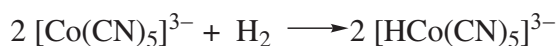


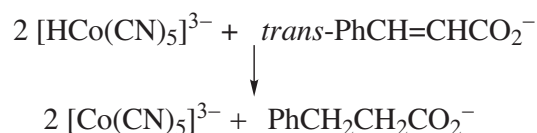
The first step involves coordination of ethene to the vacant site of the catalyst (6) to give the alkene-complex (7). Migratory insertion of ethene gives the ethyl-complex $[\text{RuCl}(\text{Et})(\text{PPh}_3)_3]$ (8). Coordination of H_2 gives the $\eta^2\text{-H}_2$ complex (9). This complex undergoes a heterolytic cleavage of H_2 , eliminating ethane and regenerating the active catalyst (6).

Hydrogenation via homolytic activation

The 17e Co(II)-complex $[\text{Co}(\text{CN})_5]^{3-}$ activates dihydrogen homolytically to give the Co(III) complex $[\text{CoH}(\text{CN})_5]^{3-}$.



This 18e-complex $[\text{CoH}(\text{CN})_5]^{3-}$ does not have a vacant site. However, it can transfer a hydrogen atom (H^\bullet) to an activated olefin, cinnamate (*trans* $\text{PhCH}=\text{CHCO}_2^-$), giving a moderately stable benzyl radical, $\text{Ph}^\bullet\text{CHCH}_2\text{CO}_2^-$ which abstracts another hydrogen radical (H^\bullet) to give 3 phenyl propionate ion, $\text{PhCH}_2\text{CH}_2\text{CO}_2^-$.



Problems

- The catalyst $[\text{MCl}(\text{PR}_3)_3]$ reacts with H_2 to give the octahedral M(III) dihydride (A). Replacement of PR_3 by $\text{MeCH}=\text{CH}_2$ in (A) gives the olefin-complex (B). In the presence of PR_3 , (B) undergoes migratory insertion to give the octahedral alkyl-complex (C). (C) reductively eliminates the alkane (D) to regenerate the catalyst $[\text{MCl}(\text{PR}_3)_3]$. Write the molecular formulae of (A), (B), (C) and (D).
- The active catalyst $[\text{RuHBr}(\text{PPh}_3)_3]$ coordinates with $\text{MeCH}=\text{CH}_2$ to give the olefin-complex (P). (P) undergoes migratory insertion to give the alkyl-complex (Q). (Q) reacts with H_2 to give the dihydrogen-complex (R) which eliminates (S) to regenerate $[\text{RuHBr}(\text{PPh}_3)_3]$. Identify (P), (Q), (R) and (S).

Student Corner

Introduction to Radiochemistry

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An **atom** consists of a very small (about 10^{-10} m in radius), dense and positively charged nucleus and negatively charged **electrons**. The **nucleus** consists of **protons** (p) and **neutrons** (n); these two particles are collectively known as **nucleons**. An element (X) with the atomic number (Z) and the mass number (A) is represented as ${}^A_Z\text{X}$, e.g. uranium-238 = ${}^{238}_{92}\text{U}$.

Chemical reactions occur by transferring **electrons** between atoms, ions or molecules. Some unstable nuclei radiate energy and/or small particles to form a new element(s); these are called **nuclear** reactions. During these reactions A and/or Z of an element **may change**. Emission of particles is a nuclear property and it is not affected by the physical state of the element, its chemical composition, temperature or pressure of the system. Henry Becquerel noticed this phenomenon of **spontaneous disintegration** and named it as

radioactivity.

Radioisotopes or radionuclides are the unstable nuclei (mainly with $Z > 83$) which emit radiation and undergo spontaneous decay or disintegration. The three main types of radiation are α , β and γ . Charge and mass of particles are given below.

Name and Symbol	Charge	Mass (amu)
α (Alpha) (${}^4_2\text{He}$)	+2	4.0015
β (Beta) (${}^0_{-1}\text{e}$)	-1	0.00055
Neutron (${}^1_0\text{n}$)	0	1.0089
Proton (${}^1_1\text{p}$ or ${}^1_1\text{H}$)	+1	1.0074
Deuterium (${}^2_1\text{H}$)	+1	2.014
Positron (${}^0_{+1}\text{e}$)	+1	0.00055
γ (Gamma)	0	-

Nuclear stability

Components in a nucleus are strongly attracted to each other; in stable nuclei, the ratio of neutron to proton is one. With increase of the n/p ratio, more neutrons are required to reduce the proton-proton repulsion forces. Extra stability is associated with nuclei having the following magic numbers for p and n.

