Text Book for

INTERMEDIATE

First Year

Chemistry

Permission and Support by

National Council of Educational Research and Training
New Delhi

Board of Intermediate Education, Andhra Pradesh
Telugu and Sanskrit Akademi, Andhra Pradesh

Intermediate
First Year

Chemistry
Text Book

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Y.S. JAGAN MOHAN REDDY

CHIEF MINISTER
ANDHRA PRADESH

AMARAVATI

MESSAGE

I congratulate Akademi for starting its activities with printing of textbooks from the academic year 2021 – 22.

Education is a real asset which cannot be stolen by anyone and it is the foundation on which children build their future. As the world has become a global village, children will have to compete with the world as they grow up. For this there is every need for good books and good education.

Our government has brought in many changes in the education system and more are to come. The government has been taking care to provide education to the poor and needy through various measures, like developing infrastructure, upgrading the skills of teachers, providing incentives to the children and parents to pursue education. Nutritious mid-day meal and converting Anganwadis into pre-primary schools with English as medium of instruction are the steps taken to initiate children into education from a young age. Besides introducing CBSE syllabus and Telugu as a compulsory subject, the government has taken up numerous innovative programmes.

The revival of the Akademi also took place during the tenure of our government as it was neglected after the State was bifurcated. The Akademi, which was started on August 6, 1968 in the undivided state of Andhra Pradesh, was printing text books, works of popular writers and books for competitive exams and personality development.

Our government has decided to make available all kinds of books required for students and employees through Akademi, with headquarters at Tirupati.

I extend my best wishes to the Akademi and hope it will regain its past glory.

(Y.S. Jagan Mohan Reddy)

Dr. Nandamuri Lakshmiparvathi
M.A., M.Phil., Ph.D.
Chairperson, (Cabinet Minister Rank)
Telugu and Sanskrit Akademi, A.P.

Message of Chairperson, Telugu and Sanskrit Akademi, A.P.

In accordance with the syllabus developed by the Board of Intermediate, State Council for Higher Education, SCERT etc., we design high quality Text books by recruiting efficient Professors, department heads and faculty members from various Universities and Colleges as writers and editors. We are taking steps to print the required number of these books in a timely manner and distribute through the Akademi's Regional Centers present across the Andhra Pradesh.

In addition to text books, we strive to keep monographs, dictionaries, dialect texts, question banks, contact texts, popular texts, essays, linguistics texts, school level dictionaries, glossaries, etc., updated and printed and made available to students from time to time.

For competitive examinations conducted by the Andhra Pradesh Public Service Commission and for Entrance examinations conducted by various Universities, the contents of the Akademi publications are taken as standard. So, I want all the students and Employees to make use of Akademi books of high standards for their golden future.

Congratulations and best wishes to all of you.

N. Lakshmiparvathi

(Nandamuri Lakshmiparvathi)

J. SYAMALA RAO, I.A.S.,
Principal Secretary to Government

Higher Education Department
Government of Andhra Pradesh

MESSAGE

I Congratulate Telugu and Sanskrit Akademi for taking up the initiative of printing and distributing textbooks in both Telugu and English media within a short span of establishing Telugu and Sanskrit Akademi.

Number of students of Andhra Pradesh are competing of National Level for admissions into Medicine and Engineering courses. In order to help these students Telugu and Sanskrit Akademi consultation with NCERT redesigned their Textbooks to suit the requirement of National Level Examinations in a lucid language.

As the content in Telugu and Sanskrit Akademi books is highly informative and authentic, printed in multi-color on high quality paper and will be made available to the students in a time bound manner. I hope all the students in Andhra Pradesh will utilize the Akademi textbooks for better understanding of the subjects to compete of state and national levels.

(J. Syamala Rao)

THE CONSTITUTION OF INDIA

PREAMBLE

WE, THE PEOPLE OF INDIA, having solemnly resolved to constitute India into a [SOVEREIGN SOCIALIST SECULAR DEMOCRATIC REPUBLIC] and to secure to all its citizens:

JUSTICE, social, economic and political;

LIBERTY of thought, expression, belief, faith and worship;

EQUALITY of status and of opportunity; and to promote among them all

FRATERNITY assuring the dignity of the individual and the [unity and integrity of the Nation];

IN OUR CONSTITUENT ASSEMBLY this twenty-sixth day of November, 1949 do HEREBY ADOPT, ENACT AND GIVE TO OURSELVES THIS CONSTITUTION.

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Foreword

The Government of India vowed to remove the educational disparities and adopt a common core curriculum across the country especially at the Intermediate level. Ever since the Government of Andhra Pradesh and the Board of Intermediate Education (BIE) swung into action with the task of evolving a revised syllabus in all the Science subjects on par with that of COBSE, approved by NCERT, its chief intention being enabling the students from Andhra Pradesh to prepare for the National Level Common Entrance tests like NEET, ISEET etc for admission into Institutions of professional courses in our Country.

For the first time BIE AP has decided to prepare the Science textbooks. Accordingly an Academic Review Committee was constituted with the Commissioner of Intermediate Education, AP as Chairman and the Secretary, BIE AP; the Director SCERT and the Director Telugu Akademi as members. The National and State Level Educational luminaries were involved in the textbook preparation, who did it with meticulous care. The textbooks are printed on the lines of NCERT maintaining National Level Standards.

The Education Department of Government of Andhra Pradesh has taken a decision to publish and to supply all the text books with free of cost for the students of all Government and Aided Junior Colleges of newly formed state of Andhra Pradesh.

We express our sincere gratitude to the Director, NCERT for according permission to adopt its syllabi and curriculum of Science textbooks. We have been permitted to make use of their textbooks which will be of great advantage to our student community. I also express my gratitude to the Chairman, BIE and the honorable Minister for HRD and Vice Chairman, BIE and Secretary (SE) for their dedicated sincere guidance and help.

I sincerely hope that the assorted methods of innovation that are adopted in the preparation of these textbooks will be of great help and guidance to the students.

I wholeheartedly appreciate the sincere endeavors of the Textbook Development Committee which has accomplished this noble task.

Constructive suggestions are solicited for the improvement of this textbook from the students, teachers and general public in the subjects concerned so that next edition will be revised duly incorporating these suggestions.

It is very much commendable that Intermediate text books are being printed for the first time by the Akademi from the 2021-22 academic year.

