3. Nuclear Chemistry

3.1 Radioactivity

The discovery of radioactivity in 1896 by Becquerel lent support to the existence of sub-atomic particles. Becquerel found that uranium- blackened, a photographic plate even in darkness. This was because uranium gave out radiations. Marie Curie showed that radium and polonium also gave out radiations.

Rutherford investigated the radiations and showed that they were of three types. He called them alpha (Î±), beta (Î²) and (Î³) gamma rays.

If uranium is put into a lead block with a hole drilled into it and the rays emitted passed through a magnetic field, they will be deflected as shown in Figure 3.1.

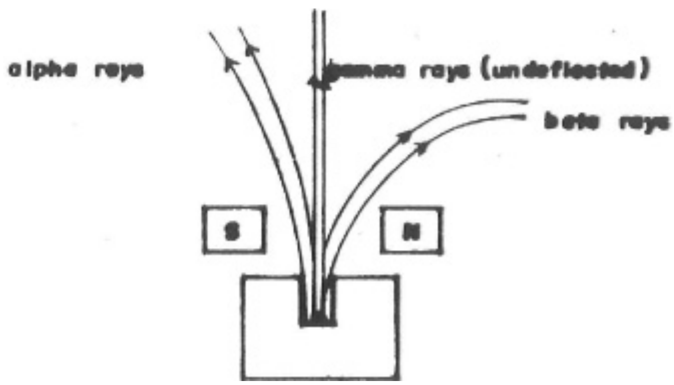


Figure 3.1 Deflection of radioactive rays

Alpha (*Î±*) rays: The deflection experiment shows that alpha rays are positively charged. They have a mass equal to the mass of the helium atom. They are positively charged helium ions, (He^{2+}). They have low penetrating power, being stopped by a thin sheet of paper, or a few centimetres of air.

Beta (*Î²*) rays: The deflection of beta rays towards a positive electrode shows that they are negatively charged. They have negligible mass. They are identical to electrons and have a speed nearly equal to the speed of light. They have much higher penetrating power than alpha particles.

Gamma (*Î³*) rays: Gamma rays have very high penetrating power. They are not deflected by magnetic or electric fields and so are not charged. They are found to be waves like x-rays, and not particles. Their high penetration makes them very dangerous as they can enter the body and destroy body tissues.

Rutherfordâ€™s explanation for those radiations was that atoms of heavy metals such as uranium, radium and polonium, disintegrate into smaller atoms with the emission of sub atomic particles or bundles of energy.

TABLE 3.1: Properties of radioactive rays

Name	Charge	Relative mass	Penetrating power
Alpha (α)	+2	4	Weak
Beta (β)	−1	Negligible	About 100 times that of α − particles.
Gamma (γ)	0	0	High

Types of Radioactivity

Three types of radioactivity have been recognised..

(a) Loss of an alpha particle from the nucleus of an atom (Î± â€“ decay): This reduces the atomic number of the atom by 2, and its mass by 4. Examples:

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

$$^{227}_{89}Ac \rightarrow ^{223}_{87}Fr + ^{4}_{2}He$$

The superscripts (mass numbers) and the subscripts (atomic numbers) must balance on both sides of the nuclear equation.

(b) Loss of a beta particle from the nucleus of an atom with a high neutron â€“ proton ratio: The effect is a change of a neutron into a proton within the nucleus *(Î² â€“* decay).

Examples:

$$^{253}_{98}Cf \rightarrow ^{253}_{99}Es + ^{0}_{-1}e$$

$$^{24}_{11}Na \rightarrow ^{24}_{12}Mg + ^{0}_{-1}e$$

$$^{28}_{13}Al \rightarrow ^{28}_{14}Si + ^{0}_{-1}e$$

(c) Capture of K electron, or emission of a positron (a positive electron) by the nucleus. This happens with nuclei that have too many protons relative to their number of neutrons. The effect is a change of a proton to a neutron within the nucleus. The mass number remains constant, but the atomic number is reduced by one.

Examples:

$$^{27}_{14}Si \rightarrow ^{27}_{13}Al + ^{o}_{+1}e \quad \text{(loss of a positron)}$$

$$^{49}_{23}V + ^{o}_{-1}e \rightarrow ^{49}_{22}Ti \quad \text{(K capture)}$$

K â€“ capture and positron emission are very rare Î±â€“ and *Î²â€”* decay are much more common. Gamma emission accompanies most nuclear reactions.

