

CHAPTER 25

SOLIDS, CRYSTALS AND CRYSTALLOGRAPHY

Polymorphism, allotropy and isomorphism :

The obvious properties of solids are their definite shape and size and rigidity. It is quite natural to suppose that the atoms and molecules in the solids have fixed positions and most of the space is occupied by the atoms themselves in contact with each other. Solids may be divided broadly into two groups :— (1) Crystalline solids, (2) Amorphous solids.

Crystals are solids having definite geometric shapes. The regular shapes of the crystals bounded by plane surfaces (called faces of the crystal) are due to the regular arrangement of the atoms in the crystal just like the arrangements of bricks in a wall. The order of arrangement of atoms in crystal in three-dimensions is so perfect that the position of each and every atom can be located if the positions of a few atoms are found out.

The faces of the crystals intersect at an angle characteristic of the substance. Thus sodium chloride forms cubic crystals and the faces of the cube in sodium chloride crystals intersect at a right angle (90°). When a crystal is broken it splits along certain preferred positions and the cleavage gives the characteristic faces and angles of the original form. *Cleavage* is thus splitting of the crystal along certain planes in which the binding forces are weak. The same crystalline state characteristics are retained even when the substance is ground to fine powder.

A particular substance may occur in different crystalline forms known as polymorphous. The phenomenon is known as *polymorphism*. Sodium chloride has cubic as well as octahedral crystalline forms. Ammonium nitrate occurs in five different crystalline forms.

When an element occurs in more than one crystalline form, it is said to have allotropic modifications and this phenomenon is called *allotropy*. Thus carbon occurs as diamond and graphite which are allotropic forms of carbon.

When a number of different substances have the same crystalline form, they are said to be *isomorphous* and the phenomenon is called *isomorphism*. Thus MgO and NaF are isomorphous substances.

Amorphous substances are those which do not have the ordered crystalline form. The atoms in such substances do not have orderly arrangements giving definite patterns. Thus glass is an example of amorphous solid. Even in some amorphous substances orderly arrangements are not lacking and polymers under certain conditions may consist of macromolecules or polycrystalline forms.

Anisotropy: It has been observed that the properties of a crystal are not the same in all directions. Many physical properties, such as solubility, magnetic susceptibility, thermal expansion, electrical conductivity etc. vary with the directions in the crystal. The variation of properties of a crystal in different directions is known as *anisotropy*. This phenomenon is exhibited because of the regular packing of atoms or molecules as shown in Fig. 25—1.

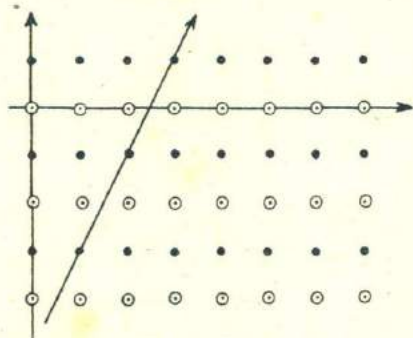


Fig. 25—1. Variation of properties of a crystal with the direction. Notice the different arrangements of points along the lines shown.

The constituent particles of a crystal are arranged in a repeating three-dimensional pattern. The pattern of points which describes the arrangements of molecules of atoms in a crystal in three-dimensions, is known as a *crystal lattice* or *space lattice*. The smallest portion of a crystal lattice which can be used to

describe the space lattice is called the *unit cell*. This is actually the repeat unit for the arrangement of atoms in the entire crystal structure. The two-dimensional crystal lattice and unit cell are shown in Fig. 25—2 (a).

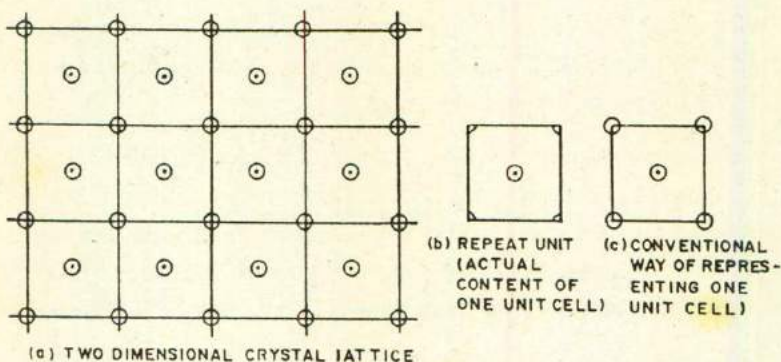


Fig. 25—2. Crystal lattice and unit cell.

It is observed that a group of repeat units combined together produce the two-dimensional pattern of the crystal lattice. The actual unit cell consists of four atoms at the corners and one full atom at the centre [Fig. 25—2 (b)]. But the conventional way of representing the unit cell is as shown in Fig. 25—2(c). The atomic surroundings at each corner of unit cell are identical. It may be noted that the pattern of crystal lattice can be divided into a sets of identical squares, rectangles or parallelograms constituting the unit cell. Any one of the possibilities may be chosen as the unit cell as shown in Fig. 25—3.

Types of Crystals

There are two different ways to classify crystals : (1) Classification on the basis of bonds between the units that occupy the lattice points and (2) classification according to the dimensions of the unit cell involving symmetry of arrangements.

Types of crystals on the basis of bonding system :

There are four types of crystals on the basis of bonding system : (1) Ionic, (2) Molecular, (3) Covalent and (4) Metallic.

In *ionic crystals* the units occupying the lattice points consist of positive and negative ions. Substances such as NaCl, MgO, CaS, Na₂SO₄ consist of

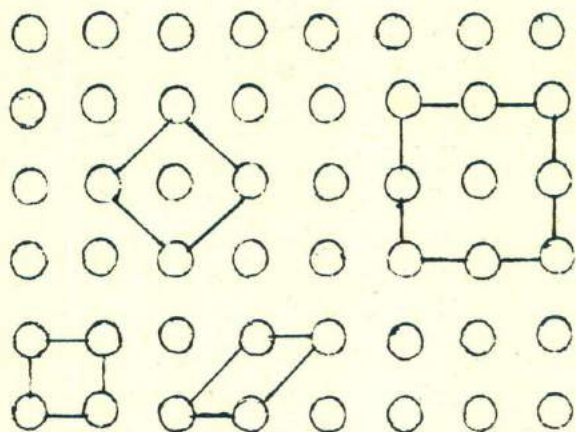


Fig. 25—3. Unit cell (4 different possibilities).

such units. The strong attractive forces between the positive and negative charges give solids of high melting point. They are brittle and show cleavage in definite directions and do not conduct electricity in the solid state but conduct electricity in the molten condition .

Molecular crystals consist of lattice points occupied by molecules. The fundamental building unit in this case is the molecule. The bonding within the molecule is covalent but the forces between the molecules give rise to the molecular crystals. The molecular forces are generally due to the dipole-dipole attraction or the van der Waals' attraction. These are weak forces and hence molecular crystals have low melting points and are soft because of easy displacement of the molecules from one position to the other. They do not conduct electricity. Ice (H_2O), gases in the solid state, iodine etc. are examples of molecular crystals.

The *covalent crystals* are those in which the shared electron-pair bonds combine all the atoms in the crystals into one giant molecule. The unit of structure is the atom. Thus in diamond every C atom is combined with all its nearest neighbours in three-dimension covalent bonds so that the bonding

extends throughout the whole crystal giving an interlocking structure. This arrangement gives the crystals the properties of hardness and high melting point. In quartz, Si and O atoms also form such a three-dimensional covalent crystal. Similar covalent crystals are formed in SiC, BN etc.

The *metallic crystals* consist of space lattice in which the unit is positive ion. The positive ions occupying the lattice point are immersed in a sea of highly mobile electrons of the valence shells. Metallic crystals are close-packed arrangements and generally belong to one of the three systems : *face-centred cubic*, *body-centred cubic* and *hexagonal close-packed*. The *electron gas*, or the sea of electrons belongs to the crystal as a whole. Because of the uniform charge distribution throughout the crystal lattice provided by the mobile electrons which also bind the positive metal atoms, the metallic crystals are good conductors of heat and electricity. These may be very hard as well as soft depending upon the forces of binding between the metal atoms in the crystals.

The different types of solid crystals on the basis of bonding systems are given in Table 25.1.

Table 25.1. Crystal lattices in terms of bonding.

<i>Types</i>	<i>Unit of structure</i>	<i>Bonding system</i>	<i>Properties</i>	<i>Examples</i>
1. Ionic	Positive and negative ions	Electrostatic attraction	Hard, brittle, high m. p., non-conductors	NaCl, K ₂ SO ₄ , MgO
2. Molecular	Molecules	van der Waal's and dipole-dipole attraction	soft, low m. p., non-conductors	Ice (H ₂ O), Solid CO ₂ , I ₂
3. Covalent	Atoms	Shared electrons	Very hard, high m. p., non-conductors	Diamond (C), Carborundum (SiC), Quartz (SiO ₂)
4. Metallic	Positive ions in electron gas	Electrical attraction between + ve ions and electrons	Hard or soft, low m. p., high m. p., conductors	Na, Cu, Fe, Ag etc.

Types of crystals on the basis of unit cell symmetry :

Crystal systems are classified in terms of the dimensions of the unit cell along its three axes (a , b , c) and the three angles between the axes (α , β , γ). The relationships between the values of the angles and the relative lengths of the three axes form the basis for the classification of the solids into seven types of crystal systems. The crystals have the same symmetry as their constituent unit cells.

These seven types of crystal represent the simple or primitive types of space lattices. The unit cells of the seven crystal systems are given in Table 25.2 and illustrated in Fig. 25—4.

Table 25.2. Seven crystal systems on the basis of symmetry.

<i>System</i>	<i>Axes</i>	<i>Angle</i>	<i>Examples</i>
1. Cubic	$a = b = c$ (all equal)	$\alpha = \beta = \gamma = 90^\circ$ (all 90°)	NaCl, CaO, Cu
2. Tetragonal	$a = b \neq c$ (Two equal)	$\alpha = \beta = \gamma = 90^\circ$ (all 90°)	MgF ₂ , MnO ₂ , Sn
3. Orthorhombic	$a \neq b \neq c$ (different lengths)	$\alpha = \beta = \gamma = 90^\circ$ (all 90°)	HgF ₂ , I ₂ , S
4. Monoclinic	$a \neq b \neq c$ (different lengths)	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$ (two 90°)	As ₂ S ₃ , B, S
5. Triclinic	$a \neq b \neq c$ (different lengths)	$\alpha \neq \beta \neq \gamma \neq 90^\circ$ (none 90°)	CuSO ₄ . 5H ₂ O, CuO
6. Hexagonal	$a = b \neq c$ (two equal)	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	SiO ₂ , AgI, C
7. Rhombo- hedral	$a = b = c$ (all equal)	$\alpha = \beta = \gamma \neq 90^\circ$ (equal but not 90°)	Al ₂ O ₃ , NiS, Bi

The seven different types of lattices have been obtained by considering the positions of the atoms at the corners of the unit cells. However, other types of lattices than the seven different types are possible and exist because the points may occupy positions in addition to the corners. Thus the cubic systems have three different lattices, e. g., simple cubic, body-centred cubic and face-centred cubic as shown in Fig. 25—5.

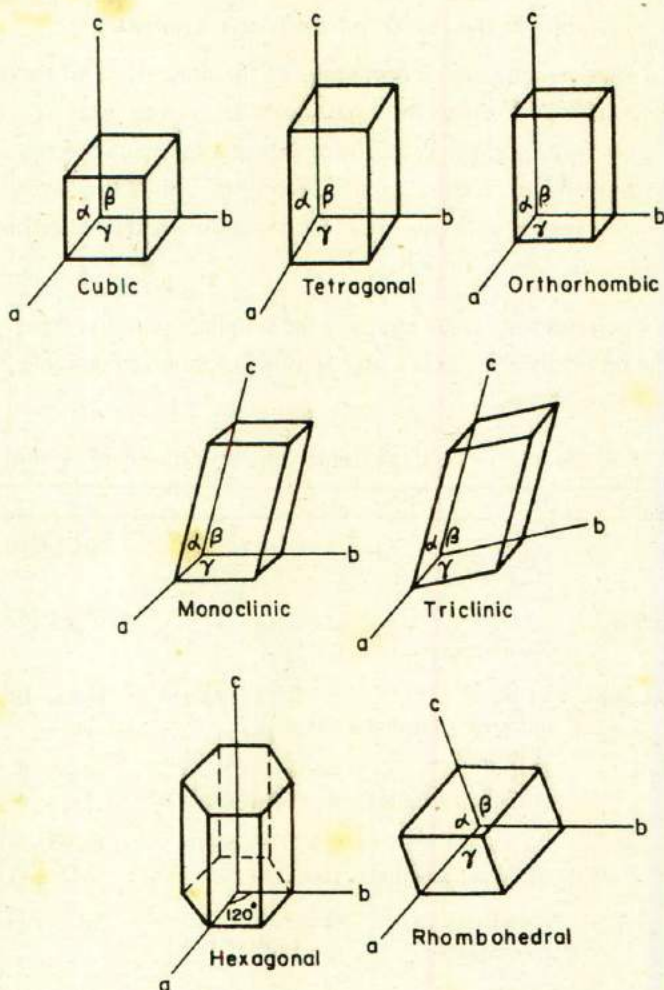


Fig. 25—4. The seven crystal systems.

Similarly, face-centred tetragonal and side-centred rhombic lattices also exist. Actually 14 distinct types of space lattices are recognised in which each point is surrounded in an identical manner by other points. These 14 space lattices are also known as Bravais Space Lattices. Further, this gives rise to 32 groups of symmetry known as *point groups* and 230 different kinds of three-dimensional arrangement of symmetry elements known as *space groups*.

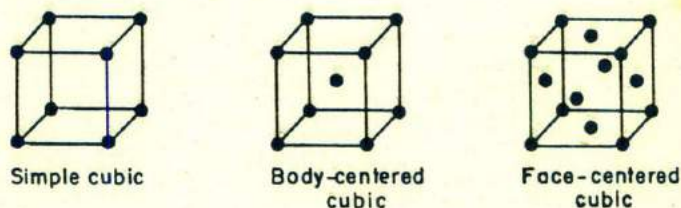


Fig. 25—5. The three different cubic lattices.

The points in the unit cell at the corners and other positions such as faces and centres represent positions occupied by an atom or a molecule.

Crystal symmetry and symmetry elements : The different types of symmetry formed in crystals are planes, axes and centre of symmetry. These are known as symmetry elements. A *plane of symmetry* divides the crystal by an imaginary plane into two parts which are mirror-images of each other in the plane. An *axis of symmetry* is an axis of revolution of the crystal which when operated makes the crystal present the same appearance more than once. The initial faces of the crystal may appear two, three, four or six times corresponding to rotation through 180° , 120° , 90° or 60° respectively as given in Fig. 25—6. A *centre of symmetry* is a point such that a line drawn through it intersects the crystal surfaces at equal distances on either side of the point.

Crystal coordination number : The unit cell in a crystal structure indicates the environment of an atom or molecule in a crystal. This environment gives the idea regarding the crystal structure when unit cells are joined together to form the lattice in three-dimensions. Coordination number in the crystal structure is the number of closest neighbours of the atom in a lattice.

