

Chapter 7 Nuclear Chemistry

"The branch of chemistry which deals with the study of composition of atomic nucleus and the nuclear transformations is known as nuclear chemistry".

The common examples of nuclear processes are radioactivity, artificial transmutations, nuclear fission and nuclear fusion. The nuclear is also an important aspect of chemistry because the energies involved in some of these are million times greater than those in ordinary chemical reactions.

Radioactivity

"Radioactivity is a process in which nuclei of certain elements undergo spontaneous disintegration without excitation by any external means." and the elements whose atoms disintegrate and emit radiations are called radioactive elements.

Henry Becquerel (1891) observed the spontaneous emission of invisible, penetrating rays from *potassium uranyl sulphate* $K_2UO_2(SO_4)_2$, which influenced photographic plate in dark and were able to produce luminosity in substances like ZnS.

Later on, *M.M. Curie and her husband P. Curie* named this phenomenon of spontaneous emission of penetrating rays as, **Radioactivity**.

Curies also discovered a new radioactive element *Radium* from *pitchblende* (an ore of *U i.e.* U_3O_8) which is about 3 million times more radioactive than uranium. Now a days about 42 radioactive elements are known.

The radioactivity may be broadly classified into two types,

(1) If a substance emits radiations by itself, it is said to possess *natural radioactivity*.

(2) If a substance starts emitting radiations on exposure to rays from some natural radioactive substance, the phenomenon is called *induced* or *artificial radioactivity*.

Radioactivity can be detected and measured by a number of devices like ionisation chamber, Geiger Muller counter, proportional counter, flow counter, end window counter, scintillation counter, Wilson cloud chamber, electroscope, etc.

Nature and characteristics of radioactive emissions

The phenomenon of radioactivity arises because of the decay of

unstable nuclei or certain element. The nature of the radiations emitted from a radioactive substance was investigated by *Rutherford* (1904) by

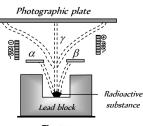


Fig. 7.1

applying electric and magnetic fields. When these radiation were subjected to electric or magnetic field, these were split into three types α , β and γ – rays.

Characteristics of radioactive rays					
Ø-Ray	β-Ray	γ-Ray			
<i>Charge and mass</i> : It carries +2 charge and 4 unit mass.	lt carries -1 charge and no mass.	It has no charge and negligible mass.			
<i>Identity</i> : Helium nuclei or helium ion $_2He^4$ or He^{2+} .	Electron $-1e^0$	High energy raditons.			
<i>Action of magnetic field</i> : Deflected towards the cathode.	Deflected to anode.	Not deflected.			
<i>Velocity</i> : 1/10 th to that of light.	Same as that of light.	Same as that of light.			
<i>lonizing power</i> : Very high nearly 100 times to that of β -rays.	Low nearly 100 times to that of γ -rays.	Very low.			
<i>Effect on ZnS plate</i> : They cause luminescence.	Very little effect.	Very little effect.			
Penetrating power : Low	100 times that of α -particles.	10 times that of β -particles.			
Range: Very small.	More than α -particles.	More			
Nature of product : Product obtained by the loss of 1 α - particle has atomic number less by 2 units and mass number less by 4 units.	Product obtained by the loss of 1 β -particle has atomic number more by 1 unit, without any change in mass number.	There is no change in the atomic number as well as in mass number.			

Theory of radioactivity disintegration

Rutherford and *Soddy*, in 1903, postulated that radioactivity is a nuclear phenomenon and all the radioactive changes are taking place in the nucleus of the atom. They presented an interpretation of the radioactive processes and the origin of radiations in the form of a theory known as **theory of radioactive disintegration**. The main points of this theory are,

 $\left(l\right)$ The atomic nuclei of the radioactive elements are unstable and liable to disintegrate any moment.

(2) The disintegration is spontaneous, *i.e.*, constantly breaking. The rate of breaking is not affected by external factors like temperature, pressure, chemical combination etc.

FSCORER 260 Nuclear Chemistry

(3) During disintegration, atoms of new elements called daughter elements having different physical and chemical properties than the parent elements come into existence.

 $\left(4\right)$ During disintegration, either alpha or beta particles are emitted from the nucleus.

The disintegration process may proceed in one of the following two ways,

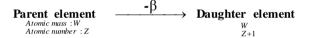
(i) α -particle emission : When an α -particle ($_2He^4$) is emitted from the nucleus of an atom of the parent element, the nucleus of the new element, called daughter element possesses atomic mass or atomic mass number less by four units and nuclear charge or atomic number less by 2 units because α -particle has mass of 4 units and nuclear charge of two units.

Parent element	$\xrightarrow{-\alpha}$	Daughter element
Atomic mass :W Atomic number :Z		W-4 Z-2

(ii) **\beta-particle emission** : β -particle is merely an electron which has negligible mass. Whenever a beta particle is emitted from the nucleus of a radioactive atom, the nucleus of the new element formed possesses the same atomic mass but nuclear charge or atomic number is increased by 1 unit than the parent element. Beta particle emission is due to the result of

decay of neutron into proton and electron. $_{0}n^{1} \rightarrow _{1}p^{1} + _{_{-1}}e^{0}$

The electron produced escapes as a beta-particle-leaving proton in the nucleus.



