B. Sc. III Semester VI
Nuclear Chemistry

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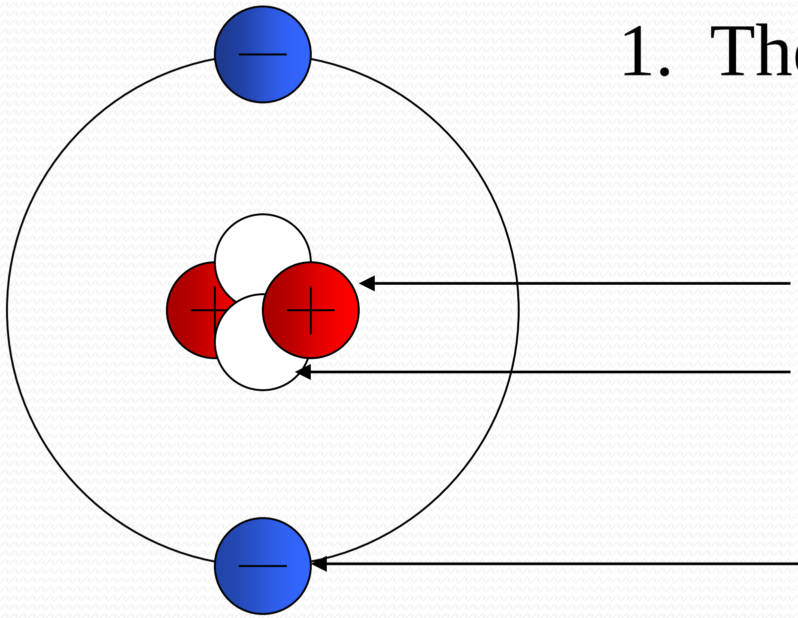
Atom

The atom consists of two parts:

1. The nucleus which contains:



protons

neutrons

2. Orbiting electrons.

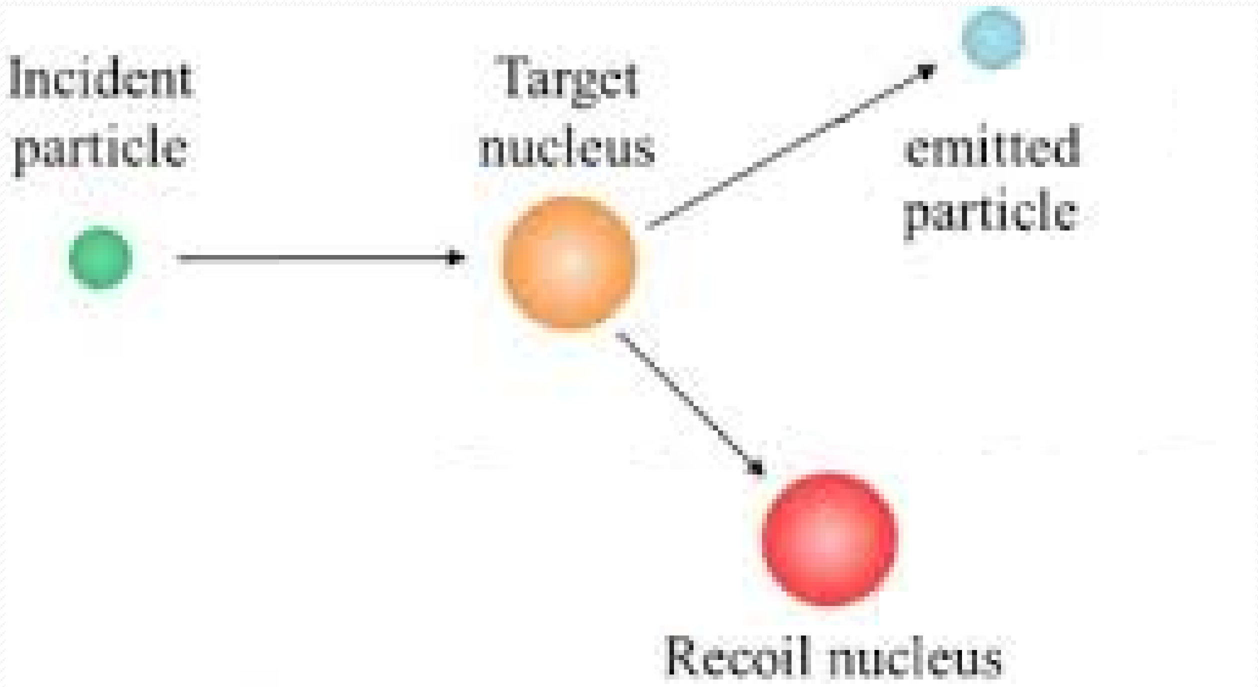
Mass number = number of protons + number of neutrons