Sri. V. Ramakrishna I.R.S.
Director
Telugu and Sanskrit Akademi,
Andhra Pradesh

Preface

In view of the recent guidelines of Central Government to have a common national curriculum which would enable children to face Nationwide common entrance tests after +2, the Board of Intermediate Education, Andhra Pradesh has thoroughly revised the syllabi of all science subjects. It is further proposed to adopt NCERT Text Book with suitable changes wherever necessary for the academic year 2012-13. Accordingly the NCERT Text Book of Class-XI has been thoroughly modified to suit the intermediate syllabus proposed by the Board of Intermediate.

The Text Book in its present form comprises of Thirteen Chapters. Chapter-1 deals with Atomic structure, quantum mechanical model of an atom and electronic configuration. Chapter-2 deals with Classification of elements and the periodicity in properties. Chapter-3 discusses Chemical bonding and molecular structure encompassing the various bonding theories and the relative merits and demerits.

Chapter-4 covers a discussion of States of matter relating to gases and liquids, namely Kinetic theory of gases, liquefaction of gases alongwith properties of liquids, vapour pressure, surface tension and viscosity.

Chapter-5 presents concepts relating to Stoichiometry, equivalent weight, mole, oxidation number and Redox reactions.

Chapter-6 deals with Thermodynamics 1st, 2nd and 3rd laws along with enthalpy calculation and criteria for spontaneity.

Chapter-7 gives a discussion on Chemical equilibrium, law of mass action, Gibbs free energy along with concept of equilibrium, acids & bases, solubility, and common ion affect.

Chapter-8 and 9 present Chemistry of Hydrogen and its compounds and the s- block elements and their compounds.

Chapter-10 and 11 deal with Elements of Group-13 and elements of Group-14. i.e. boron family and carbon family.

Chapter-12 discusses environmental concepts relating to chemistry highlighting types of pollution and strategies to control environmental pollution.

Chapter-13 gives some basic principles and techniques of Organic chemistry, discussion of hydrocarbons including aromatic hydrocarbons.

Some chapters like Acids and bases, Chemical equilibrium and Thermodynamics have been included. to suit the requirements of the proposed first intermediate syllabus of Board of Intermediate Education. Each chapter has a good number of examples and solved numerical problems. At the end of each chapter, questions covering very short, short and long answers have been provided. The content of each chapter is designed to stimulate the readers and generate fascination for the subject.

We hope this book will be highly helpful for Intermediate students appearing for National level common entrance examinations. In a book of this complex nature, though we tried our best with utmost care, there may still be some occasional errors. We will be glad to rectify them in future editions of the book and constructive criticism in this regard will be taken up for further improvement of quality of teaching and learning.

EDITORIAL BOARD

Contents

Group 1 Elements

Group 2 Elements

HYDROCARBONS

Chapter
1

ATOMIC STRUCTURE

Objectives

After studying this chapter you will be able to

- know about the discovery of electron, proton and neutron and their characteristics;
- describe Thomson, Rutherford and Bohr atomic models;
- understand the important features of the quantum mechanical model of atom;
- understand nature of electromagnetic radiation and Planck's quantum theory;
- explain the photoelectric effect and describe features of atomic spectra;
- state the de Broglie relation and Heisenberg uncertainty principle;
- define an atomic orbital in terms of quantum numbers;
- state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity;
- write the electronic configurations of atoms.

> ***The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements.***

The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word '*a-tomio*' which means 'uncut-able' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century.

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called **Dalton's atomic theory**, regarded the atom as the ultimate particle of matter.

In this chapter we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms can be further divided into sub-atomic particles, i.e., **electrons, protons** and **neutrons**— a concept very different from that of Dalton. The major problems before the scientists at that time were:

- to account for the stability of atom after the discovery of sub-atomic particles,
- to compare the behaviour of one element from other in terms of both physical and chemical properties,
- to explain the formation of different kinds of molecules

by the combination of different atoms and,

- to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

1.1 SUB-ATOMIC PARTICLES

Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur generate electricity. Many different kinds of sub-atomic particles were discovered in the twentieth century. However, in this section we will talk about only two particles, namely electron and proton.

1.1.1 Discovery of Electron

In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in second year. These results suggested the particulate nature of electricity.

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other".

In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as **cathode ray discharge tubes**. It is depicted in Fig. 1.1(a). A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode).

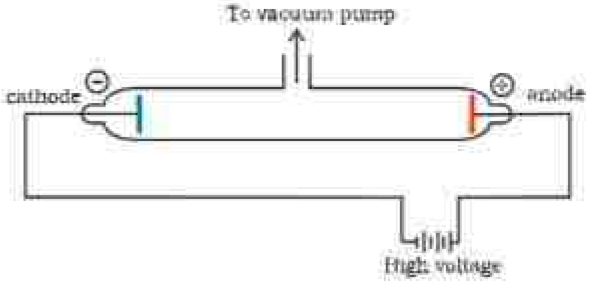

Fig. 1.1(a) *A cathode ray discharge tube*

These were called **cathode rays or cathode ray particles**. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot on the coating is developed(same thing happens in a television set) [Fig. 1.1(b)].

The results of these experiments are summarised below.

(i) The cathode rays start from cathode and move towards the anode.

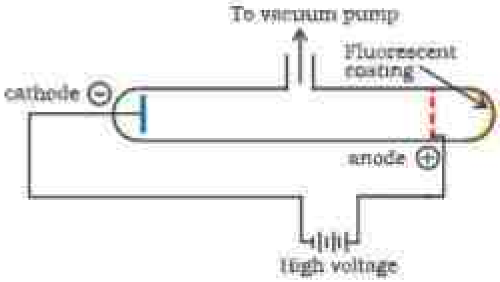

Fig. 1.1(b) *A cathode ray discharge tube with perforated anode*

(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials.

(iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 1.2).

(iv) In the presence of electrical or magnetic field, the behaviour of cathode rays is similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called **electrons.**

(v) The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

Thus, we can conclude that electrons are basic constituents of all the atoms.

1.1.2 Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 1.2). Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon:

(i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection.

(ii) the mass of the particle — lighter the particle, greater the deflection.

(iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path followed as in the absence of electric or magnetic field and they hit the screen at point B. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of e/m_e as:

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ \mathrm{C\ kg^{-1}} \qquad (1.1)$$

Where m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulombs (C). Since electrons are negatively charged, the charge on electron is $-e$.