Half-life

Observation shows that no matter the mass of a radioactive isotope one starts with, it takes a definite length of time for half of that mass to disintegrate. This length of time is known as the half-life of the radioactive isotope. It is a measure of the stability of the isotope, for if the half-life is a thousand years, such isotope is more stable than one whose half-life is only a few days. Uraniumâ€”238 has a half-life of 4.5 Ã— 10^9 years, but the half-life of sodiumâ€”14 is only 15 hours.

EXERCISE 3.1

If it takes 15 hours for 10 g of sodiumâ€”24, in 20 g of the isotope to decay, how long does it take 0.5 g out of 1 g of the isotope to decay?

Worked Example

Question:

10 g of a radioactive isotope with a half-life of 2 hours is left in a cupboard at 8.00 a.m. What mass of it remains at 6.00 p.m. the same day?

Solution:

Between 8.00 a.m and 6.00 p.m. there are five, two â€“ hour intervals. After the first two hour interval $\frac{10}{2}$ g disintegrate, leaving $\frac{10}{2}$ g.

âˆ´ after the five 2 â€”hour intervals, mass remaining is:

$$\frac{10}{2^5}g = \frac{10}{32}g$$
$$= 0.3125 \text{ g.}$$

3.2 Detection of Radiation

The detection of radioactive emission of alpha, beta and gamma rays is based on the ionization which these rays cause along their path. Alpha rays cause much ionization. Beta rays cause less, and gamma rays only a little. Ionization is caused by these rays when they strike off outer electrons from atoms through which they pass.

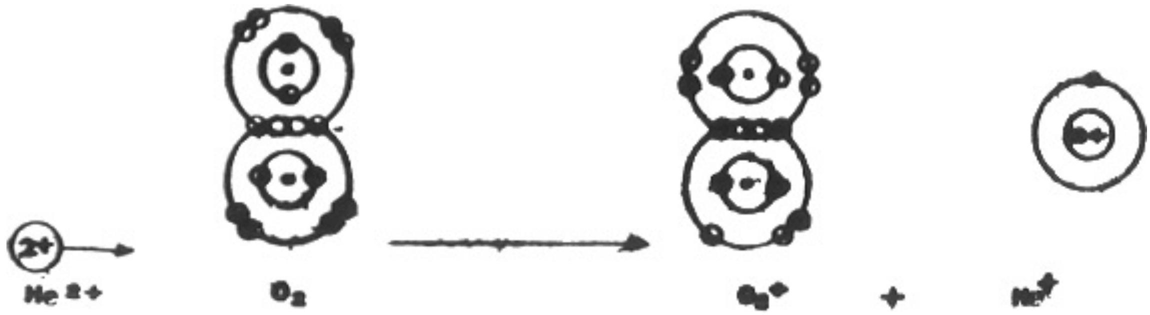
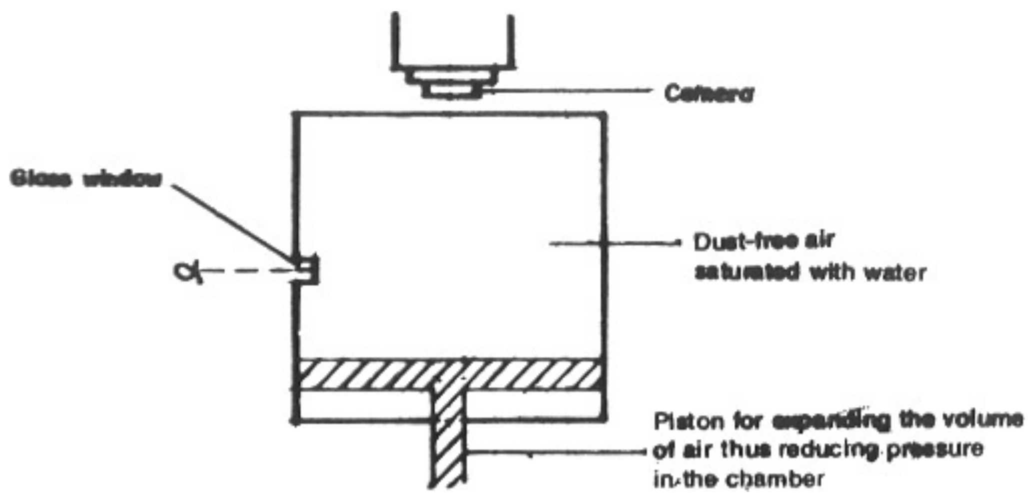


