Extension 23: Nuclear and Radiochemistry

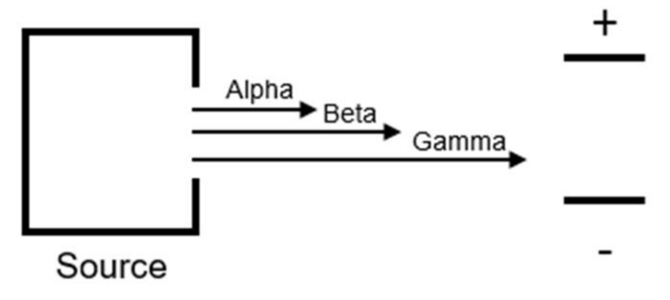
1. Concepts

In this extension unit we extend the work of Unit 23 in the book. To get you 'into the swing of things', start by attempting the following exercises.

EXERCISE 23A

alpha, beta and gamma radiation

The following diagram shows a mixture of radionuclides which emit alpha, beta and gamma radiation. Two electrically charged plates, one positive and one negative, are placed in front of the radioactive source. Redraw the diagram, showing the deflection (if any) of the three types of nuclear radiation as they approach the plates. Which radiation suffers the greatest deflection? Why? Assume that the size of the charge on each plate is the same.



Answer

Alpha particles are attracted to the negatively charged plate. Beta particles are attracted to the positively charged plate. The path of the gamma radiation is unaffected by the plates. Since the charges on the plates are equal in size (but opposite in charge), the beta particles (being less massive than the alpha particles) will be deflected more severely from their straight-line path.

EXERCISE 23B

Ionisation caused by nuclear radiation

Energies of 10^9–10^7 kJ per mole of particles correspond to $1.7–0.017\ 10^{-15}$ kJ per particle. The first ionisation energy of hydrogen is 1310 kJ per mole of H atoms. Estimate the number of hydrogen atoms that could be ionised by one particle of nuclear radiation.

Answer

Ionisation energy per H atom = $1310/6.022 \times 10^{23}$

$\approx 2 \times 10^{-21}$ kJ. An energy of 1.7×10^{-15} kJ is bigger than this by the factor

$$\frac{1.7 \times 10^{-15}}{2 \times 10^{-21}} = 850\ 000$$

therefore, 850 000 H atoms could be ionised by one particle. An energy of 0.017×10^{-15} kJ per particle would be sufficient to ionise 8500 H atoms.

Unit of activity – the Becquerel

The **activity** of a radioactive sample is the rate at which nuclear radiation is emitted from that sample. To calculate the activity of a mass of a radionuclide, we multiply the number of atoms of radionuclide present at that instant (N_t) by the decay constant of the radionuclide:

activity = $N_t \times k$

Activity is measured in disintegrations per second. If a sample has a low activity this is because

1. only a small mass of radionuclide is present; or
2. the sample is a weak emitter, i.e. a radionuclide with a long half-life (small k).

The SI unit of activity is the **Becquerel** (symbol Bq), with one becquerel being defined as one atomic disintegration per second. A mass of 1.00 g of radium-226 undergoes 3.7×10^{10} disintegrations per second. 3.7×10^{10} disintegrations is known as a **curie** (symbolised Ci):

3.7×10^{10} Bq = 1Ci

For example, radioactive sources sold for use in school laboratories typically undergo 2×10^5 disintegrations per second (equivalent to 5 microcuries, 5 μCi). (It is sometimes stated that the source 'contains' 5μCi of radioactive material.) About 7×10^7 Ci of radionuclides were blown into the air during the Chernobyl disaster. This is equivalent to the activity of 7×10^7 g (70 tonnes) of radium-226.

EXERCISE **23C**

Becquerels and curies

(i) At what rate will beta particles be emitted from 10 μCi of pure cobalt-60?

(ii) The contamination of some vegetables due to iodine-131 in Alsace, France, after the Chernobyl disaster in 1986 temporarily produced activities of 35 000 Bq per kilogram of food. (500 Bq kg^{-1} was declared the safe limit after the accident.) What mass of radium-226 would be needed to be added to 1 kg of food to produce the same number of disintegrations per second?

