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).

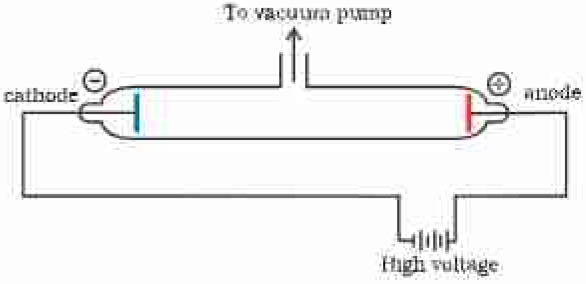


Fig. 1.1(a) A cathode ray discharge tube

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.

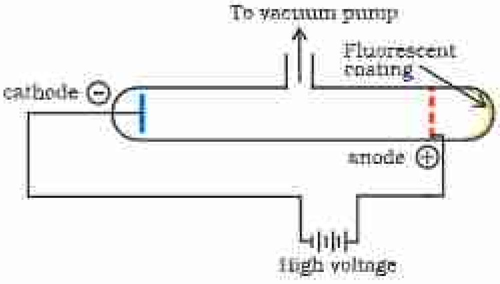


Fig. 1.1(b) A cathode ray discharge tube with perforated anode

(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

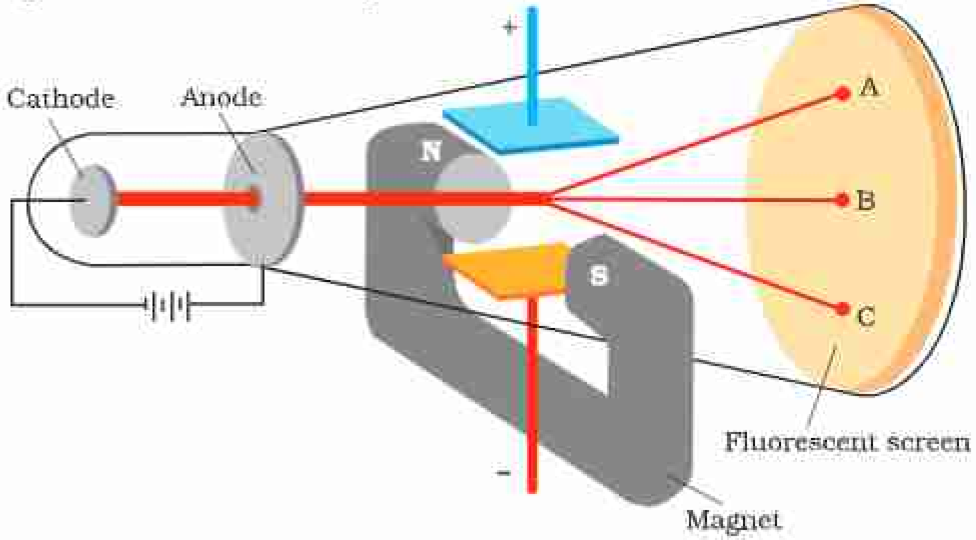


Fig. 1.2 *The apparatus to determine the charge to the mass ratio of electron*

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.

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... .

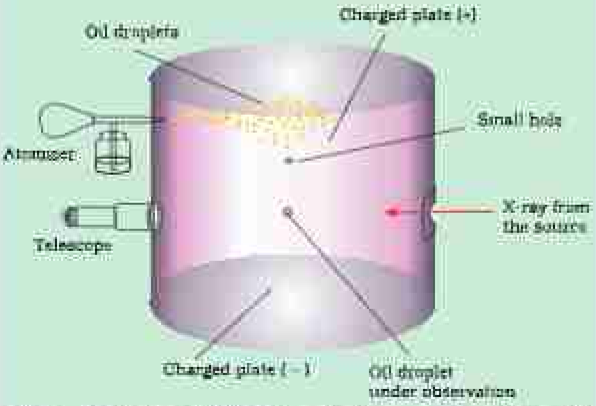


Fig. 1.3 *The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

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.

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.*

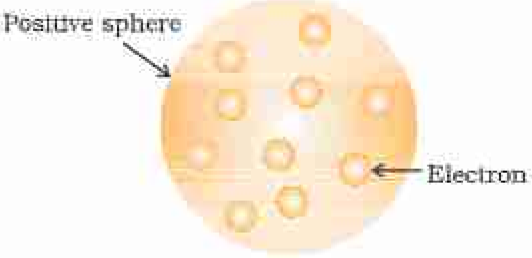


Fig.1.4 *Thomson model of atom*

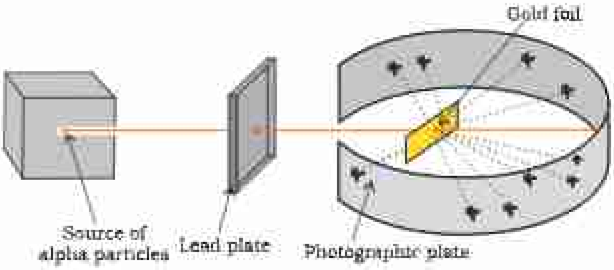
Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases.

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).

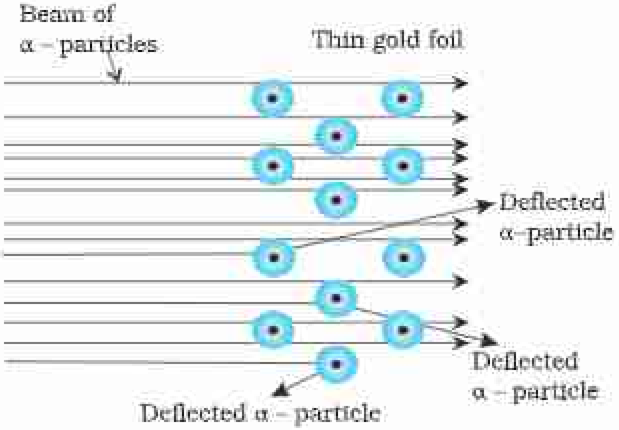
Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their own and named this phenomenon as **radioactivity** and the elements known as **radioactive elements.** This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed 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 radiations like X-rays, but are neutral in nature and do not consist of particles. As regards penetrating power, α-particles possess the least, followed by β-rays (100 times that of α–particles) and γ-rays (1000 times of that α-particles).

1.2.2 Rutherford's Nuclear Model of Atom

Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous **α–particle scattering experiment** is represented in Fig. 1.5. A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point.



A. *Rutherford's scattering experiment*



B. *Schematic molecular view of the gold foil*

Fig.1.5 *Schematic view of Rutherford's scattering experiment. When a beam of alpha (α) particles is "shot" at a thin gold foil, most of α-particles pass through without much effect. Some, however, are deflected.*

The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α– particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that :

(i) most of the α– particles passed through the gold foil undeflected.

(ii) a small fraction of the α–particles was deflected by small angles.

(iii) a very few α– particles (~1 in 20,000) bounced back, i.e., were deflected by nearly 180°.

On the basis of these observations, Rutherford drew the following conclusions regarding the structure of atom :

(i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected.

(ii) A few positively charged α– particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α– particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m. One can appreciate this difference in size by realising that if a cricket ball represents a nucleus, then the radius of atom would be about 5 km.

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom (after the discovery of protons).

According to this model :

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called **nucleus** by Rutherford.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called **orbits**. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons play the role of revolving planets.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

1.2.3 Atomic Number and Mass Number

The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number (Z). For example, the number of protons in the hydrogen nucleus is 1, in sodium nucleus it is 11, therefore their atomic numbers are 1 and 11 respectively. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively.

Atomic number (Z) = number of protons in the nucleus of an atom

= number of electrons in a neutral atom (1.3)

While the positive charge of the nucleus is due to protons, the mass of the nucleus is due to protons and neutrons. As discussed earlier protons and neutrons present in the nucleus are collectively known as **nucleons**. The total number of nucleons is termed as **mass number (A)** of the atom.

mass number (A) = number of protons (Z) + number of neutrons (n) (1.4)

1.2.4 Isobars and Isotopes

The composition of any atom can be represented by using the normal element symbol (X) with super-script on the left hand side as the atomic mass number (A) and subscript (Z) on the left hand side as the atomic number (i.e., $^{A}_{Z}X$).

Isobars are the atoms with same mass number but different atomic numbers for example, $^{14}_{6}C$ and $^{14}_{7}N$. On the other hand, atoms with identical atomic number but different atomic mass numbers are known as **Isotopes**. In other words (according to equation 1.4), it is evident that difference between the isotopes is due to the presence of different number of neutrons present in the nucleus. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called **protium($^{1}_{1}H$)**. Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called **deuterium** ($^{2}_{1}D$, 0.015%) and the other one possessing 1 proton and 2 neutrons is called **tritium** ($^{3}_{1}T$). The latter isotope is found in trace amounts on the earth. Other examples of commonly occuring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons ($^{12}_{6}C$, $^{13}_{6}C$, $^{14}_{6}C$); chlorine atoms containing 18 and 20 neutrons besides 17 protons ($^{35}_{17}Cl$, $^{37}_{17}Cl$).