Figure 3.2: Ionization of oxygen molecule by an alpha particle

Wilsonâ€™s Cloud Chamber

This is an apparatus for observing the trail of ions induced by radioactive radiations. A dust-free air is saturated with water vapour or alcohol, and put into a chamber. By suddenly reducing the pressure inside the chamber, the temperature falls. If there are nuclei inside the chamber, condensation takes place on them.

Radiation is sent into the chamber through a glass window. Ionization takes place in the atoms which are on the path of the radiation. Condensation occurs on the ions and this forms a cloud. The path of the radiation, that is the track of the cloud formation, is photographed by a camera. Figure 3.3 (a) shows the Wilson cloud chamber, and (b) a typical track produced by alpha rays.



(a) Wilson cloud chamber.

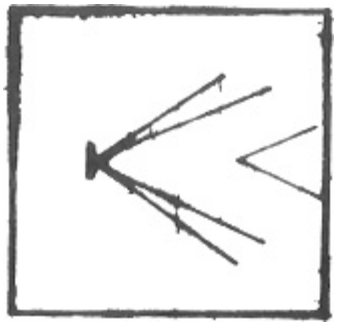


Figure 3.3 (b): Track produced by Î±â€“ rays.

Geiger-Muller Counter

The Geiger-Muller counter is another device for detecting the path of ionized gaseous molecules produced by radiations. It is a gasâ€“filled glass tube containing two. electrodes maintained at a potential difference of about 1000 volts. When a radiation such as Î±, Î² or Î³ ray enters the tube, it causes a lot of ionization. The electrons of the induced ionization move to the anode while the positive ions move to the cathode. The rapid increase in current is recorded on a counter.

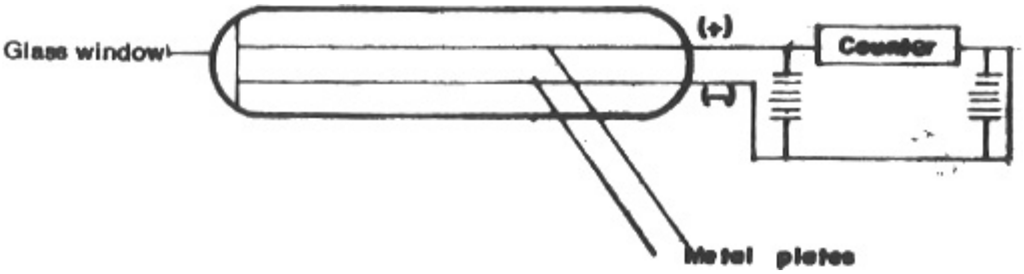


Figure 3.4: Geiger - Muller counter.

EXERCISE 3.2

1. Why must the air in the cloud chamber be dust-free?
2. The gas inside the Geiger-Muller counter is usually an â€œinertâ€ gas such as argen, helium etc. Why is an inert gas desirable? Name other suitable â€œinertâ€ gases.
3. As the electrons produced by ionization in the Geiger counter move to the anode, what happens to the positive ions formed? Do they get to the cathode before, after or at the same time as the electrons get to the anode? (Recall that heavier particles move more slowly than lighter ones).
4. Why can a single radioactive particle produce an avalanche of electrons? The answer to Question 4 is represented schematically in Figure 3.5.

