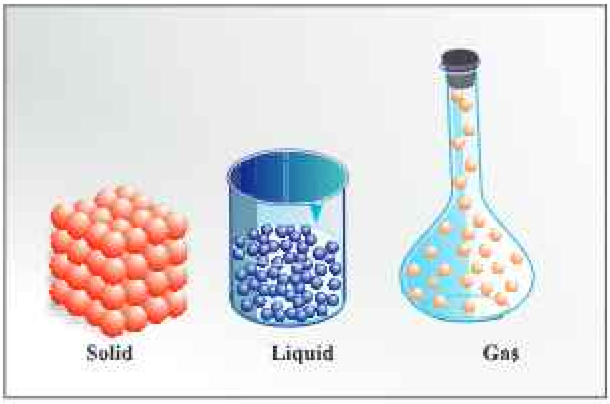


Fig. 5.1 *Arrangement of particles in solid, liquid and gaseous state*

Everything around us, for example, book, pen, pencil, water, air, all living beings etc. are composed of matter. You know that they have mass and they occupy space.

Matter can exist in three physical states *viz.* **solid**, **liquid** and **gas**. The constituent particles of matter in these three states can be represented as shown in Fig. 5.1. In **solids**, these particles are held very close to each other in an orderly fashion and there is not much freedom of movement. In **liquids**, the particles are close to each other but they can move around better than in solids. However, in **gases**, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. Because of such arrangement of particles, different states of matter exhibit the following characteristics:

(i) Solids have *definite volume* and *definite shape.*

(ii) Liquids have *definite volume* but *not* the *definite shape*. They take the shape of the container in which they are placed.

(iii) Gases have *neither definite volume nor definite shape*. They completely occupy the container in which they are placed.

These three states of matter are interconvertible by changing the conditions of temperature and pressure.

$$\text{Solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{liquid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{Gas}$$

On heating a solid usually changes to a liquid. The liquid on further heating changes to the gaseous (or vapour) state. In the reverse processes, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid.

At the macroscopic or bulk level, matter can be classified into 2 types. **mixtures** or **pure substances**. These can be further sub-divided as shown in Fig. 5.2.

Many of the substances present around you are **mixtures**. For example, sugar solution in water, air, tea etc., are all mixtures. **A mixture contains two or more substances present in it (in any ratio) which are called its components.** A mixture may be **homogeneous** or **heterogeneous**. In a **homogeneous mixture**, the components completely mix with each other and its composition is uniform throughout. Sugar solution, and air are the examples of homogeneous mixtures. In contrast to this, in **heterogeneous mixtures**, the composition is not uniform throughout and sometimes the different components can be seen. For example, the mixtures of salt and sugar, grains and pulses along with some dirt (often stone) pieces, are heterogeneous mixtures. You can think of many more examples of mixtures which you come across in the daily life. It is worthwhile to mention here that the components of a mixture can be separated by using physical methods such as simple hand picking, filtration, crystallisation, distillation etc.

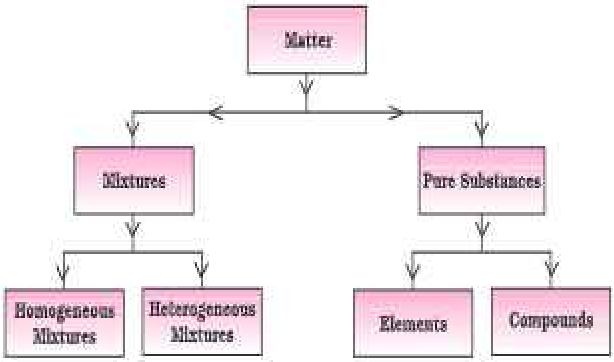


Fig. 5.2 *Classification of matter*

Pure substances have characteristics different from the mixtures. They have fixed composition, whereas mixtures may contain the components in any ratio and their composition is variable. Copper, silver, gold, water, glucose are some examples of pure substances. Glucose contains carbon, hydrogen and oxygen in a fixed ratio and thus, like all other pure substances has a fixed composition. Also, the constituents of pure substances cannot be separated by simple physical methods.

Pure substances can be further classified into **elements** and **compounds**. An **element** consists of only one type of atoms . You may be familiar with atoms and molecules from the previous classes; however, you will be studying about them in detail in this chapter. Sodium, copper, silver, hydrogen, oxygen etc. are some examples of elements. They all contain atoms of one type. However, the atoms of different elements are different in nature. Some elements such as sodium or copper, contain single atoms held together as their constituent particles whereas in some others, two or more atoms combine to give **molecules** of the element. Thus, hydrogen, nitrogen and oxygen gases consist of molecules in which two atoms combine to give their respective molecules. This is illustrated in Fig. 5.3.

When two or more atoms of different elements combine, the molecule of a **compound** is obtained. The examples of some compounds are water, ammonia, carbon

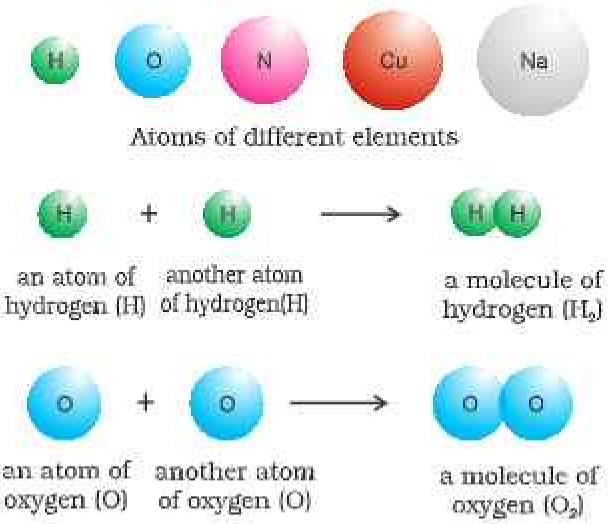
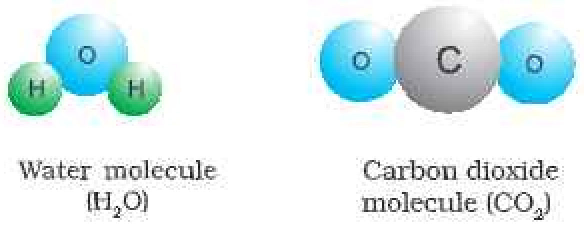


Fig. 5.3 *A representation of atoms and molecules*

dioxide, sugar etc. The molecules of water and carbon dioxide are represented in Fig 5.4.