(iii) γ -ray emission : γ -rays are emitted due to secondary effects. The excess of energy is released in the form of γ -rays. Thus γ -rays arise from energy re-arrangements in the nucleus. As γ -rays are short wavelength electromagnetic radiations with no charge and no mass, their emission from a radioactive element does not produce new element.

Special case : If in a radioactive transformation 1 alpha and 2 betaparticles are emitted, the resulting nucleus possesses the same atomic number but atomic mass is less by 4 units. A radioactive transformation of this type always produces an isotope of the parent element.

$${}_{Z}A^{W} \xrightarrow{-\alpha} {}_{Z-2}B^{W-4} \xrightarrow{-\beta} {}_{Z-1}C^{W-4} \xrightarrow{-\beta} {}_{Z}D^{W-4}$$

A and D are isotopes.

Group displacement law

Soddy, Fajans and Russell (1911-1913) observed that when an α -particle is lost, a new element with atomic number less by 2 and mass number less by 4 is formed. Similarly, when β -particle is lost, new element with atomic number greater by 1 is obtained. The element emitting then α or β -particle is called *parent element* and the new element formed is called *daughter element*. The above results have been summarized as,

(1) When an α -particle is emitted, the new element formed is displaced two positions to the **left** in the periodic table than that of the parent element (*because the atomic number decreases by 2*).

(2) When a β -particle is emitted, the new element formed is displaced one position to the **right** in the periodic table than that of the parent element (*because atomic number increased by i*).

(3) When a positron is emitted, the daughter element occupies its position one group to the left of the parent element in periodic table.

Group displacement law should be applied with great care especially in the case of elements of lanthanide series (57 to 71), actinide series (89 to 103), VIII group (26 to 28; 44 to 46; 76 to 78), IA and IIA groups. To determine the number of α - and β - particles emitted during the nuclear transformation. It can be done in following manner, ${}_{c}^{a}X \rightarrow {}_{d}^{b}Y + x {}_{2}^{4}He + y {}_{-1}e^{0}$

$$= b + 4x$$
 or $x = \frac{a-b}{4}$ (i)

$$c = d + 2x - y \qquad \qquad \dots \dots (ii)$$

where x = no. of α -emitted, y = no. of β -emitted

$$c = a + \left(\frac{1}{4}\right)^2 - y ; y = a + \left[\frac{1}{2}\right]^{-1}$$

a

Radioactive disintegration series

The phenomenon of natural radioactivity continues till stable nuclei are formed. All the nuclei from the initial element to the final stable element constitute a series known as disintegration series. Further we know that mass numbers change only when α -particles are emitted (and not when β -particles are emitted) causing the change in mass of 4 units at each step. Hence the mass numbers of all elements in a series will fit into one of the formulae. 4n, 4n+1, 4n+2 and 4n+3, hence there can be only four disintegration series.

	4 <i>n</i>	4 <i>n</i> + 1	4 <i>n</i> + 2	4 <i>n</i> + 3
п	58	59	59	58
Parent element	$_{90} Th^{232}$	$_{94} Pu^{241}$	$_{92}U^{238}$	$_{92}U^{235}$
Half life (yrs)	1.39 × 10 ¹⁰	10	4.5×10^{9}	7.07×10^8
Half life (yrs)	1.39 × 10 ¹⁰	2.2×10^{6}	4.5×10^{9}	13.5
Name of series	Thorium (Natural)	Neptunium (Artificial)	Uranium (Natural)	Actinium (Natural)
End product	$_{82}Pb^{208}$	$_{83} Bi^{209}$	$_{82}Pb^{206}$	$_{82} Pb^{207}$
п	52	52	51	51
Number of lost particles	$\alpha = 6$ $\beta = 4$	$\alpha = 8$ $\beta = 5$	$\alpha = 8$ $\beta = 6$	$\alpha = 7$ $\beta = 4$

Nuclear structure and Nuclear forces

According to an earlier hypothesis, the nucleus is considered as being composed of two building blocks, proton's and neutron's, which are collectively called **nucleons**. The *forces, which hold the nucleons together* means stronger proton – proton, neutron – neutron and even proton – neutron attractive forces, exist in the nucleus. These attractive forces are called nuclear forces. Nuclear forces operate only within small distance of about $1 \times 10^{-15} m$ or 1 fermi (1 fermi = $10^{-13} cm$) and drops rapidly to zero at a distance of $1 \times 10^{-13} cm$. These are referred to as short range forces. Nuclear forces are nearly 10^{21} times stronger than electrostatic forces.

Yukawa in 1935, put forward a postulate that neutrons and protons are held together by very rapid exchange of nuclear particles called *Pimesons* (π -*mesons have mass equal to 275 times of the mass of an electron and a charge equal to +1, 0 or -1. These are designated as* π π *and* π *respectively*). The nuclear force which is used in rapid exchange of *Pi*mesons between nucleons are also called *exchange forces*.

The binding forces between unlike nucleons (*p* and *n*) are explained by the oscillation of a charged π -meson (π or π^-)

(a)
$$p_1 + n_2 = n_1 + \pi^+ + n_2 = n_1 + p_2$$

(b) $p_1 + n_2 \rightleftharpoons n_1 + \pi^- + p_2 \rightleftharpoons n_1 + p_2$

Binding forces between like nucleons (p - p or n - n) result from the exchange of neutral mesons (π) as represented below.

