RADIOCHEMISTRY OR NUCLEAR CHEMISTRY

CHAPTER 19

NUCLEAR CHEMISTRY

The chemical properties of elements depend upon the electronic arrangements of the atoms and the behaviour of electrons in the valency shells. Nothing happens to the nuclei of the atoms during chemical changes.

Recently, a new type of transformation of matter involving changes in the atomic nuclei is studied under a new branch of chemistry called *Nuclear Chemistry. Nuclear Chemistry is the study of properties, compositions and reactions of the atomic nuclei.*

The atoms of certain elements (uranium and radium) undergo spontaneous disintegration to produce atoms of other elements alongwith emission of radioactive rays. In 1895, Becquerel discovered that uranium salt, potassium uranyl sulphate, $K_2UO_2(SO_4)_2$ gave out rays which affected photographic plates kept in darkness and wrapped in a black paper. These rays are called *radioactive rays* and the phenomenon is *called radioactivity. Radioactivity is the phenomenon of spontaneous production of invisible rays from chemical substances. The invisible rays affect the photographic plate and ionize the gas or air through which they pass.*

Radioactive substances emit three type of rays :

(*a*) **α—Rays (Alpha rays) :**

1. These rays are actually helium nuclei having charge +2 (He^{+2}).

2. The kinetic energy of α-rays is between 3 to 9 MeV. They cannot penetrate the matter to large extent. They are obstructed even by thick paper.

3. The velocity of α—rays is about 20,000 miles per hour. They ionize the air while passing through it.

4. They are deflected from straight path by a magnetic or electric field indicating their positive charge.

(*b*) **β—Rays (Beta rays) :**

1. They are negatively charged and are actually electrons having negative charge.

2. They are deflected from straight path by a magnetic or electric field indicating their negative charge.

3. β—rays are more penetrating than α—rays. A 3 mm. thick lead plate will be able to obstruct them.

4. The velocity of β—rays is almost equal to the velocity of light.

5. They ionize the air or molecules while passing through them.

(c) γ—**Rays (Gamma rays)** :

1. They are photons and consist of electromagnetic radiations.
2. They travel with the velocity of light and have strong penetrating power.
3. These rays do not carry any charge and, therefore, are not deflected by magnetic and electric fields.
4. They ionize the air or gas while passing through it.

Natural Radioactivity : Rutherford and Soddy suggested that radioactivity (of uranium) involves a decomposition of its nuclei into other elements. The alpha, beta and gamma rays are emitted from the nucleus during the course of this transformation. The spontaneous decomposition of uranium into thorium involves the emission of alpha rays in the first step as :

Uranium	→	Thorium	+	α—particle
(Mass No. = 238, Atomic No. = 92)		(Mass No. = 234, Atomic No. = 90)		(Mass No. = 4, Atomic No. = 2)

This change may be represented as :

$$_{92}U^{238} \rightarrow \ _{90}Th^{234} + \ _{2}He^{4}$$

It should be noted that the sum of the atomic numbers and atomic masses of reactants and products should be equal.

Radioactivity is a nuc'ear property and is independent of the state of chemical combination or physical conditions. Thus, uranium will have the same radioactivity whether it is in metallic, solution, solid or mineral form. It has been seen that $_{92}U^{238}$ disintegrates with the emission of α – rays. The thorium isotope, Th^{234} disintegrates with emission of β – rays to give proactinium (Pa^{234}).

$$_{90}Th^{234} \rightarrow \ _{91}Pa^{234} + \ _{-1}e^{0} \ (\beta - \text{rays})$$

Group Displacement Law : The emission of α and β—rays from atomic nuclei of radioactive elements gives rise to the displacement in positions of the products of disintegration in the periodic table. This is due to the change in atomic number of the parent element. These displacements of the elements of disintegration are described by *Group Displacement Law*. It states that ;

1. *When an element emits an α - particle, the product obtained moves to the left of the periodic table by two positions (atomic No. decreases by 2) and mass of the element is decreased by 4 units.*

2. *When an element emits a β*—particle, the product moves by one *position to the right (higher) in the periodic table (atomic number is increased by 1).*

Radioactive elements may undergo successive disintegrations to give a chain of species known as *radioactive series*. There are three naturally occurring radioactive series which include most of the naturally occurring elements.