Water molecule (H_2O)

Carbon dioxide molecule (CO_2)

Fig. 5.4 *A depiction of molecules of water and carbon dioxide*

You have seen above that a water molecule comprises of two hydrogen atoms and one oxygen atom. Similarly, a molecule of carbon dioxide contains two oxygen atoms combined with one carbon atom. Thus, the atoms of different elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound. Also, the properties of a compound are different from those of its constituent elements. For example, hydrogen and oxygen are gases whereas the compound formed by their combination *i.e.*, water is a liquid. It is interesting to note that hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher.

Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods.

Properties of Matter and their Measurement

Every substance has unique or characteristic properties. These properties can be classified into two categories – **physical properties** and **chemical properties**.

Physical properties are those properties which can be measured or observed without changing the identity or the composition of the substance. Some examples of physical properties are colour, odour, melting point, boiling point, density etc. The measurement or observation of **chemical properties** require a chemical change to occur. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility etc.

Many properties of matter such as length, area, volume, etc., are quantitative in nature. Any quantitative observation or measurement is represented by a number followed by units in which it is measured. For example length of a room can be represented as 6 m; here 6 is the number and m denotes *metre* – the unit in which the length is measured.

Two different systems of measurement, i.e. the **English System** and the **Metric System** were being used in different parts of the world. The metric system which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. The need of a common standard system was being felt by the scientific community. Such a system was established in 1960 and is discussed below in detail.

The International System of Units (SI)

The International System of Units (in French *Le Systeme International d'Unités* – abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from *Conference Generale des Poids et Measures*). The CGPM is an inter governmental treaty organization created by a diplomatic treaty known as Metre Convention which was signed in Paris in 1875.

The SI system has seven *base units* and they are listed in Table 5.1. These units pertain to the seven fundamental scientific quantities. The other physical quantities such as speed, volume, density etc. can be derived from these quantities.

The definitions of the SI base units are given in Table 5.2.

The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit. These prefixes are listed in Table 5. 3.

Let us now quickly go through some of the quantities which you will be often using in this book.

Table 5.1 Base Physical Quantities and their Units

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

Table 5.2 Definitions of SI Base Units

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

Table 5.3 Prefixes used in the SI System

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

Mass and Weight

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

The mass of a substance can be determined very accurately in the laboratory by using an analytical balance (Fig. 5.5).

The SI unit of mass as given in Table 5.1 is kilogram. However, its fraction gram (1 kg = 1000 g), is used in laboratories due to the smaller amounts of chemicals used in chemical reactions.

Volume

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

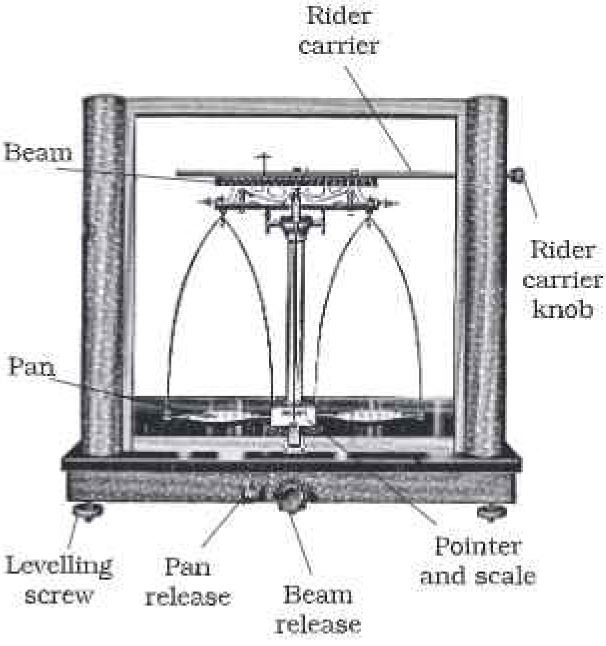


Fig. 5.5 *Analytical balance*

Maintaining the National Standards of Measurement

The system of units including unit definitions keeps on changing with time. Whenever the accuracy of measurement of a particular unit was enhanced substantially by adopting new principles, member nations of *metre treaty* (signed in 1875), agreed to change the formal definition of that unit. Each modern industrialized country including India has a National Metrology Institute (NMI) which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL), New Delhi. This laboratory establishes experiments to realize the *base units* and *derived units* of measurement and maintains National Standards of Measurement. These standards are periodically inter-compared with standards maintained at other National Metrology Institutes in the world as well as those established at the International Bureau of Standards in Paris.

A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids.

$$1 \text{ L} = 1000 \text{ mL}, \quad 1000 \text{ cm}^3 = 1 \text{ dm}^3$$

Fig. 5.6 helps to visualise these relations.

In the laboratory, volume of liquids or solutions can be measured by graduated cylinder, burette, pipette etc. A volumetric flask is used to prepare a known volume of a solution. These measuring devices are shown in Fig. 5.7.