(a)
$$p_1 \rightleftharpoons p_2 + \pi^0 \text{ or } p_1 + \pi^0 \rightleftharpoons p_2$$

(b) $n_1 \rightleftharpoons n_2 + \pi^0 \text{ or } n_1 + \pi^0 \rightleftharpoons n_2$

Nuclear stability

Nuclides can be grouped on the basis of nuclear stability, i.e. stable and unstable nucleus. The most acceptable theory about the atomic nuclear stability is based upon the fact that the observed atomic mass of all known isotopes (except hydrogen) is always less from the sum of the weights of protons and neutrons present in it. Electron (β - particle) from a radioactive nucleus may be regarded as derived from a neutron in the following way,

Neutron \rightarrow Proton + Electron

Similarly, photons are produced from internal stresses within the nucleus.

The stability of nucleus may be discussed in terms of any one of the following,

(1) Nuclear Binding Energy and Mass defect : It is observed that atomic mass of all nuclei (except hydrogen) is different from the sum of masses of protons and neutrons. The difference is termed *mass defect*.

Mass defect = Total mass of nucleons - obs. atomic mass

The mass defect is converted into energy. This energy is called the *binding energy*. This is the energy required to break the nucleus into is constituents (p and n).

Binding energy = Mass defect $\times 931 MeV$

The stability of the nucleus is explained on the value of binding energy per nucleon and not on the basis of total binding energy. Binding energy per nucleon is maximum (8.7 MeV) in the case of iron (56). The value of binding energy per nucleon can be increased either by fusion of lighter nuclei or fission of heavier nuclei.

Value of binding energy predicts the relative stability of the different isotopes of an element. If the value of binding energy is negative, the product nucleus or nuclei will be less stable than the reactant nucleus. Thus the relative stability of the different isotopes of an element can be predicted by the values of binding energy for each successive addition of one neutron to the nucleus.

$${}_{2}He^{3} + {}_{0}n^{1} \longrightarrow {}_{2}He^{4} + 20.5MeV$$
$${}_{2}He^{4} + {}_{0}n^{1} \longrightarrow {}_{2}He^{5} - 0.8MeV$$

Therefore, $_2He^4$ is more stable than $_2He^3$ and $_2He^5$.

(2) **Packing fraction :** The difference of actual isotopic mass and the mass number in terms of packing fraction is defined as,

$$Packing fraction = \frac{Actualisotopicmass - Mass number}{Mass number} \times 10^4$$

The value of packing fraction depends upon the manner of packing of the nucleons with in the nucleus. Its value can be negative, positive or even zero. A negative packing fraction generally indicates stability of the nucleus.

In general, lower the packing fraction, greater is the binding energy per nucleon and hence greater is the stability. *The relatively low packing fraction of He, C and O implies their exceptional stability, packing fraction is least for Fe (negative) and highest for H* (+78).

(3) Magic number : Nucleus of atom, like extra-nuclear electrons, also has definite energy levels (shells).

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons have been found to be particularly stable with a large number of isotopes. These numbers, commonly known as *Magic numbers* are defined as the number of

Nuclear Chemistry 261 SE

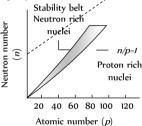
nucleons required for completion of the energy levels of the nucleus. Nucleons are arranged in shells as two protons or two neutrons (with paired spins) just like electrons arranged in the extra-nuclear part. Thus the following nuclei $_{2}He^{4}$, $_{8}O^{16}$, $_{20}Ca^{40}$ and $_{82}Pb^{208}$ containing protons 2, 8, 20 and 82 respectively (all magic numbers) and neutrons 2, 8, 20 and 126 respectively (all magic numbers) are the most stable.

Magic numbers for protons : 2, 8, 20, 28, 50, 82,114

Magic numbers for neutrons : 2, 8, 20, 28, 50, 126, 184, 196

When both the number of protons and number of neutrons are magic numbers, the nucleus is very stable. That is why most of the radioactive disintegration series terminate into stable isotope of lead (magic number for proton = 82, magic number for neutron = 126). Nuclei with nucleons just above the magic numbers are less stable and hence these may emit some particles to attain magic numbers.

(4) **Neutron-proton ratio or causes of radioactivity** It has been found that the stability of nucleus depends upon the neutron to proton ratio (n/p). If we plot the number of neutrons against number of protons for nuclei of various elements, it has been observed that most of the stable (non-radioactive) nuclei lie in a belt shown by shaded region in figure this is called **stability belt** or **stability zone**. The nuclei whose n/p ratio does not lie in the belt are unstable and undergo spontaneous radioactive disintegration.



It has been observed that,

(i) n/p ratio for stable nuclei lies quite close to unity for elements with low atomic numbers (20 or less) but it is more than one for nuclei having higher atomic numbers. Nuclei having n/p ratio either very high or low undergo nuclear transformation.

(ii) When n/p ratio is higher than required for stability, the nuclei have the tendency to emit β – rays *i.e.*, a neutron is converted into a proton.

(iii) When n/p ratio is lower than required for stability, the nuclei increase the ratio, either by emitting α – particle or by emitting a position or by *K*-electron capture.

Rate of radioactive decay

"According to the law of radioactive decay, the quantity of a radioelement which disappears in unit time (rate of disintegration) is directly proportional to the amount present."

The law of radioactive decay may also be expressed mathematically.

