Higher

Chemistry

HSN13300
Unit 3 Topic 3

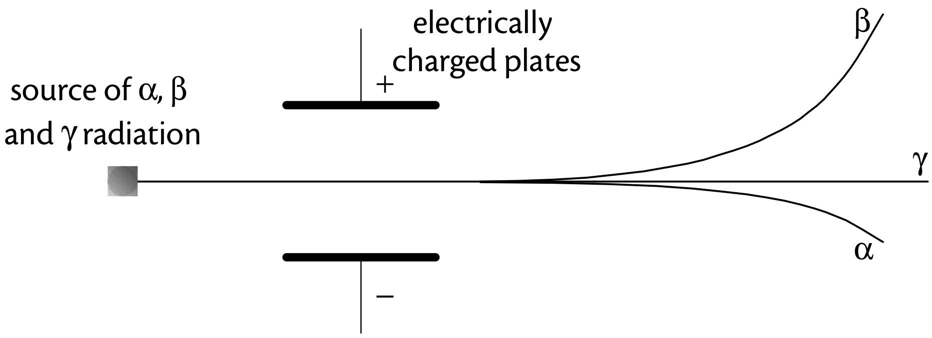
Contents

Topic 3 – Nuclear Chemistry

Topic 3 – Nuclear Chemistry

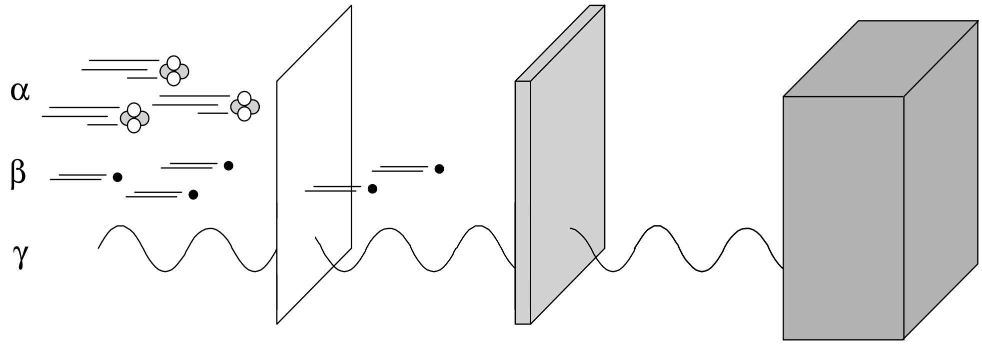
Radioactivity

As the title suggests this topic is about the chemistry of the nucleus and not about the orbitting electrons which have had an influence on the chemical reactions we have studied so far. In 1896, Becquerel discovered that compounds of uranium could 'fog' photographic plates which had been kept in the dark. The phenomenon became known as radioactivity and such substances were said to be radioactive. They emit radiation which can be of 3 types: α-, β- and γ-radiation. The radiation was affected by electric fields as shown:



This shows that α-radiation is positively charged, β-radiation is negative and γ-radiation has no charge.

α-, β- and γ-radiations also have different penetrating powers:



Some of the properties of these radiations are summarised in the table:

Name	Penetration	Nature	Charge	Mass (amu)
α (alpha)	few cm in air	He nucleus	2+	4
β (beta)	thin metal foil	electron	1–	1/2000 (approx)
γ (gamma)	thick concrete	emr*	none	None

*electromagnetic radiation

α-particles are identical to helium nuclei, ${}^{4}_{2}He^{2+}$. They are positively charged.