$$^{A}_{Z}\mathrm{X}$$

Element symbol

Atomic number = number of protons

Nuclear Reaction



$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$$

$^{14}_{7}N$ - target nucleus, $^{4}_{2}He$ - projectile, $^{17}_{8}O$ - daughter nucleus, $^{1}_{1}H$ – ejectile

Particles involved in Nuclear Reaction

alpha particles	α	$^{4}_{2}He$
beta particles	β	$^{0}_{-1}e$
positron	β^{+}	$^{0}_{+1}e$
neutron	n	$^{1}_{0}n$
proton	p	$^{1}_{1}H$ / $^{1}_{1}P$
deuteron	d	$^{2}_{1}H$
tritium	t	$^{3}_{1}H$
gamma rays	γ	-

Particles involved in Nuclear Reaction

- **Energetics of nuclear reactions:**
- Nuclear reactions are associated with changes in both mass and energy.
- According to Einstein's mass-energy equation, (which relates energy and mass in nuclear reactions)

$$\mathbf{E = mc^2}$$

"m" is the net change in mass in kg and

"c" is a constant (the speed of light) in m/sec.

- Two units to express nuclear energy are joules (J) and megaelectronvolts (MeV).

$$1.6022 \times 10^{-13} \text{ J} = 1 \text{ MeV}$$

Particles involved in Nuclear Reaction

- **Energetics of nuclear reactions:**
- The energy of 1 **atomic mass unit** is:

  1 amu = 1.4924 x 10^{-10} J = 931.5 MeV

- By knowing the mass change in amu, the energy released can be directly calculated.
- Nuclear Binding Energy = Mass Defect * c^2

  or $E = \Delta m * c^2$

- If the energy is released during nuclear reaction, it is termed as **Exoergic** and

  if the energy is absorbed during nuclear reaction, it is termed as **Endoergic**.

Types of Nuclear Reactions

- **A) Artificial transmutation :**

When an atom of one element is converted into atom of another element by artificial means, the nuclear reactions are called as artificial transmutation. In artificial transmutation, a non-radioactive nucleus is bombarded by high-speed projectile like α-particle & nucleus of new element is formed.

- $^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$ (α , p)
- $^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n$ (α , n)

Types of Nuclear Reactions

- **A) Artificial transmutation :**

Artificial transmutation can be carried out by using other projectiles like deuterons, protons, neutrons, etc.

$$^{14}_{7}N + ^{2}_{1}H \longrightarrow ^{12}_{6}C + ^{4}_{2}He \qquad (d, \alpha)$$

$$^{14}_{7}N + ^{1}_{1}H \longrightarrow ^{11}_{6}C + ^{4}_{2}He \qquad (p, \alpha)$$

$$^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{27}_{12}Mg + ^{1}_{1}H \qquad (n , p)$$

$$^{9}_{4}Be + \gamma \longrightarrow ^{8}_{4}Be + ^{1}_{0}n \qquad (\gamma , n)$$

Types of Nuclear Reactions

- **B) Artificial (induced) radioactivity :**

A nuclear process in which radioactivity is induced in a stable element, is called as artificial radioactivity. Scientist Irene Curie first discovered artificial radioactivity. Radioactivity can be induced by using particles like α, n, p, d & γ-rays.