Suppose N be the number of atoms of the radioactive element present at the commencement of observation, t = 0 and after time t, the number of atoms remaining unchanged is N_t . The rate of disintegration

$$\left(-\frac{dN_t}{dt}\right)$$
 at any time *t* is directly proportional to *N*. Then, $-\frac{dN_t}{dt} = \lambda N$

where λ is a radioactive constant or decay constant. Various forms of equation for radioactive decay are,

$$N_t = N_0 e^{-\lambda t}; \log N_0 - \log N_t = 0.4343 \lambda t$$

$$N_0 = \lambda t = 2.303 \quad N_0$$

$$\log \frac{N_0}{N_t} = \frac{\lambda t}{2.303}; \ \lambda = \frac{2.303}{t} \log \frac{N_0}{N_t}$$

F SCORER 262 Nuclear Chemistry

This equation is similar to that of first order reaction, hence we can say that radioactive disintegration are examples of first order reactions. However, unlike first order rate constant (K), the decay constant (λ) is independent of temperature.

Rate of decay of nuclide is **independent** of temperature, so its energy of activation is zero.

(1) **Half-life period (7 or t)**: The half-life period of a radioelement is defined, as the time required by a given amount of the element to decay to one-half of its initial value.

$$t_{1/2} = \frac{0.693}{\lambda}$$

Now since λ is a constant, we can conclude that half-life period of a particular radioelement is independent of the amount of the radioelement. In other words, whatever might be the amount of the radioactive element present at a time, it will always decompose to its half at the end of one half-life period.

Let the initial amount of a radioactive substance be N_0

Amount of radioactive substance left after n half-life periods

$$N = \left(\frac{1}{2}\right)^n N_0$$

Total time $T = n \times t_{1/2}$ where *n* is a whole number.

(2) Average-life period (7) : Since total decay period of any element is infinity, it is meaningless to use the term total decay period (total life period) for radioelements. Thus the term **average life** is used.

Average life $(T) = \frac{\text{Sum of livesofthe nuclei}}{\text{Total number of nuclei}}$

Average life (T) of an element is the inverse of its decay constant,

i.e., $T = \frac{1}{\lambda}$, Substituting the value of λ in the above equation,

$$T = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

Thus, Average life (7) = $1.44 \times \text{Halflife}(T_{1/2}) = \sqrt{2} \times t_{1/2}$

Thus, the average life period of a radioisotope is approximately under-root two times of its half life period.

(3) Activity of population or specific activity : It is the measure of radioactivity of a radioactive substance. It is defined as ' the number of radioactive nuclei, which decay per second per gram of radioactive isotope.' Mathematically, if 'm' is the mass of radioactive isotope, then

Specific activity =
$$\frac{\text{Rate of decay}}{m} = \frac{\lambda N}{m} = \lambda \times \frac{\text{Avogadro number}}{\text{Atomic mass in } g}$$

where ${\it N}$ is the number of radioactive nuclei which undergoes disintegration.

(4) **Radioactive equilibrium :** Suppose a radioactive element A disintegrates to form another radioactive element B which in turn disintegrates to still another element C.

$$A \longrightarrow B \longrightarrow C$$

B is said to be in radioactive equilibrium with A if its rate of formation from A is equal to its rate of decay into C.

It is important to note that the term equilibrium is used for reversible reactions but the radioactive reactions are irreversible, hence it is preferred to say that B is in a steady state rather than in equilibrium state.

At a steady state,
$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{T_A}{T_B} = \frac{(t_{1/2})_A}{(t_{1/2})_B}$$

Thus at a steady state (at radioactive equilibrium), the amounts (number of atoms) of the different radioelements present in the reaction series are inversely proportional to their radioactive constants or directly proportional to their half-life and also average life periods.

(5) **Units of radioactivity**: The standard unit in radioactivity is curie (*c*) which is defined as that amount of any radioactive material which gives 3.7×10^{10} disintegration's per second (*dps*), *i.e.*,1*c* = Activity of 1*g* of $Ra^{226} = 3.7 \times 10^{10} dps$

The millicurie (*mc*) and microcurie (μc) are equal to 10^{-3} and 10^{-6} curies *i.e.* 3.7×10^{7} and 3.7×10^{4} *dps* respectively.

$$1c = 10^{3}mc = 10^{6}\mu c; 1c = 3.7 \times 10^{10} dps$$
$$1mc = 3.7 \times 10^{7} dps; 1\mu c = 3.7 \times 10^{4} dps$$

But now a day, the unit curie is replaced by rutherford (rd) which is defined as the amount of a radioactive substance which undergoes $10^6 dps$. *i.e.*, $1rd = 10^6 dps$. The *millicurie* and *microcurie* correspondingly rutherford units are *millirutherford* (*mrd*) and *microrutherford* (μrd) respectively.

$$1c = 3.7 \times 10^{10} \, dps = 37 \times 10^3 \, rd$$

$$1mc = 3.7 \times 10^7 \, dps = 37 \, rd$$

 $1 \mu c = 3.7 \times 10^4 dps = 37 mrd$

However, in SI system the unit of radioactivity is **Becquerel** (Bq)

1
$$Bq$$
 = 1 disintegration per second = 1 dps = 1 μrd ,
10⁶ Ba = 1 rd , 3.7 × 10¹⁰ Ba = 1 c

(6) The Geiger-Nuttal relationship : It gives the relationship between decay constant of an α - radioactive substance and the range of the α -particle emitted.

$$\log \lambda = A + B \log R$$

Where *R* is the range or the distance which an α -particle travels from source before it ceases to have ionizing power. *A* is a constant which varies from one series to another and *B* is a constant for all series. It is obvious that the greater the value of λ the greater the range of the α particle.