1. *The Uranium series.*

2. *The Actinium series*
3. *The Thorium series.*

These three series undergo transformations from the parent elements (U, Ac and Th) to the end product of stable isotopes (Table 19.1).

TABLE 19.1

The Uranium Series

$_{92}U^{238}$
$\downarrow \alpha$
$_{90}Th^{234}$
$\downarrow \beta$
$_{91}Pa^{234}$
$\downarrow \beta$
$_{92}U^{234}$
$\downarrow \alpha$
$_{90}Th^{230}$
$\downarrow \alpha$
$_{88}Ra^{226}$
$\downarrow \alpha$
$_{86}Rn^{222}$
$\downarrow \alpha$
$_{84}Po^{218}$
$\downarrow \alpha$
$_{82}Pb^{214}$
$\downarrow \beta$
$_{83}Bi^{214}$
$\downarrow \beta$
$_{84}Po^{214}$
$\downarrow \alpha$
$_{82}Pb^{210}$
$\downarrow \beta$
$_{83}Bi^{210}$
$\downarrow \beta$
$_{84}Po^{210}$
$\downarrow \alpha$
$_{82}Pb^{206}$
(Stable)

α, β, β, α, α, α, α, α, β, β, α, β, β, α.
1 : 2 : 5 : 2 : 1 : 2 : 1

The Actinium Series

$_{92}U^{235}$
$\downarrow \alpha$
$_{90}Th^{231}$
$\downarrow \beta$
$_{91}Pa^{231}$
$\downarrow \alpha$
$_{89}Ac^{227}$
α ↙ ↘ β
$_{87}Fr^{223}$ $_{90}Th^{227}$
β ↘ ↙ α
$_{88}Ra^{223}$
$\downarrow \alpha$
$_{86}Rn^{219}$
$\downarrow \alpha$
$_{84}Po^{215}$
$\downarrow \alpha$
$_{82}Pb^{211}$
$\downarrow \beta$
$_{83}Bi^{211}$
$\downarrow \beta$
$_{84}Po^{211}$
$\downarrow \alpha$
$_{82}Pb^{207}$
(Stable)

α, β, α, α β / β α, α, α, α, β, β, α.
1 : 1 : 1 : 3 : 2 : 1

The Thorium Series

$_{90}Th^{232}$
$\downarrow \alpha$
$_{88}Ra^{228}$
$\downarrow \beta$
$_{89}Ac^{228}$
$\downarrow \beta$
$_{90}Th^{228}$
$\downarrow \alpha$
$_{88}Ra^{224}$
$\downarrow \alpha$
$_{86}Rn^{220}$
$\downarrow \alpha$
$_{84}Po^{216}$
$\downarrow \alpha$
$_{82}Pb^{212}$
$\downarrow \beta$
$_{83}Bi^{212}$
$\downarrow \beta$
$_{84}Po^{212}$
$\downarrow \alpha$
$_{82}Pb^{208}$
(Stable)

α, β, β, α α, α, β, β, α

Equation of Radioactive Disintegration or Decay : The rate of radioactive disinitegration is independent of all physical and chemical characteristics. The rate of radioactive disintegration is a first order reaction.

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.

If N is the number of atoms of a radioactive element present at time t, the number of atoms present in a small interval of time dt would be dN. The rate of disintegration would be $-\frac{dN}{dt}$ (minus sign indicates that the amount decreases with time).