Types of Nuclear Reactions

- **B) Artificial (induced) radioactivity :**
- **α - induced reactions :**
- e.g. i) when ^{27}Al is bombarded by α-particle, radioactive $^{30}_{15}P^*$ is formed with emission of neutron. The radioactive $^{30}_{15}P^*$ emits positron even after removal of source of α - particle & get transformed into stable ^{30}Si nucleus.
- $^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P^* + ^{1}_{0}n$

  $^{30}_{15}P^* \longrightarrow ^{30}_{14}Si + ^{0}_{+1}e$
- ii) $^{24}_{12}Mg + ^{4}_{2}He \longrightarrow ^{27}_{14}Si^* + ^{1}_{0}n$

  $^{27}_{14}Si^* \longrightarrow ^{27}_{13}Al + ^{0}_{+1}e$

Types of Nuclear Reactions

- **B) Artificial (induced) radioactivity :**

P - induced reactions :

e.g. $^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N^{*}$

$^{13}_{7}N^{*} \longrightarrow ^{13}_{6}C + ^{0}_{+1}e$

Types of Nuclear Reactions

- **C) Nuclear fission reaction :**
- The nuclear reaction in which a heavy nucleus is broken into two or more smaller nuclei of medium mass numbers, is called as nuclear fission reaction. Heavy nucleus like $^{235}_{92}U$ is bombarded with slow neutrons. It captures the neutron to form unstable $^{236}_{92}U*$ isotope. This isotope breaks into two fragments & neutrons are emitted alongwith emission of large amount of energy.

- $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{236}_{92}U* \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\ ^{1}_{0}n + E$

Types of Nuclear Reactions

- **C) Nuclear fission reaction :**
- Initially every nucleus absorbs one neutron, to emit two or more neutrons called secondary neutrons These neutrons are again used in fission of more uranium nuclei. So this reaction is known as chain reaction. This reaction continues without break & large amount of energy is evolved in every reaction.

Types of Nuclear Reactions

- **C) Nuclear fission reaction :**
- This reaction can be used for destructive purpose as in atomic bomb and also for peaceful purpose as in nuclear reactors. In nuclear reactors controlled chain reactions are carried out by using cadmium rods. These cadmium rods are used to absorb some neutrons or to slow down fast neutrons. Thus energy is released at slower rates.

Types of Nuclear Reactions

- **D) Nuclear fusion reactions :**
- The nuclear reaction in which two nuclei of lighter elements fuse or combine to form relatively heavier nucleus, is called as nuclear fusion. Large amount of energy is evolved during nuclear fusion.
- $^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n + \text{energy}$

Use of Thorium, Uranium & Plutonium in atomic energy

- The energy evolved during nuclear reactions is used on large scale. It is called as atomic energy / nuclear energy. The nuclear energy is obtained in nuclear reactors, from fission reactions. In nuclear reactors fission chain reaction is controlled by using control rods. Thus amount of energy evolved can be controlled in fission reactions.

Use of Thorium, Uranium & Plutonium in atomic energy

- In nuclear reactors, some isotopes of uranium, thorium are used as atomic fuel.
- i) $^{233}_{92}U$, $^{235}_{92}U$ & $^{238}_{92}U$ are used in nuclear reactors. $^{235}_{92}U$ & $^{238}_{92}U$ occur naturally, while $^{233}_{92}U$ is obtained from $^{232}_{90}Th$. Out of these $^{233}_{92}U$ & $^{235}_{92}U$ are fissile. $^{238}_{92}U$ undergo transformation to give fissile $^{239}_{94}Pu$.
- $^{238}_{92}U \xrightarrow{(n,\gamma)} {}^{239}_{92}U \xrightarrow{-\beta} {}^{239}_{93}Pa \xrightarrow{-\beta} {}^{239}_{94}Pu$

Use of Thorium, Uranium & Plutonium in atomic energy

- ii) $^{239}_{94}Pu$ does not occur in nature. It is obtained from $^{238}_{92}U$.
- iii) Thorium nuclides do not undergo fission. They undergo transmutation in nuclear reactor to produce fissionable product like ^{233}U.

$$^{232}_{90}Th \xrightarrow{(n,\gamma)} {}^{233}_{90}Th \xrightarrow{-\beta} {}^{233}_{91}Pa \xrightarrow{-\beta} {}^{233}_{92}U$$

- The fissionable nuclides like $^{233}_{92}U$, $^{235}_{92}U$ & $^{239}_{94}Pu$ are used as atomic fuel in the nuclear reactors. During fission reaction heat energy is released. This heat energy is then converted into electrical energy.