Artificial transmutation of elements

The conversion of one element into another by artificial means, *i.e.*, by means of bombarding with some fundamental particles, is known as artificial transmutation. The phenomenon was first applied on nitrogen whose nucleus was bombarded with α -particles to produce oxygen.

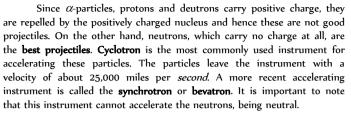
$$_7N^{14} + _2He^4 \rightarrow _8O^{17} + _1H^1$$

Nitrogen isotope Alpha particle Oxygen isotope Proton

The element, which is produced, shows radioactivity, the phenomenon is known as *Induced radioactivity*. The fundamental particles which have been used in the bombardment of different elements are,

$$\alpha$$
-particle : $_{2}He^{4}$; Proton : $_{1}H^{1}$
Deutron : $_{1}H^{2}$ or $_{1}D^{2}$; Neutron : $_{0}n^{1}$

Nuclear Chemistry 263



When a target element is bombarded with neutrons, product depends upon the speed of neutrons. **Slow neutrons** penetrate the nucleus while a **high-speed neutron passes through the nucleus**.

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239}; {}_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{237} + {}_{0}n^{1}$$

Thus slow neutrons, also called **thermal neutrons** are more effective in producing nuclear reactions than high-speed neutrons.

Alchemy : The process of transforming one element into other is known as alchemy and the person involved in such experiments is called alchemist. Although, gold can be prepared from lead by alchemy, the gold obtained is radioactive and costs very high than natural gold.

(i) Transmutation by a menticles

(i) Transmutation by departicles
(a)
$$\alpha$$
, n type
 $_{4}Be^{9}(\alpha,n)_{6}C^{12}$ i.e. $_{4}Be^{9} + _{2}He^{4} \rightarrow _{6}C^{12} + _{0}n^{1}$
 $_{94}Pu^{239}(\alpha,n)_{96}Cm^{242}$ i.e. $_{94}Pu^{239} + _{2}He^{4} \rightarrow _{94}Cm^{242} + _{0}n^{1}$
(b) α , p type
 $_{9}F^{19}(\alpha,p)_{10}Ne^{22}$ i.e. $_{9}F^{19} + _{2}He^{4} \rightarrow _{10}Ne^{22} + _{1}H^{1}$
 $_{7}N^{14}(\alpha,p) = 0^{17}$ i.e. $_{7}N^{14} + _{2}He^{4} \rightarrow _{29}Cu^{63} + _{-1}e^{0}$
(ii) Transmutation by protons
(a) p, n type
 $_{26}Fe^{59}(\alpha,\beta)_{29}Cu^{63}$ i.e. $_{26}Fe^{59} + _{2}He^{4} \rightarrow _{29}Cu^{63} + _{-1}e^{0}$
(ii) Transmutation by protons
(a) p, n type
 $_{6}C^{12}(p,\gamma)_{7}N^{13}$ i.e. $_{6}C^{12} + _{1}H^{1} \rightarrow _{16}S^{31} + _{0}n^{1}$
(b) p, γ type
 $_{6}C^{12}(p,\gamma)_{7}N^{13}$ i.e. $_{6}C^{12} + _{1}H^{1} \rightarrow _{7}N^{13} + _{2}He^{4}$
(c) p, d type
 $_{4}Be^{9}(p,d)_{4}Be^{8}$ i.e., $_{4}Be^{9} + _{1}H^{1} \rightarrow _{4}Be^{8} + _{1}H^{2}$
(d) p, α type
 $_{8}O^{16}(p,\alpha)_{7}N^{31}$ i.e. $_{8}O^{16} + _{1}H^{1} \rightarrow _{7}N^{13} + _{2}He^{4}$
(iii) Transmutation by neutrons
(a) np type
 $_{13}Al^{27}(n,p)_{12}Mg^{27}$ i.e., $_{13}Al^{27} + _{0}n^{1} \rightarrow _{12}Mg^{27} + _{1}H^{1}$
(b) $n\alpha$ type
 $_{8}O^{16}(n,\alpha)_{12}Mg^{27}$ i.e., $_{8}O^{16} + _{0}n^{1} \rightarrow _{6}C^{13} + _{2}He^{4}$
(c) n, γ type
 $_{92}U^{238}(n,\lambda)_{92}U^{239}$ i.e., $_{92}U^{238} + _{0}n^{1} \rightarrow _{92}U^{238} + \lambda$
(d) $n\beta$ type
 $_{8}O^{18}(n,\beta)_{9}F^{19}$ i.e., $_{8}O^{18} + _{0}n^{1} \rightarrow _{9}F^{19} + _{-1}e^{0}$
(iv) Transmutation by deutrons
(a) dp type
 $_{3}Li^{6}(d,p)_{3}Li^{7}$ i.e., $_{3}Li^{6} + _{1}H^{2} \rightarrow _{3}Li^{7} + _{1}H^{1}$
 $_{32}As^{75}(d,p)_{32}As^{76}$ i.e., $_{32}As^{75} + _{1}H^{2} \rightarrow _{32}As^{76} + _{1}H^{1}$
(v) Transmutation by γ -radiations
(a) χ , n type

$$_{4}Be^{9}(\lambda,n)_{4}Be^{8}$$
 i.e., $_{4}Be^{9} + \gamma \rightarrow _{4}Be^{8} + _{0}n^{1}$

Synthetic elements : Elements with atomic number greater than 92 *i.e.* the elements beyond uranium in the periodic table are not found in nature like other elements. All these elements are prepared by artificial transmutation technique and are therefore known as *transuranic elements* or *synthetic elements*.