Answer

(i) 1 Ci = 3.7×10^{10} disintegrations per second. 10 μCi = $10 \times 10^{-6} \times 3.7 \times 10^{10} = 3.7 \times 10^5$ beta particles per second.

(ii) 1 g of pure radium-226 undergoes 3.7×10^{10} disintegrations per second, i.e. 1 g ^{226}Ra ≡ 3.7×10^{10} Bq. The mass of ^{226}Ra that is needed to produce an activity of 35 000 Bq is 35 000/3.7×10^{10} = 9.5×10^{-7} g (0.95 μg).

2. Radioactive series

What is a radioactive series?

The radioactive decay of a radioisotope does not usually consist of a single step because the daughter nuclei themselves decay. The overall sequence of decays is known as a **radioactive series**. There are three radioactive series known which start with naturally-occurring radioisotopes:

1. The **uranium series** has ${}^{238}_{92}U$ as its parent. After 14 successive decays, ${}^{206}_{82}Pb$ is produced as the final 'stable' (i.e. non-radioactive) isotope.
2. The **thorium series** has ${}^{232}_{90}Th$ as its parent. After 10 stages ${}^{208}_{82}Pb$ is produced as the stable isotope.
3. The **actinium series** has ${}^{235}_{92}U$ as its parent. The decay series involves 11 stages, ending with ${}^{207}_{82}Pb$ as the stable nucleus.

Not surprisingly, the lead isotopes produced at the end of these series are all widespread in nature. Their percentage natural abundances in natural lead are ${}^{208}_{82}Pb$ 52.3%, ${}^{206}_{82}Pb$ 23.6% and ${}^{207}_{82}Pb$ 22.6%. The rest (1.5%) is ${}^{204}_{82}Pb$.

A fourth radioactive series, the **neptunium series**, involves 11 stages and starts with the artificially produced radionuclide ${}^{237}_{93}Np$ and produces ${}^{209}_{83}Bi$ as the stable nuclide.

Uranium series

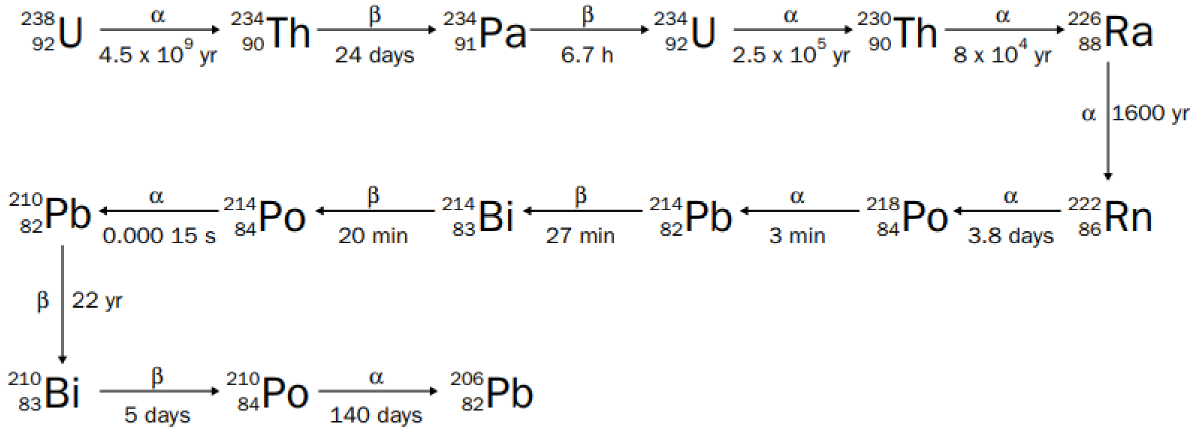


Fig. 23.1 The uranium decay series (simplified)

The main details of the uranium series are shown in Fig. 23.1. The type of decay is shown above the arrow with the half-life of the isotope shown below. The overall equation for the decay of uranium-238 to lead-206 is:

$${}^{238}_{92}U \xrightarrow{4.5 \times 10^{9}\ \text{yr}} {}^{206}_{82}P + 8\,{}^{4}_{2}He^{2+} + 6\,{}^{0}_{-1}e$$

3. Stability of radionuclides

There are about 260 stable nuclei, about 160 of which possess even numbers of protons and also even numbers of neutrons. Only five stable nuclei possess odd numbers of protons and odd numbers of neutrons. Nuclei with even numbers of protons and neutrons are generally more stable than those having any other combination.