Density

Density of a substance is its amount of mass per unit volume. So SI units of density can be obtained as follows:

$$\text{SI unit of density} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}}$$

$$= \frac{\text{kg}}{\text{m}^3} \text{ or kg m}^{-3}$$

This unit is quite large and a chemist often expresses density in g cm^{-3}, where mass is expressed in gram and volume is expressed in cm^3.

Temperature

There are three common scales to measure temperature — °C (degree celsius), °F (degree fahrenheit) and K (kelvin). Here, K is the SI unit. The thermometers based on these scales are shown in Fig. 5.8. Generally, the thermometers with celsius scale are calibrated from 0° to 100° where these two temperatures are the freezing point and the boiling point of water respectively. The fahrenheit scale is represented between 32° to 212°.

The temperatures on two scales are related to each other by the following relationship:

$$°\text{F} = \frac{9}{5}(°\text{C}) + 32$$

The kelvin scale is related to celsius scale as follows :

$$\text{K} = °\text{C} + 273.15$$

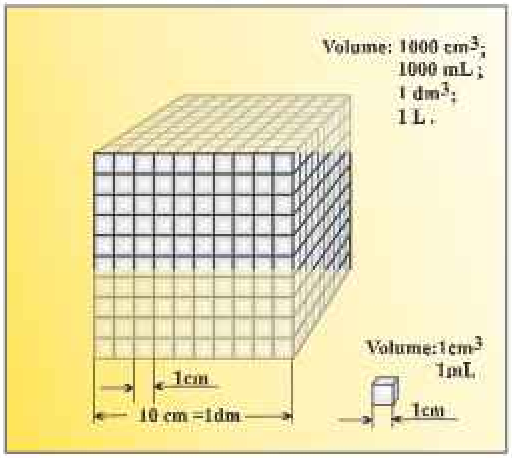


Fig. 5.6 *Different units used to express volume*

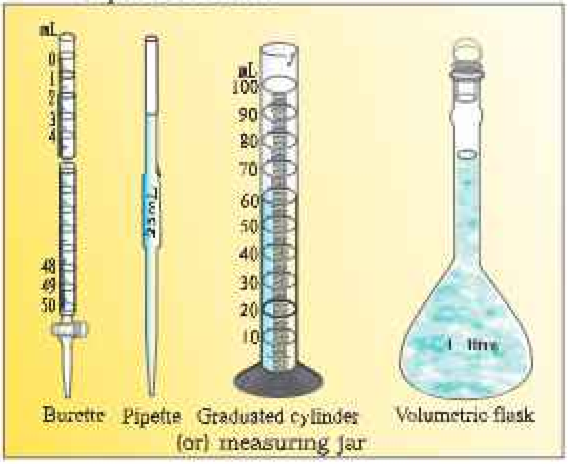


Fig 5.7 *Some volume measuring devices*

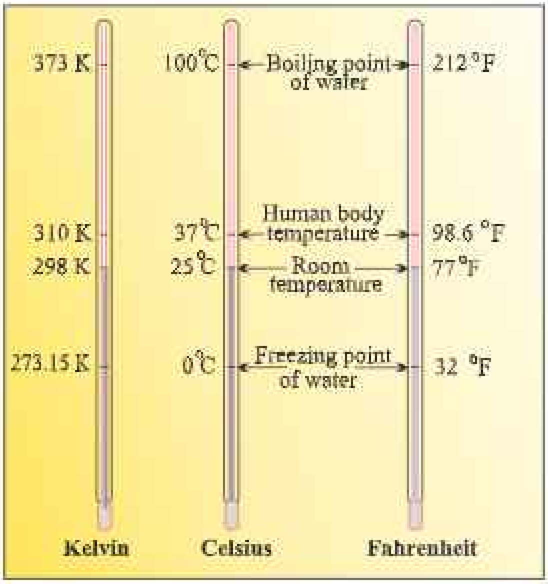


Fig. 5.8 *Thermometers using different temperature scales*

It is interesting to note that temperature below 0 °C (i.e. negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.

Reference Standard

After defining a unit of measurement such as the kilogram or the metre, scientists agreed on reference standards that make it possible to calibrate all measuring devices. For getting reliable measurements, all devices such as *metre sticks* and *analytical balances* have been calibrated by their manufacturers to give correct readings. However, each of these devices is standardised or calibrated against some reference. The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time.

Scientists are in search of a new standard for mass. This is being attempted through accurate determination of Avogadro constant. Work on this new standard focuses on ways to measure accurately the number of atoms in a well-defined mass of sample. One such method, which uses X-rays to determine the atomic density of a crystal of ultrapure silicon, has an accuracy of about 1 part in 10^6 but has not yet been adopted to serve as a standard. There are other methods but none of them are found to be adequate to replace the Pt-Ir cylinder. No doubt, changes are expected within this decade.

The metre was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0°C (273.15 K). In 1960 the length of the metre was defined as 1.65076373×10^6 times the wavelength of light emitted by a krypton laser. Although this was a cumbersome number, it preserved the length of the metre at its agreed value. The metre was redefined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Similar to the length and the mass, there are reference standards for other physical quantities.

5.1.2 UNCERTAINTY IN MEASUREMENT

Many a times in the study of chemistry, one has to deal with experimental data as well as theoretical calculations. There are meaningful ways to handle the numbers conveniently and present the data realistically with certainty to the extent possible. These ideas are discussed below in detail.

Scientific Notation

As chemistry is the study of atoms and molecules which have extremely low masses and are present in extremely large numbers, a chemist has to deal with numbers as large as 602, 200,000,000,000,000,000,000 for the molecules of 2 g of hydrogen gas or as small as 0.00000000000000000000000166 g mass of a H atom. Similarly other constants such as Planck's constant, speed of light, charges on particles etc., involve numbers of the above magnitude.