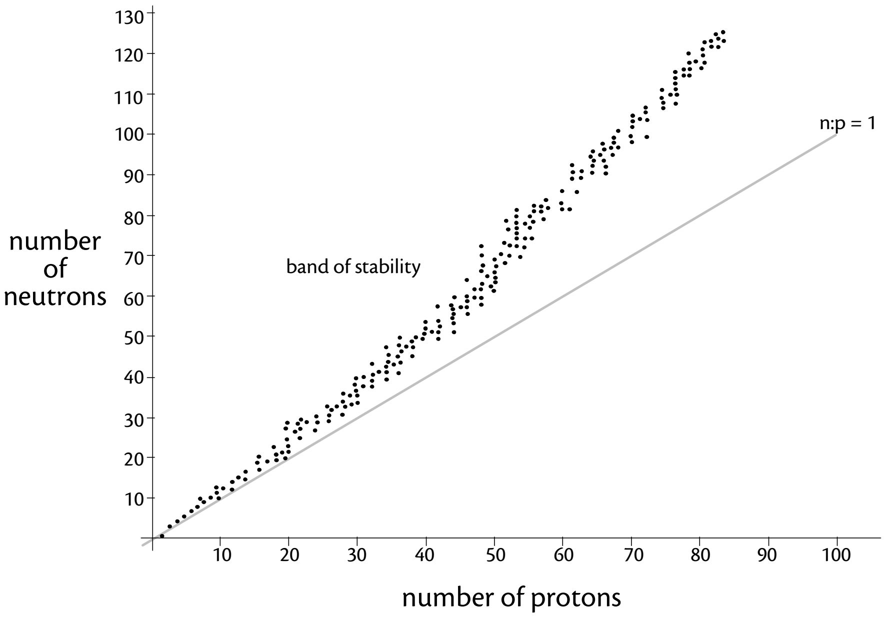
β-particles are electrons, ${}^{0}_{-1}e$. They are negatively charged.

γ-rays are very high energy electromagnetic radiation, similar to X-rays, hence the great penetrative powers. They have no charge.

Radioactivity is connected solely with the nucleus of the element concerned. This means that its chemical state is totally unimportant! Uranium compounds are as radioactive as the element.

Radioactivity is a feature of unstable nuclei and emitting radiation is a means by which the nuclei can become stable. So what makes a nucleus unstable? Protons are positively charged and it is thought that the neutrons prevent the protons repelling each other. The proton:neutron ratio is an important factor in deciding whether a nucleus is stable or not. For small stable atoms, the number of protons and neutrons are approximately the same but as the atoms become larger, the number of neutrons needs to be greater than the number of protons if the atom is to be stable. Look at the graph below:

If an atom has too many or too few neutrons for the number of protons, the atom will not lie on the belt of stability and will be unstable and so, radioactive. Very large atoms (>83 protons) are always unstable, irrespective of the number of neutrons in the nucleus. It is generally found that where a nucleus has too many neutrons, it changes a neutron into a proton and an electron and ejects the electron as β-radiation.



$$^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}e \qquad \beta\text{-emission}$$

This extra proton results in an increase in atomic number.

eg ^{14}C emits a β-particle and becomes a stable isotope of nitrogen

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

The opposite might happen if the neutron:proton ratio is too low – electron capture happens from the first 'shell'. This combines with a proton to form a neutron and the other electrons rearrange themselves to fill the first shell.

$$^{37}_{18}Ar + {}^{0}_{-1}e \longrightarrow {}^{37}_{17}Cl$$

It is found that very large nuclei (generally those with atomic number beyond 83) can become more stable by becoming smaller ie decreasing mass – this can be done by emitting α-particles. An α-particle consists of a helium nucleus ($^{4}_{2}He$) so its emission means a loss in mass of 4. These radiations come from the nucleus and as a result the nucleus is changed. We must look at this in more detail.

α-emission

The nucleus loses 2 protons and 2 neutrons; this decreases the charge on the nucleus by 2 and the mass of the nucleus by 4.

eg thorium 232 is an α-emitter. We can show this in a nuclear equation. Note: both the mass (top number) and the charge (bottom number) must be balanced in a nuclear equation.

$$^{232}_{90}\text{Th} \longrightarrow\ ^{228}_{88}\text{Ra} +\ ^{4}_{2}\text{He}$$

Since the emission also involves the loss of two protons the atomic number must decrease by 2 and we have made a new element. This is called transmutation.

β-emission

A β-particle is an electron, yet the nucleus does not contain any electrons. It is thought that a neutron changes into a proton and an electron and this electron is emitted as β-radiation. The other result is that the nucleus contanins an extra proton and the atomic number increases by 1. This another example of transmutation.

$$^{228}_{88}\text{Ra} \longrightarrow\ ^{228}_{89}\text{Ac} +\ ^{0}_{-1}\text{e}$$

γ-emission

Emission of γ-radiation often occurs along with the other types of radiation. It is a means by which nuclei can lose energy but, as it is not particle in nature and so has no mass or charge it does not affect mass number or atomic number.