The ratio of neutrons to protons appears to be an important factor in deciding whether or not a particular nuclide undergoes radioactive decay. The stable isotopes of lighter elements ($Z < 20$) all possess neutron:proton ratios close to 1. Nuclei with more neutrons than protons often decay by beta emission (in which a neutron changes into a proton).

All nuclei with more than 83 protons are unstable. Such nuclides usually decay by alpha emission followed (in the radioactive series) by beta or positron emission until a stable nucleus of lead or bismuth is achieved.

Nuclei with 'magic numbers' of protons (or of neutrons) are particularly stable. The magic numbers are 2, 8, 20, 28, 50, 82 and 126.

EXERCISE 23D

Nuclear stability

(i) Predict which of the following nuclides are stable (a) ${}^{238}_{93}\mathrm{Np}$ (b) ${}^{24}_{11}\mathrm{Na}$ (c) ${}^{16}_{8}\mathrm{O}$

(ii) Why are ${}^{4}_{3}\mathrm{He}$, ${}^{12}_{6}\mathrm{C}$ and ${}^{16}_{8}\mathrm{O}$ particularly stable nuclei?

(iii) Lead ($Z = 82$) is the end product of the three natural radioactive series. Bismuth-209 ($Z = 83$) is the end product of the neptunium radioactive series. What is special about these elements?

Answer

(i) ${}^{238}_{93}\mathrm{Np}$ is radioactive because it contains more than 83 protons. ${}^{24}_{11}\mathrm{Na}$ has an odd number of protons and neutrons and we predict that it is probably radioactive (which it is). ${}^{16}_{8}\mathrm{O}$ contains an even number of neutrons and we would (correctly) predict that it is stable.
(ii) They possess even numbers of protons and neutrons.
(iii) Pb possesses a magic number of protons. Bismuth-209 possesses a magic number of neutrons.

4. Uses of radionuclides

We now discuss the other applications of radionuclides.

(a) Nuclear fission of uranium-235

Natural uranium contains about 99.3% ${}^{238}_{92}\mathrm{U}$ and 0.7% ${}^{235}_{92}\mathrm{U}$, usually in the form of uranium oxide (UO_2). Purified uranium oxide is used as the 'fuel' for most types of nuclear reactor, with the percentage of the ${}^{235}_{92}\mathrm{U}$ artificially raised (**enriched**) to 2-3% in order to achieve sufficient fission.

Nuclear fission involves the splitting of the nucleus into two nuclei of roughly equal mass. Uranium-235 and uranium-238 naturally undergo a type of fission (known as **spontaneous fission**) in which the uranium nucleus, without assistance, breaks up into two nuclei and produces a neutron, but this process is incredibly slow – even slower than the radioactive decay of these radioisotopes by alpha emission. (Note that the greater the isotopic mass of the nuclide the faster the spontaneous fission. This may put a limit on the number of transuranium elements which can exist, since if spontaneous fission is rapid enough the nucleus of the element will never remain intact.)

Neutrons may be absorbed by uranium-235 nuclei in a process called **induced nuclear fission**, commonly simply referred to as **nuclear fission**. (Initially, the neutrons originate from the spontaneous fission of uranium or from cosmic rays which come from outer space). The equations:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n}\ (\text{slow}) \rightarrow ^{139}_{54}\mathrm{Xe} + ^{95}_{38}\mathrm{Sr} + 2^{1}_{0}\mathrm{n}$$

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n}\ (\text{slow}) \rightarrow ^{142}_{56}\mathrm{Ba} + ^{92}_{36}\mathrm{Kr} + 2^{1}_{0}\mathrm{n}$$

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n}\ (\text{slow}) \rightarrow ^{139}_{56}\mathrm{Ba} + ^{94}_{36}\mathrm{Kr} + 3^{1}_{0}\mathrm{n}$$

Are a few of the many observed fission reactions involving ^{235}U. Note that neutrons are made in fission reactions. Gamma rays are also produced in each case, together with about 10^{10} kJ of energy per mole of ^{235}U consumed. (This energy is distributed in the kinetic energy of the new nuclei and in the energy of the accompanying gamma rays.) It is this type of fission reaction which is exploited in commercial nuclear power stations.