$$p = 2, 8, 20, 28, 50, 82$$

$$n = 2, 8, 20, 28, 50, 82, 126$$

$$\text{e.g. } {}^4_2\text{He}, {}^{40}_{20}\text{Ca}, {}^{208}_{82}\text{Pb}$$

Binding energy

The energy required to decompose a nucleus into protons and neutrons is defined as the binding energy. The binding energy can also be considered as the energy associated with the formation of the nucleus from its constituent protons and neutrons. When a nucleus is formed, some of the mass of its constituents is converted into binding energy.

Actual mass of a He nucleus or α particle is 4.0015 amu. But expected mass is 4.0326 amu ($2p+2n$). Thus, **mass defect** (Δm) is 0.0311 amu.

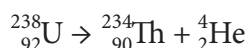
$$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$$

The average binding energy per nucleon for an α particle can be calculated by using the Einstein's equation ($E = mc^2$), which is 7.245 MeV, ($c = 2.99776 \times 10^8 \text{ m s}^{-1}$). For most of the stable nuclei it varies between 6-9 MeV.

$$1 \text{ MeV} = 1.60210 \times 10^{-13} \text{ J}$$

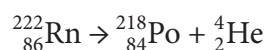
Nuclear reactions

Nuclear equation symbolizes a nuclear reaction where one element is transformed into another element(s). The sum of Z and A on one side of the arrow should be equal to those on the other side. For example,



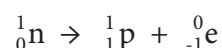
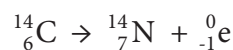
Examples for some nuclear reactions are as follows.

1. **α emission:** The α particle is identical to a helium nucleus. It carries a charge of +2 but the charge is omitted from its symbols. It can be deflected by electric and magnetic fields.

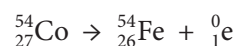
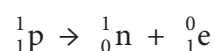


Elements below atomic number 66 do not usually emit α -particles.

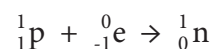
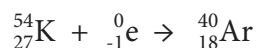
2. **β emission:** β -particle can be deflected by electric and magnetic fields. β emission decreases the n/p ratio since a neutron is converted into a proton.



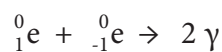
3. **Positron emission:** The positron emission is equivalent to the conversion of a proton to a neutron.



4. **Electron capture:** An unstable nucleus decays by capturing an electron from an inner orbital of an atom.



5. **γ emission:** There is no change of atomic number or mass number. Often γ emission occurs very quickly after a radioactive decay. Excited nuclei emit gamma photons ($\lambda \sim 10^{-12} \text{ m}$) in order to lower their energies. The reaction between positron and electron (annihilation collision) generate photons and energy (511 keV).



Rate of radioactive decay

The rate at which a radioactive element (isotope) disintegrates is proportional to the number of radioactive nuclei present. Radioactive decay obeys a first-order rate law.

$$-\frac{dN}{dt} \propto N; \quad -\frac{dN}{dt} = \lambda N$$

$$N = N_0 e^{-\lambda t}$$

N is the number of nuclei at time t and N_0 is the initial number at $t = 0$. λ (Lambda) is the **decay constant**, which is a characteristic of that isotope. The rate of decay

is generally expressed in counts per second. Thus, the unit of the decay constant (λ) is s^{-1} .

Radioactivity can also be expressed in term of activity (measured as disintegrations per second). A_0 = initial activity, A = activity after time t .

$$A = A_0 e^{-\lambda t}$$

The older non-SI unit of radioactivity is Curie (C_i). One Curie is equal to the disintegration rate of 1 g of radium-226. That is equal to 3.7×10^{10} disintegrations per second (dps). *i.e.* $1 C_i = 3.7 \times 10^{10}$ dps. The SI unit of activity is the Becquerel (Bq), where $1 Bq = 1$ dps.

Half-life

The half-life ($t_{1/2}$) of a radioactive isotope is the time required for an isotope to reduce the number of initial radioactive atoms (or activity) by half of the initial value.

i.e. when $t = t_{1/2}$; $N = N_0/2$.

$$\therefore \ln 2 = \lambda t_{1/2} \rightarrow \lambda t_{1/2} = 0.693$$

The half-life of Ra-226 is about 1600 y. Thus, 1 g of Ra becomes $\frac{1}{2}$ g in 1600 y, and $\frac{1}{4}$ g in another 1600 y, and so on.