Artificial Radioactivity

The examples above are natural radioisotopes but it is possible to make radioactive isotopes, and many are made for special purposes. They can be made by bombarding stable isotopes with neutrons in a nuclear reactor. Since neutrons are uncharged they are not repelled by the nucleus.

$$^{27}_{13}\text{Al} +\ ^{1}_{0}\text{n} \longrightarrow\ ^{24}_{11}\text{Na} +\ ^{4}_{2}\text{He}$$

The sodium isotope produced by the above can decay by β-emission to produce magnesium:

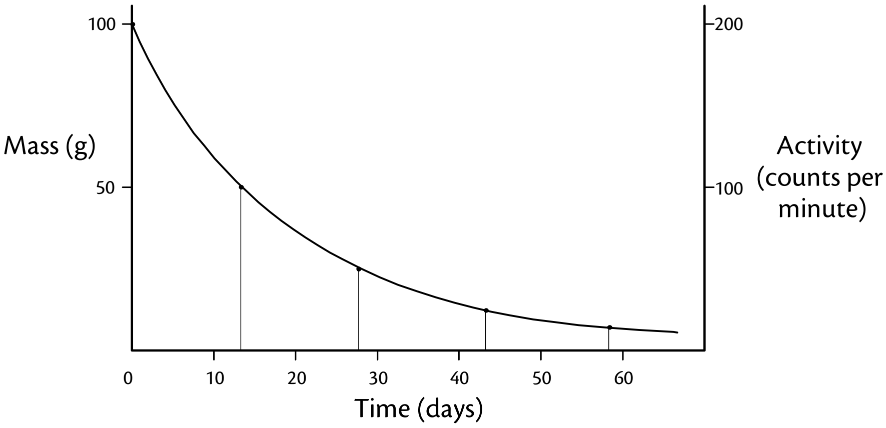
$$^{24}_{11}\text{Na} \longrightarrow\ ^{24}_{12}\text{Mg} +\ ^{0}_{-1}\text{e}$$

This source of radioactive isotopes is employed for making some of the useful radioisotopes which we will meet later. Very high energy particle accelerators have now been developed which allow positively charged particles to be used for bombardment.

Predictability of Radioactive Decay

When unstable nuclei emit radiation they are said to be decaying. It is impossible to predict exactly when one particular nuclide will in fact decay – this is a purely random event. However, with the massive numbers of radioactive nuclides in any measurable quantity, the laws of probability allow us to determine when a certain defined fraction of them will have decayed – the fraction is in fact ½ of the original. The time that this takes to happen is called the 'half-life'.

Half-life for any radioactive isotope is a constant, irrespective of how much of the isotope is left. It is also independent of the form (element, mixture or compound), temperature or applied pressure – it is fixed! However the intensity of the radiation will depend on the quantity of the radioisotope present. The graph below shows the decay of ^{32}P.



It is an example of an exponential decay curve. The percentage of the original left after n half-lives is $(\frac{1}{2})^n$. Here are some examples of half life calculations:

Example 1

A radioisotope of phosphorus has a mass of 80g and a half-life of 14 days. Calculate the mass of the isotope remaining after 56 days.

56 days = 4 half-lives

$$80g \xrightarrow{t_{1/2}} 40g \xrightarrow{t_{1/2}} 20g \xrightarrow{t_{1/2}} 10g \xrightarrow{t_{1/2}} 5g$$

So the mass remaining after 56 days is 5g

Example 2

The initial radioactivity of a radioisotope was 100 counts/minute. If the activity fell to 25 counts/minute in 24 days, what is the half-life of the radioisotope?

$$100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25$$

2 half-lives have elapsed in 24 days, so the half-life of the radioisotope is 12 days.

Example 3

A radioisotope has a half life of 7×10^3 years. How long will it take for 48g of the radioisotope to decay to leave 6g?

$$48g \xrightarrow{t_{1/2}} 24g \xrightarrow{t_{1/2}} 12g \xrightarrow{t_{1/2}} 6g$$

3 half-lives = $3\times7\times10^3$ = 2.1×10^4 years

Uses of radioisotopes

1. Medical Uses

For many years now, radiotherapy has been used for the treatment of some cancers.