Use of Thorium, Uranium & Plutonium in atomic energy

$^{232}_{90}Th$

$^{233}_{92}U$ $^{235}_{92}U$ $^{238}_{92}U$

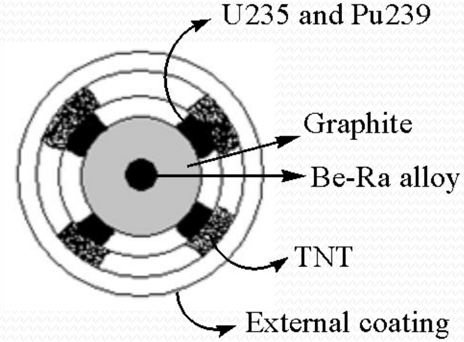
$^{233}_{92}U$ $^{235}_{92}U$ $^{239}_{94}Pu$

- $^{238}_{92}U \ (n, \gamma) \ ^{239}_{92}U \xrightarrow{-\beta} {}^{239}_{93}Np \xrightarrow{-\beta} {}^{239}_{94}Pu$
- $^{232}_{90}Th \ (n, \gamma) \ ^{233}_{90}Th \xrightarrow{-\beta} {}^{233}_{91}Pa \xrightarrow{-\beta} {}^{233}_{92}U$

Atomic Bomb

- The main principle of atomic bomb is uncontrolled chain reaction. During explosion, several thousands of Uranium nuclei break up instantaneously and enormous amount of energy is released at a time.
- **Construction of atomic bomb:**
- At the center of the bomb there is Ra-Be alloy which initiates the production of slow neutrons. The alloy is covered with graphite in which U-235 and Pu-239 are kept apart from each other. Surrounding this the explosives such as TNT (trinitrotoluene) are placed.

Atomic Bomb



- During working the neutrons are generated by Ra-Be alloy and start fission of U-235 and Pu-239. Uncontrolled nuclear fission reaction occurs which results in atomic explosion and tremendous heat is given out. One gram of U-235 give out 8.4×10^{27} kJ mol^{-1} of energy on fission.

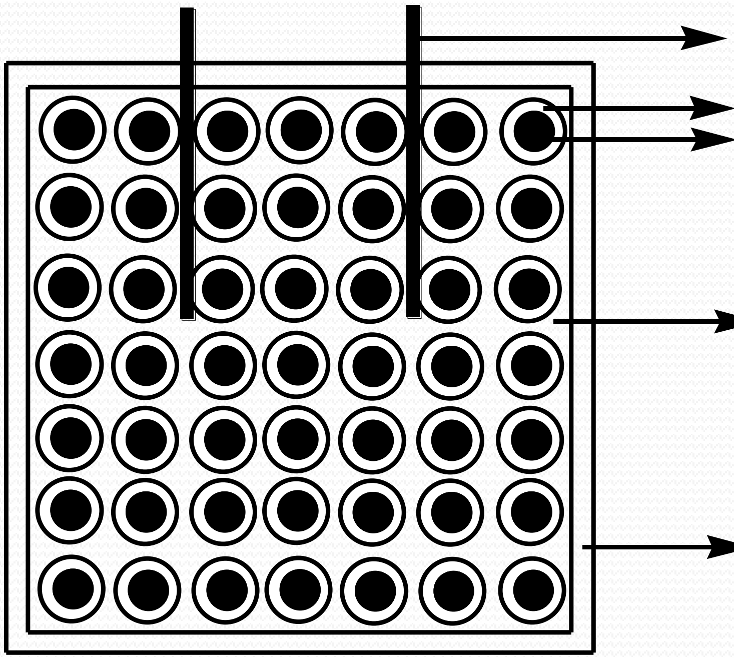
Nuclear Reactor

- Nuclear reactor/atomic reactor is a device in which nuclear reactions are carried out under controlled condition.
- The reactor consists of small bars of natural uranium(containing both U-235 & U-238) sealed in individual Al cans & packed in a large block of graphite. Graphite acts as moderator to slow down the high speed neutrons, so that they may be captured by the uranium nuclei.
- When the reactor starts operating automatically under the influence of slow neutrons, the nuclei of U-235 undergo fission and high speed neutrons are ejected. These secondary neutrons pass through graphite moderator and slow down. Some of these slow neutrons are absorbed by U-238 forming Pu-239.