It may look funny for a moment to write or count numbers involving so many zeros but it offers a real challenge to do simple mathematical operations of addition, subtraction, multiplication or division with such numbers. You can write any two numbers of the above type and try any one of the operations you like to accept the challenge and then you will really appreciate the difficulty in handling such numbers.

This problem is solved by using **scientific notation** for such numbers, *i.e.*, **exponential notation** in which any number can be represented in the form $N \times 10^n$ where n is an exponent having positive or negative values and N is a number (called digit term) which varies between 1.000... and 9.999....

Thus, we can write 232.508 as 2.32508×10^2 in scientific notation. Note that while writing it, the decimal had to be moved to the *left* by two places and so 2 is the exponent of 10 in the scientific notation.

Similarly, 0.00016 can be written as 1.6×10^{-4}. Here the decimal has to be moved four places to the *right* and (– 4) is the exponent in the scientific notation.

Now, for performing mathematical operations on numbers expressed in scientific notations, the following points are to be kept in mind.

Multiplication and Division

These two operations follow the same rules which are there for exponential numbers, i.e.

$$
\begin{aligned}
\left(5.6\times10^{5}\right)\times\left(6.9\times10^{8}\right) &= (5.6\times6.9)\left(10^{5+8}\right)\\
&= (5.6\times6.9)\times10^{13}\\
&= 38.64\times10^{13}\\
&= 3.864\times10^{14}
\end{aligned}
$$

$$
\begin{aligned}
\left(9.8\times10^{-2}\right)\times\left(2.5\times10^{-6}\right) &= (9.8\times2.5)\left(10^{-2+(-6)}\right)\\
&= (9.8\times2.5)\left(10^{-2-6}\right)\\
&= 24.50\times10^{-8}\\
&= 2.450\times10^{-7}
\end{aligned}
$$

$$
\begin{aligned}
\frac{2.7\times10^{-3}}{5.5\times10^{4}} &= (2.7\div5.5)\left(10^{-3-4}\right) = 0.4909\times10^{-7}\\
&= 4.909\times10^{-8}
\end{aligned}
$$

Addition and Subtraction

For these two operations, first the numbers are written in such a way that they have same exponent. After that, the coefficients are added or subtracted as the case may be.

Thus, for adding 6.65×10^4 and 8.95×10^3, $6.65 \times 10^4 + 0.895 \times 10^4$ exponent is made same for both the numbers.

Then, these numbers can be added as follows $(6.65 + 0.895) \times 10^4 = 7.545 \times 10^4$

Similarly, the subtraction of two numbers can be done as shown below :

$2.5 \times 10^{-2} - 4.8 \times 10^{-3}$

$= (2.5 \times 10^{-2}) - (0.48 \times 10^{-2})$

$= (2.5 - 0.48) \times 10^{-2} = 2.02 \times 10^{-2}$

5.1.3 Significant Figures

Every experimental measurement has some amount of uncertainty associated with it. However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk about the measurement.

Precision refers to the closeness of various measurements for the same quantity. However, **accuracy** is the agreement of a particular value to the true value of the result. For example, if the true value for a result is 2.00 g and a student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate. Another student repeats the experiment and obtains 1.94 g and 2.05 g as the results for two measurements. These observations are neither precise nor accurate. When a third student repeats these measurements and reports 2.01g and 1.99g as the result. These values are both precise and accurate. This can be more clearly understood from the data given in Table 5.4

Table 5.4 Data to Illustrate Precision and Accuracy

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

The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. **Significant figures** are meaningful digits which are known with certainty. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be ±1 in the last digit. Unless otherwise stated, an uncertainty of ±1 in the last digit is always understood.

There are certain rules for determining the number of significant figures. These are stated below:

(1) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.

(2) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point.

Thus, 0.03 has one significant figure and 0.0052 has two significant figures.

(3) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.

(4) Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures.

But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100. has three significant figures and 100.0 has four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×10^2 for one significant figure, 1.0×10^2 for two significant figures and 1.00×10^2 for three significant figures.

(5) Counting numbers of objects, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000

In numbers written in scientific notation, all digits are significant e.g., 4.01×10^2 has three significant figures, and 8.256×10^{-3} has four significant figures.

Addition and Subtraction of Significant Figures

The result cannot have more digits to the right of the decimal point than that at original number which has the least number of digits to the right of the decimal point in it.

$$\begin{array}{r} 12.11 \\ 18.0 \\ 1.012 \\ \hline 31.122 \end{array}$$

Here, 18.0 has only one digit after the decimal point and the result should be reported only up to one digit after the decimal point. Hence the answer is 31.1.

Multiplication and Division of Significant Figures

In these operations, the result must be reported with no more significant figures as are there in the measurement with the few significant figures.

$2.5\times1.25 = 3.125$

Since 2.5 has two significant figures, the result should not have more than two significant figures, thus, it is 3.1.

While limiting the result to the required number of significant figures as done in the above mathematical operation, one has to keep in mind the following points for rounding off the numbers

1. The digit on the extreme right (i.e., the last digit) of a number may be removed.
2. If the rightmost digit to be removed is more than 5, the preceding number is increased by one. for example, 1.386

   If we have to remove 6, we have to round off 8. Then it becomes to 1.39
3. If the digit to be removed is less than 5, the preceding number is not changed. For example, 4.334 if 4 is to be removed, then the result is rounded upto 4.33.
4. If the digit to be removed is 5, then the preceding number is not changed if it is an even number but it is increased by one if it is an odd number. For example, if 6.35 is to be rounded by removing 5, we have to increase 3 to 4 giving 6.4 as the result. However, if 6.25 is to be rounded off it is rounded off to 6.2 only.