1.1.3 Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found

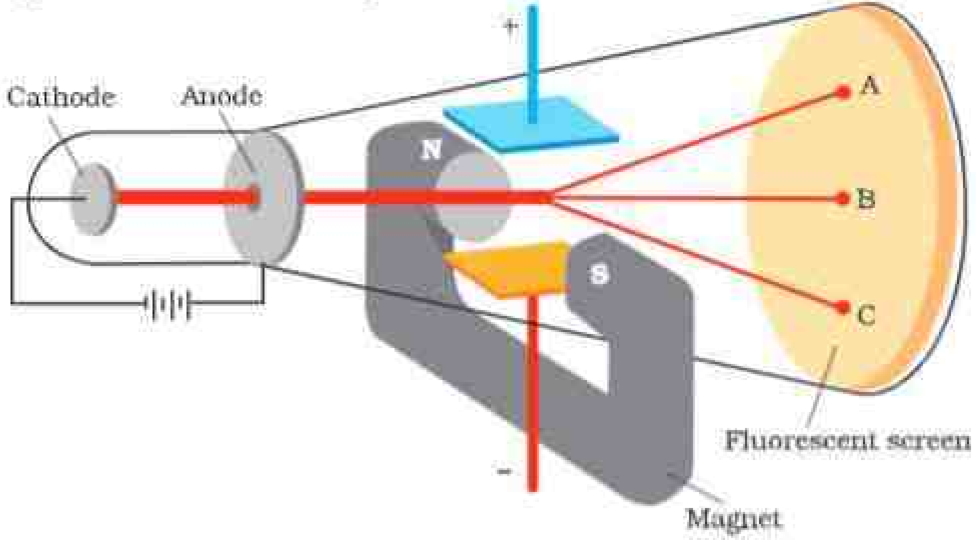

Fig. 1.2 *The apparatus to determine the charge to the mass ratio of electron*

that the charge on the electron to be -1.6×10^{-19} C. The present accepted value of electrical charge is -1.6022×10^{-19} C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_e = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19}\text{C}}{1.758820 \times 10^{11}\text{C kg}^{-1}}$$

$$= 9.1094 \times 10^{-31}\,\text{kg} \qquad (1.2)$$

1.1.4 Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as **canal rays.** The characteristics of these positively charged particles are listed below.

(i) unlike cathode rays, the nature of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions.

(ii) The charge to mass ratio of the particles is found to depend on the gas from which these originate.

(iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

(iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays.

The smallest and lightest positive ion was obtained from hydrogen gas and was called **proton**. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituents of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles, when electrically neutral particles having a mass slightly greater than that of the protons were emitted. He named these particles as **neutrons**. The important properties of these fundamental particles are given in Table 1.1.

1.2 ATOMIC MODELS

Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, proposed by J. J. Thomson and Ernest Rutherford are discussed below.

Millikan's Oil Drop Method

In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, $q = n\,e$, where n = 1, 2, 3... .

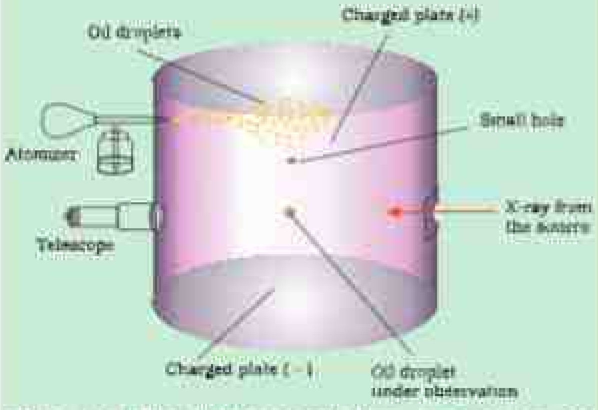

Fig. 1.3 *The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

Table 1.1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.00054	0
Proton	p	$+1.6022\times10^{-19}$	$+1$	1.67262×10^{-27}	1.00727	1
Neutron	n	0	0	1.67493×10^{-27}	1.00867	1

1.2.1 Thomson Model of Atom

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 1.4). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.** This model can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. *An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom.*

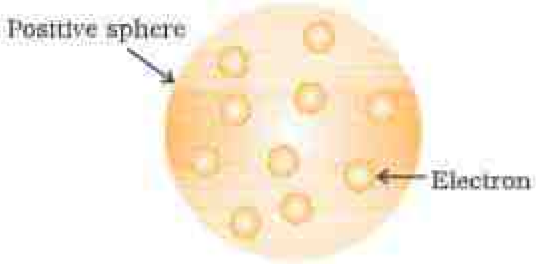

Fig.1.4 *Thomson model of atom*

Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhalm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since Röentgen did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called target. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electro-magnetic character (Section 1.3.1).

Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as **radioactivity** and the elements known as **radioactive elements.** This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed that three kinds of rays i.e., α, β- and γ-rays are emitted. Rutherford found that α-rays consist of high energy particles carrying two units of positive charge and four units of atomic mass. He concluded that α- particles are helium nuclei as when α- particles combined with two electrons yielded helium gas. β-rays are negatively charged particles similar to electrons. The γ-rays are high energy

RMS speed (u_{rms}) = $u_{rms} = \sqrt{\frac{3RT}{M}}$

$T = 27^0C + 273 = 300K; R = 8.314 J\ mol^{-1} K^{-1}$

M = gram molecular mass of CO_2 = 44 g mol^{-1}

($1J = Kg\ m^2\ s^{-2}$)

$$\sqrt{\frac{3 \times 8.314 kg\ m^2 s^{-2} K^{-1} mol^{-1} \times 300K}{0.044\ kg\ mol^{-1}}}$$

$= 4.12 \times 10^2 m\ s^{-1}$

Average speed (u_{av}) = 0.9213 x RMS speed

$= 0.9213 \times 4.12 \times 10^2 m\ s^{-1}$

$= 3.8 \times 10^2\ m\ s^{-1}$

Most probable speed

(u_{mp}) $= 0.8166 \times 4.12 \times 10^2 m\ s^{-1}$

$= 3.36 \times 10^2\ m\ s^{-1}$.