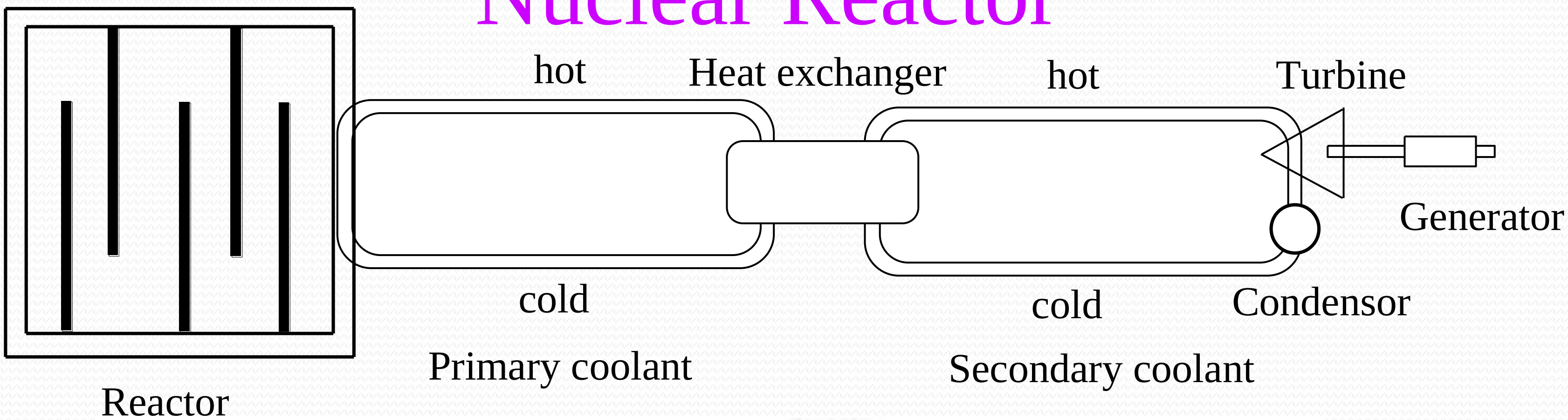
Nuclear Reactor

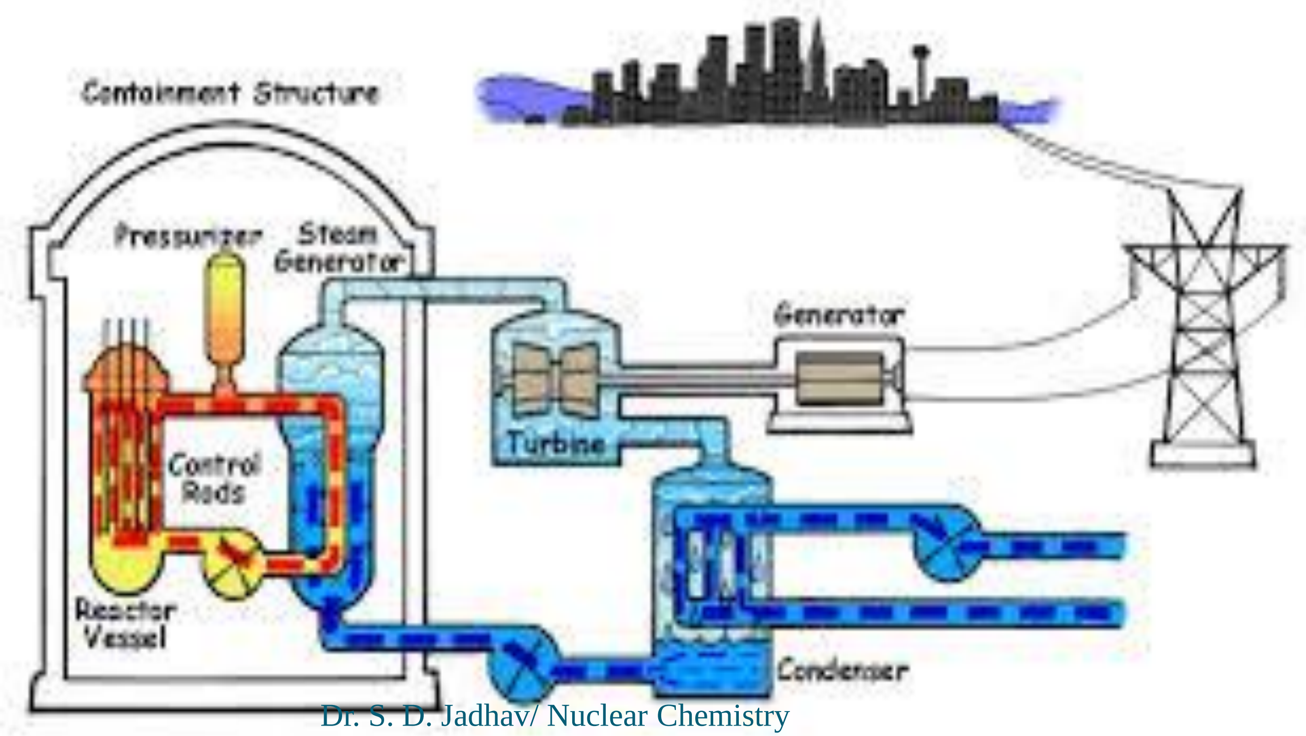
- The nuclear reactor is provided with cadmium rods which absorb neutrons easily and control the neutron number. Thus the chain reaction is always kept under control.
- Tremendous heat is evolved during fission reaction. It is removed by constant circulation of cold water (or molten sodium) by primary coolant system. This energy is transferred to heat exchanger and thereby to secondary coolant system (water), where steam is generated. This steam operates a turbine which generates electricity.
- The entire nuclear reactor is heavily shielded behind a massive layer of steel and concrete that absorbs the highly dangerous radiation products and safeguard the workers in the plant.