Rational lines and planes : Considering the pattern of particles in two dimensions, as in Fig. 25—7, it is seen that a line AB, passing through a point in the lattice, will not necessarily pass through any other points. But the lines passing through two points must pass through an infinite number of points in the lattice as the lines XYZ and XPQ indicate. This is because such a line represents the side or diagonal of a square or a rectangle. These are called *rational lines*. In a three-dimensional lattice any plane passing through *three* points

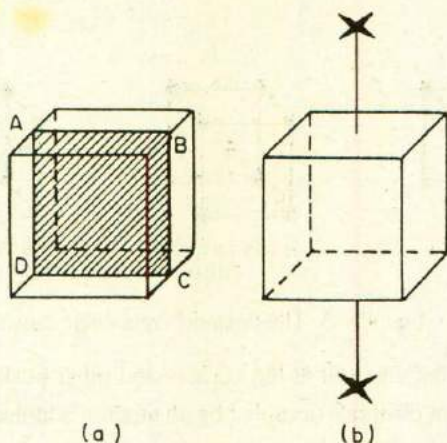


Fig. 25—6. An axis of symmetry and a plane of symmetry in a cube : (a) A plane of symmetry (ABCD) in a cube, (b) a four-fold axis of symmetry in a cube.

which are not in the same straight line will also pass through an infinite number of lattice points. These planes are called *rational planes*. Movement of the plane along the axes of the lattice by the unit-cell distance will give a number of parallel planes which will be separated from one another by equal distance which

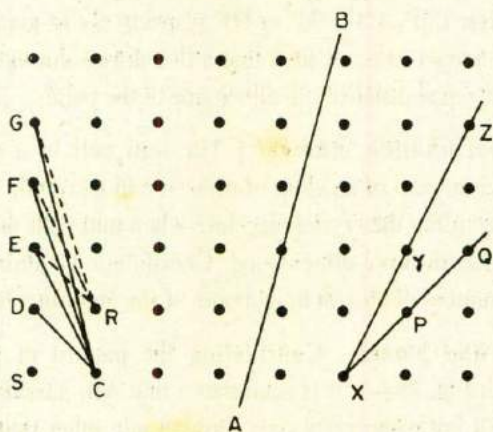


Fig. 25—7. Two-dimension rational lines.

is the same as that of the first plane from the lattice origin. This is illustrated in Fig. 25—8 with cubic lattices.

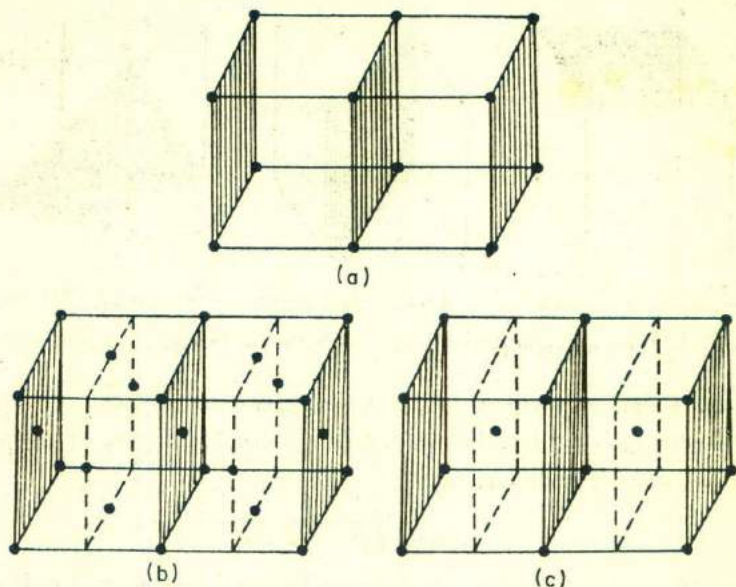


Fig. 25—8. Parallel planes passing through identical sets of points in (a) Simple cubic lattice, (b) Face-centered cubic lattice. (c) Body-centred cubic lattice.

In Fig. 25—7, showing the two-dimensional lattice, the lines CD, CE, CF and CG divide the horizontal line RD and all the lines parallel to it by 1, 2, 3 and 4 respectively. Similarly, the other pairs of lines CD and RE, CE and RF, CF and RG have the same intercept on the side of a unit cell. Since these lines are at equal distances in the lattice, the divisor or the intercept along base must be a whole number. In the same way the rational planes of three-dimensional lattice is identified by the divisor or intercept along each axis. The planes make intercepts with the three axis of the unit cell. The divisors or the intercepts are indicated by labels h, k, l and are known as the Miller Indices. Fig. 25—9 gives the values of h, k, l for the planes ABC. This plane at a unit distance from the origin O is designated as 1, 1, 1 plane or briefly written as (111). Similarly, other planes are designated as given in Fig. 25—9.

The distances between the similar parallel planes having identical arrangements of atoms are called *interplanar distances* or spacing distances of plane. This value is designated by the letter d .

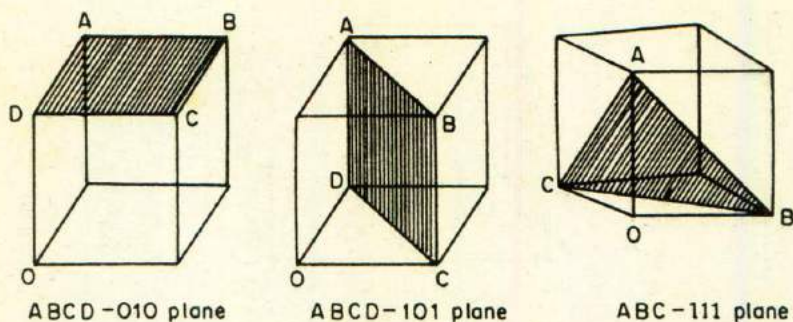


Fig. 25—9. Three different planes designated by Miller Indices in a cubic unit cell.

From simple geometry it can be proved easily that in a cube having the length of the side equal to a , known as *lattice constant*, the value of interplanar distances d is given by the equation :

$$a = d\sqrt{h^2 + k^2 + l^2}$$

Table 25.3. Relationship between 'a', 'd' and h, k, l value of cubic crystals.

hkl	$h^2 + k^2 + l^2$	d	Values of $h^2 + k^2 + l^2$ for		
			Simple Cubic	Body-centred Cubic	Face-centred Cubic
100	1	a	1	2	2
110	2	$a/\sqrt{2}$	3	4	4
111	3	$a/\sqrt{3}$	5	6	6
				8	8
200	4	$a/2$	9	10	10
210	5	$a/\sqrt{5}$	11	12	12
211	6	$a/\sqrt{6}$	13	14	14
				16	16
220	8	$a/\sqrt{8}$	17	18	18
221	9	$a/3$	19	20	20
300					

The possible values of the distances between atomic planes in cubic crystals may be calculated as given in Table 25.3. The values of $h^2 + k^2 + l^2$ indicate the crystal symmetry and planes of reflections. Knowing the values it is possible to identify the crystal symmetry from the systematic absences.

Determination of Structure

Crystallography is the study of solid substances for the determination of their identity and their crystal structure in terms of atomic configurations.

A great deal of informations about the internal structure of crystals have been obtained by X-ray diffraction experiments. X-rays are electromagnetic radiations of very short wavelengths. X-rays are generated by the impact of high-speed electrons from the cathode on a metal target (anode) in a vacuum tube (Fig. 25-10). The targets are generally copper, molydenum chromium, cobalt etc. The X-rays are directed at the sample crystals through a slit. The diffracted rays are recorded by a photographic film or other devices. The sample may be in the

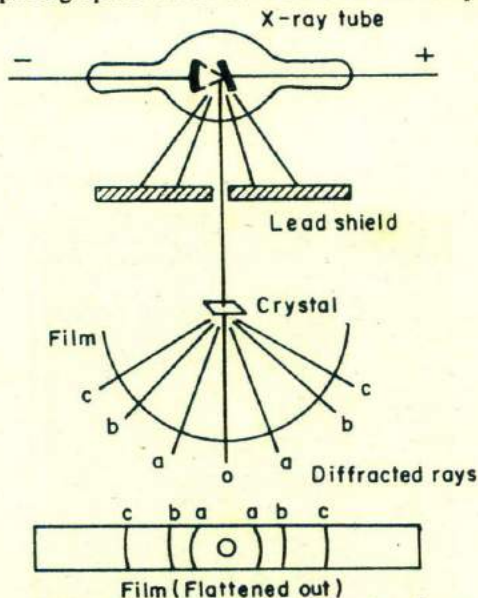


Fig. 25-10. Schematic of X-ray diffraction of crystals.

form of a single crystal or a large number of minute crystals (powder form). The diffraction of X-rays by crystals is similar to diffraction of ordinary light by a grating. The incoming X-rays interact with electrons that are present in the atoms of the crystals having a regular arrangements. The X-rays beam is scattered or deflected by the regular arrangements of atoms in the crystal. A photographic film is placed to record the scattered or deflected X-rays. On

developing the film a pattern is found which is characteristic of the structure of the crystals illustrated in Fig. 25—10. It is noted that in three-dimensional lattices a beam of X-rays striking one plane at angle permitting diffraction must strike all parallel planes having the same set of indices at the same angle and be diffracted similarly.

A monochromatic beam of X-rays is unlikely to hit a single and stationary crystal at all its planes. X-rays beam with a range of wavelengths is used or the single crystal is rotated or a large number of minute crystals (powder form) is used, so that a number of diffracted beams are obtained from the sample. The general techniques used to obtain an X-ray photographic pattern are : (1) Laue Method, (2) Powder Method and (3) Single Crystal Method.

Laue Method consists of obtaining X-ray photograph by using polychromatic X-ray beam on a single crystal. This method is no longer important and gives some information regarding the symmetry of the crystal structure. A sketch of the Laue pattern of NH_4Cl crystals is given in Fig. 25—11.

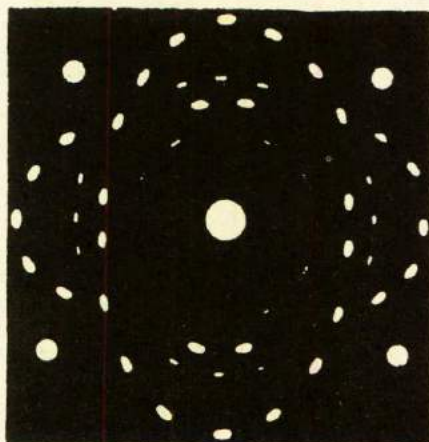


Fig. 25—11. A sketch of the Laue pattern of NaCl crystal.

The Powder Method employs monochromatic radiation with a large number of very small crystals (in the powder form) oriented at random. This is used chiefly for identification of crystalline substances and also to determine the structure in simple cases. A diffraction pattern by the powder method is given in Fig. 25—10 (bottom) when the film is flattened out.

The *Single Crystal Method* employs a single crystal of the sample which is rotated or oscillated on an axis perpendicular to the path of the incident X-rays of monochromatic radiation. When the developed film is flattened out a pattern as shown in Fig. 25—12 is obtained. This method is important for the determination of crystal structure. The crystal structure determinations have now been made fully automatic with the help of computers and applied for all types of extremely complex molecules (Fig. 25-14)

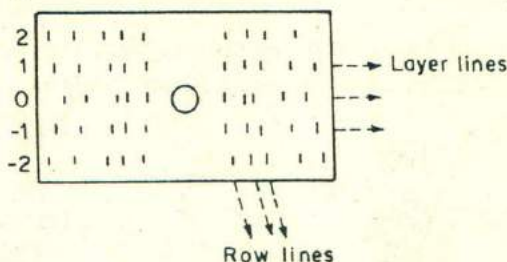


Fig. 25—12. Single crystal rotation pattern.

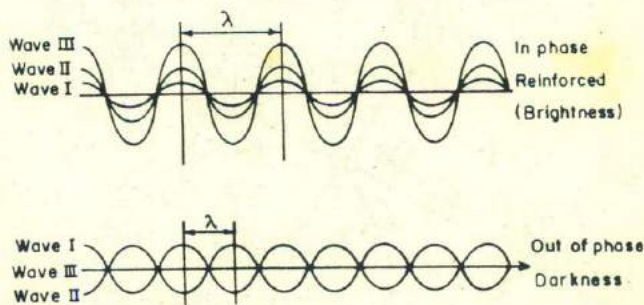


Fig. 25—13. Reinforcement of in-phase waves (top) and destructive interference of out-of-phase waves (bottom)

Origin of the Pattern

It has been mentioned that the diffraction of X-rays by crystal is similar to diffraction of light by a ruled grating which produces areas of brightness and darkness. The regular arrangements of atoms in space having the line of atoms in crystals also behave like tiny slits for the X-rays. Two waves that are in-phase reinforce each other and produce a resultant wave that has greater amplitude but the wavelength remains the same. Such waves produce areas of brightness. Two waves that are out-of-phase cancel each other by destructive interference. The resultant wave has no amplitude or intensity and produces areas of darkness. This

point is illustrated in Fig. 25—13 in which waves I and II give the resultant wave III.

A careful mathematical analysis of the patterns of the X-ray diffraction photographs gives the informations regarding the interplanar spacings (d values) and enables a crystallographer to calculate the positions of the atoms or molecules in the crystal which produces the pattern under examination.

Bragg's Equation

The basic relationship of the X-ray crystallography is given by the Bragg's equation. Considering that a beam of X-rays having single wavelength, λ , hits a

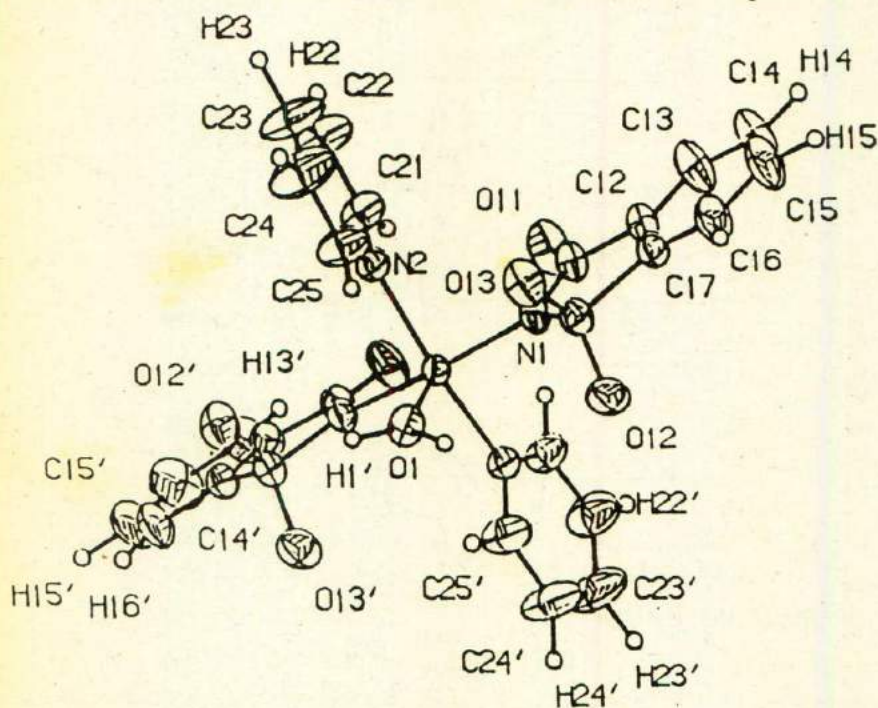


Fig. 25—14. Crystal structure of bis (saccharinato pyridine) copper (II) hydrate $\text{Cu}(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2(\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{O}$.

number of parallel planes of atoms within the crystal and taking only two such planes of atom the Bragg's equation can be easily derived as illustrated in Fig. 25—15. The wave-front AD approaches the two parallel planes xx and yy

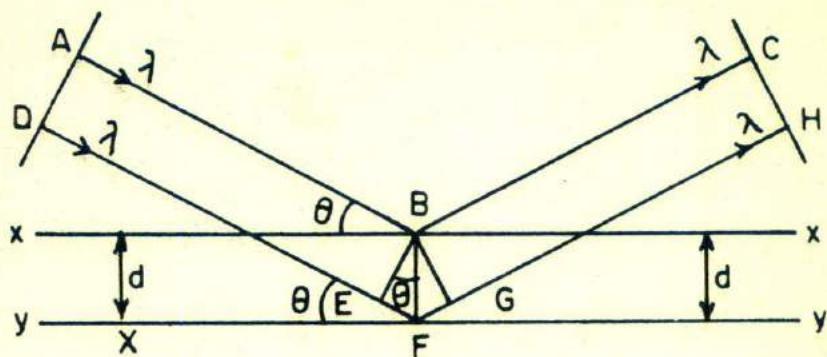


Fig. 25—15. X-ray diffraction from two parallel planes.

separated by the interplanar distance d , the angle of incidence is θ . Some of the rays are reflected from the upper plane and some from the second plane at points B and D respectively along BC and FH giving the reflection angle also equal to θ . A strong reflected beam will be produced only if the reflected rays are in-phase. It is seen from the illustration in Fig. 25—14 that path length of the ray DFH is greater than the path-length of the ray ABC by the distance $EF + FG$. These rays will be in-phase at CH only if the difference of path-lengths $DFH - ABC$ (i.e., $EF + FG$) is equal to a whole number of wavelength $n\lambda$. Thus the condition for reflection of X-rays without destructive interference is

$$EF + FG = n\lambda$$

Angle BEF is 90° since BE is perpendicular to DF. Hence the sum of the angles EBF and EFB = 90° . Angle XFB is 90° and angle XFE = θ . Therefore,

$$\angle EBF + 90^\circ - \theta = 90^\circ \text{ and hence } \angle EBF = \theta$$

$$\text{Since } \sin EBF = \sin \theta = \frac{EF}{BF} = \frac{EF}{d}$$

$$\text{Therefore, } EF = d \sin \theta$$

$$\text{Similarly, } FG = d \sin \theta$$

$$\text{Therefore, } EF + FG = 2d \sin \theta$$

$$\text{or } n\lambda = 2d \sin \theta$$

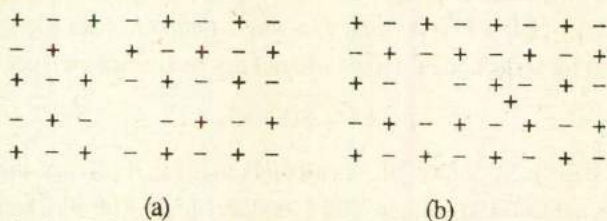
This is the Bragg's equation and may also be written as

$$\sin \theta = \frac{n\lambda}{2d}$$

Thus X-rays of definite wavelengths give reflections at various angles for a given set of planes with interplanar distance equal to d . These reflections correspond to $n = 1, 2, 3, 4$ etc. and are called *order of reflections*. As the order of reflection increases the angle also increases and the intensity of the reflected beam becomes weak. Thus the measurement of the angle at which diffraction occurs gives a method to calculate the distances between the planes of atoms within the crystal. It is to be noted that there are a number of interplanar spacings in a crystal corresponding to different sets of planes.