Rate of disintegration $\left(-\frac{dN}{dt}\right)$ would be proportional to N (the total amount of radioactive element). Thus,

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

or $$-\frac{dN}{dt} = KN$$

K is called *decay or disintegration constant*. If $dt=1$ second, we have,

$$-dN = KN$$

or $$-\frac{dN}{N} = K$$

Hence, K or the decay constant is defined as *the fraction of the total number of atoms of the radioactive element which disintegrates per second*. The value of K is characteristic of the radioactive disintegration. However, the most dependable property of a radioactive substance is its *half-life*.

Half-Life : *The half-life of a radioactive element is the time required to disintegrate one half of it.* A radioactive element would disintegrate in proportion to its quantity present at that time. So, the half life would also mean the time required to get 50% of the total activity of the radioactive element of a given amount. If N_t is the number of atoms present at time t and N_o, the number of atoms initially present,

$$\frac{N_t}{N_o} = \frac{1}{2} = 0.5$$

or $$\ln \frac{1}{2} = -Kt_{\frac{1}{2}}$$

or $$Kt_{\frac{1}{2}} = -2.303 \log \frac{1}{2}$$

$$= 2.303 \log 2 = 0.693$$

or $$t_{\frac{1}{2}} = \frac{0.693}{K}$$

Half-life of a radioelement is independent of its total mass. The half life of radium is 1590 years and that of U^{238} is 4.5×10^9 years but Po^{214} has $t_{1/2} = 19^{-5}$ seconds.

If a radioactive substance has half-life of one day and we have 100 grams of it, 50 grams would be left after one day, 25 grams of it after 2 days and 12.5 grams after the end of 3 days and so on.

Units of Radioactivity : **Curie** is the unit of radioactivity. A curie is defined as the quantity of a radioactive substance which undergoes 3.7×10^{10} disintegrations per second.

Artificial Radioactivity : Some of the elements do not disintegrate as such but are made to disintegrate by the bombardment of high energy α-particles or neutrons. Sometimes, these elements are found to retain the radioactive phenomenon even after the removal of α-rays etc., source. *The process of getting radioactive products by the bormbardment of high energy particles is generally called artificial radioactivity.*

Artificial radioactivity gained by the bombardment of particles is exampli-fied below :

1. *By the bombardment of neutrons :*

$$_{7}N^{14} + {}_{0}n^{1} \rightarrow {}_{6}C^{14} + {}_{1}H^{1}$$

$$_{47}Ag^{107} + {}_{0}n^{1} \rightarrow {}_{47}Ag^{108}$$

2. *By the bombardment of alpha particles :*

$$_{5}B^{10} + {}_{2}He^{4} \rightarrow {}_{7}N^{13} + {}_{0}n^{1}$$

$$_{12}Mg^{24} + {}_{2}He^{4} \rightarrow {}_{14}Si^{27} + {}_{0}n^{1}$$

3. *By the bombardment of deuterons :*

$$_{12}Mg^{24} + {}_{1}H^{2} \rightarrow {}_{11}Ne^{22} + {}_{2}He^{4}$$

$$_{3}Li^{7} + {}_{1}H^{2} \rightarrow {}_{4}Be^{8} + {}_{0}n^{1}$$

4. *By the bombardment of protons :*

$$_{8}O^{18} + {}_{1}H^{1} \rightarrow {}_{9}F^{18} + {}_{0}n^{1}$$

$$_{5}B^{11} + {}_{1}H^{1} \rightarrow {}_{2}He^{4} + {}_{4}Be^{8}$$

Nuclear Fission :

When $_{92}U^{235}$ is bombarded with slow neutrons the uranium nucleus is split into two fragments. *Such process is called nuclear fission.*

$$_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{56}Ba^{141} + {}_{36}Kr^{92} + 2 \text{ to } 3 \; {}_{0}n^{1} + E$$

The products written on the right side of eqation are called *fission products.* In this type of process loss of mass occurs which releases large amount of energy according to the equation $E = mc^2$. If we take equal weight of U^{235} and C to get energy, uranium will produce 2.5 million times more energy.

The neutrons produced alongwith the products of the nuclear fission would initiate further reaction and a *chain process* would start.