4.10.1 Kinetic Energy : According to Kinetic gas equation $pV = (1/3)mnu^2_{rms}$. For one mole of a gas' n' the number of molecules is equal to Avogadro's number 'N'. Then 'mN'represents the molar mass of the gas 'M'

$$p = \frac{1}{3}Mu^2_{rms} = \frac{2}{3}(\frac{1}{2}Mu^2_{rms}) = \frac{2}{3}E_k \qquad (4.58)$$

Where E_k is the kinetic energy of one mole of gas. For one mole of a gas, the ideal gas equation is

$$pV = RT \qquad (4.59)$$

From equations (4.58) and (4.59) we have

$$\frac{2}{3}E_k = RT \text{ or } E_k = \frac{3}{2}RT \qquad (4.60)$$

For 'n' moles of a gas $\quad E_k = \frac{3}{2}nRT \qquad (4.61)$

Kinetic energy is directly proprtional to the temperature in Kelvin scale

$$E_k \propto T$$

It means that one mole of any gas has the same kinetic energy at a given temperature. The kinetic energy for one molecule of a gas

$$\frac{E_k}{N} = \frac{3}{2}\left(\frac{R}{N}\right)T = \frac{3}{2}\ kT$$

Where 'k' is called Boltzmann constant and is equal to ($\frac{R}{N}$). It is the gas constant per molecule.

The value of Boltzmann constant is

$k = 1.38 \times 10^{-16}$ erg K^{-1} $molecule^{-1}$

$= 1.38 \times 10^{-23} J\ K^{-1}$ $molecule^{-1}$

Problem 4.8

Calculate kinetic energy of 5 moles of Nitrogen at 27°C

Solution

Kinetic energy $= \frac{3}{2}$ n RT

where n = 5 moles; $R = 8.314\ J\ mol^{-1}\ k^{-1}$

$T = 27°C + 273 = 300k$

Kineticenergy

$$E_k = \frac{3}{2} \times 5\ mol \times 8.314J\ mol^{-1}K^{-1} \times 300K = 18706.50\ J$$

Problem 4.9

Calculate kinetic energy (in SI units) of 4 g of methane at -73°C

Solution

n= No of moles of methane

$$\frac{4g}{16g\ mol^{-1}} = 0.25\ mol$$

$R = 8.314\ J\ mol^{-1}K^{-1}$

$T = -73°C + 273 = 200\ K$

Kinetic energy

$$= \frac{3}{2} \times 0.25 mol \times 8.314 J mol^{-1} K^{-1} \times 200K = 623.6J$$

Problem 4.10

Calculate the ratio of kinetic energies of 3 g of Hydrogen and 4g of Oxygen at a given temperature.

Solution

Since the temperature is same for the two gases, we can write the ratio of kinetic energies is in the moles of H_2 : moles of O_2

$$=\frac{3\text{ g of }H_2}{2\text{ g mol}^{-1}}:\frac{4\text{ g of }O_2}{32\text{ g mol}^{-1}}=\frac{3}{2}:\frac{1}{8}=12:1$$

4.11 BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

Our theoritical model of gases corresponds very well with the experimental observations. Difficulty arises when we try to test how far the relation $pV = nRT$ reproduce actual pressure-volume-temperature relationship of gases. To test this point we plot pV *vs* p plot of gases because at constant temperature, pV will be constant (Boyle's law) and pV *vs* p graph at all pressures will be a straight line parallel to x-axis. Fig. 4.10 shows such a plot constructed from actual data for several gases at 273 K.

It can be seen easily that at constant temperature pV *vs* p plot for real gases is not a straight line parallel to p axis. There is a significant deviation from ideal behaviour. Two types of curves are seen.In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases. The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. It is thus, found that real gases do not follow ideal gas equation perfectly under all conditions.

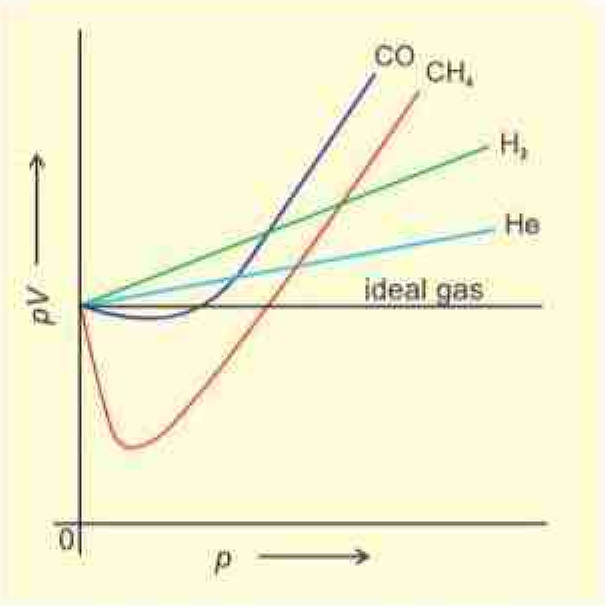

Fig. 4.10 *Plot of pV vs p for real gas and ideal gas*

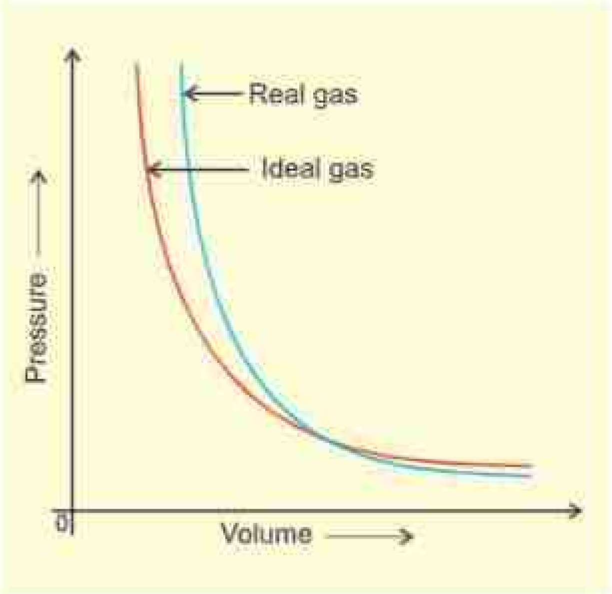

Fig. 4.11 *Plot of pressure vs volume for real gas and ideal gas*

Deviation from ideal behaviour also becomes apparent when pressure *vs* volume plot is drawn. The pressure *vs* volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Fig 4.11 shows these plots. It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

It is found that real gases do not follow, Boyle's law, Charles law and Avogadro law perfectly under all conditions. Now two questions arise.