Not all the induced fission reactions involving ^{235}U are equally likely, and experiments have shown that, on average, there are 2.5 neutrons produced for every ^{235}U atom that is broken up. This means that more neutrons are generated in nuclear fission than are used up (Fig. 23.2). It is this fact that allows, in principle, the fission of ^{235}U to be self-sustaining, the fission occurring at a faster and faster rate as the neutrons produced induce fission in the remaining U-235 nuclei, causing a **chain reaction**.

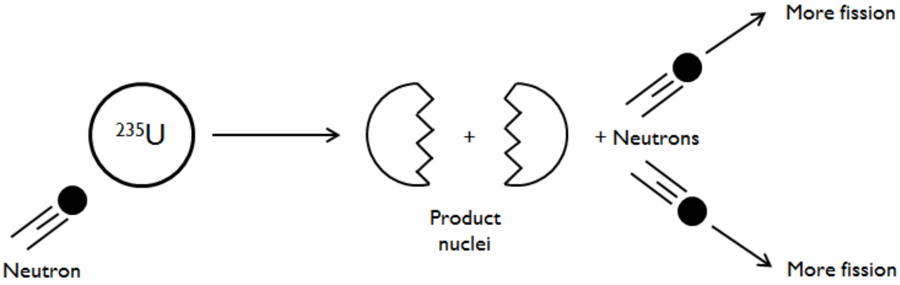


Fig. 23.2 Nuclear fission can be thought of as the breaking of a big ball (the ^{235}U nucleus) into two roughly equal halves (the product nuclei) using a small ball (a neutron) as ammunition. 2-3 neutrons are also produced, and these may cause fission in more ^{235}U nuclei, so setting up a chain reaction. The chain reaction is controlled in a nuclear power station, and uncontrolled in a nuclear bomb.

Key points about nuclear fission reactors

- In practice, a chain reaction will only occur if the absorption of neutrons by ^{235}U nuclei is efficient. If neutrons are travelling too fast, they are not absorbed, they simply pass through the ^{235}U nuclei and no fission occurs. For this reason, the neutrons must be slowed down using a moderator (commonly graphite or water) which absorbs the excess energy of the neutrons (Fig. 23.3). Because ^{235}U undergoes fission using ‘slow’ neutrons, it is said to be fissile.

- Slow neutrons will not cause fission in uranium-238 nuclei, which only undergo fission if highly energetic neutrons are used, i.e. ^{238}U is non-fissile. Fission using high-energy neutrons is less efficient than fission using slow neutrons. This means that the overall gain in energy from the use of ^{238}U as fuel is much less than that for ^{235}U, and so ^{238}U is not commercially viable.

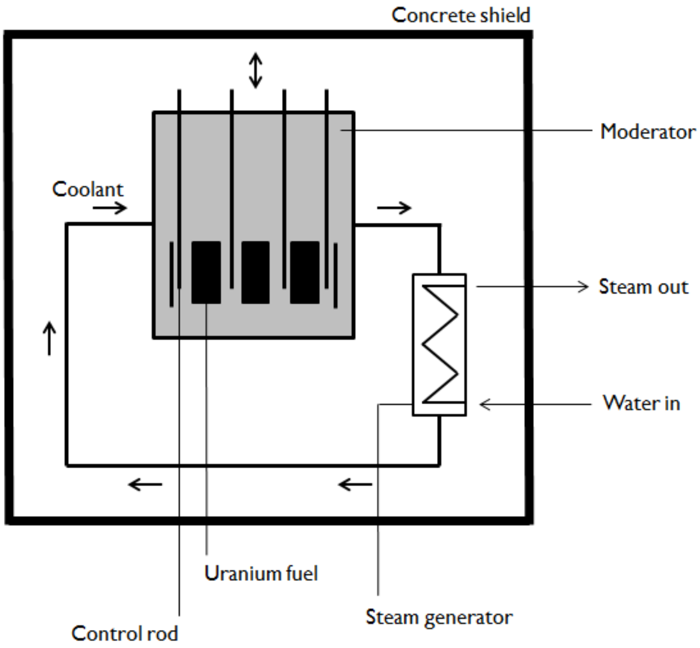


Fig. 23.3 The main parts of a nuclear reactor. Heat is transferred outside the nuclear reactor using a liquid or gas as coolant, such as water or carbon dioxide. The coolant then transfers the heat to a heat exchanger which converts water to steam to drive turbines which produce electricity.