Lastly an important point to mention regarding isotopes is that *chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus.* Number of neutrons present in the nucleus have very little effect on the chemical properties of an element. Therefore, all the isotopes of a given element show same chemical behaviour.

Problem 1.1

Calculate the number of protons, neutrons and electrons in $^{80}_{35}Br$.

Solution

In this case, $^{80}_{35}Br$, $Z = 35$, $A = 80$, species is neutral

Number of protons = number of electrons = Z = 35

Number of neutrons = 80 – 35 = 45, (equation 1.4)

Problem 1.2

The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species.

Solution

The atomic number is equal to number of protons = 16. The element is sulphur (S).

Atomic mass number = number of protons + number of neutrons

= 16 + 16 = 32

Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = 18 – 16 = 2. Symbol is ${}^{32}_{16}\mathrm{S}^{2-}$.

Note : Before using the notation ${}^{A}_{Z}\mathrm{X}$, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (1.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by A–Z, whether the species is neutral or ion.

1.2.5 Drawbacks of Rutherford Model

Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role of the massive sun and the electrons being similar to the lighter planets. Further, the coulombic force (kq_1q_2/r^2 where q_1 and q_2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus. This is mathematically similar to the gravitational force $\left(G.\frac{m_1m_2}{r^2}\right)$ where m_1 and m_2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements. The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. However, when a body is moving in an orbit, it undergoes acceleration (even if the body is moving with a constant speed in an orbit, it is accelerated because of changing direction). So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this is not happening. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons towards the nucleus to form a miniature version of Thomson's model of atom.

Another serious drawback of the Rutherford model is that it says nothing about the electronic structure of atoms i.e., how the

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* *Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects.*

electrons are distributed around the nucleus and what are the energies of these electrons.

1.3 DEVELOPMENTS LEADING TO THE BOHR'S MODEL OF ATOM

Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were:

(i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and

(ii) Experimental results regarding atomic spectra which can be explained only by assuming quantized (Section 1.4) electronic energy levels in atoms.

1.3.1 Wave Nature of Electromagnetic Radiation

James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves called **electromagnetic waves** or **electromagnetic radiations**.

Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscules). It was only in the 19th century the wave nature of light was established.

Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic characters (Fig. 1.6). Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties.

(i) The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 1.6.

(ii) Unlike sound waves or water waves, electromagnetic waves do not require medium and can move in vacuum.

(iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called **electromagnetic spectrum** (Fig. 1.7). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around 10^6Hz, used for broadcasting; microwave region around 10^{10} Hz used for radar; infrared region around 10^{13} Hz used for heating; ultraviolet region around 10^{16}Hz a component of sun's radiation. The small portion around 10^{15} Hz, is what is ordinarily called **visible light**. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation.

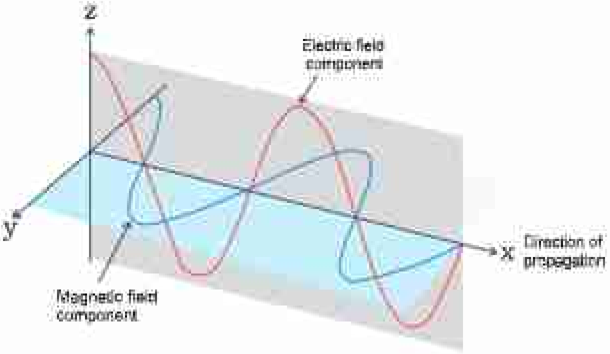

Fig.1.6 *The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.*

(iv) Different kinds of units are used to represent electromagnetic radiation.

These radiations are characterised by the properties, namely, frequency (ν) and wavelength (λ).

The SI unit for frequency (ν) is hertz (Hz, s^{-1}), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second.

Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig.1.7 shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies.

In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., 3.0×10^8 m s^{-1} (2.997925×10^8 m s^{-1}, to be precise). This is called **speed of light** and is given the symbol 'c'. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (1.5).

$$c = \nu \lambda \qquad (1.5)$$

The other commonly used quantity specially in spectroscopy, is the **wavenumber** ($\bar{\nu}$). *It is defined as the number of wavelengths per unit length.* Its units are reciprocal of wavelength unit, i.e., m^{-1}. However commonly used unit is cm^{-1} (not SI unit).

Problem 1.3

The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to?

Solution

The wavelength, λ, is equal to c/ν, where c is the speed of electromagnetic radiation in vacuum and ν is the frequency. Substituting the given values, we have

$$\lambda = \frac{c}{\nu}$$

$$= \frac{3.00 \times 10^8 \text{m s}^{-1}}{1368 \text{ kHz}}$$

$$= \frac{3.00 \times 10^8 \text{m s}^{-1}}{1368 \times 10^3 \text{s}^{-1}}$$

$$= 219.3 \text{m}$$

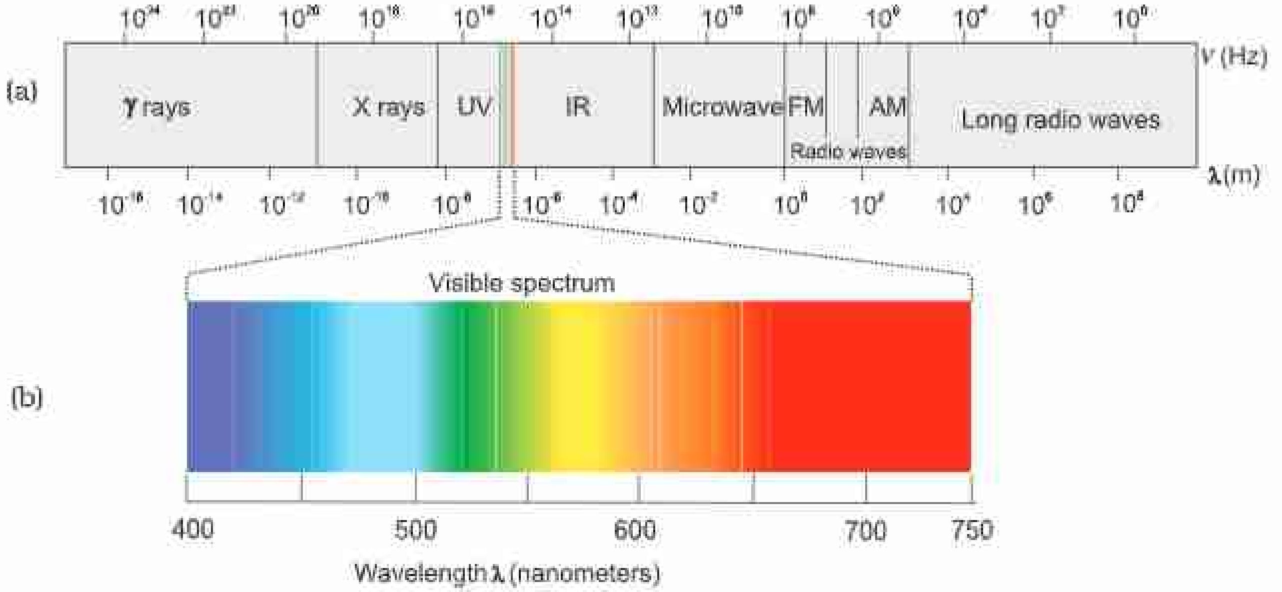

Fig. 1.7 *(a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum .*

This is a characteristic radiowave wavelength.

Problem 1.4

The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). ($1 \text{nm} = 10^{-9} \text{m}$)

Solution

Using equation 1.5, frequency of violet light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \text{m s}^{-1}}{400 \times 10^{-9} \text{m}}$$

$= 7.50 \times 10^{14} \text{Hz}$

Frequency of red light

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8} \text{ms}^{-1}}{750 \times 10^{-9} \text{m}} = 4.00 \times 10^{14} \text{Hz}$$

The range of visible spectrum is from 4.0×10^{14} to 7.5×10^{14} Hz in terms of frequency units.

Problem 1.5

Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å.

Solution

(a) Calculation of wavenumber ($\bar{\nu}$)

$$\lambda = 5800 \text{Å} = 5800 \times 10^{-8} \text{cm}$$
$$= 5800 \times 10^{-10} \text{m}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5800 \times 10^{-10} \text{m}}$$
$$= 1.724 \times 10^{6} \text{m}^{-1}$$
$$= 1.724 \times 10^{4} \text{cm}^{-1}$$

(b) Calculation of the frequency (ν)

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{8} \text{m s}^{-1}}{5800 \times 10^{-10} \text{m}} = 5.172 \times 10^{14} \text{s}^{-1}$$

1.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies Ex: (black -body radiation)

(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature

(iv) line spectra of atoms with special reference to hydrogen.