^{60}Co is often used for the treatment of deep seated tumours – it is a γ-emitter so is able to penetrate to the site of the tumour. Skin cancers can be treated with less penetrating radiation from ^{32}P which is a β-emitter. It is also possible to monitor biological processes in the body. For example, radioactive iodine, ^{132}I or ^{123}I, is used to investigate possible disease of the thyroid gland. After injection of a solution containing some of the isotope its uptake in the thyroid gland can be determined – this allows diseased areas to be traced.

2. Industrial uses

Measurements and monitoring of various industrial processes can be made using radioactive isotopes. For example, imperfections in metal castings and welded joints can be examined using very penetrating radiation (γ-radiation from ^{60}Co or ^{192}Ir). Photographic film can be used as the detector. Continuous measurements and control of continuous processes can be made such as in the monitoring of thickness of paper, plastic and thin metal sheets. β- or γ-sources can be used to pass radiation through the sheets – one beam goes through a reference sheet of correct thickness. Any difference in signals between the two sources shows difference in thickness and this can trigger a response to make a correction.

3. Agricultural uses

Isotopes ^{32}P and ^{14}C can be used to determine the uptake of phosphates and carbon dioxide in plants. This is called 'isotopic labelling'.

γ-radiation can be used to kill bacteria and moulds in crops and this helps to increase the storage life.

4. Dating

The age of materials can be determined from the half life of certain isotopes. Carbon dating is probably the most familiar form of this technique.

^{14}C is a radioactive isotope which exists naturally due to its formation in the upper atmosphere from nitrogen bombarded by neutrons.

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

Carbon-14 has a half-life of 5600 years and decays by β-emission.

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

The rate of formation is equal to the rare of decay so there is a constant level of carbon-14 in the atmosphere. So carbon in the atmosphere is mostly the common isotope carbon-12 but with a small fixed proportion of carbon-14. Carbon-14 is absorbed by plants during photosynthesis so all living plants and animals contain the radioisotope. The level of carbon-14 in living materials is also constant since the rate of decay equals the rate of uptake from the atmosphere. When the plant or animal dies it no longer absorbs carbon-14 so the level of radioactivity will decrease. By comparing the activity of plant or animal remains with that of living material and knowing that the half life of carbon-14 is 5600 years, it is possible to calculate the age of the remains.

Example

Carbon from a wooden beam in a tomb has an activity of 3.75 counts per minute per gram of carbon. New wood has an activity of 15 counts per minute. What is the age of the beam?

$$15 \xrightarrow{t_{1/2}} 7.5 \xrightarrow{t_{1/2}} 3.75$$

2 half-lives = 2×5600 = 11200 years

5. Production of energy

Nuclear Fission involves the splitting of atoms by slow moving neutrons. The resulting nuclei are more stable than the original so energy is liberated in the process. The pattern of fragmentation varies. Here are three possible ways in which ^{235}U undergoes fission:

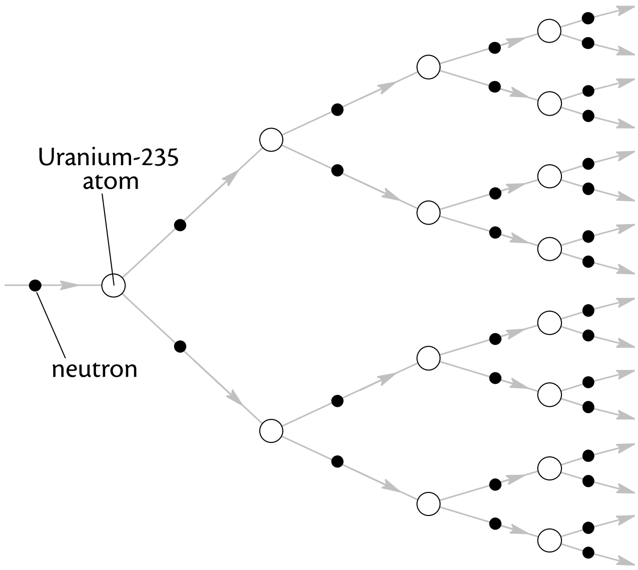
$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{90}_{38}Sr + ^{144}_{54}Xe + 2\,^{1}_{0}n \quad \text{a}$$

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{95}_{42}Mo + ^{139}_{50}Sn + 2\,^{1}_{0}n \quad \text{b}$$

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{92}_{36}Kr + ^{141}_{56}Ba + 3\,^{1}_{0}n \quad \text{c}$$

The fission process emits further neutrons. These can cause fission in other ^{235}U atoms and a chain reaction develops. The diagram on the right show what happens when two neutrons are released, as in reactions **a** and **b** above.