Nuclear Reactors and Atomic Energy : The system of producing self-sustaining nuclear reaction is referred to as *atomic reactor or pile or nuclear reactor*. The chain process can be controlled by means of substances called *moderators*, such as graphite, heavy water or water. They lower down the speed of neutrons.

Nuclear reactors are essentially sources of neutrons under controlled conditions. They are used to produce radioactive isotopes such as Co^{60}, P^{32} and C^{14} etc.

Atomic Energy : The heat energy generated during the fission reaction in atomic reactor can be utilised for power production through dynamos and turbines. The technological advancements regarding atomic energy as a source of energy would play an important role in near future. The uncontrolled nuclear chain reaction results in ultimate liberation of tremendous amount of heat and other forms of energy which is the principle of atom bomb. In this connection the *critical mass* of the fissionable material is essentially attained.

Nuclear Fusion (The Hydrogen Bomb) :

Two or more nuclei may fuse to produce new nuclei and the process is called *nuclear fusion.* Nuclear fusion involving hydrogen and its isotopes is an exothermic reaction. Examples of nuclear fusion reactions are :

$$_{1}H^{2} + {}_{1}H^{3} \rightarrow {}_{2}He^{4} + {}_{0}n^{1}$$

$$_{1}H^{3} + {}_{1}H^{3} \rightarrow {}_{2}He^{4} + 2\,{}_{0}n^{1}$$

$$_{3}Li^{7} + {}_{1}H^{2} \rightarrow 2\,{}_{2}He^{4} + {}_{0}n^{1}$$

Fusion reactions are highly exothermic and release tremendous amounts of energy and are used in hydrogen bombs. Large amounts of energy are required to start these reactions. High energy required for fusion may be derived from the nuclear fission.

It is believed that solar energy is due to a series of hydrogen fusion reactions taking place in the sun. Hydrogen is transformed to He with the release of large amounts of energy.

$$4\ {}_{1}H^{1} \rightarrow {}_{2}He^{4} + 2e^{+} + \gamma$$

The two positrons ($2e^{+}$) and two electrons interact and release large amount of energy.

Transuranium Elements :

Uranium (Atomic No. 92) was the last element known uptill 1940. Afterwards, a few other elements were artificially prepared from uranium (U^{238}) by bombarding it with high velocity electrons or deutrons or neutrons. *The elements which are made artificially and occur after uranium in the periodic table are known as transuranium elements.* The higher transuranium elements up to atomic number 104 have been reported and are usually prepared as shown by the following reactions.

$${}_{92}U^{238} + {}_{1}H^{2} \rightarrow {}_{92}U^{239} + {}_{1}H^{1}$$

$${}_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$

(Neptunium).

$${}_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^{0}$$

(plutonium)

$${}_{94}Pu^{239} + {}_{2}He^{4} \rightarrow {}_{96}Cm^{242} + {}_{0}n^{1}$$

(Curium)

$${}_{96}Cm^{242} + {}_{2}He^{4} \rightarrow {}_{98}Cf^{244} + 2\,{}_{0}n^{1}$$

(Californium)

$${}_{98}Cf^{252} + {}_{5}B^{11} \rightarrow {}_{103}Lr^{257} + 6\,{}_{0}n^{1}$$

(Lawrencium)

Nuclear Structure and Nuclear Stability :

The protons and neutrons are held together within the nucleus by means of forces known as *Nuclear Forces*. Neutrons and protons together are called *nucleons*. Nuclear forces are at least millions of times more than those which bind atoms in molecules.

It is found that as the number of protons increases in nucleus the number of neutrons also correspondingly becomes more. It is assumed that neutrons provide a type of '*Nuclear Glue*' for the nucleus. Nuclei containing even number of nucleons (protons + neutrons) are found to be more stable. Similarly, nuclei containing protons or neutrons equal to 2, 8, 20, 50, 82 or 126 are also stable.