It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation was given by Max Planck in 1900. This phenomenon is given below:

When solids are heated they emit radiation over a wide range of wavelengths. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. In terms of frequency, it means that the frequency of emitted radiation goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies in the lower frequency region while blue colour belongs to the higher frequency region of the

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* *Diffraction is the bending of wave around an obstacle.*

** *Interference is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the algebraic or vector sum of disturbances at that point resulting from each interfering wave.*

electromagnetic spectrum. *The ideal body, which emits and absorbs radiations of all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation.* The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature. At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength, as shown in Fig. 1.8.

The above experimental results cannot be explained satisfactorily on the basis of the wave theory of light. Planck suggested that atoms and molecules could emit (or absorb) energy only in discrete quantities and not in a continuous manner, a belief popular at that time. Planck gave the name **quantum** to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (ν) and is expressed by equation (1.6).

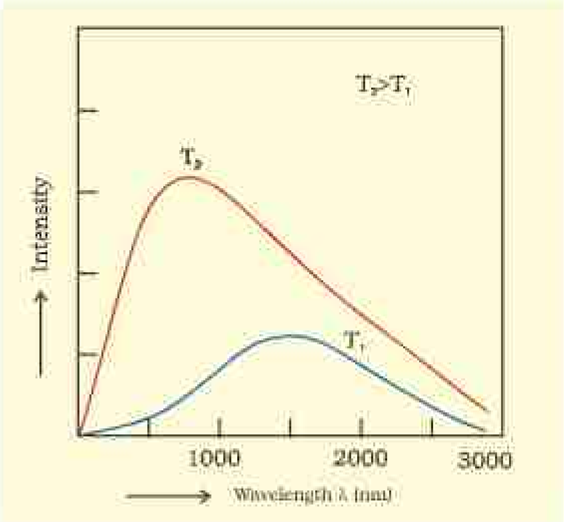


Fig. 1.8 *Wavelength-intensity relationship*

$$E = h\nu \qquad (1.6)$$

The proportionality constant, 'h' is known as Planck's constant and has the value 6.626×10^{-34} J s.

With this theory, Planck was able to explain the distribution of intensity of the radiation from black body as a function of frequency or wavelength at different temperatures.

Photoelectric Effect

In 1887, H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown in Fig.1.9. The phenomenon is called **Photoelectric effect**. The results observed in this experiment were:

(i) The electrons are ejected from the clean metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.

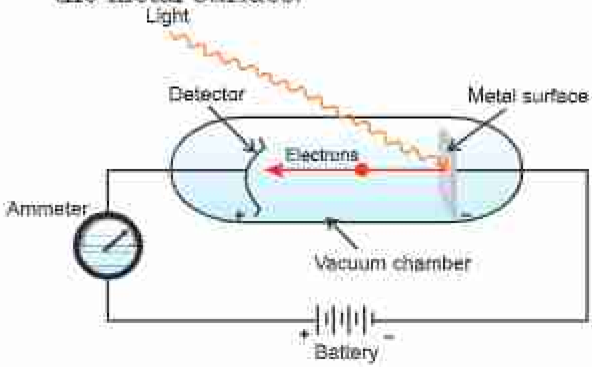


Fig.1.9 *Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.*

Max Planck
(1858 – 1947)

Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

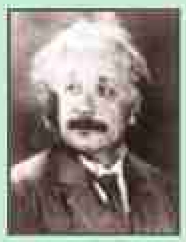
(ii) The number of electrons ejected is proportional to the intensity or brightness of light.

(iii) For each metal, there is a characteristic minimum frequency, ν_0 (also known as **threshold frequency**) below which photoelectric effect is not observed. At a frequency $\nu > \nu_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used.

All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [$\nu = (4.3 \text{ to } 4.6) \times 10^{14}$ Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light ($\nu = 5.1\text{–}5.2 \times 10^{14}$ Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency (ν_0) for potassium metal is 5.0×10^{14} Hz.

Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.



Albert Einstein (1879 - 1955)

Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0; Table 1.2), then the difference in energy $(h\nu - h\nu_0)$ is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 1.7.

$$h\nu = h\nu_0 + \frac{1}{2} m_e v^2 \qquad (1.7)$$

where m_e is the mass of the electron and v is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

Dual Behaviour of Electromagnetic Radiation

The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that

Table 1.2 Values of Work Function (W_0) for a Few Metals

Metal	Li	Na	K	Mg	Cu	Ag
W_0 /eV	2.42	2.3	2.25	3.7	4.8	4.3

light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wave like properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this wave-particle duality.

Problem 1.6

Calculate energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz.

Solution

Energy (E) of one photon is given by the expression

$E = h\nu$

$h = 6.626 \times 10^{-34}$ J s

$\nu = 5 \times 10^{14}$ s^{-1} (given)

$E = (6.626 \times 10^{-34}$ J s$) \times (5 \times 10^{14}$ s$^{-1})$

$= 3.313 \times 10^{-19}$ J

Energy of one mole of photons

$= (3.313 \times 10^{-19}$ J$) \times (6.022 \times 10^{23}$ mol$^{-1})$

$= 199.51$ kJ mol^{-1}

Problem 1.7

A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

Solution

Power of the bulb = 100 watt

= 100 J s^{-1}

Energy of one photon $E = h\nu = hc/\lambda$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{m s}^{-1}}{400 \times 10^{-9}\ \text{m}}$$

$= 4.969 \times 10^{-19}$ J

Number of photons emitted

$$\frac{100\ \text{J s}^{-1}}{4.969 \times 10^{-19}\ \text{J}} = 2.012 \times 10^{20}\ \text{s}^{-1}$$

Problem 1.8

When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68×10^{5} J mol^{-1}. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted ?

Solution

The energy (E) of a 300 nm photon is given by

$h\nu = hc/\lambda$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.0 \times 10^{8}\ \text{m s}^{-1}}{300 \times 10^{-9}\ \text{m}}$$

$= 6.626 \times 10^{-19}$ J

The energy of one mole of photons

$= 6.626 \times 10^{-19}$ J $\times 6.022 \times 10^{23}$ mol^{-1}

$= 3.99 \times 10^{5}$ J mol^{-1}

The minimum energy needed to remove one mole of electrons from sodium

$= (3.99 - 1.68)\ 10^{5}$ J mol^{-1}

$= 2.31 \times 10^{5}$ J mol^{-1}

The minimum energy for one electron

$$= \frac{2.31 \times 10^{5}\ \text{J mol}^{-1}}{6.022 \times 10^{23}\ \text{electrons mol}^{-1}}$$

$= 3.84 \times 10^{-19}$ J

This corresponds to the wavelength

$$\therefore \lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.0 \times 10^{8}\ \text{m s}^{-1}}{3.84 \times 10^{-19}\ \text{J}}$$

= 517 nm

(This corresponds to green light)

Problem 1.9

The threshold frequency ν_0 for a metal is $7.0 \times 10^{14}\ s^{-1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency $\nu = 1.0 \times 10^{15}\ s^{-1}$ hits the metal.

Solution

According to Einstein's equation

Kinetic energy = $\frac{1}{2} m_e v^2 = h(\nu - \nu_0)$

$= (6.626 \times 10^{-34}\ J\ s)\ (1.0 \times 10^{15}\ s^{-1} - 7.0 \times 10^{14}\ s^{-1})$

$= (6.626 \times 10^{-34}\ J\ s)\ (10.0 \times 10^{14}\ s^{-1} - 7.0 \times 10^{14}\ s^{-1})$

$= (6.626 \times 10^{-34}\ J\ s) \times (3.0 \times 10^{14}\ s^{-1})$

$= 1.988 \times 10^{-19}\ J$

1.3.3 Evidence for the quantized* Electronic Energy Levels: Atomic spectra

The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called **spectrum**. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50×10^{14} Hz to red at 4×10^{14} Hz. Such a spectrum is called **continuous spectrum.** Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.1.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be "**excited**". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra** or **atomic spectra** because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig. 1.10)

Line emission spectra are of great interest in the study of electronic structure. Each

---

* *The restriction of any property to discrete values is called quantization.*

element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements.

Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms are produced. These emit electromagnetic radiation of *discrete frequencies*. The hydrogen spectrum consists of several series of *lines* named after their discoverers. Balmer showed in 1885 on the basis of experimental observations that if spectral lines are expressed in terms of wavenumber ($\bar{\nu}$), then the visible lines of the hydrogen spectrum obey the following formula :

$$\bar{\nu} = 109,677 \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \text{cm}^{-1} \qquad (1.8)$$

where n is an integer equal to or greater than 3 (i.e., $n = 3,4,5,....$)

The series of lines described by this formula are called the **Balmer series**. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

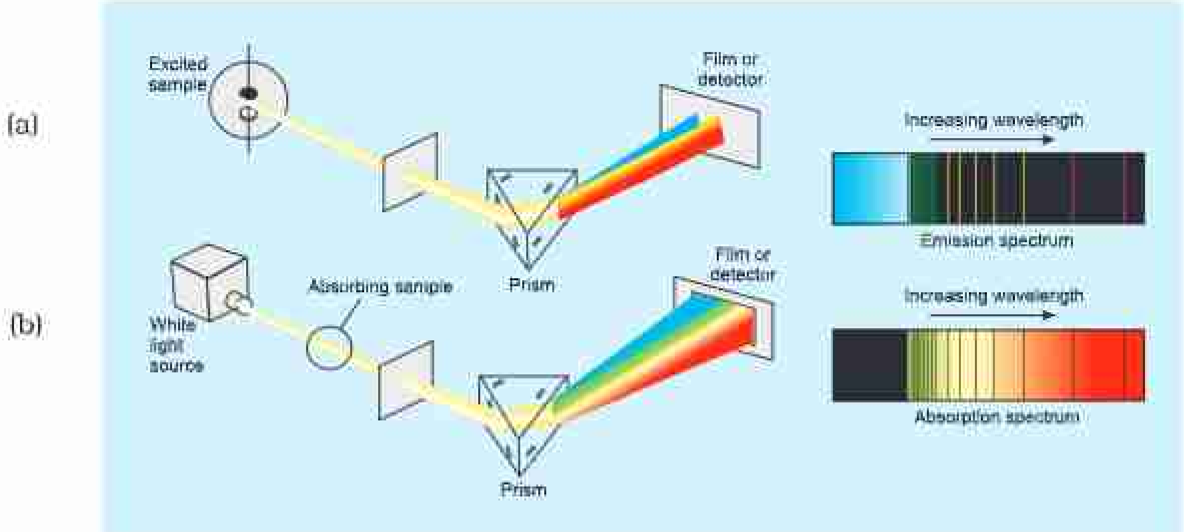


Fig. 1.10 (a) Atomic emission. *The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum.* ***(b) Atomic absorption.*** *When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.*

$$\bar{\nu} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1} \qquad (1.9)$$

where $n_1 = 1, 2, \ldots\ldots$

$n_2 = n_1 + 1,\ n_1 + 2 \ldots\ldots$

The value 109,677 cm^{-1} is called the **Rydberg constant** for hydrogen atom. The first five series of lines that correspond to $n_1 = 1, 2, 3, 4, 5$ are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively. Table 1.3 shows these series of transitions in the hydrogen spectrum. Fig 1.11 shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom.

Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum becomes more and more complex for heavier atom. There are however certain features which are common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are : What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements.

1.4 BOHR'S MODEL FOR HYDROGEN ATOM

Neils Bohr (1913) was the first to explain quantitatively the general features of hydrogen atom structure and its spectrum. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates:

i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called **orbits**, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 1.16). The energy change does not take place in a continuous manner.

Table 1.3 The Spectral Lines for Atomic Hydrogen

Series	n_1	n_2	Spectral Region
Lyman	1	2,3....	Ultraviolet
Balmer	2	3,4....	Visible
Paschen	3	4,5....	Infrared
Brackett	4	5,6....	Infrared
Pfund	5	6,7....	Infrared

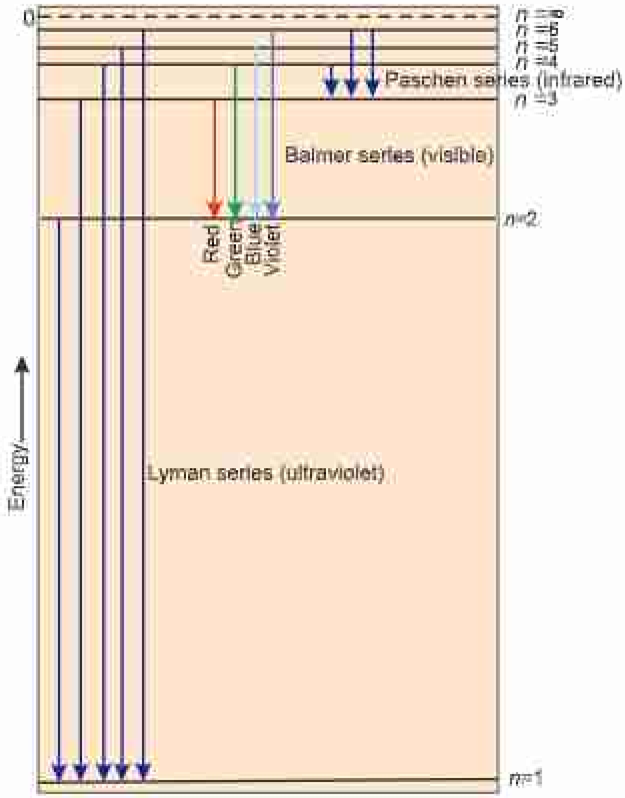


Fig. 1.11 *Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)*

iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by :

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h} \qquad (1.10)$$

Where E_1 and E_2 are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

iv) Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass m_e, moving in a circular path of radius r around the nucleus,

angular momentum = $I \times \omega$

Since $I = m_e r^2$, and $\omega = v/r$ where v is the linear velocity,

angular momentum = $m_e r^2 \times v/r = m_e vr$

The angular momentum of an electron in a given stationary state can be expressed as in equation (1.11)

$$m_e vr = n.\frac{h}{2\pi} \qquad n = 1,2,3..... \qquad (1.11)$$

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of $h/2\pi$ that is why only certain fixed orbits are allowed.

Niels Bohr
(1885–1962)

Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922.

The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom:

a) The stationary states for electron are numbered $n = 1,2,3$.......... These integral numbers (Section 1.6.2) are known as **Principal quantum numbers**.

b) The radii of the stationary states are expressed as :

$$r_n = n^2 a_0 \qquad (1.12)$$

where $a_0 = 52.9$ pm. Thus the radius of the first stationary state, called the **Bohr orbit**, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n=1). As n increases the value of r will increase. In other words the electron will be present away from the nucleus.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression.

$$E_n = -\mathrm{A}_H\left(\frac{1}{n^2}\right) \qquad n = 1,2,3.... \qquad (1.13)$$

where A_H is a constant and its value is 2.18×10^{-18} J. The energy of the lowest state, also called as the ground state, is $E_1 = -2.18\times10^{-18}\,(\frac{1}{1^2}) = -2.18\times10^{-18}$ J. The energy of the stationary state for n = 2, will be : $E_2 = -2.18\times10^{-18}\text{J}\,(\frac{1}{2^2}) = -0.545\times10^{-18}$ J. Fig. 1.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram.

When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number = $n = \infty$ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation (1.13) and depicts its stability relative to the reference state of zero energy and $n = \infty$.

What does the negative electronic energy (E_n) for hydrogen atom mean?

The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 1.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting n equal to infinity in the equation (1.13) so that $E_\infty=0$. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value and more and more negative. The most negative energy value is given by $n=1$ which corresponds to the most stable orbit. We call this the ground state.

d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18\times10^{-18}\left(\frac{Z^2}{n^2}\right)\text{J} \qquad (1.14)$$

and radii by the expression

$$r_n = \frac{52.9\,(n^2)}{Z}\,\text{pm} \qquad (1.15)$$

where Z is the atomic number and has values 2, 3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus.

e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number.

1.4.1 Explanation of Line Spectrum of Hydrogen

Line spectrum observed in case of hydrogen atom, as mentioned in section 1.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the lower orbit to the higher orbit, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (1.16).

$$\Delta E = E_f - E_i \qquad (1.16)$$

Combining equations (1.13) and (1.16)

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right)$$ (where n_i and n_f stand for initial orbit and final orbits)

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = 2.18\times10^{-18}\,\text{J}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (1.17)$$

The frequency (ν) associated with the absorption and emission of the photon can be evaluated by using equation (1.18)

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= \frac{2.18\times10^{-18}\,\text{J}}{6.626\times10^{-34}\,\text{J s}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (1.18)$$

$$= 3.29\times10^{15}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\text{Hz} \qquad (1.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{R_H}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad (1.20)$$

$$= \frac{3.29\times10^{15}\,\text{s}^{-1}}{3\times10^{8}\,\text{m s}^{-1}}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$= 1.09677 \times 10^{7} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{m}^{-1} \quad (1.21)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, ΔE is negative and energy is released.

The expression (1. 17) is similar to that used by Rydberg (1.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted.

Problem 1.10

What are the frequency and wavelength of a photon emitted during a transition from $n = 5$ state to the $n = 2$ state in the hydrogen atom?