In a nuclear reactor the rate of this chain reaction must be controlled by lowering boron rods into the reactor. This nuclear reaction yields a huge amount of energy in the form of heat and this can be used to generate electricity.



Nuclear Fusion is when two nuclei join ('fuse'), causing energy to be released. This is another possible source of energy for the future. One such possibility is:

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

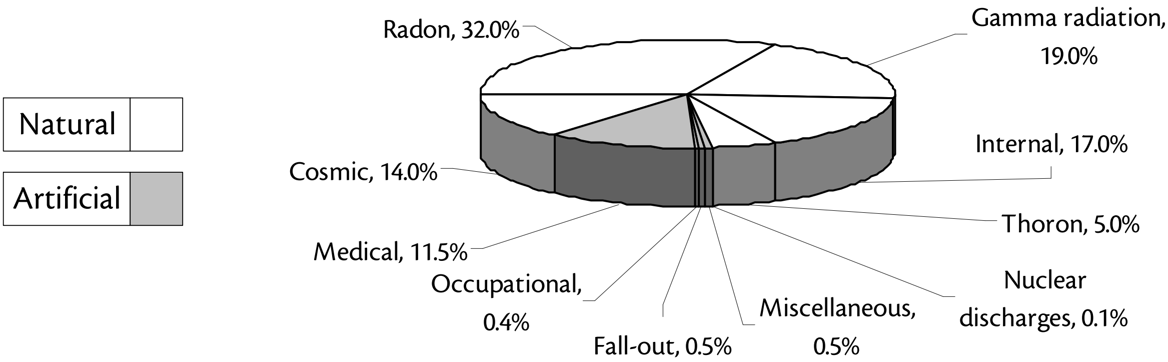
The above reaction creates even more energy than can be obtained from any fission reaction – only one ton ^{2}H and ^{3}H per year would be required for a 1000 MW power station. However it is very difficult to make two nuclei fuse because they are positively charged and the repulsion between them has to be overcome. It can only be achieved at exceptionally high temperatures, as found in our sun and stars. A great deal of research into this possibility is being conducted and it may well be a power source for the future.

Nuclear or Fossil Fuels for Generation of Electricity?

Calculations of energy released from the above equation show that 1 mole (235g) of ^{235}U would yield the equivalent energy of 60 tonnes of high quality coal (which would deliver 220 tonnes of CO_2 to the atmosphere)! This is of extreme environmental importance as nuclear reactors would reduce the consequences of the greenhouse effect and also reduce a contribution to acid rain. There are, however, some serious drawbacks of energy production from nuclear reactors. Serious accidents at nuclear plants would result in immensely catastrophic problems (probability of this is claimed to be low but accidents have happened – such as Chernobyl, 1986). The waste from some fission reactions is still very radioactive and needs to be re-processed or stored, perhaps for thousands of years, until the radioactivity has decayed to a safe level. Its disposal is a matter of great concern and debate.

Background Radiation

Many people think that the radiation surrounding us (in the air etc) comes purely from man's work with radioactive materials – eg from nuclear reactors, fallout from nuclear explosions etc. However, much of our surrounding radiation is natural, from atmospheric radon and cosmic radiation. The pie chart below shows the relative contributions to our 'background radiation'.



The Origin of the Elements

Nuclear fusion reactions occur in our sun:

$$^{1}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He$$

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

In the heaviest stars with the hottest and most compressed centres, further fusion can take place:

$$3\ ^{4}_{2}He \longrightarrow ^{12}_{6}C$$

$$^{12}_{6}C + ^{4}_{2}He \longrightarrow ^{16}_{8}O$$

All the naturally occurring elements have been formed in stars in this way.