- The uranium is stored inside the reactor core in alloy tubes called **fuel rods**. A minimum mass of ^{235}U is needed in each fuel rod in order to ensure that there are enough ^{235}U nuclei to absorb the neutrons emitted during the induced fission, so that further fission may continue. This **critical mass** of ^{235}U depends upon the shape of the uranium fuel. It is usually several kilograms.
- Many of the fission products (such as $^{142}_{56}Ba + ^{92}_{36}Kr$) are intensely radioactive in their own right. This makes the intensity of nuclear radiation in the nuclear core thousands of millions of times more intense than that generated by the natural radioactivity of the uranium radioisotopes alone. (A typical fission reactor may contain about 200 tonnes of uranium, with an activity of about 10^{10} Bq. Once fission has started, the reactor core possesses an activity of $\approx 10^{21}$ Bq!) Elaborate shielding (including thick concrete walls) is therefore needed to protect workers and members of the public.
- A chain reaction cannot be allowed to proceed unchecked in a nuclear reactor because, although there is no danger of a nuclear explosion (since this requires that the ^{235}U nuclei be smashed together at high speeds), the tremendous heat generated by uncontrolled fission might cause structural damage to the reactor itself. This would make it very likely that some of the intensely radioactive material in the core of the reactor would escape into the surrounding environment – this happened at Chernobyl. For this reason, **control rods** made of neutron-absorbing material (such as boron or cadmium) are lowered into the

nuclear reactor. To speed up fission, some of the control rods are withdrawn. When demand for electricity is low (as at night), extra control rods are lowered into the reactor.

- The nuclei and neutrons produced as fission products possess considerable kinetic energy and, due to collisions with the reactor coolant, this energy is ultimately converted to heat. This heat is utilised to produce electricity using a conventional steam turbine.
- In any nuclear reactor only about 0.1% of the initial mass of fuel is converted into energy, and it becomes necessary to replace the fuel rods 2-3 times a year. The main reason for changing the fuel rods is to remove the fission products which would otherwise absorb too many neutrons and slow down nuclear fission.

(b) Nuclear fusion

Nuclear fusion reactions are the source of the sun's energy, on which life on earth ultimately depends. The possibility of obtaining energy from controlled fusion reactions on earth is now a major research interest in several countries, with most projects using deuterium and tritium as the fuels. The fusion reaction is:

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

About 5×10^9 kJ of energy is released per mole of tritium consumed.

Positive nuclei repel each other, and it has been found that deuterium and tritium nuclei must possess huge amounts of kinetic energy before they can 'fuse' together. Such kinetic energies require a temperature of about 100 million °C. At such temperatures all atoms are ionised, and the mixture of positively charged nuclei and free electrons is called a **plasma**. If the particles in the plasma were to strike the walls of the reactor vessel, other nuclei would mix with the plasma and any fusion would stop.

The remarkable solution to this problem is to confine the plasma in the form of a ring using a powerful magnetic field. To date, fusion has been achieved only for a fraction of a second, and the commercial production of electricity from nuclear fusion has yet to be realised.

'Cold fusion', i.e. nuclear fusion at ambient temperatures, has been claimed but not proved.

(c) Radioactive dating

The fact that the half-life of a radionuclide is a constant (and independent of the molecule containing the nuclide or the temperature of the radioactive source) is used to determine the age of rocks or archaeological relics. An example is provided by the use of 'carbon-14 dating' to find the age of dead plants. Although most carbon atoms in nature are stable $^{12}_{6}\text{C}$, a tiny amount of radioactive $^{14}_{6}\text{C}$ is also present and the $^{14}_{6}\text{C}:{}^{12}_{6}\text{C}$ ratio remains approximately constant during the life of the plant. The level of $^{14}_{6}\text{C}$ in the plant begins to fall immediately after death. $^{14}_{6}\text{C}$ has a half-life of 5700 yr. Mass spectrometers are used to measure the $^{14}_{6}\text{C}:{}^{12}_{6}\text{C}$ ratio in a sample of the dead plant. Knowing the ratio for a living plant of a similar type, the time that has elapsed since the death of the organism may be calculated.