Nuclear fission and Nuclear fusion

(1) **Nuclear fission :** The splitting of a heavier atom like that of uranium – 235 into a number of fragments of much smaller mass, by suitable bombardment with sub-atomic particles with liberation of huge amount of energy is called **Nuclear fission**. Hahn and Startsman discovered that when uranium-235 is bombarded with neutrons, it splits up into two relatively lighter elements.

$$_{92}U^{235} +_0 n^1 \rightarrow _{56}Ba^{140} +_{36}Kr^{93} + 3_0n^1$$
 + Huge amount of energy

Spallation reactions are similar to nuclear fission. However, they differ by the fact that they are brought by high energy bombarding particles or photons.

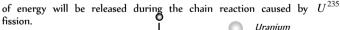
Elements capable of undergoing nuclear fission and their fission products. Among elements capable of undergoing nuclear fission, uranium is the most common. The natural uranium consists of three isotopes, namely U^{234} (0.006%), U^{235} (0.7%) and U^{238} (99.3%). Of the three isomers of uranium, nuclear fission of U^{235} and U^{238} are more important. Uranium-238 undergoes fission by fast moving neutrons while U^{235} undergoes fission by slow moving neutrons; of these two, U^{235} fission is of much significance. Other examples are Pu^{239} and U^{233} .

Uranium-238, the most abundant (99.3%) isotope of uranium, although itself does not undergo nuclear fission, is converted into plutonium-239.

$${}_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} ; {}_{92}U^{239} \rightarrow {}_{92}NP^{239} + {}_{-1}e^{0}$$
$${}_{93}Np^{238} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^{0}$$

Which when bombarded with neutrons, undergo fission to emit three neutrons per plutonium nucleus. Such material like U-238 which themselves are non-fissible but can be converted into fissible material (Pu-239) are known as **fertile materials**.

Nuclear chain reaction: With a small lump of U^{235} , most of the neutrons emitted during fission escape but if the amount of U^{235} exceeds a few kilograms (*critical mass*), neutrons emitted during fission are absorbed by adjacent nuclei causing further fission and so producing more neutrons. Now since each fission releases a considerable amount of energy, vast quantities



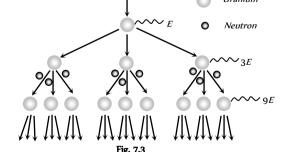


Fig. 7.3 Atomic bomb: An atomic bomb is based upon the process of that nuclear **fission** in which no secondary neutron escapes the lump of a fissile material for which the size of the fissile material should not be less than a minimum size called the critical size. There is accordingly a sudden release LF SCORER 264 Nuclear Chemistry

of a tremendous amount of energy, which represents an explosive force much greater than that of the most powerful TNT bomb. In the world war II in 1945 two atom bombs were used against the Japanese cities of Hiroshima and Nagasaki, the former contained U-235 and the latter contained Pu-239.

Atomic pile or Nuclear reactor : It is a device to obtain the nuclear energy in a controlled way to be used for peaceful purposes. The most common reactor consists of a large assembly of graphite (an allotropic form of carbon) blocks having rods of uranium metal (fuel). Many of the neutrons formed by the fission of nuclei of $_{92}U^{235}$ escape into the graphite, where they are very much slow down (from a speed of about 6000 or more *miles/sec* to a *mile/sec*) and now when these low speed neutrons come back into the uranium metal they are more likely to cause additional fissions. Such a substance like graphite, which slow down the neutrons without absorbing them is known as a **moderator**. Heavy water, DO is another important moderator where the nuclear reactor consists of rods of uranium metal suspended in a big tank of heavy water (swimming pool type reactor). Cadmium or boron are used as control rods for absorbing excess neutrons.

Plutonium from a nuclear reactor: For such purposes the fissile material used in nuclear reactors is the natural uranium which consists mainly (99.3%) of *U*-238. In a nuclear reactor some of the neutrons produced in *U*-235 (present in natural uranium) fission converts *U*-238 to a long-lived plutonium isotope, *Pu*-239 (another fissionable material). Plutonium is an important nuclear fuel. Such reactors in which neutrons produced from fission are partly used to carry out further fission and partly used to produce some other fissionable material are called **Breeder reactors**. *Nuclear reactors in India*: India is equipped with the five nuclear

reactors, namely

(i)	Apsara	a (19	52)			(ii)	Ci	rus (19	960)		
(ii	i) Zerlii	na (19	961)			(iv)	Pu	rnima	(1972)	and	<i>R</i> -5
		1.		C	1	1.1	.1	.1	1.		

Purnima uses plutonium fuel while the others utilize uranium as fuel.