Defect structure : Examples of perfect crystals are not many. An ideal crystal is one which does not contain any *lattice defects* and can be completely described by the unit cell. There are several kinds of lattice defects.

Point defects are caused by missing ions giving *lattice vacancies* known as Schottky defect. The defects due to misplaced ions give *lattice interstitials* (Frenkel defect). In lattice vacancies, some of the lattice points are unoccupied, and in lattice interstitial, the atoms occupy positions between lattice points. Lattice defects in NaCl and AgBr are illustrated in Fig. 25—15.



(a)

(b)

Fig. 25—15. Lattice defects : (a) vacancies in NaCl. Some of the Na(+) and Cl(-) ions are missing. (b) Misplaced Ag⁺(+) in AgBr at interstitial site.

Distortion is the type of defect in crystal where planes of atoms are misaligned. The two types of distortion are known as *edge distortion* and *screw distortion*. Edge distortion results when a plane of atoms is inserted only partly into a crystal. Screw distortion has a line of atoms as an axis about which the crystal planes give the effect of screw threads.

The above-mentioned defects do not alter the stoichiometry of the crystal. But certain crystal defects arise due to *non-stoichiometry*. Thus a crystal of FeO contains more oxygen atoms than Fe atoms and ZnO contains more of Zn atoms to the extent of about 0.1%. The *non-stoichiometric* compounds contain extra

metal atoms or non-metal atoms in the interstitial positions between the ions of the crystals or they may occupy the ionic lattice positions. The structure as a whole is electrically neutral. The presence of impurities also imparts crystal defects. Mg^{+2} ion in NaCl gives rise to crystal defect. Similarly, As or B are added to Ge crystal to produce defect structures. Ge has the diamond structure but addition of B replaces a Ge (4 electron) atom with B (three electrons) atom. This gives rise to an electron hole. Similarly, an extra electron enters the structure of germanium by the substitution of an As atom (5 electrons) for a Ge. This type of defect due to the presence of impurities in crystal structure makes it conductor of electricity generally known as *semi-conductivity*. These materials are intermediate between conductors and non-conductors. Semiconductors differ from conductors in one important aspect. The conductivity of semiconductors is increased with the increase of temperature and also when the material is exposed to a beam of light. This is not observed in conductors. Hence semiconductors find applications as photocells, transistors and thermistors. Conductivity of the semiconductors are due to the motion of extra electrons or the existence of electron holes.

Certain optical properties, such as fluorescence and phosphorescence of some compounds, have been found to depend on the nature and extent of crystal defects. ZnS when precipitated from aqueous solution and dried at low temperatures does not show fluorescence upon exposure to ultraviolet light. But on heating ZnS to $900^{\circ}C$, the product contains a higher Zn/S ratio than that of ZnS. Irradiation of this ZnS to ultraviolet light produces an intense blue fluorescence. If the ignited ZnS contains 0.0001% CuS, the product gives a green fluorescence which persists after the source of radiation has been removed (that is, it also shows phosphorescence).

CHAPTER 26

NUCLEAR CHEMISTRY

The physical and chemical properties of all substances and the changes that these undergo from one form to another involve the electronic rearrangements of the atoms particularly the electrons in the outermost energy level. Nothing happens to the nuclei of the atoms during chemical reactions. Physical and chemical properties and reactions are, therefore, essentially associated with the electrons of the atoms.

However, a new type of transformation of matter involving changes in the atomic nuclei has attained tremendous advancement and has given rise to a new major branch of chemistry known as *Nuclear Chemistry*.

Nuclear Chemistry is the study of the properties, compositions and reactions of the nuclei of atoms.

In connection with the discovery of atomic nucleus it has been mentioned that certain elements, such as uranium, radium etc. undergo spontaneous disintegration to produce atoms of other elements together with radioactive rays. It is also seen that some elements are naturally radioactive such as uranium, thorium, radium, radon etc. but all others can be made radio-active by artificial means. The study of the chemistry of radioactive substances has given rise to the branch of chemistry known as *Radiochemistry*.

Radiochemistry is the study of the properties, compositions and reactions of radioactive elements and their compounds.

Nuclear chemistry thus embraces the study of radiochemistry which is a part of the general study of nuclear phenomenon. It may be noted that a very large number of isotopes occur in nature and can be made artificially which are not radioactive and can be studied by means of their nuclear properties other than radioactivity.

Discovery of Radioactivity

In 1895, Röntgen accidentally discovered X-rays which are able to penetrate materials that are opaque to light, produce ionization in their path, cause certain substances to emit light, and affect photographic films.

In 1896, the French scientist Becquerel discovered that uranium salt, such as potassium uranyl sulphate, $K_2UO_2(SO_4)_2$ gave out penetrating rays which affected a photographic plate wrapped in a black paper and kept in darkness. This seemed remarkable to Becquerel who observed that some X-rays like radiations must have been emitted by the chemical compound and penetrated through the black paper to affect the photographic plate even in the dark. Becquerel thus discovered an entirely new natural phenomenon that chemical substances spontaneously give out invisible rays which have properties like X-rays. These rays emitted by chemical substances are now known as *radioactive rays* and the phenomenon is known as *radioactivity*.

Thus radioactivity is the phenomenon of spontaneous production of invisible rays from chemical substances having the power of ionizing gas or air in its vicinity and affecting photographic plate or films.

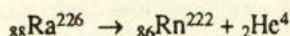
Radioactive substances generally emit three types of rays:— mid

* (1) α - Rays : These are helium-nuclei having charge + 2, (He^{+2}) and travel at a high speed. They are deflected from the straight path by a magnetic field or an electric field indicating positive charge. These rays have strong ionizing power but of short range.

* (2) β - Rays : These are electrons having charge -1, (e^-) travelling at a very high speed. They are deflected by a magnetic field and also electric field indicating the negative charge. They are more penetrating than α - rays and ionize gases and have long range.

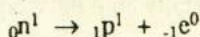
* (3) γ - Rays : These are photons (units of radiant energy) and consist of electromagnetic radiation of very short wavelength like those of X-rays. They travel with the speed of light and have intense penetrating power. These rays carry neither mass nor charge.

Radioactivity is a nuclear phenomenon : Radioactivity is a nuclear property and is independent of the state of chemical combination or physical conditions. For example, a given quantity of radium has the same radioactivity regardless of whether the radium atoms are present in the metal, in solution, in solid salts or in the mineral. The radioactive rays emanate from the nucleus of the atom as it undergoes a process of spontaneous disintegration. When an atom emits α - or β -radiation, it becomes a new kind of atom. Due to the emission of α -particle from the nucleus, the mass of the nucleus is decreased by four units and the charge is decreased by two units. This happens because the loss of an α -particle is equivalent to the loss of 2 neutrons and 2 protons from the nucleus. The loss of 2 protons from the nucleus is accompanied by the loss of two planetary electrons whereby the electrical balance in the atom is retained. The spontaneous disintegration of the radium nucleus may be represented by the following equation :

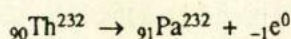


226 is the mass number and 88, the atomic number of radium. 222 is the mass number and 86, the atomic number of radon.

When a β -particle is ejected from the nucleus, a neutron in the nucleus evidently undergoes a transformation to give a proton and electron :



Due to the formation of a new proton at the expense of a neutron in the nucleus, a net increase in the positive charges takes place, as a result the atomic number of the new elements is increased by one unit. The expulsion of an electron from the nucleus does not affect the mass of the nucleus. This is illustrated when an isotope of thorium changes to protoactinium:



The emission of an α - or β -particle may be accompanied by γ -radiation. The emission of γ -rays does not change the atomic number or the mass number of an atom because γ -rays possess neither mass nor charge.

The above observations together with the experimental determination of the rate of disintegration and half-lives of radio-elements (a characteristic property

described later) led scientists to conclude that radioactivity is a nuclear property. The radioactive disintegration takes place in the nucleus of an atom. α -particles with mass 4 and charge +2 could come out only from the nucleus which contains the mass and positive charges. The change in atomic number does indicate that β -particle must come from the nucleus. The loss of a unit negative charge increases the positive charge on the nucleus through neutron to proton conversion mechanism involving loss of β -rays known as β -decay.

Group Displacement Law

The emission of α - and β -particles from atomic nuclei obviously give rise to displacement in the positions of the product of disintegration in the Periodic Table because of the change of the atomic number of the parent element. These displacements are described by the so-called *Group Displacement Law*:

(1) When an element gives out an α -particle, the product obtained moves two positions lower than the parent element in the Periodic Table (atomic number decreased by 2). Mass of the element is decreased by 4 units.

(2) When an element gives out a β -particle, the product obtained moves one position higher than the parent element in the Periodic Table (atomic number increased by 1). Mass of the element remains the same.

Elements undergoing successive disintegrations and producing a number of elements which are radioactive isotopes give rise to a chain of species known as *radioactive series*. There are three different radioactive series of elements which are of natural origin and include most of the natural radioactive elements of the Periodic Table. Besides there is the fourth series discovered during World War II. This series is called the Neptunium series which was discovered by the production of the series members by artificial means. Thus there are four radioactive series, namely :

- (1) The Uranium series,
- (2) The Actinium series,
- (3) The Thorium series,
- (4) The Neptunium series.

Each series is characterized by a parent (first element) of long life and the ultimate end product leads to a stable isotopé which is not radioactive. The

various series consisting of transformation from the parent element to the end product of stable isotopes are outlined as follows:

The Uranium series	The Actinium series	The Thorium series	The Neptunium series
${}_{92}\text{U}^{238}$	${}_{92}\text{U}^{235}$	${}_{90}\text{Th}^{232}$	${}_{93}\text{Np}^{237}$
↓ α	↓ α	↓ α	↓ α
${}_{90}\text{Th}^{234}$	${}_{90}\text{Th}^{231}$	${}_{88}\text{Ra}^{228}$	${}_{91}\text{Pa}^{233}$
↓ β	↓ β	↓ β	↓ β
${}_{91}\text{Pa}^{234}$	${}_{91}\text{Pa}^{231}$	${}_{89}\text{Ac}^{228}$	${}_{92}\text{U}^{233}$
↓ β	↓ α	↓ β	↓ α
${}_{92}\text{U}^{234}$	${}_{89}\text{Ac}^{227}$	${}_{90}\text{Th}^{228}$	${}_{90}\text{Th}^{229}$
↓ α	$\alpha \swarrow \searrow \beta$	↓ α	↓ α
${}_{90}\text{Th}^{230}$	${}_{87}\text{Fr}^{223}$ ${}_{90}\text{Th}^{227}$	${}_{88}\text{Ra}^{224}$	${}_{88}\text{Ra}^{225}$
↓ α	$\beta \searrow \swarrow \alpha$	↓ α	↓ β
${}_{88}\text{Ra}^{226}$	${}_{88}\text{Ra}^{223}$	${}_{86}\text{Rn}^{220}$	${}_{89}\text{Ac}^{225}$
↓ α	↓ α	↓ α	↓ α
${}_{86}\text{Rn}^{222}$	${}_{86}\text{Rn}^{219}$	${}_{84}\text{Po}^{216}$	${}_{87}\text{Fr}^{221}$
↓ α	↓ α	↓ α	↓ α
${}_{84}\text{Po}^{218}$	${}_{84}\text{Po}^{215}$	${}_{82}\text{Pb}^{212}$	${}_{85}\text{At}^{217}$
↓ α	↓ α	↓ β	↓ α
${}_{82}\text{Pb}^{214}$	${}_{82}\text{Pb}^{211}$	${}_{83}\text{Bi}^{212}$	${}_{83}\text{Bi}^{213}$
↓ β	↓ β	↓ β	↓ β
${}_{83}\text{Bi}^{214}$	${}_{83}\text{Bi}^{211}$	${}_{84}\text{Po}^{212}$	${}_{84}\text{Po}^{213}$
↓ β	↓ β	↓ α	↓ α
${}_{84}\text{Po}^{214}$	${}_{84}\text{Po}^{211}$	${}_{82}\text{Pb}^{203}$	${}_{82}\text{Pb}^{209}$
↓ α	↓ α	(stable)	↓ β
${}_{82}\text{Pb}^{210}$	${}_{82}\text{Pb}^{207}$		${}_{83}\text{Bi}^{209}$
↓ β	(stable)		(stable)
${}_{83}\text{Bi}^{210}$			
↓ β			
${}_{84}\text{Po}^{210}$			
↓ α			
${}_{82}\text{Pb}^{206}$			
(stable)			

It may be noted that expulsion of one α -particle from an element and subsequent expulsion of two β -particles bring the element back to the same position in the Periodic Table thus giving rise to an isotope which are elements having the same atomic number.

It is to be remembered that in general, γ -rays are emitted each time the atomic nuclei undergo disintegration. The disintegration of uranium stops with the formation of lead 206. Samples of lead occurring in nature and from different radioactive minerals have different atomic weights. The actinium series starting from ${}_{92}\text{U}^{235}$ and the thorium series starting with ${}_{90}\text{Th}^{232}$ both also end with the formation of lead as the end product giving isotopes ${}_{82}\text{Pb}^{207}$ and ${}_{82}\text{Pb}^{208}$ respectively. Thus natural lead is a mixture of four isotopes having mass number 206, 207, 208 and 209. The proportions in which these isotopes are present give natural lead (Pb) its atomic weight of 207.21. This happens in the case of all elements. Recently the fourth radioactive series known as the neptunium series was discovered. ${}_{93}\text{Np}^{237}$ is the longest lived member which is the starting element and the series end at ${}_{83}\text{Bi}^{209}$ which is the stable product.

Radioactive Equilibrium

It may also be noted that the rate of disintegration of all the radio-elements are not the same. Some element, such as U^{238} , disintegrates very slowly whereas Ra disintegrates rapidly. Those radio-elements which are decaying at a rapid rate are also produced by their predecessor exactly at the same rate in nature. Hence they can not disintegrate out of existence because the parent element is producing the element at the same rate at which it is disintegrating. Such condition is known as *radioactive equilibrium* and is not reversible as in the case of chemical equilibrium which is a reversible phenomenon. Thus if an element A changes to B which again changes to C, then B will be at radioactive equilibrium if the rate of change of A to B, i. e., dA/dt (disintegration of A) and the rate of change of B to C, i. e., dB/dt (disintegration of B) are the same.

$$\text{If } A \rightarrow B \rightarrow C, \text{ then } \frac{dA}{dt} = \frac{dB}{dt}$$

Disintegration or Decay Constant

The rate of disintegration of a radio-element is absolutely independent of all physical or chemical factors and is also different for different elements. Experimentally it has been found that every radioactive disintegration occurs at a rate that is directly proportional to the quantity of disintegrating material present. Hence the rate of disintegration of a radio-element follows the first-order reaction. Thus we have the following statement.