(i) Why do gases deviate from the ideal behaviour?

(ii) What are the conditions under which gases deviate from ideality?

We get the answer of the first question if we look into postulates of kinetic theory once again. We find that two assumptions of the kinetic theory do not hold good. These are

(a) There is no force of attraction between the molecules of a gas.

(b) Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If assumption (a) is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress. This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volume. If assumption (b) is correct, the pressure *vs* volume graph of experimental data (real gas) and that theoritically calculated from Boyles law (ideal gas) should coincide.

Real gases show deviations from ideal gas law because molecules interact with one another other. At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{ideal} = \underset{\text{observed pressure}}{p_{real}} + \underset{\text{correction term}}{\frac{an^2}{V^2}} \qquad (4.63)$$

Here, a is a constant.

Repulsive forces also become significant. Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres. The volume occupied by the molecules also becomes significant because instead of moving in volume *V*, these are now restricted to volume (*V*–*n*b) where *n*b is approximately the total volume occupied by the molecules themselves. Here, b is a constant. Having taken into account the corrections for pressure and volume, we can rewrite equation (4.17) as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad (4.64)$$

Equation (4.64) is known as van der Waals equation. In this equation *n* is number of moles of the gas. Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas. Value of 'a' is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

Also, at very low temperature, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces. Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

The deviation from ideal behaviour can be measured in terms of **compressibility factor** *Z*, which is the ratio of product *pV* and *n*R*T*. Mathematically

$$Z = \frac{pV}{n\,RT} \qquad (4.65)$$

For ideal gas $Z = 1$ at all temperatures and pressures because $pV = n\,RT$. The graph of *Z* *vs* *p* will be a straight line parallel to pressure axis (Fig. 4.12). For gases which deviate from ideality, value of *Z* deviates from unity. At very low pressures all gases have $Z \approx 1$ and behave as ideal gas. At high pressure all the gases have $Z > 1$. These are more difficult to compress. At intermediate pressures, most gases have $Z < 1$. **Thus gases show ideal**

behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it. In other words, the behaviour of the gas becomes more ideal when pressure is very low. Upto what pressure a gas will follow the ideal gas law, depends upon nature of the gas and its temperature. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point.** Boyle point of a gas depends upon its nature. Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very feeble. Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously. Above explanation shows that at low pressure and high temperature gases show ideal behaviour. These conditions are different for different gases.

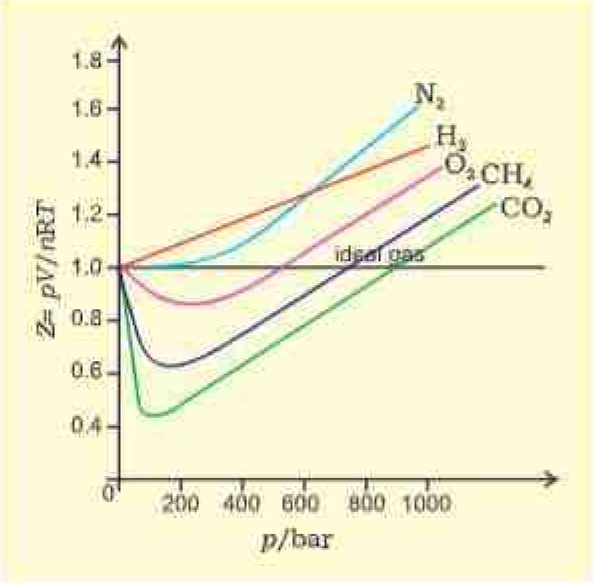

Fig. 4.12 *Variation of compressibility factor for some gases*

More insight is obtained in the significance of Z if we note the following derivation

$$Z = \frac{pV_{\text{real}}}{nRT} \qquad (4.66)$$

If the gas shows ideal behaviour then $V_{\text{ideal}} = \frac{nRT}{p}$. On putting this value of $\frac{nRT}{p}$ in equation (4.66) we have

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \qquad (4.67)$$

From equation (4.67) we can see that compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

In the following sections we will see that it is not possible to distinguish between gaseous state and liquid state and that liquids may be considered as continuation of gas phase into a region of small volumes and very high molecular attraction. We will also see how we can use isotherms of gases for predicting the conditions for liquefaction of gases.

4.12 LIQUEFACTION OF GASES

First complete data on pressure - volume - temperature relations of a substance in both gaseous and liquid state was obtained by Thomas Andrews on carbon dioxide. He plotted isotherms of carbon dioxide at various temperatures (Fig. 4.13). Later on it was found that real gases behave in the same manner as carbon dioxide. Andrews noticed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquified even at very high pressure. As the temperature is lowered, shape of the curve changes and data shows considerable deviation from ideal behaviour. At 30.98 °C carbon dioxide remains gas upto 73 atmospheric pressure. (Point E in Fig. 4.13). At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. The temperature 30.98 °C is called **critical temperature (T_c)** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed. Above this temperature it is gas. Volume of one mole of the gas at critical temperature and critical pressure is called

critical volume (V_C) and pressure at this temperature is called **critical pressure (p_C)**. The critical temperature, pressure and volume are called critical constants. Further increase in pressure simply compresses the liquid carbon dioxide and the curve represents the compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in steep rise in pressure indicating very low compressibility of the liquid. Below 30.98 °C, the behaviour of the gas on compression is quite different. At 21.5 °C, carbon dioxide remains as a gas only upto point B. At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide coexist and further application of pressure results in the condensation of more gas until the point C is reached. At point C, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by steep line. A slight compression from volume V_2 to V_3 results in steep rise in pressure from p_2 to p_3 (Fig. 4.13). Below 30.98 °C (critical temperature) each curve shows the similar trend. Only length of the horizontal line increases at lower temperatures. At critical point horizontal portion of the isotherm merges into one point. Thus we see that a point like A in the Fig. 4.13 represents gaseous state. A point like D represents liquid state and a point under the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium. All the gases upon compression at constant temperature (isothermal compression) show the same behaviour as shown by carbon dioxide. Also above discussion shows that gases should be cooled below their critical temperature for liquefication. Critical temperature of a gas is highest temperature at which liquefaction of the gas first occurs. Liquefaction of so called permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.

