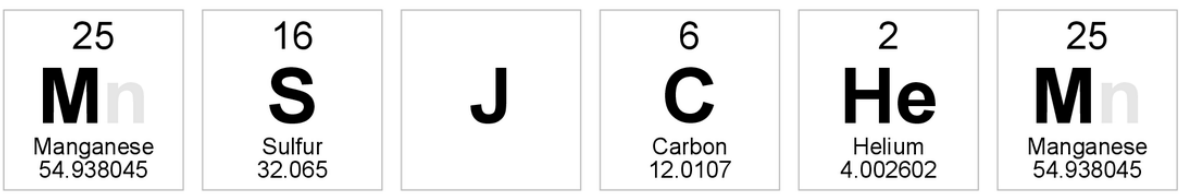
Reactivity 3.3

IB CHEMISTRY SL



Reactivity 3.3.1 and 3.3.2

Understandings:

- A radical is a chemical entity that has an unpaired electron. Radicals are highly reactive (3.3.1).
- Radicals are produced by homolytic fission, e.g. of halogens, in the presence of ultraviolet (UV) light or heat (3.3.2).

Learning outcomes:

- Identify and represent radicals (3.3.1).
- Explain, including with equations, the homolytic fission of halogens, known as the initiation step in a chain reaction (3.3.2).

Additional notes:

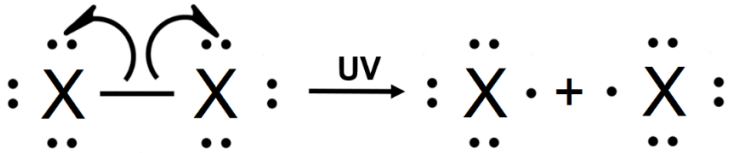
- The use of a single-barbed arrow (fish hook) to show the movement of a single electron should be covered.

Linking questions:

- Structure 2.1 How is it possible for a radical to be an atom, a molecule, a cation or an anion? Consider examples of each type.
- Reactivity 1.2 Why do chlorofluorocarbons (CFCs) in the atmosphere break down to release chlorine radicals but typically not fluorine radicals?
- Structure 2.2 What is the reverse process of homolytic fission?
- Structure 2.2 Chlorine radicals released from CFCs are able to break down ozone, O_3, but not oxygen, O_2, in the stratosphere. What does this suggest about the relative strengths of bonds in the two allotropes?

Homolytic bond fission

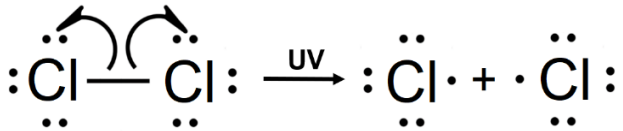
- In homolytic bond fission, (also known as homolytic bond cleavage), a covalent bond between two atoms in a molecule breaks with each atom taking one electron from the bond.
- The breaking of the bond requires energy in the form of UV radiation or heat.
- Homolytic fission results in the formation of radicals (or free radicals) which are highly reactive species with unpaired electrons.
- For example, the covalent bond between two atoms of X breaks with each atom taking one electron from the bond.



- The single-barbed arrows (known as fish hooks) show the movement of a single electron.
- The radicals formed are represented with a single dot such as X•.

Homolytic fission of the halogens

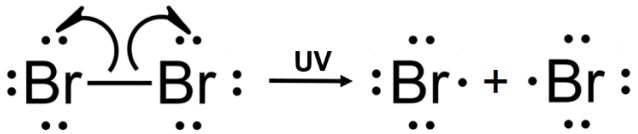
- The bond between the two atoms in chlorine, Cl_2, can undergo homolytic fission in the presence of ultraviolet (UV) radiation.



- The products of the fission are two chlorine radicals, represented as Cl•.

$$Cl_2 \rightarrow 2Cl\bullet \qquad \textit{or} \qquad Cl_2 \rightarrow Cl\bullet + Cl\bullet$$

- The formation of radicals is the first step, known as the initiation step, in the free-radical substitution reactions of the alkanes.
- The bond between the two atoms in Bromine, Br_2, can also undergo homolytic fission in the presence of UV radiation.



- The products of the fission are two bromine radicals, represented as Br•.

$$Br_2 \rightarrow 2Br\bullet \qquad \textit{or} \qquad Br_2 \rightarrow Br\bullet + Br\bullet$$

Exercise: Outline the type of bond fission taking place in the reaction below.

Reactivity 3.3.3

Understandings:

- Radicals take part in substitution reactions with alkanes, producing a mixture of products.

Learning outcomes:

- Explain, using equations, the propagation and termination steps in the reactions between alkanes and halogens.

Additional notes:

- Reference should be made to the stability of alkanes due to the strengths of the C–C and C–H bonds and their essentially non-polar nature.

Linking questions:

- Reactivity 2.2 Why are alkanes described as kinetically stable but thermodynamically unstable?

Radical substitution reactions of the alkanes

- Alkanes undergo radical substitution reactions which take place in three stages: initiation, propagation and termination.
- Example – methane and chlorine react as follows in the presence of UV light as follows.

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Initiation

- The bond between the chlorine atoms undergoes homolytic fission in the presence of UV light.
- Each chlorine atom takes one electron from the single bond resulting in the production of reactive chlorine radicals with unpaired electrons.

$$Cl_2 \rightarrow 2Cl\bullet$$

Propagation

- The first propagation step shows methane reacting with a chlorine radical to produce a methyl radical and hydrogen chloride.
- The second step shows the methyl radical reacting with a chlorine molecule to produce chloromethane and a chlorine radical.

$$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$$

$$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

- Two more propagation steps are shown below.

$$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$$

$$\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$$

Termination

- In the termination step, radicals pair up to form molecules.

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$$

$$\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$$

Exercise: Ethane, C_2H_6, reacts with bromine to form bromoethane, C_2H_5Br, in a radical substitution reaction. Write initiation, propagation and termination steps for the reaction.