(2) Nuclear fusion : "Oposite to nuclear fission, nuclear fusion is defined as a process in which lighter nuclei fuse together to form a heavier nuclei. However, such processes can take place at reasonable rates only at very high temperatures of the order of several million degrees, which exist only in the interior of stars. Such processes are, therefore, called Thermonuclear reactions (temperature dependent reactions). Once a fusion reaction initiates, the energy released in the process is sufficient to maintain the temperature and to keep the process going on.

$$4_1 H^1 \rightarrow {}_2 H e^4 + 2_{+1} e^0 + \text{Energy}$$

Hydrogen Helium Positron

This is not a simple reaction but involves a set of the thermonuclear reactions, which take place in stars including sun. In other words, *energy of sun is derived due to nuclear fission*.

Controlled nuclear fusion : Unlike the fission process, the fusion process could not be controlled. Since there are estimated to be some 10^{17} pounds of deuterium $(_1H^2)$ in the water of the earth, and since each pound is equivalent in energy to 2500 tonnes of coal, a controlled fusion reactor would provide a virtually inexhaustible supply of energy.

Hydrogen bomb : Hydrogen bomb is based on the *fusion of hydrogen nuclei into heavier ones by the thermonuclear reactions with release of enormous energy.*

As mentioned earlier the above nuclear reactions can take place only at very high temperatures. Therefore, it is necessary to have an external source of energy to provide the required high temperature. For this purpose, the atom bomb, (*i.e., fission bomb*) is used as a *primer*, which by exploding provides the high temperature necessary for successful working of hydrogen bomb (*i.e., fusion bomb*). In the preparation of a hydrogen bomb, a suitable quantity of deuterium or tritium or a mixture of both is enclosed in a space surrounding an ordinary atomic bomb. The first hydrogen bomb was exploded in November 1952 in Marshall Islands; in 1953 Russia exploded a powerful hydrogen bomb having power of 1 million tonnes of TNT A hydrogen bomb is far more powerful than an atom bomb. Thus if it is possible to have sufficiently high temperatures required for nuclear fusion, the deuterium present in sea (as DO) is sufficient to provide all energy requirements of the world for millions of years. The first nuclear reactor was assembled by Fermi in 1942.

Difference between Nuclear fission and fusion

Nuclear fission	Nuclear fusion				
The process occurs only in the nuclei of	The process occurs only in the nuclei				
heavy elements.	of light elements.				
The process involves the fission of the	The process involves the fission of the				
heavy nucleus to the lighter nuclei.	lighter nuclei to heavy nucleus.				
The process can take place at ordinary	The process takes place at higher				
temperature.	temperature $(10^{8} C)$.				
The energy liberated during this process	The energy liberated during the				
is high	process is comparatively low				
(200 <i>MeV</i> per fission)	(3 to 24 MeV per fusion)				
Percentage efficiency of the energy	Percentage efficiency of the energy				
conversion is comparatively less.	conversion is high (four times to that				
	of the fission process).				
The process can be controlled for useful	The process cannot be controlled.				
purposes.					

Application of radioactivity

Radioisotopes find numerous applications in a variety of areas such as medicine, agriculture, biology, chemistry, archeology, engineering and industry.

(1) Age determination : The age of earth has been determined by uranium dating technique as follows. Samples of uranium ores are found to contain Pb^{206} as a result of long series of α - and β -decays. Now if it is assumed that the ore sample contained no lead at the moment of its formation, and if none of the lead formed from U^{238} decay has been lost then the measurement of the Pb^{206} / U^{238} ratio will give the value of time *t* of the mineral.

$$\frac{\text{No. of atoms of } Pb^{206}}{\text{No. of atoms of } U^{238} \text{ left}} = e^{-\lambda t - 1}$$

where λ is the decay constant of uranium-238

Alternatively,

$$t = \frac{2.303}{\lambda} \log \frac{\text{Initial amount of } U^{238}}{\text{Amount of } U^{238}}$$
 in the mineral present till date

Similarly, the less abundant isotope of uranium, U^{235} eventually decays to Pb^{207} ; Th^{232} decays to Pb^{208} and thus the ratios of Pb^{207} / U^{235} and Pb^{208} / Th^{232} can be used to determine the age of rocks and minerals.

14

 $_6C^{14}$ (half-life 5760 years) was used by *Willard Libby* (Nobel lauret) in determining the age of carbon-bearing materials (*e.g.* wood, animal fossils, etc.) Carbon-14 is produced by the bombardment of nitrogen atoms present in the upper atmosphere with neutrons (from cosmic rays).

$$_7 N^{14} + _0 n^1 \rightarrow _6 C^{14} + _1 H^1$$

Thus carbon-14 is oxidised to CO_2 and eventually ingested by plants and animals. The death of plants or animals puts an end to the intake of C^{14} from the atmosphere. After this the amount of C^{14} in the dead tissues starts decreasing due to its disintegration.

$$_{6}C^{14} \rightarrow _{7}N^{14} + _{-1}e^{0}$$

It has been observed that on an average, one gram of radioactive carbon emits about 12 β -particles per minute. Thus by knowing either the amount of *C*-14 or the number of β -particles emitted per minute per gram of carbon at the initial and final (present) stages, the age of carbon material can be determined by using the following formulae.