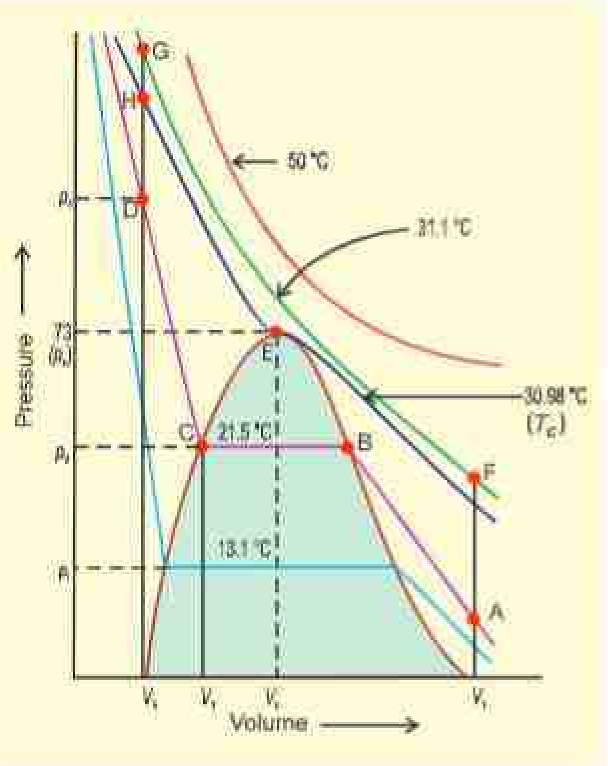

Fig. 4.13 *Isotherms of carbon dioxide at various temperatures*

It is possible to change a gas into liquid or a liquid into gas by a process in which always a single phase is present. For example in Fig. 4.13 we can move from point A to F vertically by increasing the temperature, then we can reach the point G by compressing the gas at the constant temperature along this isotherm (isotherm at 31.1°C). The pressure will increase. Now we can move vertically down towards D by lowering the temperature. As soon as we cross the point H on the critical isotherm we get liquid. We end up with liquid but in this series of changes we do not pass through two-phase region. If process is carried out at the critical temperature, substance always remains in one phase.

Thus there is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognise this continuity. Thus a liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears. A gas below the critical temperature can be liquified by applying pressure, and is called **vapour** of the substance. Carbon dioxide gas below its critical temperature is called carbon dioxide vapour. Critical constants for some common substances are given in Table 4.4.

Table 4.4 Critical Constants for Some Substances

Substance	T_c /K	p_c /bar	V_c/dm^3 mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Problem 4.11

Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the gas particles. Critical temperatures of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquify first when you start cooling from 500 K to their critical temperature ?

Solution

Ammonia will liquify first because its critical temperature will be reached first. Liquefaction of CO_2 will require more cooling.

4.13 LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.

Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

4.13.1 Vapour Pressure

If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases. After some time it becomes constant, an equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as **equilibrium vapour pressure or saturated vapour pressure.**. Since process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid.

When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is given in (Fig. 4.14). At 1 atm pressure boiling temperature is called **normal boiling point**. If pressure is 1 bar then the boiling point is called **standard boiling point** of the liquid. Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100 °C (373 K), its standard boiling point is 99.6 °C (372.6 K).

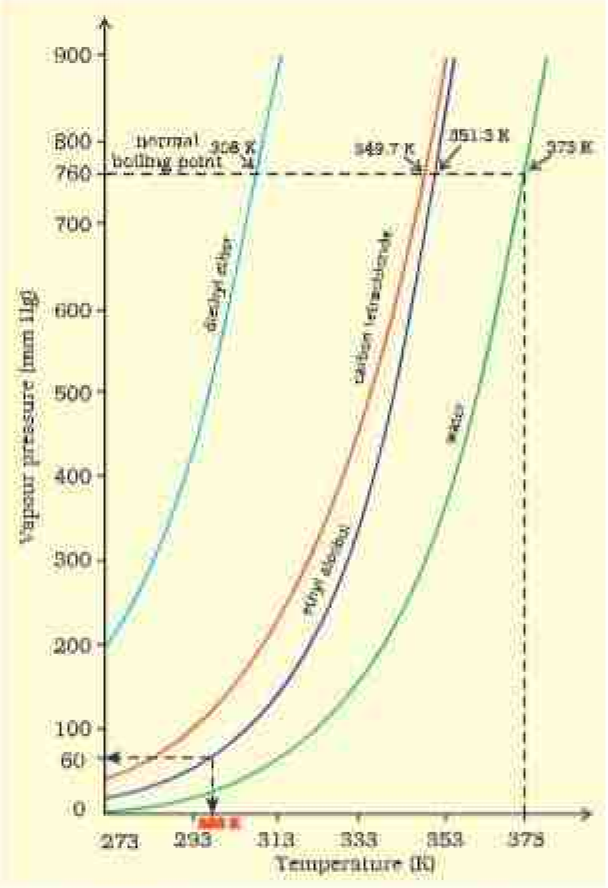

Fig. 4.14 *Vapour pressure vs temperature curve of some common liquids.*

At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food. In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called **critical temperature** about which we have already discussed.

4.13.2 Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface. Why do particles of soil at the bottom of river remain separated but they stick together when taken out ? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid ? All these phenomena are caused due to the characteristic property of liquids, called **surface tension**. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule, therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Fig. 4.15), due to the molecules below it. Since there are no molecules above it.

Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are J m^{-2}. Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ

(Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1}. The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition, that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.

The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

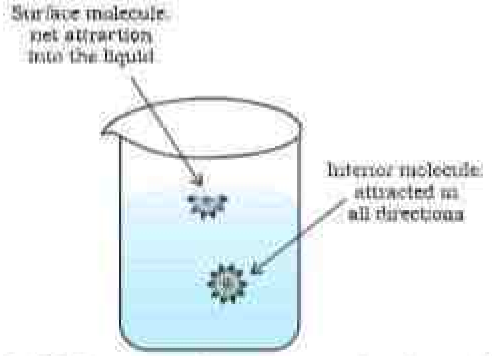

Fig. 4.15 *Forces acting on a molecule on liquid surface and on a molecule inside the liquid*

4.13.3 Viscosity

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.

When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called **laminar flow**. If we choose any layer in the flowing liquid (Fig.4.16), the layer above it accelerates its flow and the layer below this retards its flow.