Solution

Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in the visible region of the Balmer series. From equation (1.17)

$$\Delta E = 2.18 \times 10^{-18} \text{J} \left[\frac{1}{5^2} - \frac{1}{2^2} \right]$$

$$= -4.58 \times 10^{-19} \text{J}$$

It is an emission energy

The frequency of the photon (taking energy in terms of magnitude) is given by

$$\nu = \frac{\Delta E}{h}$$

$$= \frac{4.58 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}}$$

$$= 6.91 \times 10^{14} \text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{8} \text{m s}^{-1}}{6.91 \times 10^{14} \text{Hz}} = 434 \text{ nm}$$

Problem 1.11

Calculate the energy associated with the first orbit of He^+. What is the radius of this orbit?

Solution

$$E_n = -\frac{(2.18 \times 10^{-18} \text{J}) Z^2}{n^2} \text{ atom}^{-1}$$

For He^+, $n = 1$, $Z = 2$

$$E_1 = -\frac{(2.18 \times 10^{-18} \text{J})(2^2)}{1^2} = -8.72 \times 10^{-18} \text{J}$$

The radius of the orbit is given by equation (1.15)

$$r_n = \frac{(0.0529 \text{ nm}) n^2}{Z}$$

Since $n = 1$, and $Z = 2$

$$r_n = \frac{(0.0529 \text{ nm}) 1^2}{2} = 0.02645 \text{ nm}$$

1.4.2 Limitations of Bohr's Model

Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He^+, Li^{2+}, Be^{3+}, and so on). However, Bohr's model was too simple to account for the following points.

i) It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect).

ii) It could not explain the ability of atoms to form molecules by chemical bonds.

In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms.

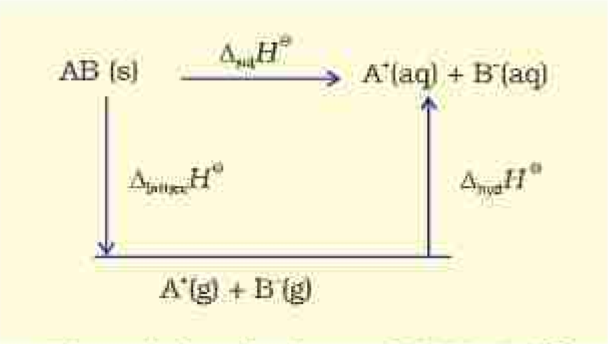
1.5 QUANTUM MECHANICAL

Louis de Broglie (1892 – 1987)

Louis de Broglie, a French physicist, studied history as an undergraduate in the early 1910's. His interest turned

enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)



The enthalpy of solution of AB(s), $\Delta_{sol}H^{\ominus}$, in water is, therefore, determined by the selective values of the lattice enthalpy,$\Delta_{lattice}H^{\ominus}$ and enthalpy of hydration of ions, $\Delta_{hyd}H^{\ominus}$ as

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$$

For most of the ionic compounds, $\Delta_{sol}H^{\ominus}$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Why do many fluorides tend to be less soluble than the corresponding chlorides? Estimates of the magnitudes of enthalpy changes may be made by using tables of bond energies (enthalpies) and lattice energies (enthalpies).

Enthalpy of dilution

It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute for the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolvsing one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. for water

$$HCl\,(g) + 10H_2O \rightarrow HCl_{\,(10\,H_2O)}$$

$$\Delta H = -69.01 \text{ kJ mol}^{-1}$$

Let us consider the following set of enthalpy changes

$$(S-1)\;\; HCl\,(g) + 25\,H_2O \rightarrow HCl_{\,(25\,H_2O)}$$

$$\Delta H = -72.03 \text{ kJ mol}^{-1}$$

$$(S-2)\;\; HCl\,(g) + 40\,H_2O \rightarrow HCl_{\,(40\,H_2O)}$$

$$\Delta H = -72.79 \text{ kJ mol}^{-1}$$

$$(S-3)\;\; HCl\,(g) + \infty\,H_2O \rightarrow HCl_{\,(aq.)}$$

$$\Delta H = -74.85 \text{ kJ mol}^{-1}$$

The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e., the value in infinite dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3).

If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain -

$$\Delta H_{(40\,H_2O)} - \Delta H_{(25\,H_2O)} = \Delta H_{(dilution)}$$

$$\Delta H_{(dilution)} = [-72.79 - (-72.03)] \text{ kJ / mol} = -0.76 \text{ kJ / mol}$$

This value (-0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn by the sourroundings from the system when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$$Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g);$$
$$\Delta_{lattice}H^\ominus = +788\,\text{kJ mol}^{-1}$$

Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy change diagram called a **Born-Haber Cycle** (Fig. 6.9).

Let us now calculate the lattice enthalpy of $Na^+Cl^-(s)$ by following steps given below :

1. $Na(s) \rightarrow Na(g)$, *sublimation of sodium metal*, $\Delta_{sub}H^\ominus = 108.4$ kJ mol^{-1}
2. $Na(g) \rightarrow Na^+(g) + e^{-1}(g)$, the *ionization of sodium atoms*, ionization enthalpy $\Delta_iH^\ominus = 496$ kJ mol^{-1}
3. $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$, the *dissociation of chlorine*, the reaction enthalpy is half the bond dissociation enthalpy.
$\frac{1}{2}\Delta_{bond}H^\ominus = 121\,\text{kJ mol}^{-1}$.

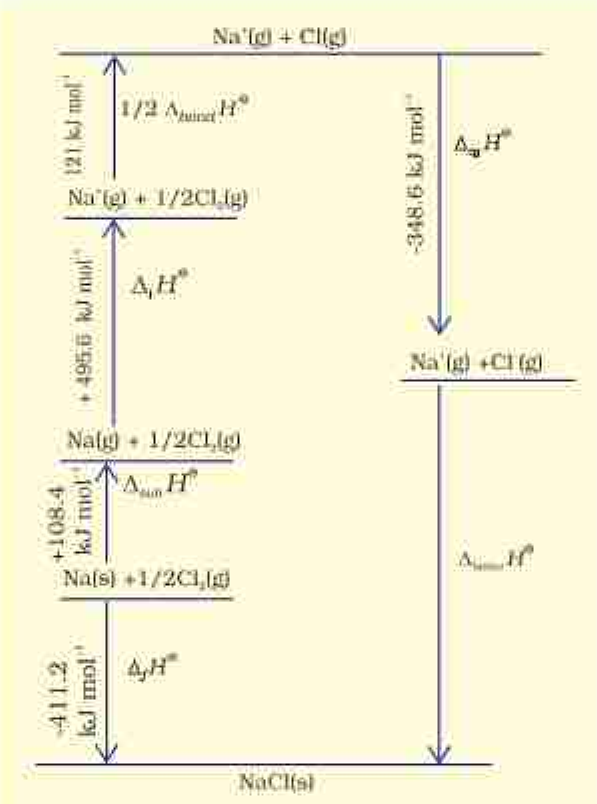


Fig. 6.9 *Enthalpy diagram for lattice enthalpy of NaCl*

4. $Cl(g) + e^{-1}(g) \rightarrow Cl^-(g)$ *electron gained* by chlorine atoms. The electron gain enthalpy, $\Delta_{eg}H^\ominus = -348.6$ kJ mol^{-1}.
You have learnt about ionization enthalpy and electron gain enthalpy in chapter 2. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms (see the box for justification).
5. $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$
The sequence of steps is shown in Fig. 6.9, and is known as a Born-Haber cycle.
6. $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s);\quad \Delta_fH^0 = -411.2$

Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for

$M(g) \rightarrow M^+(g) + e^-$ (for ionization)
$M(g) + e^- \rightarrow M^-(g)$ (for electron gain)

at temperature, T is

$$\Delta_rH^\ominus(T) = \Delta_rH^\ominus(0) + \int_0^T \Delta_rC_p^\ominus dT$$

The value of C_p for each species in the above reaction is 5/2 R ($C_V = 3/2R$)
So, $\Delta_rC_p^\ominus = +\,5/2$ R (for ionization)
$\Delta_rC_p^\ominus = -\,5/2$ R (for electron gain)
Therefore,
$\Delta_rH^\ominus$ (ionization enthalpy)
$= E_0$ (ionization energy) + 5/2 RT
$\Delta_rH^\ominus$ (electron gain enthalpy)
$= -$ A(electron affinity) – 5/2 RT

The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero.

Applying Hess's law, we get,

$$\Delta_{lattice}H^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{lattice}H^\ominus = +788\,\text{kJ}$$

for $NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$

Internal energy is smaller by 2RT (because $\Delta n_g = 2$) and is equal to + 783 kJ mol^{-1}.

Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$$

For one mole of NaCl(s),
lattice enthalpy = + 788 kJ mol^{-1}
and $\Delta_{hyd}H^{\ominus}$ = – 784 kJ mol^{-1}(from the literature)

$$\Delta_{sol}H^{\ominus} = + 788 \text{ kJ mol}^{-1} - 784 \text{ kJ mol}^{-1}$$
$$= + 4 \text{ kJ mol}^{-1}$$

The dissolution of NaCl(s) is accompanied by very little heat change.

6.6 SPONTANEITY

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes ? What determines the direction of a spontaneous change ? In this section, we shall establish some criterion for these processes whether these will take place or not.

Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means *'having the potential to proceed without the assistance of external agency'*. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows:

> ***A spontaneous process is an irreversible process and may only be reversed by some external agency.***

(a) Is decrease in enthalpy a criterion for spontaneity ?

If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g) \; ; \quad \Delta_r H^{\ominus} = -46.1 \text{ kJ mol}^{-1}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g) \; ; \quad \Delta_r H^{\ominus} = -92.32 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \; ; \quad \Delta_r H^{\ominus} = -285.8 \text{ kJ mol}^{-1}$$

The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 6.10(a).

Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far !

Now let us examine the following reactions:

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g); \quad \Delta_r H^{\ominus} = +33.2 \text{ kJ mol}^{-1}$$

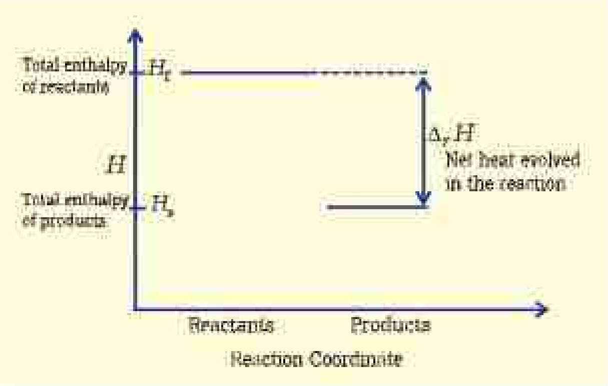


Fig. 6.10 (a) *Enthalpy diagram for exothermic reactions*

C(graphite, s) + 2 S(l) → CS_2(l);

$$\Delta_r H^\ominus = +128.5 \text{ kJ mol}^{-1}$$

These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 6.10(b).

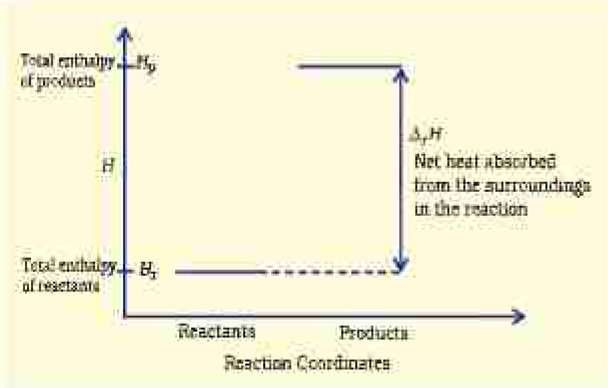


Fig. 6.10 (b) *Enthalpy diagram for endothermic reactions*

Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(b) Entropy and spontaneity

Then, what drives the spontaneous process in a given direction ? Let us examine such a case in which $\Delta H = 0$ i.e., there is no change in enthalpy, but still the process is spontaneous.

Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 6.11.

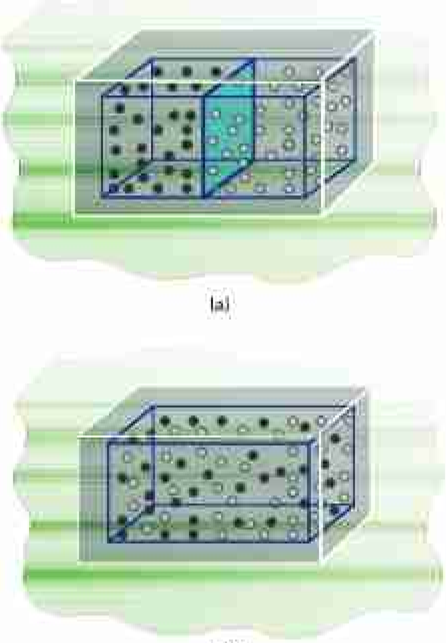


Fig. 6.11 *Diffusion of two gases*

The two gases, say, gas A and gas B are represented by black dots and white dots respectively and separated by a movable partition [Fig. 6.11 (a)]. When the partition is withdrawn [Fig.6.11(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete when homogeneous mixture is formed.

Let us examine the process. Before taking out the partition, if we were to pick up the gas molecules from left portion of the container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right portion of the container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change !

Entropy

At this point, we introduce another thermodynamic function, **entropy** denoted as *S*. The **above mentioned disorder is the manifestation of entropy. To form a mental picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy.** As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered). The gaseous state is state of highest entropy.

Now let us try to quantify entropy. One way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy *U* and enthalpy *H* is a state function and ΔS is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus **heat (*q*) has randomising influence** on the system. Can we then equate ΔS with q ? Wait ! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, **temperature is the measure of average chaotic motion of particles in the system**. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T} \qquad (6.18)$$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0 \qquad (6.19)$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Problem 6.9

Predict in which of the following, entropy increases/decreases :

(i) A liquid crystallizes into a solid.

(ii) Temperature of a crystalline solid is raised from 0 K to 115 K.

(iii) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(iv) $H_2(g) \rightarrow 2H(g)$

Solution

(i) After freezing, the molecules attain an ordered state and therefore, entropy decreases.

(ii) At 0 K, the contituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

(iii) Reactant, $NaHCO_3$ is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy.

(iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule.

Problem 6.10

For oxidation of iron,

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

entropy change is – 549.4 $JK^{-1}mol^{-1}$at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous?

($\Delta_r H^{\ominus}$for this reaction is -1648×10^3 J mol^{-1})

Solution

One decides the spontaneity of a reaction by considering

ΔS_{total} i.e., $(\Delta S_{sys} + \Delta S_{surr})$. For calculating ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H^{\ominus}$. At temperature T, entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{\Delta_r H^{\ominus}}{T} \text{ (at constant pressure)}$$

$$= -\frac{(-1648\times10^3\ J\,mol^{-1})}{298\,K}$$

$$= 5530\ JK^{-1}mol^{-1}$$

Thus, total entropy change for this reaction

$$\Delta_r S_{total} = 5530\ JK^{-1}mol^{-1} + (-549.4\ JK^{-1}mol^{-1})$$

$$= 4980.6\ JK^{-1}mol^{-1}$$

This shows that the above reaction is spontaneous.

6.6.(b)Entropy; spontaneity and second Law of Thermodynamics

We know that for an ioslated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

Statements of the second law of Thermodynamics

1. It is impossible to construct a machine working in cycles which transforms heat from a lower temperature region to higher temperature region without the intervention of any external agency. Such a machine which transfers heat from lower temperature to higher temperature on its own is called perpetual motion machine of second kind. This is not possible.
2. Heat can not flow from a cooler body to a hotter body on its own.
3. Heat can not be coverted into work completely without causing some permanant changes in the system involved or sourroundings.
4. All spontaneous processes are thermodynamically irrerversible and entropy of the system increases in all spontaneous processes.

6.6.(c)Gibbs energy and spontaneity

We have seen that for a system, it is the total entropy change, ΔS_{total} which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, Gibbs proposed a new thermodynamic function called the Gibbs energy or Gibbs function, G, as

$$G = H - TS \qquad (6.20)$$

Gibbs function, G is an extensive property and a state function.

The change in Gibbs energy for the system, ΔG_{sys} can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$$

At constant temperature, $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

$$\Delta G = \Delta H - T\Delta S \qquad (6.21)$$

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of ΔH) and entropy (ΔS, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that ΔG has units of energy because, both ΔH and the $T\Delta S$ are energy terms, since $T\Delta S$ = (K) (J/K) = J.

Now let us consider how ΔG is related to reaction spontaneity.

We know,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

Rearranging the above equation:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontaneous process, $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$\Rightarrow -\left(\Delta H_{sys} - T\Delta S_{sys}\right) > 0$$

Using equation 6.21, the above equation can be written as

$$-\Delta G > 0$$

$$\Delta G = (\Delta H - T\Delta S) < 0 \qquad (6.22)$$

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

ΔG gives a criteria for spontaneity at constant pressure and temperature.

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non spontaneous. (except coupled reactions)

Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh ΔH. This can happen in two ways; (a) The positive entropy change of the system can be 'small' in which case T must be large. (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 6.4 summarises the effect of temperature on spontaneity of reactions.

6.7 GIBBS ENERGY CHANGE AND EQUILIBRIUM

We have seen how a knowledge of the sign and magnitude of the Gibbs energy change of a chemical reaction allows:

(i) Prediction of the spontaneity of the chemical reaction.