Nuclear Reactor



Nuclear Reactor





Nuclear Reactor

- **Stage I – Pressurized Heavy Water Reactor**
- In the first stage of the programme, natural uranium fuelled pressurized heavy water reactors (PHWR) produce electricity while generating plutonium-239 as by-product. PHWRs was a natural choice for implementing the first stage because it had the most efficient reactor design in terms of uranium utilization, and the existing Indian infrastructure in the 1960s allowed for quick adoption of the PHWR technology. India correctly calculated that it would be easier to create heavy water production facilities (required for PHWRs) than uranium enrichment facilities (required for LWRs). Natural uranium contains only 0.7% of the fissile isotope **uranium-235**. Most of the remaining **99.3% is uranium-238** which is not fissile but can be converted in a reactor to the **fissile isotope plutonium-239**. Heavy water (deuterium oxide, D_2O) is used as moderator and coolant.

Nuclear Reactor

- **Stage II – Fast Breeder Reactor**
- In the second stage, fast breeder reactors (FBRs) would use **a mixed oxide (MOX) fuel** made from **plutonium-239**, recovered by reprocessing spent fuel from the first stage, and natural uranium. In FBRs, plutonium-239 undergoes fission to produce energy, while the uranium-238 present in the mixed oxide fuel transmutes to additional plutonium-239. Thus, the Stage II FBRs are designed to "breed" more fuel than they consume. Once the inventory of plutonium-239 is built up thorium can be introduced as a blanket material in the reactor and transmuted to uranium-233 for use in the third stage.

Applications of radioisotopes as tracers

- Nowadays radioactive isotopes are used as tracers in various processes. It is a most advanced technique. In this technique, a radioactive isotope is applied at one point of system & then its movement is traced by measuring radioactivity in different parts of the system.

Applications of radioisotopes as tracers

- **i) Chemical investigation : (Esterification)**
- Ester can be prepared by carrying out reaction between an acid & an alcohol.
- e.g. $CH_3COOH + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + H_2O$
- In esterification, it can't be estimated experimentally that H_2O eliminated is from OH of alcohol & H of acid or from OH of acid & H of alcohol. This mechanism can be investigated by using $^{18}O^*$ radioactive isotope.
- A labeled alcohol is used for the reaction & during reaction $^{18}O^*$ is traced. It is found that $^{18}O^*$ goes into ester, indicating that H_2O is formed from H of alcohol & OH of acid.
- $CH_3COOH + HO^*C_2H_5 \longrightarrow CH_3COO^*C_2H_5 + H_2O$

Applications of radioisotopes as tracers

ii) Structural determination : (Phosphorus pentachloride)

The problem regarding structural equivalence can be solved by using tracers.

e.g. in phosphorus pentachloride, five Cl atoms are structurally equivalent or not; it may be determined by using $^{36}Cl^*$ as tracer.