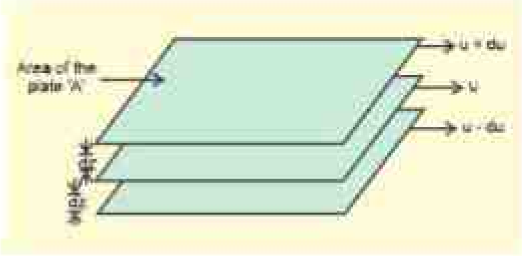

Fig. 4.16 *Gradation of velocity in the laminar flow*

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\frac{du}{dz}$. A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$F \propto A$ (A is the area of contact)

$F \propto \frac{du}{dz}$ (where, $\frac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$$F \propto A.\frac{du}{dz}$$

$$\Rightarrow F = \eta A\frac{du}{dz} \qquad (4.68)$$

'η' is proportionality constant and is called **coefficient of viscosity**. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m^{-2}) = pascal second (Pa s = 1kg $m^{-1}s^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = 1 g $cm^{-1}s^{-1}$ = 10^{-1}kg $m^{-1}s^{-1}$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

SUMMARY

Intermolecular forces operate between the particles of matter. These forces differ from pure electrostatic forces that exist between two oppositely charged ions. Also, these do not include forces that hold atoms of a covalent molecule together through covalent bond. Competition between thermal energy and intermolecular interactions determines the state of matter. "Bulk" properties of matter such as behaviour of gases, characteristics of solids and liquids and change of state depend upon energy of constituent particles and the type of interaction between them. Chemical properties of a substance do not change with change of state, but the reactivity depends upon the physical state.

Forces of interaction between gas molecules are negligible and are almost independent of their chemical nature. Interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental studies on gases. **Boyle's law** states that under isothermal condition, pressure of a fixed amount of a gas is inversely proportional to its volume. **Charles' law** is a relationship between volume and absolute temperature under isobaric condition. It states that volume of a fixed amount of gas is directly proportional to its absolute temperature $(V \propto T)$. If state of a gas is represented by p_1, V_1 and T_1 and it changes to state at p_2, V_2 and T_2, then relationship between these two states is given by combined gas law according to which $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$. Any one of the variables of this gas can be found out if other five variables are known. **Avogadro law** states that equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules. **Graham's Law** of diffusion states that the rate of diffusion of a gas is inversely proportional to the squre root of its density. Thus $r \propto \frac{1}{\sqrt{d}}$. **Dalton's law of partial pressure** states that total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them. Thus $p = p_1+p_2+p_3+ \dots$. Relationship between pressure, volume, temperature and number of moles of a gas describes its state and is called equation of state of the gas. Equation of state for ideal gas is $pV=nRT$, where R is gas constant and its value depends upon units chosen for pressure, volume and temperature. According to Kinetic molecular theory, gases consist of small and tiny particles called molecules and pressure of a gas is due to collisions of gas molecules on the walls of the container. According to Kinetic gas equation

$pV = \frac{1}{3} mnu_{rms}^2$ and all the gas laws can be derived from it. The molecules of gases possess different types of speeds like rms, average and most probable speeds. Kinetic energy of gas molecules is given by $E_k = \frac{1}{2} mu^2$ and as temperture increases the kinetic energy of gas molecules also increases.

At high pressure and low temperature intermolecular forces start operating strongly between the molecules of gases because they come close to each other. Under suitable temperature and pressure conditions gases can be liquified. Liquids may be considered as continuation of gas phase into a region of small volume and very strong molecular attractions. Some properties of liquids *e.g.*, surface tension and viscosity are due to strong intermolecular attractive forces.

QUESTIONS

Very short answer type questions

1. Name the different intermolecular forces experienced by the molecules of a gas.
2. State Boyle's law. Give its mathematical expression.
3. State Charle's law. Give its mathematical expression.
4. What are Isotherms?
5. What is Absolute Temperature?
6. What are Isobars?
7. What is Absolute Zero?
8. State Avogadro's law.
9. What are Isochores?
10. What are S T P Conditions?
11. What is Gram molar Volume?
12. What is an Ideal gas?
13. Why the gas constant 'R' is called Universal gas constant?
14. Why Ideal gas equation is called Equation of State?
15. Give the values of gas constant in different units.
16. How are the density and molar mass of a gas related?
17. State Graham's law of diffusion.
18. Which of the gases diffuses faster among N_2 , O_2 and CH_4? Why?
19. How many times methane diffuses faster than sulphurdioxide?
20. State Dalton's law of Partial pressures.
21. Give the relation between the partial pressure of a gas and its mole fraction.

22. What is aqueous tension?
23. Give the two assumptions of Kinetic molecular theory of gases that do not hold good in explaining the deviation of real gases from ideal behaviour.
24. Give the Kinetic gas equation and write the terms in it.
25. Give an equation to calculate the kinetic energy of gas molecules.
26. What is Boltzman's constant? Give its value.
27. What is R M S speed?
28. What is Average speed?
29. What is Most probable speed?
30. What is the effect of temperature on the speeds of the gas molecules?
31. What is the effect of temperature on the kinetic energy of the gas molecules?
32. Give the ratio of RMS average and most probable speeds of gas molecules.
33. Why RMS speed is taken in the derivation of Kinetic gas equation?
34. What is Compressibility factor?
35. What is Boyle Temperature?
36. What is critical temperature? Give its value for CO_2.
37. What is critical Volume?
38. What is critical Pressure?
39. What are critical constants?
40. Define vapour Pressure of a liquid.
41. What are normal and standard boiling points? Give their values for H_2O.
42. Why pressure Cooker is used for cooking food on hills?
43. What is surface tension?
44. What is laminar flow of a liquid?
45. What is coefficient of Viscosity? Give its units.

Short answer type questions

46. State and explain Boyle's law.
47. State and explain Charle's law.
48. Derive Ideal gas equation.
49. State and explain Graham's law of Diffusion.
50. State and explain Dalton's law of Partial pressures.
51. Deduce (a) Boyle's law and (b) Charle's law from Kinetic gas equation.
52. Deduce (a) Graham's law and (b) Daltons law from Kinetic gas equation.
53. Derive an expression for Kinetic Energy of gas molecules.
54. Define (a) rms (b) average and (c) most probable speeds of gas molecules. Give their interrelationship.
55. Explain the physical significance of van der Waals paramaters.