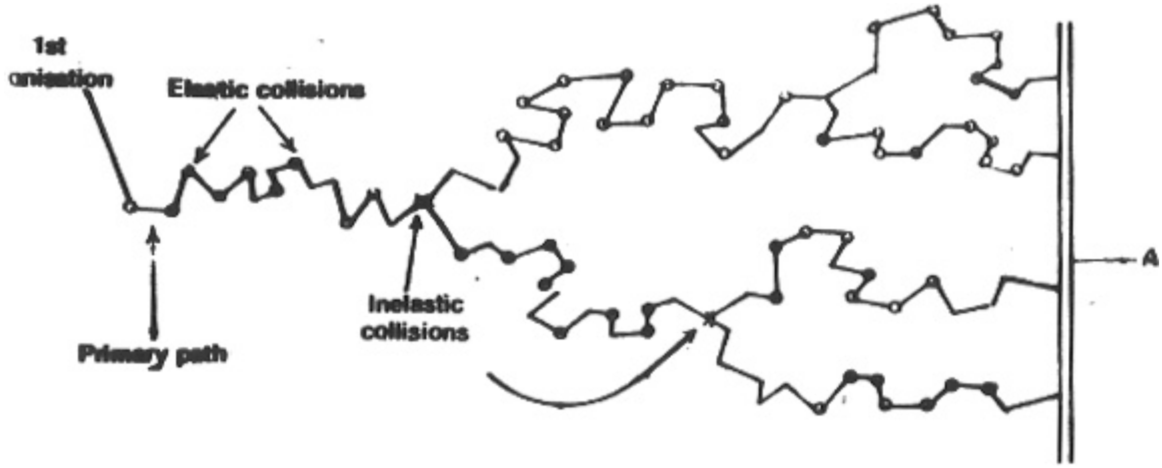


Figure 3.5: Primary and secondary paths of electrons towards the anode

3.3 Nuclear Reactions

Nuclear reactions are reactions which cause changes in the composition of the nucleus of the atom. In our earlier discussion of natural radioactivity as evidence for the existence of sub-atomic particles, we saw that some nuclei disintegrate spontaneously. Such nuclei were said to be unstable. Half-life has also been described as a measure of their stability. But how does the composition of a nucleus affect its stability? What forces in the nuclei, are responsible for this instability?

The nucleus occupies a very small portion of an atom. Protons must therefore be very closely packed. The repulsive forces between them must be high. These could be responsible for nuclear instability.

The dependence of nuclear stability on the number of protons and neutrons in a nucleus can be summarised thus:

(i) Nuclei with atomic numbers 1 â€“ 20 are stable if they contain equal numbers of protons and neutrons.

(ii) Between atomic numbers 21 â€“ 83 only nuclei with more neutrons than protons are stable.

(iii) No atom with more than 83 protons is stable.

These are shown in a plot of the number of neutrons against number of protons in the atoms in Figure 3.6. Atoms whose neutron â€“ proton ratios are outside the belt of nuclear stability are radioactive.

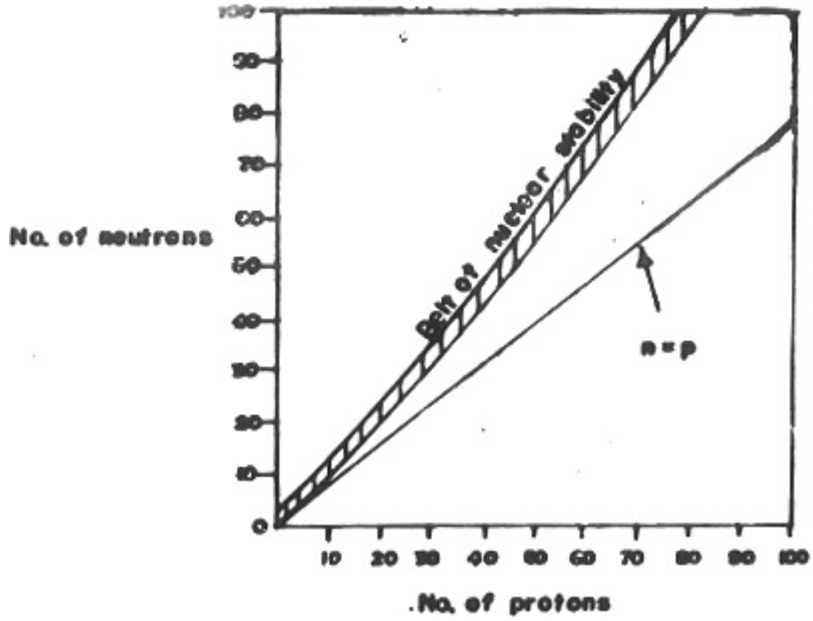


Figure 3.6: A plot of number of neutrons against number of protons showing belt of nuclear stability