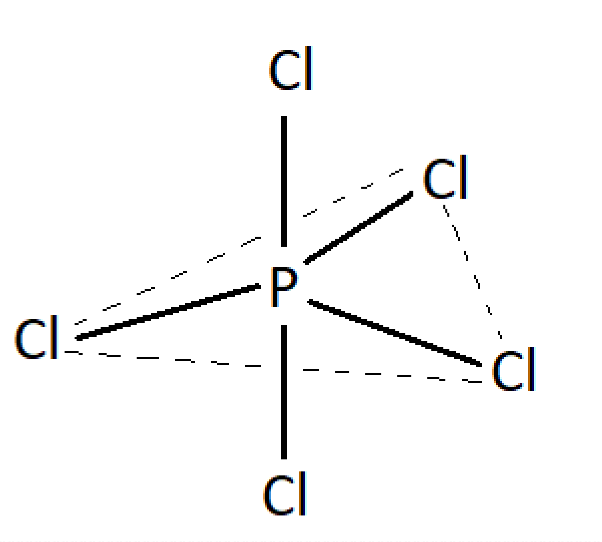
PCl_5 is synthesized by using PCl_3 & Cl_2 labeled with $^{36}Cl^*$.

$$PCl_3 + Cl^*_2 \longrightarrow PCl^*_5$$

This product is then hydrolyzed.

$$PCl^*_5 + H_2O \longrightarrow POCl_3 + HCl^*$$

Thus all the radioactive Cl^* atoms remain with HCl & $POCl_3$ contains no radioactive $^{36}Cl^*$. This indicates that two Cl occupy different positions from other three Cl. This shows that PCl_5 has TBP structure, in which 3Cl atoms are arranged in triangular planar manner while 2Cl atoms are perpendicular to that plane, with P-Cl distance slightly longer than P-Cl in plane.


Cl
Cl
P
Cl
Cl
Cl

Applications of radioisotopes as tracers

- **iii) Analytical chemistry : (Isotopic dilution method for determination of volume of blood)**

The volume of blood present in patient's body can be determined by isotopic dilution method. Initially 1cm^3 of blood of patient is withdrawn & labeled with $^{24}Na^*$ as NaCl. The activity of 0.1cm^3 of blood (s_1) is determined. Then remaining labeled blood sample is reinjected (y = 0.9cm^3). After 15 minutes, again 1cm^3 blood is withdrawn & its activity (s_2) is measured. Total volume of blood in patient's body can be determined by using the equation,

$$y \cdot s_1 = (x + y) \cdot s_2$$

$$y \cdot s_1 = x \cdot s_2$$

as y = 0.9 cm^3 is very less & can be neglected

$$x = y \cdot (s_1 / s_2)$$

where, y = labeled blood injected

x = total volume of blood

Thus total volume of blood can be determined.

Applications of radioisotopes as tracers

iv) Age determination : (C –14 dating)

The age of historical samples of plants can be determined by using radioactive $^{14}C^{*}$.In atmosphere carbon is present in the form of CO_2, where small amount of CO_2 contains $^{14}C^{*}$.

(In atmosphere $^{14}C^{*}$ is formed due to bombardment of ^{14}N by neutrons from cosmic rays.

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

Living plants always use atmospheric CO_2 for photosynthesis. Thus small amount of $^{14}C^{*}O_2$ is also taken by plants. Plants prepare their food by the process of photosynthesis. Once the life process of plants stops, it can not take atmospheric CO_2. Hence, after death $^{14}C^{*}$ present in plant tissues start decaying. Thus amount of $^{14}C^{*}$ goes on decreasing.

(half life of $^{14}C^{*}$ is = 5730 years)

Applications of radioisotopes as tracers

iv) Age determination : (C –14 dating)

The radioactivity of $^{14}C^{*}$ in historical sample wood can be determined & compared with that present in living wood sample. From this age of historical sample can be calculated by using the equation :

$$t = \frac{2.303}{\lambda} . \log \frac{No}{N}$$

where, N_0 = initial activity

and $\lambda = \frac{2.303}{t_{1/2}}$ N = final activity

For this technique, very small amount of sample i.e. about 0.01 gm is required for radioactivity measurement.

THANK YOU