(d) Treatment of cancer

Although high levels of X-ray and nuclear radiation cause cancer, such radiation may also be used to kill cancer cells, which are particularly sensitive to radiation because of their high rate of growth. The use of nuclear radiation in this way is called **radiotherapy**. The aim of radiotherapy is to deliver as high a dose as possible to the malignant tissue without causing severe injury to the surrounding healthy tissue.

(e) Radioisotopes as tracers

Radioisotopes have the same *chemical* reactions as non-radioactive isotopes of the same element, but they have the advantage that their position may be located using suitable detection equipment, i.e. they can be *traced*. In medicine, tracers consisting of compounds containing technetium $^{99}_{43}\mathrm{Tc}$, are used to locate brain tumours. The use of salt which contains radioactive $^{24}_{11}\mathrm{Na}$ allows doctors to follow movements of sodium ions in the kidney. In positron emission tomography (PET) positronemitting nuclides, such as $^{15}_{8}\mathrm{O}$, are used to provide an image of the flow of blood in the brain.

(f) Miscellaneous uses

These include the use of the beta emitter $^{241}_{95}\mathrm{Am}$ ($t_{½}$ = 432 yr) in smoke detectors, the sterilisation of food using nuclear radiation, the use of gamma sources to estimate the thickness of metal pipes, and the use of radioisotopes in an analytical technique called neutron activation analysis.

5. Energy and mass changes in nuclear reactions

The energy changes involved in nuclear reactions are about one-million times larger than those resulting from chemical reactions, although this is usually only obvious in rapid nuclear reactions on a large scale, such as the fission of uranium in nuclear power stations. Even early workers realised that intensely radioactive isotopes, such as radium-226, got warm as they decayed. 1 g of radium gives out about 100 kJ of heat energy per hour. This is remarkable in view of the fact that only 0.000 005% of the radium has decayed during this period, and it follows that enormous amounts of energy must be released during the atomic disintegrations that do occur.

Although we shall use the joule and the kilojoule as our units of energy, it is worth noting that in nuclear physics it is customary to use the mega electronvolt, MeV, as the unit of energy. 1 MeV = 1.602×10^{16} kJ. 1 MeV per *nucleus* is equivalent to $9.65\ 10^{7}$ kJ per mole of nuclei.

Equivalence of mass and energy

As a result of the work of Albert Einstein (1879–1955) and others, it is now known that matter and energy can be *interconverted*.

This remarkable idea has an important consequence. If a collection of atoms or molecules is found to give out energy for any reason (whether it be the result of chemical change, of changes in state or from nuclear reaction) then the total mass of the reacting particles must fall during the change. The reverse applies to endothermic reactions. This means that the law of conservation of mass is disobeyed.

The change in mass, m (in kg), that accompanies the energy change E joules for any process, may be calculated from the famous **Einstein equation**.

$$E = mc^2$$

where *c* is the speed of light in a vacuum. Since *c* is a very big number (3.00×10^{8} m s^{-1}), the square of *c* is enormous, and the conversion of even a small mass produces a huge amount of energy.

Mass loss in a chemical reaction

Suppose that a mass of fuel is burned in oxygen to give 1000 kJ (1 000 000 J) of heat. This means that E = − 1 000 000 J (minus because heat is given out). The change in mass is then

$$m = \frac{E}{c^2} = \frac{-1\,000\,000}{(3.00\ \times\ 10^{8})^{2}} = \ -1.11\ \times 10^{-11}\ \mathrm{kg, or} - 1.11\ \times\ 10^{-8}\ \mathrm{g}$$

where the negative sign attached to the mass shows that mass has been lost. The loss in mass from the fuel and oxygen molecules is too small to be detected by laboratory balances. This explains why, in practice, the law of conservation of mass appears such a good approximation for chemical reactions.