The rate of disintegration of a radioactive element at any time is proportional to the number of atoms of the element present at that time.

Let N be the number of atoms present at time t . If in the small interval of time dt the number of atoms which disintegrates is dN , then the rate of disintegration is $-\frac{dN}{dt}$ (minus sign indicates decrease in amount with time). Since the rate of disintegration is proportional to N (total quantity of radioelement), therefore, we have :

$$-\frac{dN}{dt} \propto N$$

$$\text{or } -\frac{dN}{dt} = \lambda N$$

where λ is a constant called Decay Constant or Disintegration Constant. When the rate of disintegration in unit time (per second) is taken into account, i.e., when $dt = 1$ second, we have,

$$-dN = \lambda N$$

$$\text{or } \lambda = -\frac{dN}{N}$$

Hence λ , the Decay Constant, is defined as the *fraction of the total number of atoms of the radio-element disintegrating per second*. This has a characteristic value for each radioelement. But the most important characteristic property of a radio-element is generally considered to be its half-life. Very often reference is made to the half-life of radioactive element which actually determines the radioisotope.

Half-life of Radio-elements

The *half-life* of a radioelement is the time required for one-half of the atoms in a sample to disintegrate.

Since the amount of the radioactivity is directly proportional to the quantity of radio-element (number of atoms of radioelement) the definition for half-life can also be stated as : The time required for a radio-element of a given amount to lose 50% of its activity. Integrating the equation

$$-\frac{dN}{dt} = \lambda N, \text{ i. e., } -\frac{dN}{N} = \lambda dt$$

between time interval zero to any time t . We have, $\int_0^t -\frac{dN}{N} = \int_0^t \lambda dt$

$$\ln N_t - \ln N_o = \lambda t$$

$$\text{or exponentially } \frac{N_t}{N_o} = e^{-\lambda t}$$

Where N_t = the number of atoms present at time t .

N_o = the number of atoms initially present, when $t = 0$

$$\text{At half-life, } t_{1/2} \text{ we have } \frac{N_t}{N_o} = 1/2 = e^{-\lambda t_{1/2}} \text{ or } \frac{N_t}{N_o} = e^{-\lambda t_{1/2}}$$

$$\text{or } \ln 1/2 = -\lambda t_{1/2}$$

$$\text{or, } t_{1/2} = \frac{2.303 \log 2}{\lambda} \text{ or } t_{1/2} = \frac{0.693}{\lambda}$$

$$= N_t = N_o e^{-\lambda t}$$

Half-life of a radio-element is thus independent of its total mass. The half-life of radium (216) is 1590 years, that of radon (222) is 3.8 days and that of polonium (218) is 3 minutes. Half-lives of different radioisotopes actually vary from small fractions of a second to billions of years. Thus in the uranium series the half-life of U^{238} is 4.5×10^9 years and that of Po^{212} is 3×10^{-7} seconds only.

Half-life of a radioelement implies that if we have 400 g. of the radioelement having half-life, say one day, then 200 g. of it will be left after one day, 100 g. at the end of two days, 50 g. at the end of 3 days, 25 g. at the end of 4 days and so on.

Average Life of Radio-elements.

It is to be noted that radio-active disintegration follows an exponential law which implies a definite probability for any particular atom disintegrating at a given moment to be proportional to the total number of atoms present at that moment. The life of any radio-element, that is, the length of time it can exist before it disintegrates can thus have all possible values from zero to infinity. This explains the gradual decay of a radio-element, for otherwise all the atoms would decay at the same time. Hence an average life or mean life for an aggregate of a large number of atoms of radio-element is taken into account.

The average life of a radio-element is the reciprocal of the disintegration constant. Thus, if T_a is the average life, we have, $T_a = \frac{1}{\lambda}$.

Detection and measurement of radioactivity and half-life: Various techniques, such as electroscope, photography, electrometer, ionization chamber etc. had been used to study radioactivity earlier. But recently the measurement of activity and determination of half-life are carried out by sophisticated electronic devices. Geiger-Muller counter, proportional counter, scintillation counter and coincidence counter are some of these modern devices. The ionization produced by a radio-element is multiplied by various techniques and measured under high voltages. The extent of ionization is proportional to the activity of radio-element.

The Geiger-Muller counter consists of a tube shown in Fig. 26—1. The radiations from a radioisotope emitting α , β or γ -rays enter the tube through a thin window. The G—M tube is filled with argon gas under low pressure. The

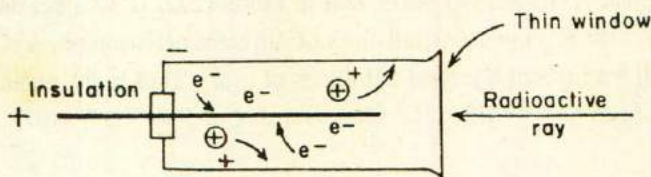


Fig. 26—1. Outline of Geiger-Muller tube for counting radioactive rays.

radioactive rays knock electrons off the argon atoms and form positive argon ions. Under a high external potential of 1000—1200 volts an avalanche of electrons is produced by successive collision and a pulse of electric current flows through the circuit. The continuous discharge is stopped by quenching agents, such as ethyl alcohol or halogen in the tube. The pulse is amplified to operate a microphone or an automatic electronic counter.

Wilson Cloud Chamber enables the path of ionizing radiation from a radioactive element to be seen and photographed. Air saturated with water vapour in a chamber on sudden expansion and cooling provides the medium to follow the track of the radioactive rays. Water vapour is condensed as droplets on the ions formed in the path.

Radioactive rays causes scintillation in some materials such as zinc sulphide or thalium activated sodium iodide crystals which gives out flashes of light on the impact of each radioactive particle or ray. The window of a photo-electric

tube is coated with such a substance and the flash of light causes a pulse of electric current which is amplified and made to operate counting devices.

Thus the radioactivity can be measured in counts per minute or count per second as the case may be.

The activity is proportional to the number of atoms or the quantity of radioisotope. When the radioactivity in terms of, say counts per minute, is plotted against time, the curve obtained is as given in Fig 26—2, which shows the decay curve of a radio-element. But in practice log activity (i. e., log counts per minute) is plotted against time, and a straight line is obtained in the case of a pure radioactive isotope as given in Fig. 26—3. This curve can be used directly to find out the half-life of a radio-element. From the graph in Fig. 26—3, it is found that the time required for the activity to become half the original value is 10 minutes (1000 counts per minute becomes 500 counts per minute in 10 minutes).

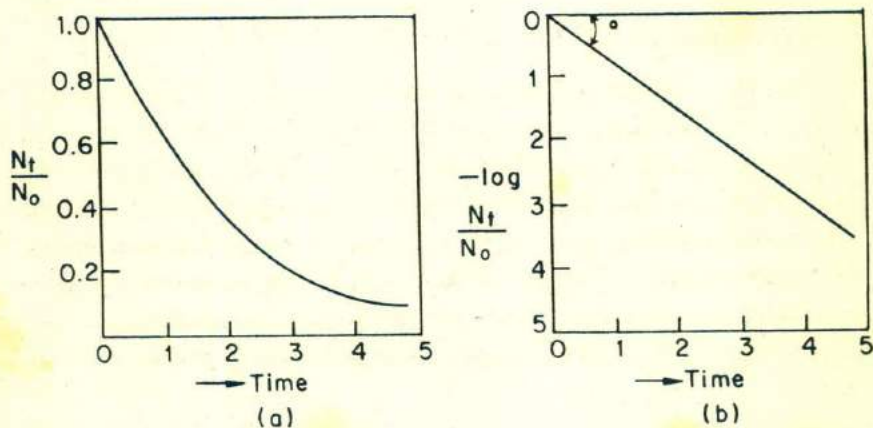


Fig. 26—2. Plot of decay against time. The asymptote curve shows that decay of radio-element follows an exponential law. The log scale gives straight line.

Unit of radioactivity : A Curie is the unit of radioactivity and is used in most practical measurements. A curie is defined as the quantity of any radioisotope which is undergoing 3.7×10^{10} disintegrations per second. A Becquerel is the quantity of a radioisotope undergoing 1 disintegration per second.

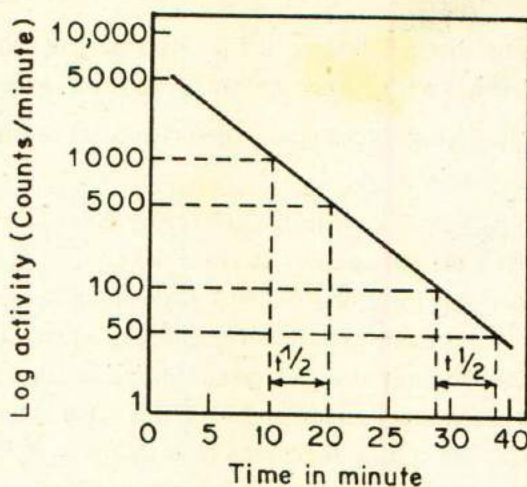


Fig. 26—3. Plot of log activity against time giving a straight line for a pure radioelement. Half-life can be directly read from the graph. $t_{1/2}$ in this case is 10 minutes as indicated.

Nuclear Reactions

It has already been described before that α -particles and electron beams were being used by scientists to investigate the structure of matter. The scattering experiments of Rutherford had already been known, as a result, the existence of a nucleus in an atom was established. Naturally this can be generalized to conclude that if a positively charged particle, such as α -particle, proton or deuteron moving with a high velocity, approaches a positively charged nucleus at rest, it tends to be deflected away because of repulsion of the positive charges on each. But if high-energy particle is used it may collide with the nucleus to produce two types of effects :

- (1) The high-energy particle is at first absorbed by the nucleus forming a compound nucleus which may be unstable and break up to give a new nucleus and another particle.
- (2) The high-energy particle may be absorbed by the nucleus which does not break up but gives out γ -rays.

A nuclear reaction is a process in which a nucleus reacts with another nucleus generally an elementary particle or a photon to produce one or more

nuclei. The high-energy particles used for bombardment in nuclear reactions are known as *projectiles*. The elements subjected to nuclear reactions by projectiles are known as *targets*.

In 1919, Rutherford and his co workers carried out the first nuclear reaction in the laboratory. Using high velocity γ -particles emanating from a radium isotope, Rutherford bombarded nitrogen atoms in a device outlined in Fig. 26—4.

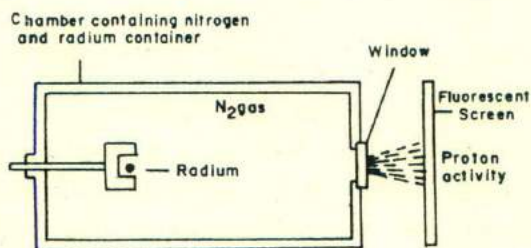
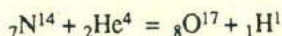
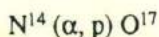


Fig. 26—4. Rutherford apparatus for transmutation of N to O indicated by proton activity on the fluorescent screen.

It was noticed that proton rays were produced when α -particle passed through nitrogen oxygen isotope ${}^8\text{O}^{17}$ was formed. ${}^8\text{O}^{17}$ is stable and no further change occurred. The nuclear reaction is expressed as :



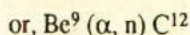
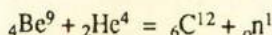
Notice that the sum of the atomic numbers 9 and the sum of the mass numbers 18, are the same, before and after the nuclear reaction. This reaction is conveniently abbreviated as,



which means " α -particle in" and "proton out" in a nuclear reaction involving nitrogen which is converted to oxygen isotope. This reaction was the first "artificial transmutation" as contrasted to "spontaneous transmutation" of elements in nature.

Interest in nuclear structure and the results of high-energy bombardments with projectiles led to the discovery of positron which is a particle similar to electron but with charge +1, by Anderson in 1932. This is designated as e^+ , ${}_{+1}e^0$

or β^+ . In the same year Chadwick discovered neutron, a neutral particle having nearly the same mass as proton by carrying out nuclear reaction :



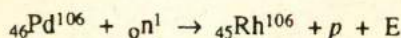
Energetics of Nuclear Reactions

Consider the nuclear reaction : $\text{N}^{14} (\alpha, \text{p}) \text{O}^{17}$

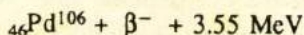
The sum of $\text{N}^{14} + \text{He}^4$ masses = 18.01141 mass units. The masses of $\text{O}^{17} + \text{H}^1 = 18.01262$ mass units. The difference of the mass units is 0.00121. An amount of energy equivalent to 0.00121 mass unit has to be supplied to make the reaction energetically feasible. Since 1 mass unit is equivalent to 931 MeV according to the Einstein's equation $E = mc^2$, the amount of energy $0.00121 \times 931 = 1.13$ MeV is required to carry out this nuclear reaction.

But it is not possible to carry out the reaction $\text{N}^{14} (\alpha, \text{p}) \text{O}^{17}$ by using α -particle having kinetic energy of 1.13 MeV. The collision between α -particle and N^{14} nucleus is subjected to the conservation of momentum for which 4/18 of kinetic energy of α -particle must be retained by the products. Thus only 14/18 of kinetic energy of α -particle is used for the reaction. But the kinetic energy of the α -particle just capable for carrying out the reaction $\text{N}^{14} (\alpha, \text{p}) \text{O}^{17}$ reaction must be = $18/14 \times 1.13 = 1.45$ MeV. However, the fraction of the kinetic energy of the projectile retained as the kinetic energy of the products becomes smaller with increasing mass of the target nucleus.

When the mass of the reacting nuclei are not known and if the product nucleus is radioactive disintegrating to the initial nucleus with known decay energy, it is possible to calculate the energy of a nuclear reaction. Thus the reaction



↓



The overall effect in the above reaction is the transformation of neutron into a proton and an electron.

Thus the energy of the nuclear reaction

$E = (1.00893 - 1.00812) \times 931 - 3.55 \text{ MeV} = 2.80 \text{ MeV}$ will be necessary.

Potential Barrier in Nuclear Reaction

Considering the nuclear reaction, ${}_7\text{N}^{14} (\alpha, p) {}_8\text{O}^{17}$ it is evident that the coulomb repulsion between the positively charged particles and the nitrogen nucleus creates the potential barrier for the nuclear reaction.

If the charge of the projectile is $Z_1 \cdot e$ and the charge of the target nucleus = $Z_2 \cdot e$, and if R_1 is the radius of the projectile particle and R_2 the radius of the target nucleus, the coulomb energy to bring these two particles in contact with each other.

$$V = \frac{Z_1 \cdot Z_2 \cdot e^2}{R_1 + R_2}$$

The energy of the α -particle must be greater than 3.4 MeV. Rutherford actually used α -particles of over 7 MeV to carry out the reaction. However, the probability of a lower energy particle of "tunnelling through the barrier" exists in accordance with the concept of quantum mechanical approach.

It is therefore visualized that in general it is much easier for neutrons to enter and leave nuclei as compared to the charged particles. Therefore, neutrons of very low energy are most conveniently used for carrying out the nuclear reactions. It is possible to control the energy of neutron to the desired level since neutrons have no charge.

Comparison between Nuclear and Chemical Reactions

1. Both the nuclear and chemical reactions are associated with the absorption and release of energy. In the chemical reaction the valence electrons only participate in the reactions, whereas nucleus are involved nuclear reactions.

2. The quantities of energy in the two types of reactions are vastly of different magnitude.

In chemical reactions the energy is expressed in terms of cal/mol or Kcal/mole or KJ/mole. But in the case of nuclear reactions it is generally expressed in terms of MeV.

3. Chemical reactions deals with macroscopic amounts of materials in the reactions.
4. Nuclear reactions are very rare and can be brought about by special equipment. Whereas chemical reactions is of common occurrence in nature and carried out for particular purposes which can be easily manipulated.