(ii) Prediction of the useful work that could be extracted from it.

So far we have considered Gibbs energy changes in irreversible reactions. Let us now examine the Gibbs energy changes in reversible reactions.

'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in Gibbs energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium

$A + B \rightleftharpoons C + D$; is

$\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^\ominus$ is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^\ominus + RT \ln K$$

or $\Delta_r G^\ominus = -RT \ln K$

or $\Delta_r G^\ominus = -2.303\, RT \log K$ (6.23)

We also know that

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -RT \ln K \qquad (6.24)$$

For strongly endothermic reactions, the value of $\Delta_r H^\ominus$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H^\ominus$ is large and negative, and $\Delta_r G^\ominus$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\Delta_r G^\ominus$ also depends upon $\Delta_r S^\ominus$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\Delta_r S^\ominus$ is positive or negative.

Using equation (6.24),

(i) It is possible to obtain an estimate of $\Delta G^\ominus$ from the measurement of $\Delta H^\ominus$ and $\Delta S^\ominus$, and then calculate K at any temperature for economic yields of the products.

(ii) If K is measured directly in the laboratory, value of $\Delta G^\ominus$ at any other temperature can be calculated.

Table 6.4 Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^\ominus$	$\Delta_r S^\ominus$	$\Delta_r G^\ominus$	Description*
–	+	–	Reaction spontaneous at all temperature
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperatures

---

* *The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

Problem 6.11

Calculate $\Delta_r G^\ominus$ for conversion of oxygen to ozone, $3/2\ O_2(g) \rightarrow O_3(g)$ at 298 K. if K_p for this conversion is 2.47×10^{-29}.

Solution

We know $\Delta_r G^\ominus = -2.303\ RT \log K_p$ and $R = 8.314\ JK^{-1}\ mol^{-1}$

Therefore, $\Delta_r G^\ominus =$

$$-2.303\ (8.314\ J\ K^{-1}\ mol^{-1}) \times (298\ K)\ (\log 2.47 \times 10^{-29})$$

$= 163000\ J\ mol^{-1}$

$= 163\ kJ\ mol^{-1}$.

Problem 6.12

Find out the value of equilibrium constant for the following reaction at 298 K.

$$2NH_3\ (g) + CO_2\ (g) \rightleftharpoons NH_2CONH_2\ (aq) + H_2O\ (l)$$

Standard Gibbs energy change, $\Delta_r G^\ominus$ at the given temperature is $-13.6\ kJ\ mol^{-1}$.

Solution

$$\text{We know, } \log K = \frac{-\Delta_r G^\ominus}{2.303\,RT}$$

$$= \frac{\left(-13.6 \times 10^3\ J\ mol^{-1}\right)}{2.303\left(8.314\ JK^{-1}\ mol^{-1}\right)(298K)}$$

$= 2.38$

Hence $K =$ antilog $2.38 = 2.4 \times 10^2$.

Problem 6.13

At 60°C, dinitrogen tetroxide is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Solution

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1-0.5}{1+0.5}\ ;\ x_{NO_2} = \frac{2 \times 0.5}{1+0.5}$$

$$p_{N_2O_4} = \frac{0.5}{1.5} \times 1\ \text{atm},\ p_{NO_2} = \frac{1}{1.5} \times 1\ \text{atm}.$$

The equilibrium constant K_p is given by

$$K_p = \frac{\left(p_{NO_2}\right)^2}{p_{N_2O_4}} = \frac{1.5}{(1.5)^2\ (0.5)}$$

$= 1.33$ atm.

Since

$\Delta_r G^\ominus = -RT \ln K_p$

$$\Delta_r G^\ominus = (-8.314\ JK^{-1}\ mol^{-1}) \times (333\ K) \times (2.303) \times (0.1239)$$

$= -763.8\ kJ\ mol^{-1}$

6.8 Absolute Entropy and Third Law of Thermodynamics

Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. **The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.** This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculations of absolute values of entropy of pure substance from the thermal data alone. For a pure substance, this can be done by summing q_{rev}/T increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

SUMMARY

Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the **first law of thermodynamics** via $\Delta U = q + w$. ΔU, change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $w = -p_{ex}\Delta V$ in case of expansion of gases. Under reversible process, we can put $p_{ex} = p$ for infinitesimal changes in the volume making $w_{rev} = -p\, dV$. In this condition, we can use gas equation, $pV = nRT$.

At constant volume, w = 0, then $\Delta U = q_V$, heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function **enthalpy**. Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$, can be found directly from the heat changes at constant pressure, $\Delta H = q_p$.

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using **Hess's law**. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H = \sum_f \left(a_i \Delta_f H_{\text{products}}\right) - \sum_i \left(b_i \Delta_f H_{\text{reactants}}\right)$$

and in gaseous state by

$\Delta_r H^\ominus = \Sigma$ *bond enthalpies of the reactants* $- \Sigma$ *bond enthalpies of the products*

First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, $\Delta U = 0$. We define another state function, S, **entropy** for this purpose. **Entropy** is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, $\Delta U = 0$, $\Delta S > 0$, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation $\Delta S = \frac{q_{rev}}{T}$ for a reversible process. $\frac{q_{rev}}{T}$ is independent of path.

Chemical reactions are generally carried at constant pressure, so we define another state function **Gibbs energy**, G, which is related to entropy and enthalpy changes of the system by the equation:

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

For a spontaneous change, $\Delta G_{sys} < 0$ and at equilibrium, $\Delta G_{sys} = 0$.

Standard Gibbs energy change is related to equilibrium constant by

$$\Delta_r G^\ominus = -RT \ln K.$$

K can be calculated from this equation, if we know $\Delta_r G^\ominus$ which can be found from $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction.

The Third law of thermodynamics interms of absolute entropy of pure crystalline substances has been stated.

QUESTIONS

Very short answer type questions

1. What is the information given by the term thermodynamics ?
2. What is the relationship between the laws of thermodynamics and equilibrium state ?
3. Define a system. Give an exmaple.
4. The wall is adiabatic and $\Delta U = W_{ad}$. What do you understand about the heat and work with respect to the system ?
5. The system loses 'q' amount of heat though no work is done on the system. What type of wall does the system have ?
6. Work is done by the system and 'q' amount of heat is supplied to the system. What type of system would it be ?
7. What is the workdone in the free expansion of an ideal gas in reversible and irreversible processes ?
8. From the equation $\Delta U = q - p_{ex}\Delta V$, if the volume is constant what is the value of ΔU ?
9. In isothermal free expansion of an ideal gas find the value of q and ΔU.
10. In isothermal irreversible change of ideal gas what is the value of q ?
11. In isothermal reversible change of an ideal gas, what is the value of q ?
12. For an adiabatic change in an ideal gas what is the relationship between its ΔU and W (adiabatic)
13. State the first law of the thermodynamics.
14. What are the sign conventions of the work done on the system and work done by the system ?
15. Volume (V) pressure (p) and Termperature (T) are state functions. Is the statement true ?
16. What are the heat (q) sign conventions when heat is transferred from the surroundings to the system and that transferred from system to the surrounding ?
17. No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ?
18. No work is done on the system, but heat (q) is taken out from the system by the surroundings. What type of wall does the system have ?
19. Work is done by the system and heat (q) is supplied to the system. What type of system would it be ?
20. $q = w = -P_{ext}(v_f - v_i)$ is for irreversible ......change.
21. $q = -w = nRT \ln(v_f/v_i)$ is for isothermal ....change.
22. What are the 'ΔH' sign conventions for exothermic and endothermic reactions ?
23. What are intensive and extensive properties ?
24. In the equation $q = c.\ m\ .\Delta T$. If ΔT is change in temperature 'm' mass of the substance, and 'q' is heat required, what is 'c'?
25. Give the equation that gives the relationship between ΔU and ΔH.
26. What is the relationship between C_p and C_v ?
27. 1g of graphite is burnt in a bomb calorimeter in excess of O_2 at 298K and 1 atm. pressure according to the equation.

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$

During the reaction the temperature rises from 298K to 299K. Heat capacity of the bomb calorimeter is $20.7kJK^{-1}$. What is the enthalpy change for the above reaction at 298K and 1 atm ?

28. For the above reaction what is the internal energy change, ΔU ?
29. What is $\Delta_r H$ for $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ interms of molar enthalpies of the respective reactants and products ?
30. Enthalpy decrease is not the criterion for spontaneity. Why ?
31. Is increase of entropy the criterion for spontaneity ? Why ?
32. Explain the relationship between Gibbs energy change and equilibrium constant.
33. If we measure ΔH^θ and ΔS^θ it is possible to estimate ΔG^θ . Is it true ? why ?
34. Equilibrium constant 'K' is measured accurately in the laboratory at given temperature. Is it possible to calcuate ΔG^θ at any other temperature ? How ?
35. Comment on the thermodynamic stability of $NO_{(g)}$ given that

$$\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)};\ \Delta_r H^\theta = 90kJ\ mol^{-1}$$

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{2(g)};\ \Delta_r H^\theta = -74kJ\ mol^{-1}$$

36. Calculate the entropy change in surroundings when 1.00 mole of $H_2O_{(l)}$ is formed under standard conditions $\Delta_f H^\theta = -286k\ Jmol^{-1}$
37. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ? R = 8.314 $JK^{-1}\ mol^{-1}$, T = 300 K.
38. State the third law of thermodynamics.