Mass loss in a nuclear reaction

As an example of the change in mass involved in **nuclear reactions**, consider the fusion of two helium atoms,

$$\begin{array}{lcccccccc} & {}^{2}_{1}\mathrm{H} & + & {}^{2}_{1}\mathrm{H} & \rightarrow & {}^{3}_{1}\mathrm{He} & + & {}^{1}_{0}\mathrm{n} \\ \textit{masses}/\mu & 2.0140 & & 2.0140 & & 3.0160 & & 1.00867 \end{array}$$

which is known to be highly exothermic. The *accurate* masses of the particles are also shown. The change in mass, when two deuterium *atoms* combine is the difference

mass of products – mass of reactants

Here,

$$(3.0160 + 1.008\,67) - (2.0140 + 2.0140) = 0.0033\ \mathrm{u}$$

the negative sign indicating that a *loss* in mass has occurred. Since 1 u = $1.660\,54 \times 10^{-24}$ g, the loss in mass in grams is:

$$0.0035 \times 1.6600\,54 \times 10^{-24} = 5.5 \times 10^{-27}\ \mathrm{g.}$$

When two moles of deuterium atoms react, the loss in mass will be:

$$5.5 \times 10^{-27} \times 6.022 \times 10^{23} = 0.0033\ \mathrm{g\ or}\ 3.3 \times 10^{-6}\ \mathrm{kg}$$

Such a loss of mass would be readily detectable using sensitive laboratory balances. Generalising,

> **Nuclear changes show significant deviations from the law of conservation of mass.**

Substitution of m = 3.3×10^{6} kg into the Einstein equation gives the energy released in the fusion reaction as approximately 3×10^{11} J per mole of helium-3 formed.

Although we usually think of mass and energy as quite distinct, the Einstein equation suggests that matter and energy are different forms of the same thing. Since even a small mass of matter can be converted into an enormous amount of energy, it is tempting to regard matter as a highly condensed form of energy.

EXERCISE **23E**

Calculate the mass change (and hence the energy change) for the reaction in which 1 mol of tritium is made from lithium-6. You are given the following accurate masses: m($^{6}_{3}$Li) = 6.0151 u, m($^{4}_{2}$He) = 4.0026 u, m($^{3}_{1}$H) = 3.0161 u, m($^{1}_{0}$n) = 1.008 67 u.

Answer

Change in mass is:

$(4.0026 + 3.0161) - (6.0151 + 1.00867) = -0.0051$ u

The mass loss associated with the production of 1 mol of tritium is therefore 0.0051 g or $5.1\ 10^{-6}$ kg. The energy change is given by:

$E = (-5.1 \times 10^{-6}) \times (3.00 \times 10^{8})^{2}$

$= -4.6 \times 10^{11}$ J (exothermic)

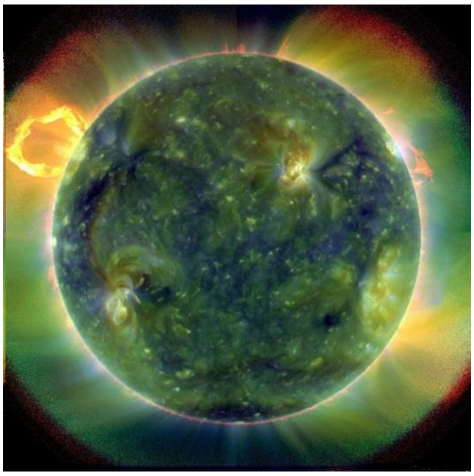


Fig. 23.4 The energy emitted by the sun is produced by nuclear fusion at its core. This image showing the ultraviolet emission from the sun. The red areas are < 60000 K and the blues and greens are > 1000000 K. Photograph courtesy of NASA.

DID YOU KNOW?

Nuclear fusion weapons (‘H bombs’) use nuclear fission bombs based on plutonium to ignite deuterium in a massively exothermic nuclear fusion reaction. Lord William Penny estimated the force of the 1957 hydrogen bomb using metal tubes of artists’ paint placed within the blast area, since the compression of the tubes caused by the blast could be calibrated by comparing the dents with those produced by known forces in the laboratory. Since toothpaste was also sold in metal tubes until recently, he might have used tubes of toothpaste instead!

Britain’s first nuclear fission bomb, Monte Bello islands, 1952.

References

Invisible Rays, A History of Radioactivity, by GI Brown, Sutton Publishing, 2002. This is an exceptionally good history of radioactivity and its uses, from the viewpoint of a chemist.