Nuclear Cross Section

The probability of a nuclear reaction is generally expressed in terms of "Cross Section" represented by σ . The cross section has the dimension of area. The reaction between a nucleus by a projectile which should be uncharged are mainly considered since charged projectiles has to overcome the potential barrier due to coulombic forces. The cross section for a nuclear reaction is expressed by the equation.

$$\sigma = \frac{N}{I.n.x}$$

10⁻²⁴ cm²

σ = Cross section for the nuclear reaction expressed in Cm^2 (unit is barn = 10^{-24}Cm^2)

N = Nature and number of nuclear reactions occurring in the target

I = Number of projectiles incident on the target nucleus

n = Number of target nuclei per Cm^3 of the target

x = Thickness of the target in Cm .

The thickness of the target material is an important factor which determines the nuclear cross section i. e. the probability of the nuclear reaction using neutron as the projectile. In most cases the reactions considered are (n, n) , (n, γ) , (n, p) and (n, α) reactions.

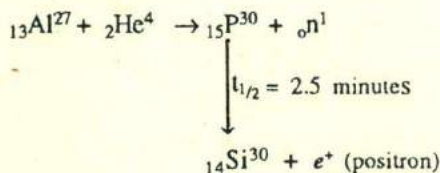
The number N of target nuclei is calculated from the relationship

$$N = \frac{\text{density of the target}}{\text{At. Wt. of the target}} \times 6,023 \times 10^{23}$$

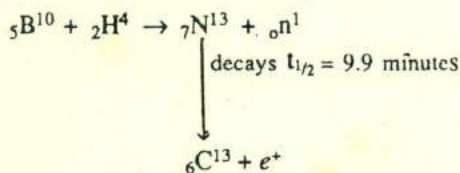
Thus in the case of $\text{Au}^{197} (n, \gamma) \text{Au}^{198}$ reaction if $x = 0.3 \text{ Cm}$ and 5 Cm^2 is the area exposed to thermal neutron flux of 10^7 per Cm^2 per sec., the capture cross section of Au^{197} is 95 barns.

Artificial Radioactivity

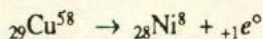
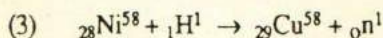
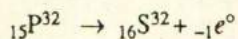
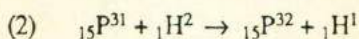
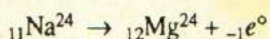
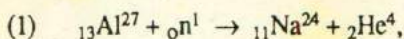
The first *artificial radioactivity* as distinguished from the natural radioactivity of uranium, thorium and actinium series was discovered by Joliot-Curie in 1934. High energy α -particle was used to bombard aluminium foils as a target. It was found that positrons were emitted and positron activity continued even after stopping the bombardment. The positron activity decreased according to the same disintegration law as the natural radioactivity. When the aluminium target was dissolved in dilute HCl, along with hydrogen PH_3 was also evolved and the solution on oxidation gave a precipitate of an insoluble phosphate. Both the evolution of PH_3 and the phosphate precipitate carried the radioactivity as an isotope of the phosphours :



Similarly, a boron target when bombarded with α -particle and dissolved in NaOH produced NH_3 gas which was radioactive due to the nuclear reaction forming radioactive isotope of nitrogen:



These experiments proved the existence of positrons. Other projectiles, other than α -particles such as protons, deuterons and neutrons also produced artificially induced radioactivity. In some cases electrons are produced :

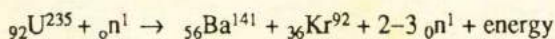


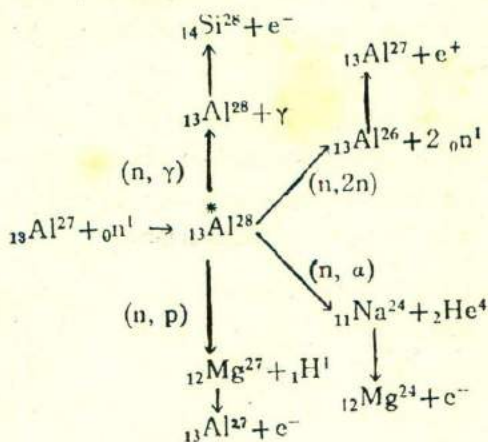
In nuclear reactions when radioactive products are formed by bombardment with high-energy particles, the process is generally known as *artificial radioactivity*.

α -particle is not the only projectile but a number of particles including atomic particles have been used as projectiles. Neutron, n, proton, p, deuteron, d, (hydrogen nucleus with mass of 2), are the most common projectiles in nuclear reactions.

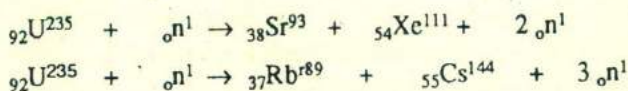
It may be noted that neutron being an electrically neutral particle is obviously more advantageous because it can penetrate into the nucleus of an atom easily. But very fast neutrons may just pass through the nucleus without any nuclear reaction. Hence neutrons of controlled energy are generally used to carry out nuclear reactions and depending upon the energy of the neutron projectile a number of different types of processes take place. Thus an aluminium target penetrated by a neutron forms a compound nucleus ${}_{13}\text{Al}^{28}$ which breaks off in a number of ways depending largely on its energy :

Nuclear Fission : A major discovery in nuclear reactions was made in 1936 by Otto Hahn and Strassman in Germany and Fermi in Italy who found that when uranium is used as a target for bombardment with thermal ("slow") neutrons, the uranium nucleus splits into two fragments. Such a process is called *nuclear fission*:





It is now known that uranium 235 undergoes fission in several different ways:



The products on the right hand side of the equation are known as *fission products*. Not only U^{235} but also Pu^{239} undergoes fission with slow neutrons. Th^{232} and U^{238} undergo fission when bombarded with high velocity neutrons.

In this type of reaction a loss of mass occurs which corresponds to the release of a fantastic quantity of energy in accordance with the equation $E = mc^2$. Weight for weight, uranium 235 will produce 2.5 million times energy than coal. On calculation energy released for such reaction are of the order of 200 MeV. Temperature rise is to the order of 10^7°C and the blast of visible, uv, x-ray, γ -rays radiation occur.

Nuclear Reactors : Neutrons are also among the fission products of nuclear reactions and thus it is possible to build an apparatus in which a self-sustaining nuclear chain reaction could occur. The apparatus is generally known as an *atomic reactor* or *pile* or *nuclear reactor*. The number of neutron build-up in the apparatus may take place so rapidly that the chain reaction may lead to the

explosive stage. The chain propagation can be controlled by means of substances called *moderators* such as graphite, heavy water or water which slow down the speed of neutrons and *neutron absorbers*, such as boron or cadmium rods which absorb neutrons.

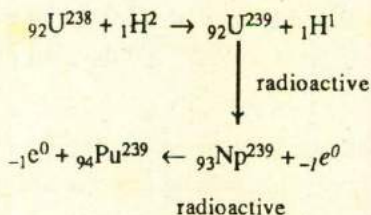
Pu^{239} is produced in the nuclear reactor by bombarding uranium rods with neutrons. It is uranium 238 which undergoes transmutation (see transuranium elements). Large quantity of cooling water is necessary to cool the reactor. Pu^{239} is separated from the uranium rods by chemical means.

Nuclear reactors are essentially sources of neutrons under controlled conditions. All types of atoms can be used for making both stable and radioactive isotopes, such as cobalt 60, phosphorus 32, sodium 24, carbon 14 etc.

Atomic Energy : The heat energy generated during the fission reaction in an atomic reactor may also be used to raise high pressure steam for turbines and to run dynamos for power production. The technological development of the use of atomic energy will undoubtedly make nuclear fission a prime source of energy in the near future. It is the heat energy which is produced during the nuclear reactions and is used to raise steam under pressure.

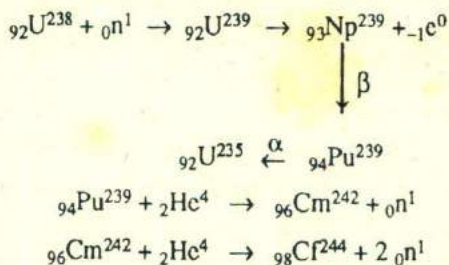
Transuranium Elements

A remarkable advancement in science was possible due to the nuclear reaction. Prior to 1940 uranium was the last element having atomic number 92; in 1940 McMillan and Abelson were able to make element 93, neptunium (Np), by bombarding uranium with high velocity deuterons i. e., with (d, p) reaction, Thus,



The elements, such as neptunium, Np, and plutonium, Pu, which were made artificially and which occur after uranium in the Periodic Table, are called

transuranium elements. Seaborg and his coworkers made a number of transuranium elements by new types of nuclear reactions. Thus:



The higher transuranium elements upto atomic number 105 have been made by various other nuclear reactions including the use of atomic particles as projectiles. These bombardment reactions, using such reactors as Van de Graff generators, *Cyclotron*, *Synchrotron*, *Betatron*, *Linear accelerators* etc. Fig. 26—5 gives an schematic diagram of a cyclotron generally used to accelerate protons and deuterons. The Van de Graff generators is used to build up huge voltage differences. The betatron is employed for obtaining high velocity electrons. The synchrotron and liner accelerator are used to produce charged particles of extremely high energies. In the cyclotron, as illustrated in Fig. 26—5, the ions produced at the source in the centre are accelerated between the "dees". Each "dee" between a high magnetic field becomes alternately charged positively, then negatively about 12 million times per second. The particles become greatly accelerated and after attaining very high energy (velocity), they leave the "dee" and strike the target to produce the desired nuclear reactions.

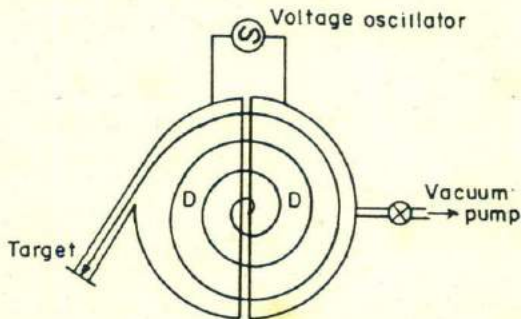
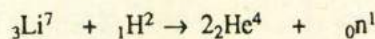
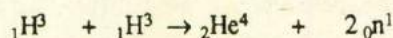
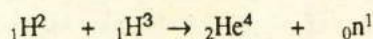


Fig. 26—5. Schematic diagram of a cyclotron for acceleration of charged particles.

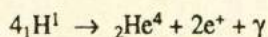
The Atomic Bomb : Although the theoretical aspects of the production of atomic bomb using uranium 235 and plutonium 239 involving nuclear fission and large energy evolution by the chain reaction appear to be simple, the technology is highly complex. In this connection the *critical mass* of the fissionable material is a necessary factor. Samples of uranium 235, less massive than the critical mass, will not explode. But a terrific explosion occurs if two or more pieces of U—235 or Pu—239 having a total mass equal to the critical mass are brought in contact with each other. A stray cosmic ray neutron is all that is necessary to trigger this nuclear chain reaction.

Nuclear Fusion (The Hydrogen Bomb) : Nuclear fusion involves reaction between two or more nuclei to produce new nuclei. Nuclear fusion involving the isotopes of hydrogen are specially exothermic because the packing fraction of a hydrogen nuclide is larger than that of any other nuclide. Examples of nuclear fusion reactions for use in hydrogen (thermonuclear) bombs are:



These reactions require very high energy to get started since they involve interaction between nuclides of like charges and comparable masses. The technology of hydrogen bomb is different from the nuclear fission bomb. There is no critical mass and no neutron is required to trigger the reaction. However, the high energy required may be derived from the nuclear fission for bringing about the nuclear fusion.

It is believed that solar energy is due to a series of nuclear fusion reactions taking place in the sun ultimately leading to the step-wise transformation from protium (${}_1\text{H}^1$) atoms to one He :



The two positrons encounter two electrons and all the four particles are annihilated releasing tremendous amount of energy.

Radioisotopes

There are about 280 stable naturally occurring isotopes, 73 natural radioisotopes and in addition about 1000 or more artificial radioisotopes which have been made and identified. All the isotopes of elements beyond bismuth, atomic number 93, are naturally radioactive.

Constitution of isotopes : Isotopes are elements occupying the same place in the Periodic Table which is based upon the atomic number of elements. Isotopes are, therefore, elements having the same atomic number but different mass numbers. The atomic number is the number of positive charges, i. e., the number of protons in the nucleus of the atom. It is also the number of extra-nuclear electrons in a neutral atom. The nucleus of an element, for all practical purposes, may be supposed to consist entirely of protons and neutrons. These together make up almost the entire mass of the atom.

An element must have fixed number of protons ; but the number of neutrons varies so that it is possible to have several kinds of nuclei of different weights. For instance, atoms having 6 protons exist in 5 different weights.

Carbon—10	6	protons	+	4	neutrons
C—11	6	"	+	5	"
C—12	6	"	+	6	"
C—13	6	"	+	7	"
C—14	6	"	+	8	"

Similarly, oxygen may have the following isotopes:

Oxygen —16	8	protons	+	8	neutrons
O—17	8	"	+	9	"
O—18	8	"	+	10	"

There are two important questions which arise :

(1) Why so many protons could be packed together within a nucleus ? The protons are expected to fly off from each other due to repulsion of positive charges.

(2) Why some isotopes are stable, whereas a large number of them are radioactive and undergo disintegration? Stable isotopes are those which do not emit any detectable radiations.

The answer to these questions are given in the considerations of nuclear stability.

Nuclear Structure and Nuclear Stability

Nuclear structure : The nuclei of elements, for all practical purposes, consist of protons and neutrons except the hydrogen nucleus which contains only one proton. Neutrons and protons together are called *nucleons*.

The protons and neutrons within a nucleus are held together by means of forces known as *Nuclear Forces*. Nuclear forces are at least millions of times greater than those which bind atoms in a molecule. These forces operate only at very close range and hence nuclear forces are short-range forces and the packing of the nuclear particles are so close that the density is 130 million tons/c.c. The radius of the nucleus varies from about 2×10^{-13} cm. for He to about 8×10^{-13} cm. for U.

The nuclear forces are quite different from the electrostatic and gravitational forces and in a nucleus they arise due to interaction between the proton and neutron. These are designated as :

proton—proton interaction	(p—p)
neutron—neutron interaction	(n—n)
proton—neutron interaction	(p—n)

When the number of protons is high as in the case of elements of higher atomic number, there is a sharp increase in the number of neutrons to hold the nucleus together. It is, therefore, assumed that neutrons must be at least partly responsible for the binding of nucleus. Thus the neutrons provide a sort of "*nuclear glue*" for the nucleus.

A number of theories have been advanced to explain the structure of the nucleus. It has been assumed that protons and neutrons are arranged in *nuclear energy levels* just as the electrons. It is also believed that the nuclear particles are held together by π -mesons. During the conversion of a proton to neutron or a

neutron to proton, π -mesons are produced and absorbed, and a nuclear particle called neutrino (ν) with almost zero mass and charge is released as a result of the exchange phenomenon. This question still remains essentially unanswered.

The liquid drop model of nucleus proposed by Bohr imagines the nucleus as consisting of neutrons and protons in a random manner like the molecules in a drop of liquid. This idea is supported by almost the same nuclear density of all the elements. The nuclear-shell model considers nuclear particles arranged in a systematic manner in different energy levels like the electrons. This is supported by the fact that Pauli Exclusion Principle is applicable on nuclear particles which have spin and momentum. Thus nuclei containing even number of nucleons of either kind are stable and plentiful and nuclei having the proton or neutron equal to the so-called *magic numbers*, 2, 8, 20, 28, 50, 82 and 126 are stable.

Nuclear Binding Energy

The nuclear binding energy is the energy released when two or more nuclear particles form a nucleus. Conversely, this is also the theoretical measure of the energy required to disrupt a nucleus into constituent parts.

The difference between the masses of the nucleus and the sum of the individual mass of the component parts (neutrons and protons) provide a measure of the energy that is liberated when the nucleus is built from its components.

Mass of each isotope is a whole number known as the *Mass Number*. The exact value of the mass of an atom is called the *atomic mass*.