The stability of the nucleus of an atom depends upon the ratio of the number of neutrons to the number of protons in it. For elements upto atomic number 20, the *n/p* ratio should be close to 1 for stability. But for elements of higher atomic numbers, the *n/p* ratio should be 1.52 at the most for stability. If the ratio of neutrons to protons is beyond 1.52, excessive neutrons impart unstability to the nuclei.

Radioisotopes : Isotopes are atoms of the same element which have same atomic number but different mass numbers. Radioisotopes (radio active isotopes) are usually produced in nuclear reactors as a result of neutron bombardments. Thus $_9F^{18}$ is conveniently obtained by irradiating $_3Li^6$ with neutrons in a reactor.

$$_3Li^6 + _0n^1 \rightarrow _1H^3 + _2He^4$$
$$_1H^3 + _8O^{16} \rightarrow _9F^{18} + _0n^1$$

Another useful source of radioisotopes is the fission of uranium in a reactor. Thus Sr^{90} can be produced from fission products. Radioisotopes can also be prepared by bombardment of protons or deutrons in the cyclotron.

The mixture of radioisotopes can be separated from the parent by *solvent extaction, volatilisation, electrodeposition, ion exchange* or *precipitation* technique.

Applications of Radioisotopes :

1. Uses in Analytical Chemistry :

(*a*) *Radiometric analysis* : The analysis of inorganic compounds can be carried out with the help of radioactive reagent. For example, labelled P^{32} is used to determine the amount of Zn (II) in the given sample. The radioactivity in the product is noticed with counters and amount of unknown Zn (II) determined. This method is less time consuming and very convenient and more accurate at the same time.

(*b*) *Isotope Dilution* : This technique is now very commonly used. It is quite helpful in separating a complicated mixture of various components to get them in free state. The purity of the separated components is tested through radiation counts.

(*c*) *Determination of Metals in Compounds* : Let us examplify this technique by taking an example of the complex $[Co(NH_3)_5H_2O]Cl_3$. A drop of $Co^{60}Cl_3$

(cobalt chloride containing Co^{60} radioisotope) is added to at least 100 mg of the complex. The complex $[Co(NH_3)_5H_2O]Cl_3$ is converted into $K_3[Co(NO_2)_6]$ and radiation count in this product would give an idea about the amount of Co present in it.

2. Uses in Physical and Inorganic Chemistry :

The radioisotopes are now commonly used in studying the molecular structures, reaction kinetics and mechanism, catalysis and diffusion of gases. The transuranium elements have been studied by this technique.

3. Uses in Organic Chemistry :

The radioisotope technique is very useful in elaborating the mechanism of organic reactions. In this way the mechanism of the reactions between alcohol and organic acids to form esters can be studied quite efficiently by means of tracers (radioisotopes). C^{14} radioisotope is usually used as tracer in organic reactions.

4. Uses in Medicines :

Radioisotopes are commonly used for diagnosis and treatment of various diseases. They are very popular in diagnosing heart disease, cancer, vitamin deficiency and for metabolism. The rate of gaining water and food by plants can be estimated by this technique.

5. Uses in Industry :

Radioactive tracers are commonly used in catalysis, detergents, dyes etc,, They are found to give excellent results in cigarette, paper, plastic industries and in various metallurical operations. They are also used in determining the structures of polymers.

The tracers are useful in detecting the cracks in pipes. I^{131} is used to detect the leakage point in underground pipes. As I^{131} has half life of only eight days, its use is harmless because its activity dies down after a short time.

6. Uses in Agriculture :

The use of radioisotopes is found to give excellent results in studying the genetic changes of plants. The preservation of food and vegetable is a problem which will hopefully be solved in future with the help of radioisotope techniques.

7. Radioisotope Dating :

The age of certain objects has been calculated by means of radioisotope tracers. C^{14} has half life of about 5568 years. The age of a dead body or fossil can be determined by noting C^{14} activity in it. The approximate age of Egyptian pyramids has been calculated by noting the activity of C^{14} and found present since 2600 B.C. Libby (1960) calculated the dates of various monuments and got Nobel Prize for that work.