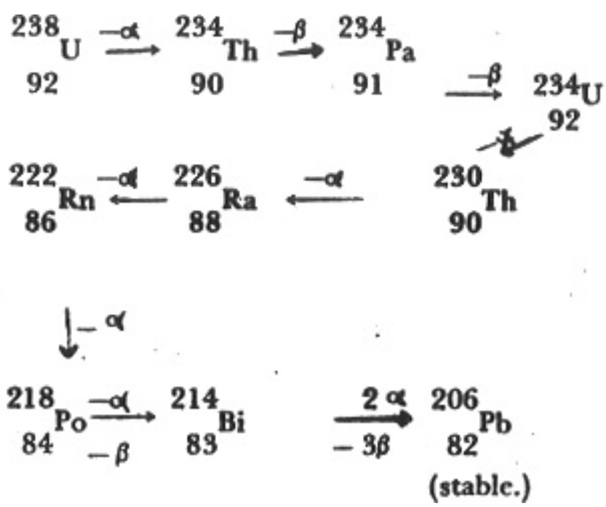
As we noted earlier, unstable or radioactive isotopes try to attain stability in three ways:

(i) by alpha emission;

(ii) by beta emission and

(iii) by Kâ€”capture (capture of an elctron from the K shell).

Many radioactive disintegration processes produce other radioactive isotopes which also disintegrate. The process continues until a stable isotope is produced. The disintegration of uraniumâ€”238 is an example of such a process.



Nuclear Energy

Mass is not conserved in nuclear reactions. The hypothetical nuclear reactions:

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

illustrates this point. We can calculate the mass defect in the reaction thus:

The mass of a mole of protons = 1.00759 g

The mass of a mole of neutrons = 1.00997 g

âˆ´ Total mass of the reactants in the hypothetical reaction

= (2 Ã— 1.00759) + (2 Ã— 1.00897) g

= 4.03312 g.

But mass of a mole of helium atoms = 4.00277 g.

âˆ´ Mass defect in the reaction = (4.03312 - 4.00277) g = 0.03035 g.

If this nuclear reaction were to take place, this mass defect of 0.03035 g would be converted into energy in accordance with Einesteinâ€™s equation, $E = mc^2$, where E is energy, m the mass defect, and c the velocity of light.

The energy, E, is in joules if the mass is in kg and c is in m sec^{-1}

Velocity of light = 3 Ã— 10^8m sec^{-1}

âˆ´ Given a mass defect of 0.03 g, i.e. 3 Ã— 10^{-5} kg,

E = 3 Ã— 10^5 N Ã— 3 Ã— 10^8 Ã— 3 Ã— 10^8 joules

= 2.7 Ã— 10^{19} kJ mol^{-1}.

Since the velocity of light, c, is very high, even a very small mass defect will give rise to a large amount of energy.

Induced Radioactivity

By bombarding a stable isotope with radioactive particles, radioactivity can be induced on the stable isotope. The absorption of an alpha particle by the nucleus of a nitrogen atom leads to a radioactive fluorine which emits a proton to form oxygenâ€”17.

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

Cobalt absorbs a neutron when placed in a uranium pile, thus becoming radioactive cobaltâ€”60 isotope.

$${}^{59}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{60}_{27}\mathrm{Co} \rightarrow {}^{56}_{25}\mathrm{Mn} + {}^{4}_{2}\mathrm{He}$$

The cobaltâ€”60 emits ah alpha particle to become manganeseâ€”56. If subjected to the same treatment, sulphur absorbs a neutron and emits a proton to become phosphorus.

$${}^{32}_{16}\mathrm{S} + {}^{1}_{0}\mathrm{n} \cdots\cdots {}^{33}_{15}\mathrm{P} + {}^{1}_{1}\mathrm{H}$$

In all these nuclear reactions mass defects are converted into high amounts of energy.

Atomic Bomb

To many people atomic energy connotes nuclear bomb. The first nuclear bomb was made from uraniumâ€“235. Natural source of uranium contains about 99.3% uraniumâ€“238, and only 0.7% of uraniumâ€“235. Separation of the isotopes was achieved by converting natural uranium to uranium fluoride which is gaseous. The fluoride of uraniumâ€“235 is lighter than that of uraniumâ€“238. The application of Grahamâ€™s law of diffusion separates the fluorides. Heating the fluorides yields the free uranium isotopes.