In view of the fact that isotopic masses are whole numbers, they can not be exact multiples of the masses of neutron (1.00893) and proton (1.00758). For example, the helium nucleus contains 2 neutrons and 2 protons. The mass of helium nucleus is:

$$(2 \times 1.00759) + (2 \times 1.00897) = 4.03312$$

But the actual mass of helium nucleus is 4.00277. The difference between the expected mass and the actual mass is $4.03312 - 4.00277 = 0.03035$ mass unit. This difference between the actual mass of an atom and that expected from the mass of its components (neutrons and protons) is known as *Mass Defect*.

Thus, in the formation of a helium nucleus with two neutrons and two protons there is actually a loss of mass (0.03035 units). This mass defect principle is true for all the nuclei.

Mass-Energy Relationship

The loss of mass during the formation of an atom from its components is explained on the basis of Einstein's theory that such reactions involve change of mass into energy according to the equation, $E = mc^2$, where E is the energy, m stands for mass and c is the velocity of light. According to this equation it can be calculated that 1 g. of matter can liberate 2.15×10^{13} calories, or 9×10^{20} ergs or 931 million electron volts (MeV) of energy. Thus one atomic mass unit (a.m.u) is equivalent to 931MeV of energy. In the case of the formation of He nucleus by using 2 protons and 2 neutrons the mass defect is equal to 0.0304 a. m. u. This is equivalent to 6.5×10^{11} calories of heat or about 28 MeV of energy. (1 MeV = 1.6×10^{-6} erg).

Thus the breakdown or the formation of a stable nucleus from its component parts involves a very large amount of energy. The decrease in mass from that of the neutrons and the protons from which the nucleus may be considered to be formed is called the *Packing Effect*. The greater the loss of mass (Packing Effect), the more stable the nucleus. Thus the mass defect is actually a measure of the nuclear binding energy.

Neutron-Proton Ratio

Stability of atomic nuclei : The stability of the nucleus of an atom is related to the ratio of the number of neutrons to the number of protons in the nucleus. For lighter elements upto atomic number 20, the neutron to proton ratio (n/p) is close to 1. For stable isotopes of elements of higher atomic numbers the n/p ratio increases until it reaches 1.52 for bismuth (${}_{83}\text{Bi}^{200}$). After bismuth the excessive number of neutrons imparts instability to the nuclei which occur in nature. Hence all isotopes with atomic number greater than 83 are radioactive. For each stable nucleus there is an optimum range of n/p within which the isotopes of that nucleus will be stable. It is observed from the curve in Fig. 26—6 that the straight line corresponds to n/p ratio of those nuclei which would have equal number of neutrons and protons ($n = p$). The light

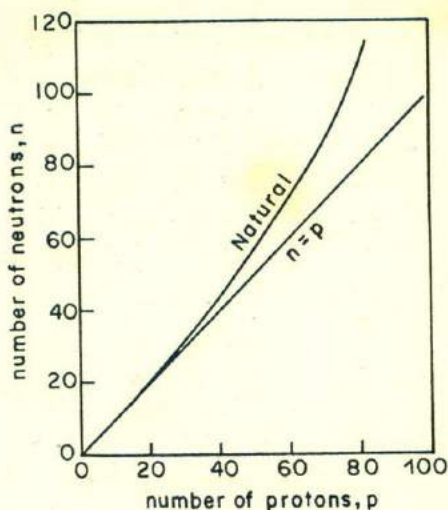
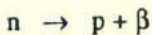


Fig 26—6. Neutron-proton ratio in nuclei of element.

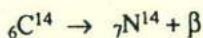
non-radioactive elements contain almost equal number of neutrons and protons as is seen from the lower portion of the curved line in the Fig. 26—6 which also shows that stable nuclei of heavier elements require more neutrons for stability.

Those nuclei having n/p ratios outside the natural stability curve are generally radioactive. In such cases, the n/p ratio is either too high or too low for stability and these have tendency to decay in order to adjust n/p ratio to more stable one by several ways :—

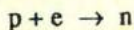
(i) The isotopes having too many neutrons will disintegrate by α - or β -emission. β -particles are formed within the nucleus due to the conversion of a neutron to proton :



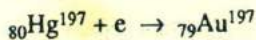
Thus



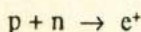
(ii) Alternatively the nucleus may capture an orbital electron (K-capture) to readjust excess proton which is converted to neutron by this process. This capture is always accompanied by emission of X-rays or γ -rays.



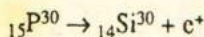
Thus



(iii) Decrease of positive charge on the nucleus may also be achieved by positron emission. This is observed in artificial radio isotopes only.

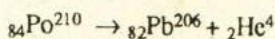


Thus

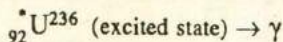


(iv) α -decay : (2p + 2n out from nucleus) = ${}_{2}\text{He}^4$

Thus



(v) γ -radiation : γ -rays are emitted due to energy changes within the nucleus when an excited nucleus drops down to a lower nuclear energy level. This is frequently accompanied during α , β or β^+ emission :



(vi) Neutron emission. Thus : ${}_{2}\text{He}^5 \rightarrow {}_{2}\text{He}^4 + {}_0n^1$

Isobars : Most elements have two or more isotopes. But we also come across with the nuclei of different elements which have the same mass number. Different elements that have the same mass numbers but different atomic numbers are called *Isobars*. The total number of neutrons and protons is the same but the number of protons is different. Thus the following elements are isobar pairs :

Cr	$24p + 30n =$	54 mass number
Fe	$26p + 28n =$	54 mass number
Cd	$48p + 68n =$	116 mass number
Sn	$50p + 66n =$	116 mass number

Methods of Separation of Isotopes

Separation of isotopes : By definition it can be seen that the isotopes of an element vary in mass but not in chemical properties. The only method which may be applied to isotopic separation depends on properties related to mass. It may be mentioned that separation of isotopes has now assumed a great importance from the practical point of view in the field of atomic energy where large quantities of fissionable materials, such as U^{235} , are required.

There are a number of methods for the separation of isotopes and only three methods are described.

The separation of isotopes depends mostly on physical properties related to mass. Thus in a gas composed of two isotopes of an element the average kinetic energy of the lighter isotope molecules and that of the heavier isotope molecules are the same. Therefore, the speed of the lighter molecules must be greater than that of the heavier molecules. Thus under the influence of external forces the lighter and heavier molecules can be made to move with different speed.

Similarly, isotopes of the same element may differ appreciably in their reactivities particularly in the case of lighter elements, such as H^1 and H^2 . This gives rise to variation in reaction rates of isotopic molecules. Based on this principle, chemical methods have also been devised for the separation of isotopes.

The various methods of separation of isotopes may be listed as follows.

1. The gaseous diffusion method ;
2. The electromagnetic method ;
3. The thermal diffusion method ;
4. The distillation method ;
5. The centrifugal method ;
6. The electrolytic method ;
7. The chemical exchange method.

Brief description of three methods are given :—

1. The gaseous-diffusion method : The rates of diffusion of different gases through a porous material are inversely proportional to the square roots of their densities at the same temperature. Thus two gases of different molecules having masses m_1 and m_2 will have velocities v_1 and v_2 . The kinetic energies of the two molecules are equal. Therefore,

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

$$\text{or} \quad \frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

which is Graham's Law of Diffusion.

Based on this principle, uranium isotopes, U^{238} and U^{235} , have been separated from the point of view of the importance of U^{235} which is a nuclear fuel. The compound used is UF_6 in the gaseous state containing $U^{238}F_6$ and $U^{235}F_6$ in the ratio of 99.3% and 0.7% respectively. After separation $U^{235}F_6$ is about 9% pure after passing through approximately 4000 diffusion stages.

2. *The electromagnetic method* : The principle of the electromagnetic separation of isotope is the same as the mass spectrograph in which isotopes of different masses when passed through a magnetic field separate into light and heavy particles. A sketch of the principle of electromagnetic separation is given in the Fig. 26—7. This method is now-a-days used to separate most of the isotopes throughout the Periodic Table mostly for the purpose of study and research. It is highly costly on commercial lines.

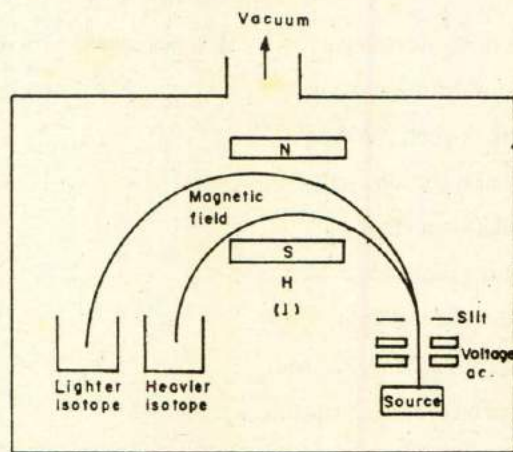


Fig. 26—7. Separation of isotopes by the electromagnetic method.

3. *The distillation method* : Separation of isotopes on the basis of their vapour pressure has been achieved in the case of mercury, deuterium (D_2O from H_2O) etc. The difference in vapour pressure arises due to different masses. Fig. 26—8 shows the arrangement for separation of mercury isotopes by partial vacuum between the walls of Dewar flask. The lighter isotopes are condensed at the bottom part of the inner flask cooled with liquid air.

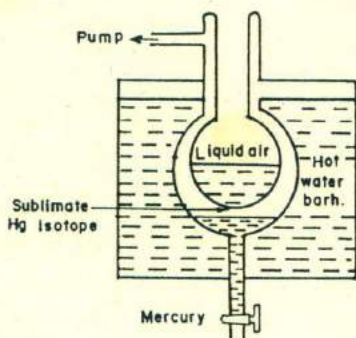


Fig. 26—8. Separation of Hg isotopes by distillation method.

Application of Radioisotopes

The characteristics of radioisotopes as displayed by its half-life and the type of radiation, make it possible for a wide range of utilization in industry, agriculture, biology and space research. The numerous fields where radioisotopes and even stable isotopes have been used are so vast that now-a-days it has given rise to a new branch of chemistry known as *Tracer Chemistry*. We shall focus upon a few instance of isolated fields of applications to illustrate this powerful technique developed in this modern time.

Techniques of applications : A number of techniques, such as isotope dilution and activation methods, have been developed for the application of isotopes. Some of the fields of application are given below as typical examples.

1. Mechanical applications : Radiation gauges have been developed for many industrial applications, such as production of linoleum, steel sheet, coated paper, plastic film, internal diameters of tubes etc. Thickness of a thin film strip of, say, aluminium or paper or plastic speeding through rollers can be measured by means of a radioisotope held below the film so that its radiation goes upward through the moving strip. A radioisotope is chosen for the job so that its radiations are substantially absorbed in the film. On the other side of the film, a detector head, such as a G. M. counter, is mounted to monitor the number of rays passing through the moving strip. The electronic output of the counter is a measure of the film thickness. Variations in counter output corres-

pond to changes in thickness. A signal advantage is that there is no mechanical contact with the moving film. The G. M. counter output can be coupled to drive mechanism of the rolling or coating machine. In this way the rolling or coating process can be subjected to automation to produce a uniform product.

2. Chemical analysis : Detection, identification and quantitative determinations of materials could be easily and advantageously carried out and could be applied where other methods simply fail. Besides analytical problems, both synthetic and reaction mechanism could be studied by using radioisotopes as "tags" to label chemical compound of extreme complexity in course of chemical reaction. Thus hydrolysis, saponification, rates of reactions and changes in structures of chemical species are advantageously investigated.

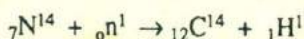
3. Radioisotopes in medicine : These are used for both diagnostic and therapeutic purposes. The application generally results from the fact that certain elements are preferentially absorbed by definite types of tissues. Destruction of cancerous tissues by cobalt—60 and natural radium is well-known. Phosphorus—32 has been used to control polycythemiavera, a condition where blood contains too many red corpuscles. The disease is located in the bone marrow. Iodine—131 is used for treatment of certain thyroid complaints. Functions of liver, mucous membrane and other vital organs of body have been studied.

4. Agricultural applications : The transportation of mineral nutrients from roots to leaves and subsequent redistribution within plants can be planned through the use of radioisotopes and radioautography. Improvement of irrigation feed water and fertilizers and their actions on the food crops have been made. Preservations of agricultural farm produce have been achieved, such as sprouting of potatoes has been prevented. Preservation of fish, meat and eggs could be done. Shelf life of perishable fruits and vegetables has been extended.

5. Industrial applications : The field of industrial applications of radioisotopes are varied and numerous. Measuring levels of liquid in closed tanks by floats containing radioisotopes, thickness of sheets, counting of tablets, pills and cigarettes in packets, functions of plasticizers in tyers and tubes, metallurgical operations producing special alloys etc. are some of them. Internal cracks can be located by radioautography. Mixing of ingredients in an industrial

product could be traced. Different grades of petroleum can be transmitted through the same pipe.

6. Measurement of time : Atomic clock which measures time by the actions of an electric current on cesium atom spinning in vacuum has an accuracy of one second in 3000 years. The age of the earth and the age of archaeological samples have been found by radiocarbon dating. The ratio of C^{14}/C^{12} is fixed in the atmosphere because of the continuous production of C^{14} by neutrons present in cosmic rays :



$C^{14}O_2$ and $C^{12}O_2$ both are taken up by living things and C^{14}/C^{12} ratio is the same as that in the atmosphere. But after death the living things does not absorb CO_2 and the C^{14} in the system begins to lose its activity. The half-life of C^{14} is 5770 years and the activity left in the system gives a measure of the date when it existed or first made. Even freshness of water and other materials can also be determined by the hydrogen isotope Tritium. Internally deposited radioisotopes are used as time markers which establish the date of origin of the product. Very small quantity of harmless radioisotopes are used for this purpose.

7. Biological applications : Tracer method by radioisotopes has been applied extensively in the field of biology and biochemistry and living things. For instance, the various biological and biochemical processes, such as transport of ions across cell membranes, metabolic interconversions, food and mineral metabolism and particularly the dynamics of the steady state in living beings have been explored to gain better understanding of living things. It has now been established that the entire structure of man changes to a new structure within the course of one year. This was possible by using calcium—44, a radioisotope of calcium. The natural phenomenon of photosynthesis has been studied with radioactive carbondioxide and it has been established that phosphoglyceric acid is the first stable compound produced by a plant in photosynthesis.

8. In forensic science : Radioisotopes help in tracking down the activities of counterfeiters who must necessarily draw upon certain commercial sources of ink, paper and other materials. Narcotic rings may be disrupted if their

sources of supply can be identified. An isotopic technique has been developed to trace drug samples back to their place of origin.

9. Isotope for power generation : Discs of strontium titanate are sealed inside a cylinder to isolate the radioactivity due to strontium—90, a hazardous radioisotope. Heat produced by the 17,500 curies of strontium—90 inside the cylinder is converted by means of thermoelectric elements into five watts of power which can run weather station and transmit atmospheric data.

10. Living molecules : Now-a-days extensive studies are being made to unravel the mystery of life and living molecules. Study of renewal rates of phosphatides and carbohydrates and the formation rate of desoxyribonucleic acid and ribonucleic acid (DNA and RNA) using phosphorus—32 and carbon—14 has revealed more mysteries of nature of living organisms and it appears probable that man would be able to create living molecules in future.

QUESTIONS AND PROBLEMS

1. Write notes on the following :—
 - (a) Half-life period of radioactive element ;
 - (b) Radioactive equilibrium ;
 - (c) Artificial radioactivity ;
 - (d) Packing fraction ;
 - (e) Half-life of a radioisotope ;
 - (f) Geiger counter ;
 - (g) Uses of radioisotopes.
2. What is radioactivity and how was it discovered? Describe the properties of radiation obtained from radium.
3. What do you understand by Isotopes and Isobars? By what methods can isotopes be identified ? Indicate the importance of isotopes.
4. How are isotopes detected ? Give an account of the basis of the method of separation of isotopes.
5. What are isotopes? How are the isotopes of an element identified ?