5.1.4 Dimensional Analysis

Often while calculating, there is a need to convert units from one system to other. The method used to accomplish this is called **factor label method** or **unit factor method** or **dimensional analysis**. This is illustrated below.

Example

A piece of metal is 3 inch (represented by in) long. What is its length in cm?

We know that 1 in = 2.54 cm

From this equivalence, we can write

$$\frac{1\ \text{inch}}{2.54\ \text{cm}} = 1$$

thus $\frac{1\ \text{inch}}{2.54\ \text{cm}}$ equals 1 and $\frac{2.54\ \text{cm}}{1\ \text{inch}}$ also equals 1. Both of these are called **unit factors**

$$2 \times 1000\ \text{cm}^3 \times \left[\frac{1\text{m}}{100\ \text{cm}}\right]^3 = \frac{2}{1000}\ \text{m}^3$$

Example

How many seconds are there in 2 days?

Here, we know 1 d

Table 7.5 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~–1.0
Human Saliva	6.4		

Solution

$2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-(aq)$

$K_w = [OH^-][H_3O^+]$

$= 10^{-14}$

Let, $x = [OH^-] = [H_3O^+]$ from H_2O. The H_3O^+ concentration is generated (i) from the ionization of HCl dissolved i.e.,

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+\ (aq) + Cl^-(aq)$,

and (ii) from ionization of H_2O. In these very dilute solutions, both sources of H_3O^+ must be considered:

$[H_3O^+] = 10^{-8} + x$

$K_w = (10^{-8} + x)(x) = 10^{-14}$

or $x^2 + 10^{-8}x - 10^{-14} = 0$

$[OH^-] = x = 9.5 \times 10^{-8}$

So, pOH = 7.02 and pH = 6.98

7.11.3 Ionization Constants of Weak Acids

Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by:

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$
Initial
concentration (M)
c 0 0
Let α be the extent of ionization
Change (M)
-cα +cα +cα
Equilibrium concentration (M)
c-cα cα cα

Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium:

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

K_a is called the **dissociation or ionization constant** of acid HX. It can be represented alternatively in terms of molar concentration as follows,

$K_a = [H^+][X^-] / [HX]$ (7.30)

At a given temperature T, K_a is a measure of the strength of the acid HX i.e., larger the value of K_a, the stronger is the acid. K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M.

Table 7.6 The Ionization Constants of Some Selected Weak Acids (at 298K)

Acid	Ionization Constant, K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Formic Acid (HCOOH)	1.8×10^{-4}
Niacin (C_5H_4NCOOH)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HClO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

The values of the ionization constants of some selected weak acids are given in Table 7.6.

The pH scale for the hydrogen ion concentration has been so useful that besides

pK_w, it has been extended to other species and quantities. Thus, we have:

$$pK_a = -\log (K_a) \qquad (7.31)$$

Knowing the ionization constant, K_a of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids / bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction

(a) Initial concentration, c.

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization.

(c) Equilibrium concentration.

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α.

Step 6. Calculate the concentration of species in principal reaction.

Step 7. Calculate $pH = -\log[H_3O^+]$

The above mentioned methodology has been elucidated in the following examples.

Problem 7.18

The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Solution

The following proton transfer reactions are possible:

1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

$$K_a = 3.2 \times 10^{-4}$$

2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$$K_w = 1.0 \times 10^{-14}$$

As $K_a >> K_w$, [1] is the principal reaction.

	HF +	$H_2O \rightleftharpoons$	H_3O^+ +	F^-
Initial concentration (M)	0.02		0	0
Change (M)	-0.02α		$+0.02\alpha$	$+0.02\alpha$
Equilibrium concentration (M)	$0.02 - 0.02\,\alpha$		$0.02\,\alpha$	0.02α

Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives:

$K_a = (0.02\alpha)^2 \,/\, (0.02 - 0.02\alpha)$

$= 0.02\,\alpha^2 \,/\, (1 - \alpha) = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$\alpha^2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0$

The quadratic equation in α can be solved and the two values of the roots are:

$\alpha = +\,0.12$ and $-\,0.12$

The negative root is not acceptable and hence,

$\alpha = 0.12$

This means that the degree of ionization, $\alpha = 0.12$, then equilibrium concentrations of other species viz., HF, F^- and H_3O^+ are given by:

$[H_3O^+] = [F^-] = c\alpha = 0.02 \times 0.12$

$= 2.4 \times 10^{-3}$ M

$[HF] = c(1 - \alpha) = 0.02\ (1 - 0.12)$

$= 17.6 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$

Problem 7.19

The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species H^+, A^- and HA at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Solution

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

Therefore, $[H^+] = 10^{-pH} = 10^{-4.50}$

$= 3.16 \times 10^{-5}$

$[H^+] = [A^-] = 3.16 \times 10^{-5}$

Thus, $K_a = [H^+][A^-] / [HA]$

$[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5}) \simeq 0.1$

$K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$

$pK_a = -\log(10^{-8}) = 8$

Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as:

Percent dissociation

$= [HA]_{dissociated} \times 100\ /[HA]_{initial}$ (7.32)

Problem 7.20

Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is 2.5×10^{-5}. Determine the percent dissociation of HOCl.

Solution

$HOCl(aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

Initial concentration (M)

0.08 0 0

Change to reach equilibrium concentration (M)

–x +x +x

equilibrium concentartion (M)

0.08 – x x x

$K_a = \{[H_3O^+][ClO^-] / [HOCl]\}$

$= x^2 / (0.08 - x)$

As x << 0.08, therefore $0.08 - x \simeq 0.08$

$x^2 / 0.08 = 2.5 \times 10^{-5}$

$x^2 = 2.0 \times 10^{-6}$, thus, $x = 1.41 \times 10^{-3}$

$[H^+] = 1.41 \times 10^{-3}$ M.