If uraniumâ€“235 is stored in small amounts, the neutrons produced by the disintegration of its nuclei escape at such a rate that a chain reaction cannot be maintained. But if a large lump is kept, then the neutrons produced are absorbed by other nuclei, producing fission at such a rapid rate that it leads to an explosion. That is, there is a critical mass of uranium â€“ 235 below which most of the neutrons produced by the fission of one nucleus escape without causing further fission. This mass is 2.5 kg. An atomic bomb is made by bringing together many sub-critical masses of uraniumâ€“235 and providing a neutron source to trigger the chain reaction. This is illustrated in Figure 3.7.

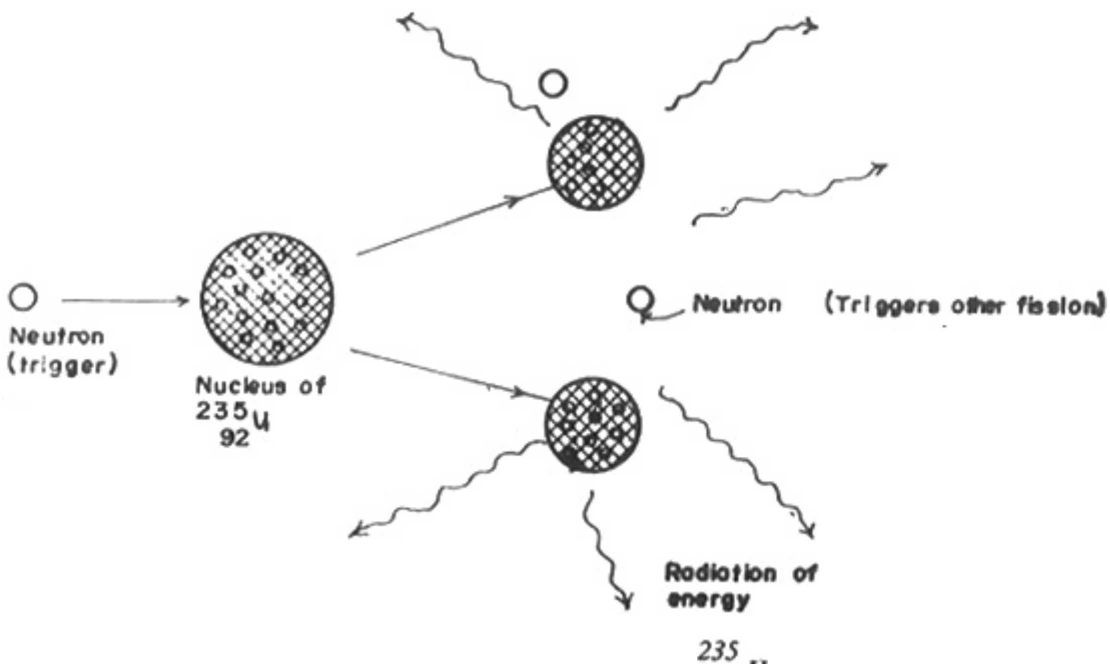


Figure 3.7: Fission of $^{235}_{92}U$

The reaction is controlled either by restricting the amount of fissionable materials, or by inserting elements which capture thermal neutrons. Boron or cadmium rods, when inserted into a mass of uraniumâ€“235 keep the uranium masses at sub-critical levels. On withdrawing the rods, the small masses combine to a mass larger than the critical mass, and then become capable of undergoing chain reaction. Graphite rods, when inserted into uraniumâ€“235, capture the neutrons produced by fission of the uraniumâ€“235. A chain reaction is thus avoided.

Fusion Processes

The fusion of small nuclei, as we saw in the hypothetical nuclear reaction between two protons and two neutrons producing a helium atom, produces tremendous amounts of energy. Examples of feasible fusion reactions that have been used in hydrogen bombs include:

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

$$^{6}_{3}Li + ^{2}_{1}H \rightarrow 2\,^{4}_{2}He + \text{Energy}$$

These reactions take place at very high temperatures, (about 10^{60}C). Such high temperatures can only be achieved by initiating the fusion reaction, using a fission bomb. The advantage of the fusion bomb over the fission one is that there is no danger of radioactive fallout, except from the detonating fission reaction

EXERCISE 3.3

$^{2}_{1}H$ is one proton, plus one neutron.