6. What is radioactivity ? Describe the properties of the radiation obtained from radium? What information has this knowledge contributed to the mechanism of radioactivity ?
7. Explain the following with illustrations :—
 - (a) Half-life of a radioelement ;
 - (b) Nuclear reaction.
8. Write a short note on radioactivity.
9. Write short notes on :—
 - (a) Isotopes ;
 - (b) Uses of radioisotopes ;
 - (c) properties of α , β and γ -rays.
10. Answer the following :—
 - (a) What are alpha particles? Describe some nuclear reactions that take place by bombardment with alpha particles. What other particles are utilized for nuclear reactions ?
 - (b) Explain, with illustrations, the term isotopes. Discuss briefly the principles underlying two methods of separation of isotopes.
11. Write a short note on discovery of radioactivity.
12.
 - (a) How will you detect and measure radioactivity?
 - (b) ${}_{13}\text{Al}^{27}$ on bombardment with alpha particles yields ${}_{15}\text{P}^{30}$ which is radioactive and emits a positron. Write the equations for the nuclear reactions involved.
13. What is the difference between natural and artificial radioactivity? Describe three types of artificial disintegration of atoms with suitable examples.
14. Write notes on :—
 - (a) Radioactivity, (b) Nuclear Reactions, (c) Heavy hydrogen, (d) Uses of Radioisotopes.
18. Write explanatory note on radioactivity equilibrium and Half-life of radioactivity.
19. The radioactive decay constant of radium is 1.36×10^{-11} . How many disintegrations per second occur in 100 g of radium.
20. How many α -particles per second would be emitted from 4×10^{-12} g of ${}^{210}\text{Po}$ ($t_{1/2} = 138$ days)?
21. 2.0 g of ${}^{33}\text{P}$ decays by β emission to 0.25 g in 75.9 days. Find the $(t_{1/2})$ of ${}^{33}\text{P}$.

CHAPTER 27

CHEMISTRY OF SOME RADIOACTIVE ELEMENTS

(Radium, Thorium, Uranium and Plutonium)

The chemistry of radioactive elements, natural or artificial, follows the pattern of the periodic relationship of the group of elements to which they belong. Apart from the special phenomenon of radioactivity, their chemistry is quite ordinary and is concerned almost entirely with the properties which depend upon the valence electrons. The phenomenon of radioactivity is connected with the nuclear structures but the chemistry is concerned with the electron arrangement of the outermost orbitals.

Radium

Radium is the last element of the alkaline earth family, group IIA, as has been mentioned before (page 372). It has almost identical physical and chemical properties with those of barium. In accordance with the gradation of group properties, the following points may be noted :—

- (i) Radium is the most reactive metal of group IIA.
- (ii) $\text{Ra}(\text{OH})_2$ is fairly soluble in water like $\text{Ba}(\text{OH})_2$ and the solution gives a strong base.
- (iii) RaSO_4 is insoluble in acids and ammonia like BaSO_4 .
- (iv) Ra-compounds are isomorphous with the corresponding compounds of Barium.

Discovery of Radium

With the help of a gold-leaf electroscope, which measures the extent of ionization produced by a radioactive substance, Madam Curie studied the residue

of the uranium ore, *pitchblende* (mostly U_3O_8), after the extraction of uranium. She found that a sample of the residue on concentration was more active than the same weight of a purified uranium salt. This indicated the presence of a more radioactive substance in the ore residue than uranium. In 1898 Madam Curie succeeded in isolating a very active substance in the form of bromide from a large quantity of pitchblende after a long and tedious process of extraction and fractional crystallization. This salt was a million times more active than the same salt of uranium. The salt isolated was radium bromide and thus the discovery of new radioactive element, radium, was announced.

Extraction of Radium

Sources : Pitchblende (mainly U_3O_8)

 Carnotite [mainly $K_2 [(UO_2)_2 (VO_4)_2 \cdot 8H_2O]$

 or $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot xH_2O$

The process of extraction depends upon the type of mineral. The precipitation of the insoluble sulphates and subsequent isolation of barium and radium are the main principles involved. A simple flow-sheet for the isolation of $RaCl_2$ is given on page 792.

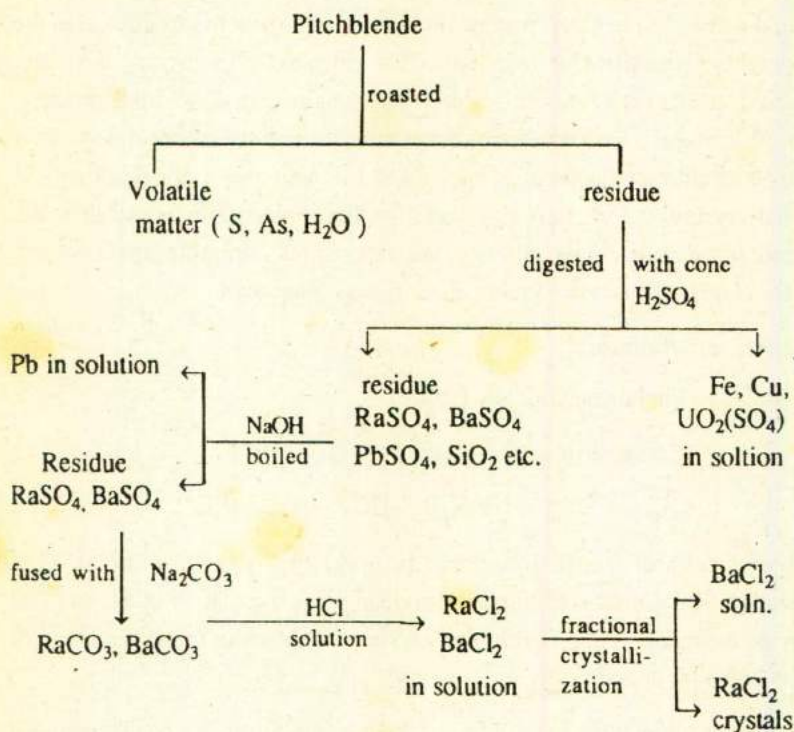
Metallic radium was first obtained by Madam Curie by electrolysing a solution of $RaCl_2$ with a Hg-cathode and platinum-iridium anode. Ra-amalgam obtained is distilled to remove mercury.

Properties of Ra : It is a white metal, rapidly tarnishes in air. It has similar physical and chemical properties as those of barium.

Ra metal reacts with water forming $Ra(OH)_2$ in solution and evolving hydrogen. It dissolves in dilute HCl giving $RaCl_2$. It also absorbs nitrogen forming nitride, Ra_3N_2 . It is the most reactive of all the alkaline earth elements.

$RaCl_2 \cdot 2H_2O$ is isomorphous with $BaCl_2 \cdot 2H_2O$ but less soluble in water than barium chloride. $RaSO_4$ is less soluble in water than $BaSO_4$. Ra-salts are obtained by the action of acid on $RaCO_3$.

Ra metal and all its compounds in any form are radioactive and disintegrate with half-life of 1590 years into radon ${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + He^4 + \text{energy}$. The



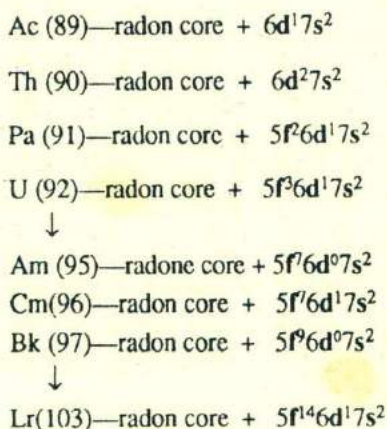
products of disintegration are both gases. The gases are obtained when a radium salt such as RaCl_2 , is dissolved in water and boiled. Radon and helium together with H_2 and O_2 (from the decomposition of H_2O) are evolved. The salts of Ra glow in the dark with green phosphorescence.

Uses : Ra-salts mixed with ZnS , fluorspar etc, are made into luminous paints. Radium is used in the treatment of cancer and malignant tumour.

THE ACTINIDE SERIES

In order to discuss the individual chemistry of thorium, uranium and plutonium from the modern stand point, it is necessary to mention that these three radioelements are members of a series of elements known as the *Actinide Series* (page 138). This series begins with Actinium, element 89, and extends upto Lawrencium, element 103. The series are analogous to the rare earth

elements known as the *Lanthanides*. The electronic configurations of the Actinide Series are built up in a similar manner as the lanthanides but electrons orbitals involved are 5f or 6d. The outer electron orbitals of some of the actinide elements are represented as follows :



Although there are some controversy regarding the electronic configurations but, in general, the chemistry of these elements follows the pattern of rare earths. These elements have characteristic valence of +3, but show much wider variations in oxidation states due to larger sizes of the atomic radii. Thorium resembles cerium in that it has a oxidation state of +4.

From element 93—103 (neptunium to lawrencium) the series is generally called as transuranium elements and are all made by artificial means (see page 774).

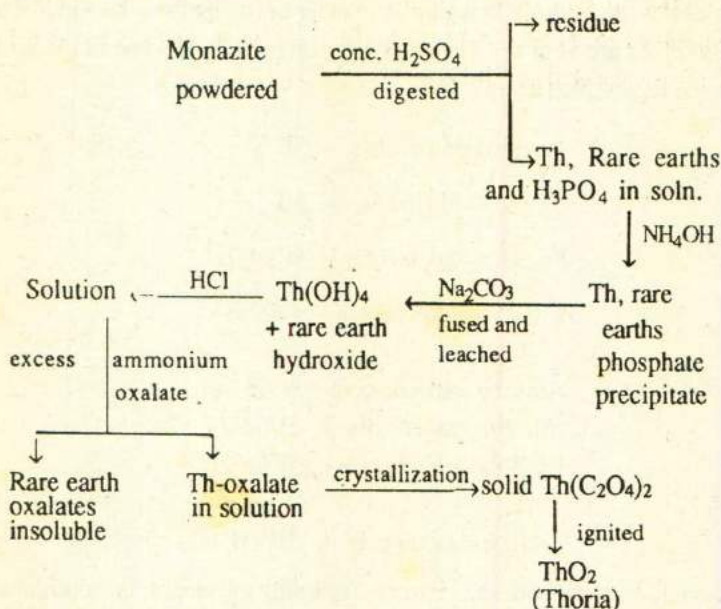
Thorium, uranium and plutonium are of great importance in this atomic age because of their use in the development of atomic energy both for war and peace.

Thorium

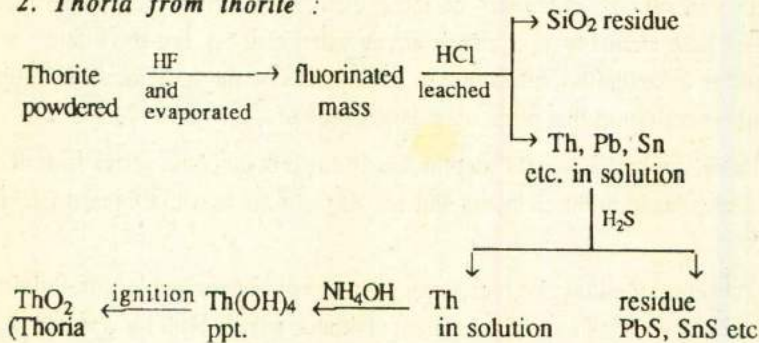
- Sources* : Thorite— ThSiO_4
 Monazite—Th, Ce, La etc. as phosphate
 Thorianite— $\text{ThO}_2 + \text{UO}_2$

Extraction : The following procedures are generally adopted to separate Th from other substances present in the mineral monazite and thorite :

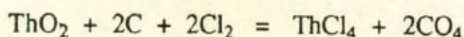
1. Thoria from monazite :



2. Thoria from thorite :



Other compounds of thorium, such as $\text{Th(NO}_3)_4$, $\text{Th(SO}_4)_2$, etc. may be obtained by dissolving Th(OH)_4 in the appropriate acids and crystallization. ThCl_4 is obtained by heating a mixture of ThO_2 and carbon in Cl_2 gas :



Metallic Th is obtained by reducing ThCl_4 with Na or K.

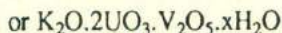
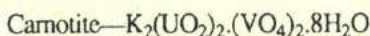
Thorium has very similar chemistry as that of the elements of group IVB (Ti, Hf, Zr). It has + 4 as the most common oxidation state. $\text{Th}(\text{OH})_4$ is much more basic and Th-salts are not appreciably hydrolysed in water.

Uses : Thoria, ThO_2 , mixed with CeO_2 , is used in the manufacture of gas mantles. Tungsten filaments in electric lamps are also given a coat of thoria to increase their efficiency. Recently thorium has acquired an strategic importance of its application in the field of atomic energy.

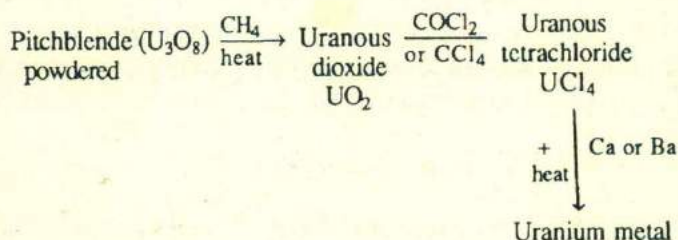
Uranium

Uranium was the first radioactive element to be discovered in pitchblende.

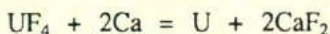
Sources : Pitchblende—(mainly U_3O_8) or (Uraninite)



Extraction of uranium : There are several methods for the processing of the uranium mineral and subsequent extraction of the metal which is of great importance in the atomic age as a nuclear fuel. One of the methods is based on the reduction of the mineral pitchblende (U_3O_8) to UO_2 by carbon or natural gas. UO_2 on chlorination with COCl_2 or CCl_4 gives UCl_4 which is reduced to metallic uranium by heating with Ca or Ba.



Uranium metal is also obtained by heating UF_4 with Mg or Ca :



Properties of uranium : Uranium metal has the appearance of nickel and is white to look at. It melts at 1850°C . It has a high density of about 19

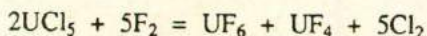
g/cm³. It occurs in several isotopes of which U²³⁸ and U²³⁵ are most abundant in nature.

Uranium is moderately active and reacts with halogens, sulphur, nitrogen and acids etc. It reacts with water slowly in the cold but rapidly on boiling. Alkali solutions have no action on uranium.

Compounds of uranium : Uranium shows oxidation states of +2, +3, +4, +5 and +6 but the most important oxidation states are +4 and +6. The chemistry of uranium follows the same pattern as the elements of group VIB (Cr, Mo, W). The +4 and +6 states are stable in aqueous solutions. UCl₃ and UCl₅ may be formed at high temperature but are unstable in water.

Uranyl compounds : The hexavalent uranium exists in acid solution as UO₂⁺² (uranyl ion) and many uranium salts, such as UO₂(NO₃)₂, UO₂(OOCCH₃)₂, UO₂SO₄, UO₂Cl₂ etc. are well-defined compounds. These compounds are also commonly called uranium salts. The processing of mineral U₃O₈ with conc H₂SO₄ and subsequent precipitation of uranium by NH₄OH or (NH₄)₂CO₃ give UO₂(OH)₂ or UO₂CO₃. These are the starting materials for all uranyl salts. Alternatively the oxides of uranium may be dissolved in HNO₃ to give uranium nitrate, UO₂(NO₃)₂. This on treatment with H₂SO₄ gives UO₂(SO₄).

Uranium hexafluoride, UF₆ : It is obtained as white crystals which sublimes at 57°C, by the action of excess of F₂ on heated metal. UF₆ is the most important halide of uranium. Mixed with UF₄ it is obtained by the action of F₂ on UCl₅. UF₄ being insoluble can be easily separated :



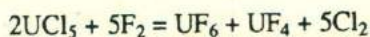
It has been used for the separation of U²³⁵ and U²³⁸ in the vapour condition because of the difference in molecular velocities of U²³⁵F₆ and U²³⁸F₆ in a gaseous diffusion apparatus.

Yellow oxide of uranium, Na₂U₂O₇·6H₂O : When pitchblende is roasted with Na₂CO₃ and the melt is extracted with H₂SO₄ it gives UO₂(SO₄) in solution. On adding alkali, such as NaOH solution, the precipitate obtained is

called uranium yellow (sodium uranate having the composition $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$). It is used for painting porcelain and manufacture of fluorescent glasses.