Short answer type questions

39. What are open, closed and isolated systems ? Give one example for each.
40. Define the state function and state variables. Give examples
41. "Internal energy is a state function". Explain.
42. "Work is not a state function". Explain.
43. What is heat ? Explain.
44. Derive the equation for 'W_{rev}' in isothermal reversible process.
45. Two litres of an ideal gas at a pressure of 10 atm expands isothermally into a vacuum until its total volume is 20 litres. How much heat is absorbed and how much work is done in the expansion ? (Ans : q = -w = p_{ex} (20-2)= (0 × 18) = 0)
46. If the ideal gas given in the problem 45 expands against constant external pressure of 1 atm what is the **q** value ? (Ans : q = -w = (1 × 18) = 18 L atm.
47. If the ideal gas given in the problem 45 expands to a final volume of 10L conducted reversibly what is **q** vlaue ? (Ans : q = -w = 2.303 × 20log 20/2 = 46.06 L atm.
48. Explain the state function 'enthalpy, H'. What is the relationship between ΔU and ΔH ?
49. Show that $\Delta H = \Delta U + \Delta n_{(g)} . RT$

50. If Water vapour is assumed to be a perfect gas, molar enthapy change for vapourisation of 1 mole of water at 1 bar and 100° C is 41 kJ mol^{-1} . Calculate the internal energy change when

    a) 1 mol of water is vapourised at 1 bar and 100° C

    b) 1 mol of water liquid is converted into ice.

51. Explain extensive and intensive properties.

52. Define heat capacity. What are C_p and C_v ? Show that $C_p - C_V = R$

53. Explain the determination of ΔU of a reaction calorimetrically

54. Explain the determination of ΔH of a reaction calorimetrically.

55. What is enthalpy of a reaction ? Explain the standard enthalpy of a reaction .

56. What is the standard enthalpy of formation ? Explain it with exmaple.

57. Define and explain enthalpy of phase transformation.

58. Define and explain the standard enthalpy of fusion (Molar enthalpy of fusion)

59. Define and explain the standard enthalpy of vapoursation (Molar enthalpy of vapourisation)

60. Define and explain the standard enthalpy of sublimation.

61. Define and explain the standard enthalpy of formation ($\Delta_f H^\theta$)

62. State and explain the Hess's law of constant Heat summation.

63. Define and explain the enthalpy of combustion ($\Delta_r H^\theta$)

64. Define and explain enthalpy of atomisation ($\Delta_a H^\theta$)

65. Define and explain the Bond enthalpy ($\Delta_{bond} H^\theta$)

66. What is the bond enthalpy of C-H bond of CH_4 ?

67. Define heat of solution ($\Delta_{sol} H^\theta$) and heat of dilution.

68. Define ionisation enthalpy and electron affinity.

69. Expain the spontaneity of a process ?

70. Is decrease in enthalpy a criterion for spontaneity ? Explain.

71. What is entropy ? Explain with examples.

72. Is increase in entropy a criterion for spontaneity ? Explain.

73. Can ΔU and ΔS discriminate between irreversible and reversible processes ? Explain.

74. In which of the following processes entropy increases ?

    a) A liquid evaporates to vapour.

    b) Temperature of a crystalline solid lowered from 115K to OK

    c) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

    d) $Cl_{2(g)} \rightarrow 2Cl_{(g)}$

75. For the oxidation of iron

    $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$, the entropy change is - 549.45 JK^{-1} mol^{-1} at 298K. Though it has negative entropy change the reaction is spontaneous. Why ? $(\Delta_r H^\theta = -1648 \times 10^3 \text{ J mol}^{-1})$

76. Which formulae in the following are correct ?

a) $G = H - TS$ b) $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$ c) $\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T}$

d) $\Delta S_{total} = \Delta S_{sys} + \frac{(-\Delta H_{sys})}{T}$ e) $T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$

77. Calculate $\Delta_r G^\theta$ for conversion of oxygen to ozone $\frac{3}{2}O_{2(g)} \rightarrow O_{3(g)}$ at 298K. Kp for the the reaction is 2.43×10^{-29} $(\Delta_r G^\theta = 163\text{kJ mol}^{-1})$

78. State the second law of thermodynamics and explain it.
79. State the third law of thermodynamics. What do you understand by it ?
80. Explain "Entropy" concept.
81. Explain spontaneity of a process in terms of Gibbs energy.
82. The sign and magnitude of Gibbs energy change of a chemical process tells about its spontaneity and useful work that could be extracted from it. Explain.
83. In a process 701 J of heat is absorbed by a system and 394J of work is done by the system. What is the change in internal energy for the process?

Ans : $q = +701\text{J};\ w = -394\text{J};\ \Delta U = 307\text{J}$

84. The reaction of cyanamide (s), with dioxygen was carried out in a bomb calorimeter and ΔU was found to be - 742.7kJ mol^{-1} at 298K. Calculate the enthalpy change for the reaction at 298K.

$$NH_2CN_{(g)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$

Ans : -741.5kJ mol^{-1}

85. Calculate the number of kJ of heat necessary to rise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacityof aluminimum is 24 J $\text{mol}^{-1}\ \text{K}^{-1}$. (Ans : 1.09 kJ)
86. Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at –10.0°C. $\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0°C.
$C_p\,[H_2O(l)] = 75.3\ \text{J mol}^{-1}\ \text{K}^{-1}$
$C_p\,[H_2O(s)] = 36.8\ \text{J mol}^{-1}\ \text{K}^{-1}$

Ans : $\Delta H = -6.415\text{kJ mol}^{-1}$

87. Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

Ans : –315kJ

88. Enthalpies of formation of CO(g), CO_2(g), N_2O(g) and N_2O_4(g) are –110, – 393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:
$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

Ans : $\Delta_r H = -778\text{kJ}$

89. Given

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta_r H^\ominus = -92.4$ kJ mol^{-1}

What is the standard enthalpy of formation of NH_3 gas?

Ans : $\Delta_f H = -46.2 \text{kJmol}^{-1}$

90. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:

$CH_3OH\ (l) + \frac{3}{2}\ O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta_r H^\ominus = -726$ kJ mol^{-1}

C(graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta_c H^\ominus = -393$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l)$; $\Delta_f H^\ominus = -286$ kJ mol^{-1}.

Ans : -239kJmol^{-1}

91. Calculate the enthalpy change for the process

$CCl_4(g) \rightarrow C(g) + 4\ Cl(g)$

and calculate bond enthalpy of C – Cl in $CCl_4(g)$.

$\Delta_{vap} H^\ominus(CCl_4) = 30.5$ kJ mol^{-1}.

$\Delta_f H^\ominus\ (CCl_4) = -135.5$ kJ mol^{-1}.

$\Delta_a H^\ominus\ (C) = 715.0$ kJ mol^{-1} , where $\Delta_a H^\ominus$ is enthalpy of atomisation

$\Delta_a H^\ominus\ (Cl_2) = 242$ kJ mol^{-1}

Ans : 327kJmol^{-1}

92. For an isolated system, $\Delta U = 0$, what will be ΔS ? Ans : $\Delta S > 0$

93. For the reaction at 298 K,

$2A + B \rightarrow C$

$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

Ans : 2000K

94. For the reaction,

$2\ Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

Ans : $\Delta H = -ve$; $\Delta S = -ve$

95. For the reaction

$2\ A(g) + B(g) \rightarrow 2D(g)$

$\Delta U^\ominus = -10.5$ kJ and $\Delta S^\ominus = -44.1$ JK^{-1}.

Calculate $\Delta G^\ominus$ for the reaction, and predict whether the reaction can occur spontaneously or not.

Ans : 0.164kJ nonspontaneous

96. The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^{\ominus}$? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

Ans : –5.744kJmol^{-1}

97. State the first law of thermodynamics. Explain its mathematical notation.

98. State the 2nd law of thermodynamics in any two ways

99. Explain Gibbs energy.

100. Explain the spontaneity of a reaction interms of Gibbs energy.

Long answer type questions

101. State and explain Hess's Law of constant heat summation. Give exinaple.

102. Explain the experiment to determine the internal energy change of a chemical reaction.

103. Explain the experiment to determine the enthalpy change of a chemical reaction.

104. Explain the spontaneity of a reaction interms of enthalpy change, entropy change and Gibb's energy change.