$^{3}_{1}H$ is one proton, plus two neutrons.

The mass of one mole of protons is 1.00759 g, and that of one mole of neutr is 1.00897 g. The mass of a mole of helium atoms is 4.00277 g. Velocity of light = 3 Ã— 10^{8} m sec^{-1}. Calculate the mass defect for the fusion reaction:

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

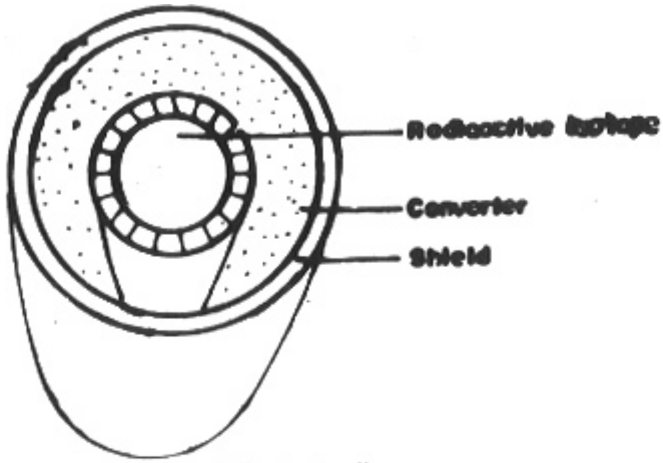
Hence, calculate the energy liberated per mole of reactants.

3.4 Applications of Radioactivity

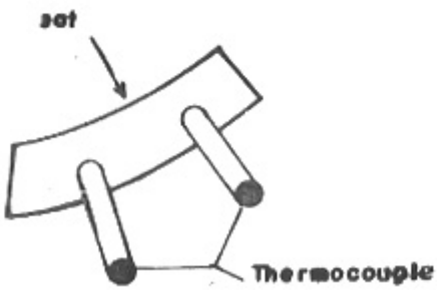
Conversion of Atomic Energy into Electricity

Several methods for converting heat energy from nuclear reactions into electricity are available. The most common is to use the heat to boil water and generate steam. The steam drives turbines which in turn drive electric generators.

A second method is based on the fact that if two dissimilar metals are joined into a closed circuit and their two ends placed at different temperatures, current flows through the circuit. The two metals so joined make up a thermocouple. One end of a thermocouple is burried in a heat insulator in a fuel capsule, and the other end outside the capsule, to generate electricity. Figure 3.8 shows such a device.



(a) Fuel cell



(b) Converter

A third method is to use the heat generated by a nuclear reaction to heat a metal used as cathode in a vacuum tube. Electrons are generated from that cathode as a result of the heating. They are made to move towards an anode. Their movement constitutes electric current. The device is termed thermionic emission

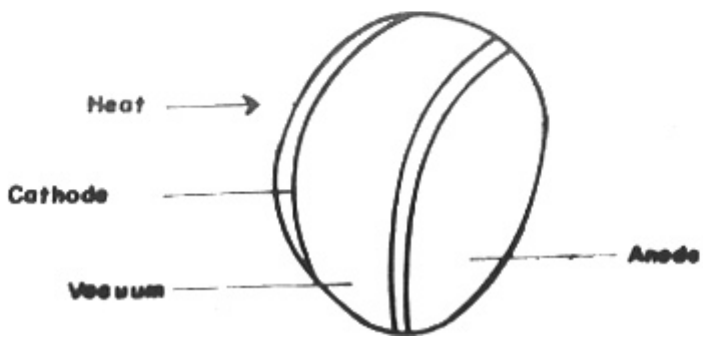


Figure 3.9: Thermionic emitter

The problems associated with the derivation of electric energy from nuclear reactions are:

(i) difficulty in controlling the amount of energy released from the nuclear reaction;

(ii) releasing the energy over a long period of time, and

(iii) the expensive process of separating the radioactive isotopes from associated non-radioactive isotopes in the element.

To release the energy steadily over long period of time and yet avoid separation of isotopes, graphite is incorporated into naturally occuring uranium. The graphite absorbs fast neutrons so that they are not absorbed by ^{238}U, but are available for the fission of ^{235}U. The chain reaction that occurs releases energy steadily.