Radioactive decay series

The series containing all the elements starting with the **parent** element and all the decay products (**daughter** elements) is called the **radioactive decay series**. The heavy radioactive elements can be grouped into four decay series and in each series, α and β emissions take place until a stable isotope of lead or bismuth is formed.

- Thorium ($4n$) Series (ends with lead 208) (the mass numbers 232, 228, 224,....., 208 are multiples of 4).
- Neptunium ($4n+1$) Series (ends with bismuth 209)
- Uranium ($4n+2$) Series (ends with lead 206)
- Actinium ($4n+3$) Series ends with lead 207)

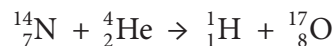
Induced nuclear reactions

There are two main types of radioactive processes namely natural and artificial.

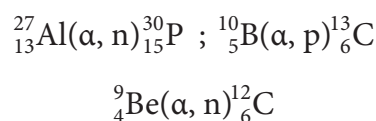
Natural radioactivity arises from naturally occurring

radioactive isotopes such as ^{235}U , ^{232}Th and ^{238}U . Artificial radioactivity or nuclear transmutation is a process that produces radioactive elements by bombarding non-radioactive elements with a suitable particle.

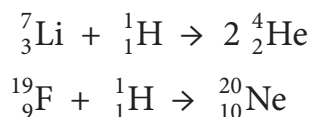
1. Bombarding with α particles: *e.g.*



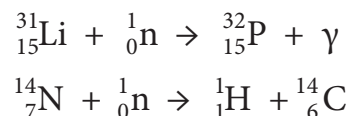
The shorthand notion of the above reaction is $^{14}_7\text{N}(\alpha, p)^{17}_8\text{O}$ representing, reactants (bombarding particle, ejected particle) products. Other examples include



2. Bombarding with protons: *e.g.*

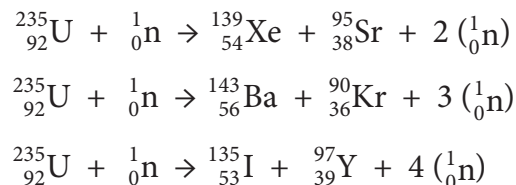


3. Bombarding with neutrons: *e.g.*



Nuclear fission

Nuclear fission is a process in which bombardment of neutrons breaks a suitable radioactive nucleus into several nuclei, neutrons and energy.



Nuclear fusion

Nuclear fusion is a process in which two light nuclei are joined to form a heavier nucleus.



Applications of radioisotopes

We are aware of the destructive aspects of nuclear energy; nuclear bombs have been used to destroy cities and millions of people. Many nuclear power stations generate electricity at a lower cost. Scientists use radioisotopes as “tracers” or “labels” to follow the pathways in many physical, chemical or biological reactions: *e.g.* to find out leaks in hidden pipelines, study the uptake of phosphorus by a plant, preserve food and estimate the age of rocks or archaeological objects (*e.g.*: radiocarbon dating). Radioisotopes are widely used in medicine; use of radiation (Co-60) to treat cancer. Some of the medicinal uses of them are given below.

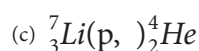
X	Importance	X	Importance
^{74}As	Locate brain tumours	^{60}Co	Treatment for cancer
^{51}Cr	Determine total blood volume	^{131}I	Treatment for thyroid cancer
^{58}Co	Determine uptake of Vitamin B ₁₂	^{24}Na	Detect obstructions in the blood circulation

Detectors used for measuring radiation

The interaction of nuclear radiation with matter is used to identify different types of radiation and their quantitative analysis. Geiger Muller counter, semiconductor detector, proportional counter and scintillation counter are some of the common devices used in this regard.

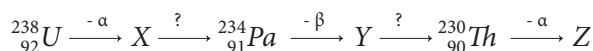
Problems

- Write complete nuclear equations for each of the following notations:



- $^{225}_{88}\text{Ra}$ decays with a half-life of 15 days to produce $^{225}_{89}\text{Ac}$.
 - Identify the type of decay involved in the above process.
 - Calculate the decay constant (λ)
 - Calculate the percentage of Ra-225 that will remain after 5 days.
 - Calculate the time taken to decay 75% of the original sample.

- Given below is a part of the $(4n+2)$ decay series



Identify the missing particles, and X, Y and Z.

- Calculate the binding energy per nucleon in MeV for iron-56 which has an atomic mass of 55.9349 amu.
- Calculate the energy released in the following nuclear reaction.