56. What is Surface Tension of liquids? Explain the effect of temperature on the suface tension of liquids.

57. What is Vapour Pressure of liquids? How the Vapour Pressure of a liquid is related to its boiling point?

58. Define Viscosity and Coefficient of Viscosity. How does the Viscosity of liquids varies with temperature.

Long answer type questions

59. Write notes on Intermolecular Forces.

60. State Boyle's law, Charle's law and Avogadro's law and derive Ideal gas equation.

61. Write notes on diffusuon of Gases.

62. State and explain Dalton's law of Partial Pressures.

63. Write the postulates of Kinetic Molecular Theory of Gases.

64. Deduce gas laws from Kinetic gas equation.

65. Explain Maxwell-Boltzmann distribution curves of molecular speeds and give the important conclusions. Discuss the effect of temperature on the distribution of molecular speeds.

66. Write notes on the behaviour of real gases and their deviation from ideal behavior.

67. Derive the van der Waals equation of state. Explain the importance of vander Waal's gas eqaution.

68. Explain the principle underlying the liquefaction of gases.

69. Write notes on the following properties of liquids

(a) Vapour Pressure (b) Surface Tension (c) Viscosity.

PROBLEMS

4.1 What will be the minimum pressure required to compress 500 dm^3 of air at 1 bar to 200 dm^3 at 30°C ? (Ans : 2.5bar)

4.2 A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35 °C. What would be its pressure? (Ans : 0.8bar)

4.3 Using the equation of state $pV=nRT$; show that at a given temperature density of a gas is proportional to gas pressure p.

4.4 At 0°C, the density of a certain oxide of a gas at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide? (Ans : 70g/mol)

4.5 Pressure of 1 g of an ideal gas A at 27 °C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature the pressure becomes 3 bar. Find a relationship between their molecular masses. (Ans : $M_B = 4M_A$)

4.6 The drain cleaner, Drainex contains small bits of aluminum which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20 °C and one bar will be released when 0.15g of aluminum reacts? (Ans : 202.50 mL)

4.7 What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in a 9 dm^3 flask at 27 °C ? (Ans : 8.314×10^4 Pa)

4.8 What will be the pressure of the gaseous mixture when 0.5 L of H_2 at 0.8 bar and 2.0 L of dioxygen at 0.7 bar are introduced in a 1L vessel at 27°C? (Ans ; 1.8 bar)

4.9 Density of a gas is found to be 5.46 g/dm^3 at 27 °C at 2 bar pressure. What will be its density at STP? (Ans : $3g/dm^3$)

4.10 34.05 mL of phosphorus vapour weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus? (Ans : $124.77g\ mol^{-1}$)

4.11 A student forgot to add the reaction mixture to the round bottomed flask at 27 °C but instead he/she placed the flask on the flame. After a lapse of time, he realized his mistake, and using a pyrometer he found the temperature of the flask was 477 °C. What fraction of air would have been expelled out? (Ans : 3/5)

4.12 Calculate the temperature of 4.0 mol of a gas occupying 5 dm^3 at 3.32 bar. ($R = 0.083$ bar $dm^3\ K^{-1}\ mol^{-1}$). (Ans : 50K)

4.13 Calculate the total number of electrons present in 1.4 g of dinitrogen gas. (Ans : 4.2154×10^{23})

4.14 How much time would it take to distribute one Avogadro number of wheat grains, if 10^{10} grains are distributed each second ? (Ans : 1.90956×10^6 year)

4.15 Ammonia gas diffuses through a fine hole at the rate 0.5 lit min^{-1}. Under the same conditions find the rate of diffusion of chlorine gas. (Ans : 0.245 lit. min^{-1})

4.16 Find the relative rates of diffusion of CO_2 and Cl_2 gases . (Ans : 1 : 1.267)

4.17 If 150mL carbon monoxide effused in 25 seconds, what volume of methane would effuse in same time. (Ans : 198.5 mL)

4.18 Hydrogen chloride gas is sent into a 100 metre tube from one end 'A' and ammonia gas from the other end 'B', under similar conditions. At what distance from 'A' will be the two gases meet. (Ans : 40.48 metres from the end 'A')

4.19 Calculate the total pressure in a mixture of 8 g of dioxygen and 4 g of dihydrogen confined in a vessel of 1 dm^3 at 27°C. $R = 0.083$ bar $dm^3\ K^{-1}\ mol^{-1}$. (56.025 bar)

4.20 Calculate the total pressure in a mixture of 3.5g of dinitrogen 3.0g of dihydrogen and 8.0g dioxgyen confined in vessel of $5dm^3$ at 27°C ($R = 0.\ 083$ bar $dm^3\ k^{-1}\ mol^{-1}$)

(Ans : 9.3375 bar)

4.21 Pay load is defined as the difference between the mass of displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1.66 bar at 27°C. (Density of air = 1.2 kg m^{-3} and $R = 0.083$ bar $dm^3\ K^{-1}\ mol^{-1}$). (Ans : 3811.1 kg)

4.22 Calculate the volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure. $R = 0.083$ bar L $K^{-1}\ mol^{-1}$. (Ans : 5.05L)

4.23 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of dihydrogen at 17 °C, at the same pressure. What is the molar mass of the gas? (Ans : $40g\ mol^{-1}$)

4.24 A mixture of dihydrogen and dioxygen at one bar pressure contains 20% by weight of dihydrogen. Calculate the partial pressure of dihydrogen. (Ans : 0.8 bar)

4.25 What would be the SI unit for the quantity pV^2T^2/n ?

4.26 In terms of Charles' law explain why –273 °C is the lowest possible temperature.

4.27 Critical temperature for carbon dioxide and methane are 31.1 °C and –81.9 °C respectively. Which of these has stronger intermolecular forces and why?

4.28 Air is cooled form 25°C to 0°C. Calculate the decrease in rms speed of the moleculas.

(Ans : About 4%)

4.29 Find the rms, most probable and average speeds of SO_2 at 27°c.

(Ans : 3.42×10^2, 2.79×10^2, $3.15\times10^2 m\ s^{-1}$)

4.30 Find the RMS, average and most probable speeds of O_2 at 27°c.

(Ans : 4.614×10^2, 4.25×10^2, $3.77\times10^2 m\ s^{-1}$)