Therefore,

Percent dissociation

$= \{[HOCl]_{dissociated} \times 100\ /\ [HOCl]_{initial}\}$

$= 1.41 \times 10^{-3} / 0.08 = 1.76$ %.

$pH = -\log(1.41 \times 10^{-3}) = 2.85.$

7.11.4 Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

$MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$

In a weak base there is partial ionization of MOH into M^+ and OH^-, the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$K_b = [M^+][OH^-] / [MOH]$ (7.33)

Alternatively, if c = initial concentration of base and α = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as:

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

Table 7.7 The Values of the Ionization Constant of Some Weak Bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO\ (NH_2)_2$	1.3×10^{-14}

The values of the ionization constants of some selected weak bases, K_b are given in Table 7.7.

Many organic compounds like *amines* are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and nicotine all behave as very weak bases due to their very small K_b. Ammonia produces OH^- in aqueous solution:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The pH scale for the hydrogen ion concentration has been extended to get:

$$pK_b = -\log (K_b) \qquad (7.34)$$

Problem 7.21

The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Solution

$$NH_2NH_2 + H_2O \rightleftharpoons NH_2NH_3^+ + OH^-$$

From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have:

$[H^+]$ = antilog (–pH)

= antilog (–9.7) = 1.67×10^{-10}

$[OH^-] = K_w / [H^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10}$

$= 5.98 \times 10^{-5}$

The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentrations of both these ions are very small so the concentration of the undissociated base can be taken equal to 0.004M.

Thus,

$K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2]$

$= (5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7}$

$pK_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04.$

Problem 7.22

Calculate the pH of the solution in which 0.2M NH_4Cl and 0.1M NH_3 are present. The pK_b of ammonia solution is 4.75.

Solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The ionization constant of NH_3,

K_b = antilog ($-pK_b$) i.e.

$K_b = 10^{-4.75} = 1.77 \times 10^{-5}$ M

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Initial concentration (M)

0.10 0.20 0

Change in concentration to reach equilibrium (M)

–x +x +x

At equilibrium (M)

0.10 – x 0.20 + x x

$K_b = [NH_4^+][OH^-] / [NH_3]$

$= (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$

As K_b is small, we can neglect x in comparison to 0.1M and 0.2M. Thus,

$[OH^-] = x = 0.88 \times 10^{-5}$

Therefore, $[H^+] = 1.12 \times 10^{-9}$

$pH = -\log[H^+] = 8.95.$

7.11.5 Relation between K_a and K_b

As seen earlier in this chapter, K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of NH_4^+ and NH_3 we see,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

$$K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = [NH_4^+][OH^-] / NH_3 = 1.8 \times 10^{-5}$$

$$\text{Net: } 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\ M^2$$

Where, K_a represents the strength of NH_4^+ as an acid and K_b represents the strength of NH_3 as a base.

It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants K_a and K_b for the reactions added. Thus,

$$K_a \times K_b = \{[H_3O^+][NH_3] / [NH_4^+]\} \times \{[NH_4^+][OH^-] / [NH_3]\}$$

$$= [H_3O^+][OH^-] = K_w$$

$$= (5.6x10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14}\ M^2$$

This can be extended to make a generalisation. **The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:**

$$K_{NET} = K_1 \times K_2 \times \ldots\ldots \qquad (7.35)$$

Similarly, in case of a conjugate acid-base pair,

$$K_a \times K_b = K_w \qquad (7.36)$$

Knowing one, the other can be obtained. It should be noted that a *strong acid will have a weak conjugate base and vice-versa.*

Alternatively, the above expression $K_w = K_a \times K_b$, can also be obtained by considering the base-dissociation equilibrium reaction:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = [BH^+][OH^-] / [B]$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get:

$$K_b = [BH^+][OH^-][H^+] / [B][H^+]$$

$$=\{[OH^-][H^+]\}\{[BH^+] / [B][H^+]\}$$

$$= K_w / K_a$$

$$\text{or } K_a \times K_b = K_w$$

It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:

$$pK_a + pK_b = pK_w = 14 \text{ (at 298K)}$$

Problem 7.23

Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 7.7. Also, calculate the ionization constant of the conjugate acid of ammonia.

Solution

The ionization of NH_3 in water is represented by equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

We use equation (7.33) to calculate hydroxyl ion concentration,

$$[OH^-] = c\,\alpha = 0.05\,\alpha$$

$$K_b = 0.05\,\alpha^2 / (1 - \alpha)$$

The value of α is small, therefore the quadratic equation can be simplified by neglecting α in comparison to 1 in the denominator on right hand side of the equation,

Thus,

$$K_b = c\,\alpha^2 \quad \text{or} \quad \alpha = \sqrt{(1.77 \times 10^{-5} / 0.05)}$$

$$= 0.018.$$

$$[OH^-] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4} M.$$

$$[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4})$$

$$= 1.06 \times 10^{-11}$$

$$pH = -\log(1.06 \times 10^{-11}) = 10.97.$$

Now, using the relation for conjugate acid-base pair,

$$K_a \times K_b = K_w$$

using the value of K_b of NH_3 from Table 7.7.

We can determine the concentration of conjugate acid NH_4^+

$$K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5}$$

$$= 5.64 \times 10^{-10}.$$

7.11.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

The ionization reactions for example for a *dibasic acid* H_2X are represented by the equations:

$$H_2X(aq) \rightleftharpoons H^+(aq) + HX^-(aq)$$
$$HX^-(aq) \rightleftharpoons H^+(aq) + X^{2-}(aq)$$

Table 7.8 The Ionization Constants of Some Common Polyprotic Acids (298K)

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic Acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic Acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous Acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric Acid	Very large	1.2×10^{-2}	
Carbonic Acid	4.3×10^{-7}	5.6×10^{-11}	
Citric Acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric Acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

And the corresponding equilibrium constants are given below:

$$K_{a_1} = \{[H^+][HX^-]\} / [H_2X] \text{ and}$$

$$K_{a_2} = \{[H^+][X^{2-}]\} / [HX^-]$$

Here, K_{a_1} and K_{a_2} are called the first and second ionization constants respectively of the acid H_2X. Similarly, for tribasic acids like H_3PO_4 we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 7.8.