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N_t} \text{ or } t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t}$$

where t = Age of the fossil, λ = Decay constant, N_0 = Initial radioactivity (in the fresh wood), N_c = Radioactivity in the fossil

The above formula can be modified as,

$$t = \frac{2.303}{\lambda} \log \frac{\text{Initial ratio of } C^{14} / C^{12} \text{ (in fresh wood)}}{C^{14} / C^{12} \text{ ratio in the old wood}}$$

Similarly, tritium ${}_{1}H^{3}$ has been used for dating purposes.

(2) **Radioactive tracers** (use of radio-isotopes) : A radioactive isotope can be easily identified by its radioactivity. The radioactivity can, therefore act as a tag or label that allows studying the behaviour of the element or compounding which contains this isotope. An isotope added for this purpose is known as isotopic tracer. The radioactive tracer is also known as an isotopic tracer. The radioactive tracer is also known as an indicator because it indicates the reaction. Radioisotopes of moderate half-life periods are used for tracer work. The activity of radioisotopes can be detected by means of electroscope, the electrometer or the Geiger-Muller counter. Tracers have been used in the following fields,

(i) **To diagnose many diseases** : For example, Arsenic -74 tracer is used to detect the presence of tumours, Sodium -24 tracer is used to detect the presence of blood clots and lodine -131 tracer is used to study the activity of the thyroid gland. It should be noted that the radioactive isotopes used in medicine have very short half-life periods.

(ii) *In agriculture* : The use of radioactive phosphorus ${}^{32}P$ in fertilizers has revealed how phosphorus is absorbed by plants. This study has led to an improvement in the preparation of fertilizers. ${}^{14}C$ is used to study the kinetics of photo synthesis.

(iii) *In industry*: Radioisotopes are used in industry to detect the leakage in underground oil pipelines, gas pipelines and water pipes. Radioactive carbon has been used as a tracer in studying mechanisms involved in many reactions of industrial importance such as alkylation, polymerization, catalytic synthesis etc.

 (iv) In analysis : Several analytical procedures can be used employing radioisotopes as tracers.

(a) A small amount of radioactive isotope is mixed with the inactive substance and the activity is studied before and after adsorption. Fall in activity gives the amount of substance adsorbed.

(b) The solubility of lead sulphate in water may be estimated by mixing a known amount of radioactive lead with ordinary lead.

 $(c) \;$ lon exchange process of separation is readily followed by measuring activity of successive fractions eluted from the column.

 $\left(d\right)$ By labelling oxygen of the water, mechanism of ester hydrolysis has been studied.

(e) The efficiency of analytical procedures may be measured by adding a known amount of radio-isotopes to the sample before analysis begins. After the completion, the activity is again determined. The comparison of activity tells about the efficiency of separation.

(3) **Use of** γ **rays** : γ rays are used for disinfecting food grains and for preserving food stuffs. Onions, potatoes, fruits and fish etc., when irradiated with γ rays, can be preserved for long periods. High yielding disease resistant varieties of wheat, rice, groundnut, jute etc., can be developed by the application of nuclear radiations. The γ rays radiations are used in the treatment of cancer. The γ radiations emitted by cobalt -60 can burn cancerous cells. The γ radiations are used to sterilize medical instruments like syringes, blood transfusion sets. etc. These radiations make the rubber and plastics objects heat resistant.

Hazards of radiations

Nuclear Chemistry 265

The increased pace of synthesis and use of radio isotopes has led to increased concern about the effect of radiations on matter, particularly in biological systems. The accident of Chernobyl occurred in 1986 in USSR is no older when radioisotopes caused a hazard there. The nuclear radiations (alpha, beta, gamma as well as X-rays) possess energies far in excess of ordinary bond energies and ionisation energies. Consequently, these radiations are able to break up and ionise the molecules present in living organisms if they are exposed to such radiations. This disrupts the normal functions of living organisms. The damage caused by the radiations, however, depends upon the radiations received. The resultant radiation damage to living system can be classified as,

(1)Somatic or pathological damage : This affects the organism during its own life time. It is a permanent damage to living civilization produced in body. Larger dose of radiations cause immediate death whereas smaller doses can cause the development of many diseases such as paralysis, cancer, leukaemia, burns, fatigue, nausea, diarrhoea, gastrointestinal problems etc. some of these diseases are fatal. Many scientists presently believe that the effect of radiations is proportional to exposure, even down to low exposures. This means that any amount of radiation causes some finite risk to living civilization.

(2) Genetic damage : As the term implies, radiations may develop genetic effect. This type of damage is developed when radiations affect genes and chromosomes, the body's reproductive material. Genetic effects are more difficult to study than somatic ones because they may not become apparent for several generations.



- The particle like mesons, positron, neutrino, *etc*, about 20 in number are created by stresses in nucleus but do not exist as component of nucleus.
- E Highest degree of radioactivity is shown by radium.
- M The nuclear forces are not governed by inverse square law.
- \bigstar About 42 radioactive nuclides (Z > 82) occur in nature. Each of these gives stable end product of an isotope of lead.
- The half life is independent of physical or chemical state of a radioactive element.
- \mathcal{E} The average life of the natural radioactive element vary from 10 s 10 years or more.
- It has been observed that fusion of 45 mg of hydrogen produce as much energy as obtained from one ton of coal.
- Beryllium has been found to be the best moderator as it occupies small space and have low absorption cross-section.
- *K* The total life span of a radioactive element is infinite.
- **\mathscr{I}** The γ radiation of total energy 1.02 *MeV*, emitted when a positron and an electron interact are known as annilation radiation.