Uranous oxide, UO_2 : When U_3O_8 is strongly heated in hydrogen the black dioxide UO_2 containing U^{+4} is obtained. UO_2 is soluble in concentrated acid giving the green solution containing UO^{+2} ion. UO^{+2} ion is also formed by reduction of UO_2^{-2} ion with zinc amalgam or $\text{Sn} + \text{HCl}$. UO^{+2} ion can be titrated with KMnO_4 solution for the quantitative determination of uranium.

Uranium tetrahalides : UCl_4 is obtained as a green crystals when UO_2 or U_3O_8 mixed with carbon is heated with Cl_2 . It is soluble in water, alcohol and benzene. It is an intermediate in the preparation of uranium metal. UF_4 is obtained by the reaction of UCl_5 with F_2 or by adding a soluble fluoride to an uranium salt solution :



UF_4 is insoluble in water.

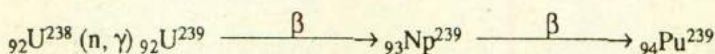
Zinc and Magnesium uranyl acetate : These are double acetates of zinc acetate or magnesium acetate with uranyl acetate and is made by mixing the two in acetic acid solution. The yellow solution produces a yellow precipitate with Na^+ ion and is used for its identification.

Uses : Uranium is a strategic metal and is of great importance in the production of nuclear power. Apart from the industrial applications of the uranium compounds, it is used for the production of plutonium and other transuranium elements. The isotope U^{235} undergoes nuclear fission reaction with neutron whereas U^{238} undergoes neutron capture giving the transuranium elements.

Plutonium

Plutonium (element 94) is a strategic metal and an important member of the transuranium elements. Trace amounts of neptunium, Np, and plutonium, Pu, occur in nature in uranium minerals due to the natural radioactivity of uranium isotope, 235.

Both Np^{239} and Pu^{239} are found in the uranium fuel of the nuclear reactor. Pu^{239} is formed by the nuclear reaction.



Isolation of Pu : The separation of Pu from the reactor fuel elements is a difficult task because of the recovery operations for the starting material (uranium) and hazards involved in handling of highly radioactive fission products and high toxicity of Pu itself. The uranium fuel element from the nuclear reactor is dissolved in HNO_3 and the solution containing uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, and Pu^{+4} is subjected to solvent extraction or precipitation or ion-exchange separation to isolate Pu from the fission products and uranium.

Metallic Pu : Metallic Pu is prepared by the same procedure as uranium. Reduction of PuF_6 with an alkali metal or Ba gives Pu metal at 1200°C . PuF_6 is a volatile solid and is less stable than UF_6 .

Compounds of Pu : Plutonium forms a number of compounds with variable oxidation states of +2, +4 and +6. Thus oxides, halides, oxyhalides, nitrates, etc. of Pu have been made. PuO_3 , PuCl_2 , PuF_2 , PuF_4 , PuF_6 , $\text{Pu}(\text{NO}_3)_4$ etc. are some examples. PuO_2^{+2} ion is less stable than uranyl, UO_2^{+2} , ion.

QUESTIONS AND PROBLEMS

1. Describe the preparation and uses of uranium tetrafluoride.
2. Write a short note on the chemistry of uranium.
3. Discuss the similarity of the chemistry of radium with that of other alkaline earth metals. How is radium extracted from pitchblende ?
4. Describe with a flow-sheet the extraction of thorium from monazite. Discuss the oxidation states of thorium.
5. Why is uranium so important in this age ? Describe a method for the extraction of uranium metal from pitchblende.
6. Write a short note on the uranyl compounds. What is the use of zinc uranyl acetate?
7. Discuss the oxidation states of Ra, Th, U, Np and Pu with respect to their electronic configurations.

8. Describe the preparation, properties and uses of uranium tetrafluoride.
9. Prove that half-life of radium could be calculated if the disintegration rate of radium is known. How the half-life is related to the average life.

SOME MODEL QUESTIONS AND PROBLEMS

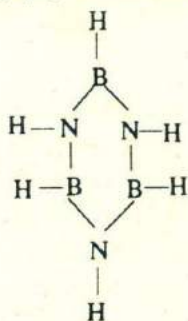
1. What are the maximum number of electrons in the following energy levels ?
 5d- 3f- 2s- 6f- 1p- 4p-
2. 6.02×10^{23} molecules of oxygen weigh 32 g., calculate the weight of one atom of oxygen.
3. What element can produce a species having no electron at all. Give its various names and symbols.
4. The value of Rydberg constant is $R = 190,500 \text{ cm}^{-1}$. Calculate the wavelength of the second line (H_{β}) in the visible region of the hydrogen spectrum.
5. Show diagrammatically that electrons are small negatively charged particles.
6. What is the difference in the nuclear structure of the two isotopes of the same element ?
7. How would you prove that matter consists of atoms ?
8. Helium consists of two isotopes having mass number 3 and 4. Indicate the atomic number, the number of protons, the number of neutrons and the nuclear charge for each of the isotopes.
9. Explain the presence of a large number of lines in the hydrogen spectrum although hydrogen contains only one electron.
10. How many valence electrons have carbon, silicon, phosphorus, hydrogen ? Write the electron configurations for neutral atom of each element.
11. Give the values of all four quantum numbers for each of the ten electrons of the neon atom.
12. Distinguish between the four general types of elements, and explain how their chemical properties differ.
13. How does the electron structure of atoms of metals differ from that of atoms of non-metals ?
14. From their positions in the Periodic Table predict the chemical properties of astatine and francium.
15. From the relative position of radium in the Periodic Table predict the solubilities of its hydroxide and sulphate.

16. Explain the small differences in the sizes of the atoms of Cu, Ag and Au and their ions as compared with the large differences in the sizes of the alkali metal atoms and their ions.
17. The atomic number of the mythical element centaurium (Ct) is 117. (a) Indicate the likely atomic structure. (b) In which family will it be found ?
18. Give brief explanations of the following :—
(a) LCAO, (b) Orbit and Orbital, (c) Radius-Ratio effect in ionic crystals, (g) Fajan's Rule.
19. Arrange the following bonds in order of their ability to distort negative ions :—
 Al^{+3} , Cs^+ , Cr^{+3} , Cr^{+6} , Rb^+ , Sr^{+2} , Xe .
20. Arrange the following bonds in order of increasing ionic character :
 Be—O , C—O , N—O , O—O , Si—O , Se—O . Indicate the Bond Order for each.
21. Predict the configuration of each of the following ions or molecules :
(a) BH_4^- , (b) NH_4^+ , (c) Br_3^- , (d) D_2Se , (e) $\text{Co}(\text{SCN})_6^{-3}$, (f) SiCl_4 , (g) $\text{Cr}(\text{NH}_3)_6^{+3}$ and (h) SbH_3 .
22. Write Lewis structure for each of the following ions and discuss about their properties :
 PO_4^{-3} , PO_3^{-3} , ClO_2^- , ClO_3^- , SO_3^{-2} , SeO_4^{-2} and IO_4^- ,
23. The molecular formula of some substances are given below. Discuss the types and nature of the chemical bonds between the respective atoms of the molecules. How the properties of the molecules are influenced by the bonds in these molecules ?
 H_2O , NH_3 , H_2SO_4 , MgO , AlCl_3 , $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, NH_4Cl , CO_2 ,
 SO_3 , NO_2 , SF_6 , KCl , HNO_3 , HF , H_2PO_3 , H_3PO_2 , H_2O_2 .
24. "HCl is a covalent compound but ionizes in water to produce H_3O^+ ion." Explain.
25. "Ionic compounds dissolve in polar liquid and covalent compounds dissolve in non-polar liquids." Is the above statement always true ? Discuss.
26. Why is sodium chloride a better conductor of electricity in a molten condition than in the solid state ?
27. What is the difference between a polar and a non-polar compound ?
28. Are all covalent compounds non-polar ? Explain.
29. Why would you expect ionic compounds normally to have higher melting points than covalent compounds ?
30. Why should you expect the melting point of NaCl to be much higher than that of AlCl_3 ?

31. Which compound should be more ionic, AlF_3 or AlCl_3 ? Give reasons for your answer.
32. Why do some elements have more than one ionization potential?
33. How can the electronegativities of the elements be used to predict what kind of bond will be formed when two elements combine? Illustrate your explanation with specific examples.
34. In general, the first ionization energies (energies required to remove one electron from the neutral atom I_1 increase as we go across the second period (see below). Why? However, boron and oxygen exhibit anomalous behaviour; their ionization energies are lower than expected. Examine the electronic configuration of these elements and suggest why:

	Li	Be	B	C	N	O	F	Ne
$I_1(\text{ev}) =$	5.4	9.3	8.3	11.3	14.5	13.6	17.6	21.6

35. Discuss the nature of bonding in the molecules H_2S , PH_3 , SiH_4 and P_2H_6 . Be specific about bond angles, number of σ and π bonds, lone pairs, type of hybridization and cores and bond orders.
36. The molecule CO_2 is linear with the carbon atom between the oxygens. Discuss with pictures the probable bonding in this molecule. Draw a classical line structure consistent with your model.
37. Suggest on the basis of orbital theory two possible geometric structures for the molecule P_4 . The four phosphorus atoms are equivalent.
38. The CO_3^{2-} ion is a planar one with the carbon atom in the centre of a triangle formed by the oxygens. Discuss the bonding in this molecules.
39. The molecule borazole, $\text{B}_2\text{N}_3\text{H}_6$, has the framework:



Discuss the bonding in this molecule.

40. Discuss reasons why the compound OF_6 has never been observed while SF_6 , in principle a member of the same family of compounds, is known.

41. What forces hold polar molecules together ? Explain their source and operation.
42. How is the polarity of a bond related to the electronegativities of the atoms which are held together by the bond ?
43. Account for the shape of the water molecule.
44. Explain the occurrence of the hydrogen bond in water and hydrogen fluoride.
45. Why would you expect H_2O to be more polar than H_2S ?
46. Discuss the properties of water in relation to the hydrogen bond.
47. Explain the wide difference between the boiling points of H_2S , and H_2O .
48. State the types of bonds which would be expected in crystals of (a) krypton, (b) ice, (c) carbon tetrachloride, (d) diamond, (e) copper, (f) magnesium nitrate, (g) potassium chloride and (h) hydrogen fluoride.
49. Explain why the boiling point of the inert gases increase with increase in atomic size.
50. KF reacts with HF to form a solid of formula, KHF_2 . Discuss the probable geometry and bonding in the HF_2^- ion.
51. The density of liquid water is considerably greater than that of solid water i.e. ice floats on water. Suggest an explanation in terms of hydrogen bonding and structure.
52. Discuss briefly the significant features in the properties and structures of the following pairs :—

(a) H_2O and H_2S	(b) AgF and AgCl
(c) NCl_5 and PCl_5	(d) SF_6 and UF_6
(e) CO_2 and SiO_2	(f) SnCl_4 and SiCl_4
(g) AlCl_3 and BCl_3	(h) Li_2CO_3 and MgCO_3
53. Explain the following observations :—
 - (a) Silver fluoride is colourless and soluble in water whereas silver iodide is coloured and insoluble.
 - (b) Water burns in fluorine, but not in oxygen.
 - (c) Hydrazine is suitable for rocket fuel.
 - (d) NCl_5 does not exist, whereas PCl_5 does.
 - (e) Zirconium and hafnium have almost identical properties.
 - (f) Liquid HCl does not conduct electricity whereas an aqueous solution of HCl is a good conductor.
 - (g) The transition metal ions are generally coloured.
 - (h) $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ is more stable than $\text{Co}(\text{NH}_3)_6\text{Cl}_2$.

54. The outermost orbitals of (i) He, (ii) alkaline earth metals, (iii) the transition metals, (iv) Zn, Cd and Hg, (v) the lanthanides and (vi) the actinides all have s^2 electrons in the outermost energy levels. Explain why their properties are vastly different.
55. Give reasons for the following :—
- Carbon, a non-metal, is a good conductor of electricity and is used as electrodes.
 - NF_3 is more stable than PCl_3 .
 - CuI_2 is unstable, $CuCl_2$ is stable.
 - AgF is colourless and soluble in water, AgI is coloured and insoluble.
 - CO_2 is a gas at ordinary temperature, SiO_2 is a solid of high melting point.
 - Cu is red, Ag is white and Au is yellow.
 - HNO_3 is a stronger acid than H_3PO_4 but H_3PO_4 has a higher boiling point than HNO_3 .
56. Mention the strengths of the following acids and arrange them in the increasing order of the strengths :
- $HClO$ H_2SO_4 HNO_3 H_4SiO_4 H_3PO_3 $HClO_4$
57. A pure ionic compound was placed in a tightly sealed flask and nearly all the air removed. After several weeks the gaseous phase in the flask was examined and an appreciable amount of helium found. Interpret this finding.
58. Write balanced nuclear reactions for the decay of :—
- Rn^{222} by α -emission.
- Cd^{115} by β -emission,
- Br^{75} by positron emission.
- Zn^{62} by K-capture.
59. Compare alpha, beta and gamma rays in terms of mass, charge and penetrating power.
60. Explain the conditions that exist in a radioactive equilibrium.
61. Explain why rates of radioactive disintegrations are given in terms of half-life periods.
62. An isotope of thorium, Th^{232} , undergoes a series of disintegration to form a stable isotope of lead, Pb^{208} , as an end product. How many alpha and beta particles are emitted in the total decay of one atom ?
63. The half-life of Fr^{221} is 4.8 min. Starting with 1 mg of the isotope, how much would remain after 30 min ?
64. Explain how the most abundant isotope of uranium, U^{238} , can be converted into plutonium.

65. It is said that plutonium—239 with a half-life of 24,000 years, is found in nature in minute traces. Account for this occurrence.
66. Explain the difference between nuclear fission and nuclear fusion.
67. Practically all artificial isotopes used in tracer investigation are beta emitters. Why should this be true ?
68. The half-life of sulphur 37 (beta emitter) is 5 min. If you were given 80 g. of the nuclide at 9 A. M. on a Monday morning, how much of it would you have at 10 A. M. the same morning ?
69. Write equations to represent the following nuclear transformation :—
(a) $\text{Be}^9 (\alpha, n)$; (b) $\text{K}^{39} (p, \alpha)$, (c) $\text{Na}^{23} (d, \alpha)$, (d) $\text{Bi}^{200} (d, n)$.
70. Suppose we have a few grams of RaSO_4 which is, of course, radioactive. Is the half-life of this material the same as the half-life of (radioactive) RaO ? Why, or why not ?
71. Prove that the Average life of a radioelement is equal to $1.34 \times$ half life time.
72. Calculate the time in which the radioactivity of a sample of thorium reduces to 90% of its activity. Given $t_{1/2}$ of Th = 1.4×10^{10} years.
73. Calculate the number of α - and β -particles emitted by ${}_{92}\text{U}^{238}$ when it changes to ${}_{82}\text{Pb}^{206}$.
74. How long it will take for 25% of the sample of Ac^{227} to disintegrate. Half-life of Ac^{227} is 22 years.
75. A piece of wood contained $\text{C}^{14}/\text{C}^{12}$ ratio = 0.7 of that in a living plant. Calculate the age of the wood "t". Half-life of C^{14} = 5760 year. Use the equation
- $$t = \frac{2.303 t_{1/2}}{0.693} \log \left[\frac{\text{C}^{14}/\text{C}^{12} \text{ ratio in the fresh wood}}{\text{C}^{14}/\text{C}^{12} \text{ ratio in the old piece of wood}} \right]$$
76. The ratio of $\text{C}^{14}/\text{C}^{12}$ in a piece of wood was found to be 13% of the atmosphere. Calculate the age of wood. Half life of C^{14} = 5700 year.
77. Complete the equation.
- (a) ${}_{92}\text{U}^{236} \longrightarrow {}_{90}\text{Th}^{234} + ?$
- (b) ${}_{11}\text{Na}^{24} \longrightarrow {}_{12}\text{Mg}^{24} + ?$
- (c) ${}_6\text{C}^{12} + {}_1\text{H}^1 \longrightarrow$
- (d) ${}_{17}\text{Cl}^{35} + {}_0\text{n}^1 \longrightarrow$