It can be seen that higher order ionization constants (K_{a_2}, K_{a_3}) are smaller than the lower order ionization constant (K_{a_1}) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-. Similarly, it is more difficult to remove a proton from a doubly charged HPO_4^{2-} anion as compared to $H_2PO_4^-$.

Polyprotic acid solutions contain a mixture of acids like H_2A, HA^- and A^{2-} in case of a diprotic acid. H_2A being a strong acid, the primary reaction involves the dissociation of H_2A, and H_3O^+ in the solution comes mainly from the first dissociation step.

7.11.7 Factors Affecting Acid Strength

Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid H-A depends on the **strength** and **polarity** of the H-A bond.

In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acid nature.

But it should be noted that while comparing acids formed by elements in the same *group* of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example,

$$\xrightarrow{\text{Size increases}}$$
$$HF << HCl << HBr << HI$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

Similarly, H_2S is stronger acid than H_2O.

But, when we discuss acids formed in elements in the same *row* of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example,

$$\xrightarrow{\text{Electronegativity of A increases}}$$
$$CH_4 < NH_3 < H_2O < HF$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

7.11.8 Common Ion Effect in the Ionization of Acids and Bases

Consider an example of acetic acid dissociation equilibrium represented as:

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

or $HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

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

Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if H^+ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example of **common ion effect**. **It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.** Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section 7.8.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again,

$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$

Initial concentration (M)

0.05 0 0.05

Let x be the extent of ionization of acetic acid.

Change in concentration (M)

–x +x +x

Equilibrium concentration (M)

0.05-x x 0.05+x

Therefore,

$K_a = [H^+][Ac^-]/[H\,Ac] = \{(0.05+x)(x)\}/(0.05-x)$

As K_a is small for a very weak acid, x<<0.05.

Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus,

$1.8 \times 10^{-5} = (x)(0.05 + x) / (0.05 - x)$

$= x(0.05) / (0.05) = x = [H^+] = 1.8 \times 10^{-5}M$

$pH = -\log(1.8 \times 10^{-5}) = 4.74$

Problem 7.24

Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$

Solution

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = [NH_4^+][OH^-] / [NH_3] = 1.77 \times 10^{-5}$

Before neutralization,

$[NH_4^+] = [OH^-] = x$

$[NH_3] = 0.10 - x \approx 0.10$

$x^2 / 0.10 = 1.77 \times 10^{-5}$

Thus, $x = 1.33 \times 10^{-3} = [OH^-]$

Therefore, $[H^+] = K_w / [OH^-] = 10^{-14} / (1.33 \times 10^{-3}) = 7.51 \times 10^{-12}$

$pH = -\log(7.5 \times 10^{-12}) = 11.12$

On addition of 25 mL of 0.1M HCl solution (i.e., 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e., 5 mmol of NH_3), 2.5 mmol of ammonia molecules are neutralized. The resulting 75 mL solution contains the remaining unneutralized 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+.

$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

2.5 2.5 0 0

At equilibrium

0 0 2.5 2.5

The resulting 75 mL of solution contains 2.5 mmol of NH_4^+ ions (i.e., 0.033 M) and 2.5 mmol (i.e., 0.033 M) of unneutralised NH_3 molecules. This NH_3 exists as NH_4OH in the following equilibrium:

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

0.033M – y y y

where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains 2.5 m mol NH_4^+ ions (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$[NH_4^+] = 0.033 + y$

As y is small, $[NH_4OH] \approx 0.033$ M and $[NH_4^+] \approx 0.033M$.

We know,

$K_b = [NH_4^+][OH^-] / [NH_4OH]$

$= y(0.033)/(0.033) = 1.77 \times 10^{-5}$ M

Thus, $y = 1.77 \times 10^{-5} = [OH^-]$

$[H^+] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$

Hence, pH = 9.24

7.11.9 Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. **The later process of interaction between water and cations/anions or both of salts is called hydrolysis.** The pH of the solution gets affected by this interaction. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., Cl^-, Br^-, NO_3^-, ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

(i) salts of weak acid and strong base e.g., CH_3COONa.

(ii) salts of strong acid and weak base e.g., NH_4Cl, and

(iii) salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionised in solution. This results in increase of OH^- ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in increased H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

CH_3COOH and NH_4OH, also remain into partially dissociated form:

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

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

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

Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their p*K* values:

$$pH = 7 + ½ (pK_a - pK_b) \qquad (7.37)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Problem 7.25

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Solution

$$pH = 7 + ½ [pK_a - pK_b]$$

$$= 7 + ½ [4.76 - 4.75]$$

$$= 7 + ½ [0.01] = 7 + 0.005 = 7.005$$

7.12 BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer solutions of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

7.12.1 DESIGNING BUFFER SOLUTION

Knowledge of pK_a, pK_b and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

Preparation of Acidic Buffer

To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant, Ka of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionises in water.