Application in Medicine

Radioactive rays, especially gamma rays, are used to kill cancerous cells in the treatment of cancer. Radioactive iodine is used to treat thyroid diseases while radioactive phosphorus is used to treat leukaemia.

These radioactive radiations used in treating cancer affect other cells of the body, hence their use in medicine is limited.

Application in Agriculture

Radioactive isotopes are used as sources of radiations to kill bacteria that cause decay in food. Agricultural products are thus preserved. They are also used in the production of species of seeds that are more resistant to diseases and even those that mature early.

Application in Carbon â€“ Dating

The nuclear reaction:

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

is brought about by cosmic rays. The radioactive carbon so produced joins in the carbon cycle and every living thing gets its fair share of it. Infact the ratio of carbonâ€“14 to carbonâ€“12 in the atmosphere and in living things remains constant. But the ratio starts to decrease and approach zero once the living thing dies, because ^{14}C is no longer replenished through the carbon cycle after death. A measure of this ratio in archeological specimens therefore tells the number of years that have elapsed since the organism died. This calculation is based on the half-life of ^{14}C which is known to be 5600 years.

Application in Industry

Radioactive isotopes are used in industry for very many purposes. Some of these are to trace leakages in pipes, to detect the level of liquids in tanks and to determine the change-point when different grades of oil are transported in the same pipe. The technique in these examples is the same. The effect of the radioactive isotope on a Geiger-Muller counter tells the tale. Figure 3.10 illustrates the principle.

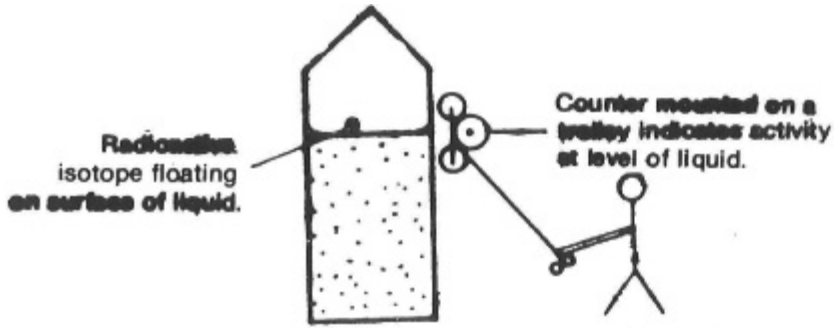


Figure 3.10: Use of radioactivity to detect level of liquid in a giant tank

Application in Research

The application of radioactivity in research is very vast and varied. For example, radioisotopes are used to follow the course of chemical reactions in determining reaction mechanism.

CHAPTER SUMMARY

â€¢ Unstable nuclei may attain stability by:

(i) alpha emission,

(ii) beta emission,

(iii) K â€“ capture.

â€¢ Mass defects accompanying these processes are converted to energy according to the Einstein equation:

$$E = mc^2.$$

â€¢ The Wilson cloud chamber and Geiger-Muller counter are used to detect radioactive particles, and hence to detect radioactivity.

â€¢ The three major radioactive particles are:

Î± â€“ particles: charged helium ions with mass of 4 a.m.u.

Î² â€“ particles : electrons in motion with neglibible mass.

Î³ â€“ rays: highly penetrating bundles of nenergy.

â€¢ Nuclear fission is the breakdown of an unstable nucleus to atoms of smaller nuclei. This is often accompanied by emission of energy and radioactive particles.

â€¢ Nuclear fusion is the combination of the nuclei of small atoms to form the nucleus of a larger atom. It is also accompanied by the emission of energy, and radioactive particles.

â€¢ Half-life is the time it takes a radioative isotope to disintegrate to half its mass. The longer this period of time, the more stable the isotope.

â€¢ Radioisotopes are used in the generation of electricity, medicine, agriculture, industry, and in warfare.

ASSESSMENT

1. Define the terms half-life, wavelength, frequency, ionization energy, electronegativity.

2. Complete the following nuclear equations:

   (i) ${}^{14}_{6}C \rightarrow {}^{14}_{7}N + ?$

   (ii) ${}^{59}_{27}Co + {}^{1}_{0}n \rightarrow ? + \alpha$

   (iii) ${}^{226}_{?}Ra \rightarrow {}^{?}_{86}Rn + {}^{4}_{2}He$

3. List 4 uses of radioisotopes/radioactivity.