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

For which we can write the expression

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearranging the expression we have,

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

Taking logarithm on both the sides and rearranging the terms we get-

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

or

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (7.38)$$

$$pH = pKa + \log \frac{[\text{Conjugate base, } A^-]}{[\text{Acid, HA}]} \quad (7.39)$$

The expression (7.39) is known **Henderson-Hasselbalch equation.**

The quantity $\frac{[A^-]}{[HA]}$ is the ratio of concentration of conjugate base (anion) of the acid and the acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base, [A$^-$], comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (7.39) take the form:

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

In the equation [7.38], if the concentration of [A$^-$] is equal to the concentration of [Ha], then pH = pK_a because value of log 1 is zero. Thus if we take molar concentration of acid and salt (conjugage base) same, the pH of the buffer solution will be equal to the pK_a of the acid. So for preparing the buffer solution of the required pH we select that acid whose pKa is close to the required pH. For acetic acid pK_a value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result.

$$pOH = pK_b + \log \frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, B}]} \quad [7.40]$$

pH of the buffer solution can be calculated by using the equation pH + pOH = 14.

We know that pH + pOH = pK_w and

$pK_a + pK_b = pK_w$ On putting these values in equation (7.40) it takes the form as follows:

$$pK_w\text{-}pH = pK_w\text{-}pK_a + \log\frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

$$\text{or}\ \ pH = pK_a - \log\frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

(7.41)

If molar concentrations of base and its conjugate acid (cation) are same then pH of the buffer solution will be same as pK_a for the base. pK_a value for ammonia is 9.25 therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium chloride solution of equal molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation (7.41) becomes:

$$pH = 9.25 - \log\frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

7.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed as insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case

Table 7.9 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298K.

Name of the Salt	Formula	K_{sp}
Silver Bromide	$AgBr$	5.0×10^{-13}
Silver Carbonate	Ag_2CO_3	8.1×10^{-12}
Silver Chromate	Ag_2CrO_4	1.1×10^{-12}
Silver Chloride	$AgCl$	1.8×10^{-10}
Silver Iodide	AgI	8.3×10^{-17}
Silver Sulphate	Ag_2SO_4	1.4×10^{-5}
Aluminium Hydroxide	$Al(OH)_3$	1.3×10^{-33}
Barium Chromate	$BaCrO_4$	1.2×10^{-10}
Barium Fluoride	BaF_2	1.0×10^{-6}
Barium Sulphate	$BaSO_4$	1.1×10^{-10}
Calcium Carbonate	$CaCO_3$	2.8×10^{-9}
Calcium Fluoride	CaF_2	5.3×10^{-9}
Calcium Hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium Oxalate	CaC_2O_4	4.0×10^{-9}
Calcium Sulphate	$CaSO_4$	9.1×10^{-6}
Cadmium Hydroxide	$Cd(OH)_2$	2.5×10^{-14}
Cadmium Sulphide	CdS	8.0×10^{-27}
Chromic Hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Cuprous Bromide	$CuBr$	5.3×10^{-9}
Cupric Carbonate	$CuCO_3$	1.4×10^{-10}
Cuprous Chloride	$CuCl$	1.7×10^{-6}
Cupric Hydroxide	$Cu(OH)_2$	2.2×10^{-20}
Cuprous Iodide	CuI	1.1×10^{-12}
Cupric Sulphide	CuS	6.3×10^{-36}
Ferrous Carbonate	$FeCO_3$	3.2×10^{-11}
Ferrous Hydroxide	$Fe(OH)_2$	8.0×10^{-16}
Ferric Hydroxide	$Fe(OH)_3$	1.0×10^{-38}
Ferrous Sulphide	FeS	6.3×10^{-18}
Mercurous Bromide	Hg_2Br_2	5.6×10^{-23}
Mercurous Chloride	Hg_2Cl_2	1.3×10^{-18}
Mercurous Iodide	Hg_2I_2	4.5×10^{-29}
Mercurous Sulphate	Hg_2SO_4	7.4×10^{-7}
Mercuric Sulphide	HgS	4.0×10^{-53}
Magnesium Carbonate	$MgCO_3$	3.5×10^{-8}
Magnesium Fluoride	MgF_2	6.5×10^{-9}
Magnesium Hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Magnesium Oxalate	MgC_2O_4	7.0×10^{-7}
Manganese Carbonate	$MnCO_3$	1.8×10^{-11}
Manganese Sulphide	MnS	2.5×10^{-13}
Nickel Hydroxide	$Ni(OH)_2$	2.0×10^{-15}
Nickel Sulphide	NiS	4.7×10^{-5}
Lead Bromide	$PbBr_2$	4.0×10^{-5}
Lead Carbonate	$PbCO_3$	7.4×10^{-14}
Lead Chloride	$PbCl_2$	1.6×10^{-5}
Lead Fluoride	PbF_2	7.7×10^{-8}
Lead Hydroxide	$Pb(OH)_2$	1.2×10^{-15}
Lead Iodide	PbI_2	7.1×10^{-9}
Lead Sulphate	$PbSO_4$	1.6×10^{-8}
Lead Sulphide	PbS	8.0×10^{-28}
Stannous Hydroxide	$Sn(OH)_2$	1.4×10^{-28}
Stannous Sulphide	SnS	1.0×10^{-25}
Strontium Carbonate	$SrCO_3$	1.1×10^{-10}
Strontium Fluoride	SrF_2	2.5×10^{-9}
Strontium Sulphate	$SrSO_4$	3.2×10^{-7}
Thallous Bromide	$TlBr$	3.4×10^{-6}
Thallous Chloride	$TlCl$	1.7×10^{-4}
Thallous Iodide	TlI	6.5×10^{-8}
Zinc Carbonate	$ZnCO_3$	1.4×10^{-11}
Zinc Hydroxide	$Zn(OH)_2$	1.0×10^{-15}
Zinc Sulphide	ZnS	1.6×10^{-24}

of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule , for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former. Each salt has its

$$1.1 \times 10^{-10} = (S)(S) = S^2$$

or $S = 1.05 \times 10^{-5}$.

Thus, molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol L^{-1}.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula