

# Reactivity 3.3 · Electron sharing reactions

International Baccalaureate · IB Diploma · Chemistry · HL

## Scope and prerequisites

This handout teaches Reactivity 3.3, Electron sharing reactions, for the course first assessed in 2025. This topic is the same at Standard Level and Higher Level.

Prerequisites: covalent bonds and electronegativity from Structure 2.2, alkanes and structural formulas from Structure 3.2, and bond enthalpies from Reactivity 1.2. You will use bond enthalpy values from the data booklet.

## Radicals

### ■ Why does sunlight matter?

Methane and chlorine can be mixed in the dark and nothing happens. Put the same mixture in sunlight and it reacts at once. The product is never pure chloromethane: it always contains  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  as well. One kind of particle explains all of this: the radical.

### ■ What a radical is

- A **free radical**, usually just called a radical, is a particle with an **unpaired electron**.
- We show the unpaired electron with a single dot:  $\text{Cl}\bullet$ ,  $\text{Br}\bullet$ ,  $\bullet\text{CH}_3$ ,  $\bullet\text{OH}$ .
- A radical can be a single atom, such as  $\text{Cl}\bullet$ , or a group of atoms, such as the methyl radical  $\bullet\text{CH}_3$ .

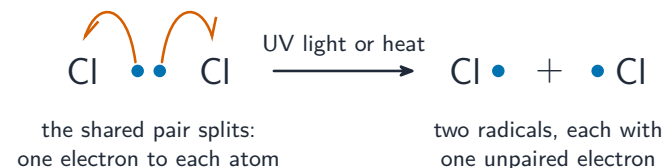
Radicals are very reactive. The unpaired electron “wants” a partner, so a radical reacts with almost any molecule it hits to make a new bond.

Do not confuse a radical with an ion.  $\text{Cl}\bullet$  has 17 electrons and no charge; the chloride ion  $\text{Cl}^-$  has 18 electrons and a full outer shell, so it is not a radical.

## Homolytic fission

### ■ Breaking a bond evenly

A covalent bond is a shared pair of electrons. When the bond breaks so that each atom keeps one electron of the pair, the break is called **homolytic fission**. It always makes two radicals.



*In homolytic fission each atom takes one electron of the shared pair*

A **single-barbed arrow** (also called a fishhook arrow) shows the movement of ONE electron. A normal double-barbed arrow shows a PAIR of electrons; you will use it in Reactivity 3.4.

### ■ What supplies the energy?

Breaking a bond is endothermic, so homolytic fission needs energy from **ultraviolet light** or from heat. The halogens split most easily because their bonds are weak:

| Bond  | Bond enthalpy / $\text{kJ mol}^{-1}$ |
|-------|--------------------------------------|
| Br–Br | 193                                  |
| Cl–Cl | 242                                  |
| C–C   | 346                                  |
| C–H   | 414                                  |

In a mixture of methane and chlorine, UV light breaks  $\text{Cl–Cl}$ , not  $\text{C–H}$ , because  $\text{Cl–Cl}$  is the weaker bond.

## Alkanes and radical substitution

### ■ Why alkanes are unreactive

Alkanes such as methane do not react with acids, alkalis or most other polar reagents. There are two reasons:

- Strong bonds.**  $\text{C–C}$  ( $346 \text{ kJ mol}^{-1}$ ) and  $\text{C–H}$  ( $414 \text{ kJ mol}^{-1}$ ) need a lot of energy to break.
- Almost no polarity.** The electronegativities of C (2.6) and H (2.2) are close, so  $\text{C–H}$  bonds are almost **non-polar**. No part of the molecule attracts a charged reagent.

Alkanes do react in two ways: they burn, and they react with radicals.

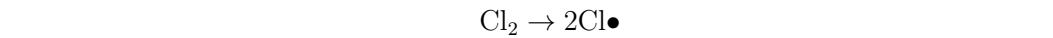
■ The chain reaction

Methane and chlorine react in UV light by **radical substitution** : a chlorine atom takes the place of a hydrogen atom. It is a **chain reaction** with three stages.

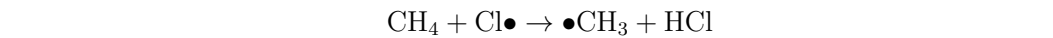
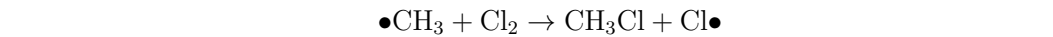
|                |                                                                                                                                                                                                                                                                                         |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1. initiation  | $\text{Cl}_2 \xrightarrow{\text{UV}} 2 \text{Cl}^\bullet$ <p>UV light splits the weakest bond, Cl–Cl, into two radicals</p>                                                                                                                                                             |
| 2. propagation | $\text{CH}_4 + \text{Cl}^\bullet \longrightarrow \text{CH}_3^\bullet + \text{HCl}$ $\text{CH}_3^\bullet + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}^\bullet$ <p>each step uses a radical and makes a new one, so the chain continues</p>                             |
| 3. termination | $\text{Cl}^\bullet + \text{Cl}^\bullet \longrightarrow \text{Cl}_2 \quad \text{CH}_3^\bullet + \text{Cl}^\bullet \longrightarrow \text{CH}_3\text{Cl} \quad \text{CH}_3^\bullet + \text{CH}_3^\bullet \longrightarrow \text{C}_2\text{H}_6$ <p>two radicals join, so the chain ends</p> |

Initiation makes radicals, propagation passes them on, termination removes them

1. **Initiation** : UV light splits chlorine molecules into radicals.

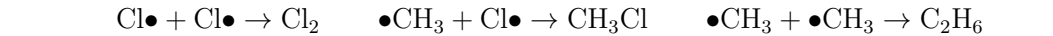


2. **Propagation** : each step uses one radical and makes another, so the chain keeps going.

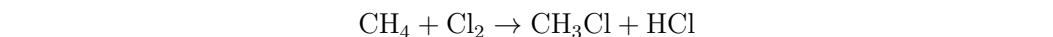


The Cl• made in the second step starts the first step again. One initiation can lead to thousands of propagation cycles.

3. **Termination** : two radicals join, so the chain stops.



The overall equation is the sum of the two propagation steps:



Note that a hydrogen atom, not •H, is taken by the chlorine radical in the first propagation step. The products of propagation are HCl and •CH<sub>3</sub>, never CH<sub>3</sub>Cl and •H.

■ Counting steps from equations

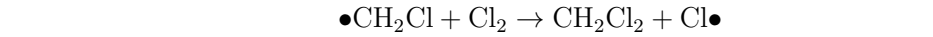
To decide which stage an equation is:

| Radicals on the left | Radicals on the right | Stage       |
|----------------------|-----------------------|-------------|
| 0                    | 2                     | initiation  |
| 1                    | 1                     | propagation |
| 2                    | 0                     | termination |

A mixture of products

■ Further substitution

Chloromethane still has C–H bonds, so a Cl• radical can attack it too:



The same can happen again to give CHCl<sub>3</sub> and finally CCl<sub>4</sub>. Termination also adds products such as ethane. So radical substitution always gives a **product mixture** (several products together), which must be separated, for example by fractional distillation.

| To get more of...  | Use...                                                          |
|--------------------|-----------------------------------------------------------------|
| CH <sub>3</sub> Cl | a large excess of methane, so Cl• usually meets CH <sub>4</sub> |
| CCl <sub>4</sub>   | a large excess of chlorine                                      |

■ Evidence for the chain model

- Nothing happens in the dark, but the reaction starts at once in UV light: radicals must be made first.
- A short burst of light causes a lot of reaction: each radical is passed on many times.
- Traces of ethane appear even though no C–C bond was in the reactants: two •CH<sub>3</sub> radicals must have joined.

■ Larger alkanes

Ethane reacts in the same way:



In propane, a chlorine radical can remove a hydrogen atom from an end carbon or from the middle carbon, so two different monochloro products form: 1-chloropropane and 2-chloropropane.

Bromine reacts in the same way, but more slowly, because the first propagation step is endothermic for bromine.

## Energy changes in the chain

Use bond enthalpies to see why the propagation steps run so easily with chlorine.

| Bond                                 | C–H | Cl–Cl | H–Cl | C–Cl | H–Br |
|--------------------------------------|-----|-------|------|------|------|
| Bond enthalpy / kJ mol <sup>-1</sup> | 414 | 242   | 431  | 324  | 366  |

**Worked example.** Find  $\Delta H$  for each propagation step of the chlorination of methane.

- $\text{CH}_4 + \text{Cl}\bullet \rightarrow \bullet\text{CH}_3 + \text{HCl}$ : break C–H, form H–Cl.  $\Delta H = 414 - 431 = -17 \text{ kJ mol}^{-1}$ .
- $\bullet\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\bullet$ : break Cl–Cl, form C–Cl.  $\Delta H = 242 - 324 = -82 \text{ kJ mol}^{-1}$ .
- Add the two steps:  $\Delta H = -99 \text{ kJ mol}^{-1}$  for  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ .

Both propagation steps are exothermic, so once a few radicals are made the chain runs quickly.

For bromine the first step is  $414 - 366 = +48 \text{ kJ mol}^{-1}$ . It is endothermic, so bromination is slower than chlorination.

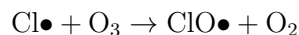
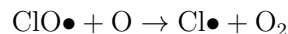
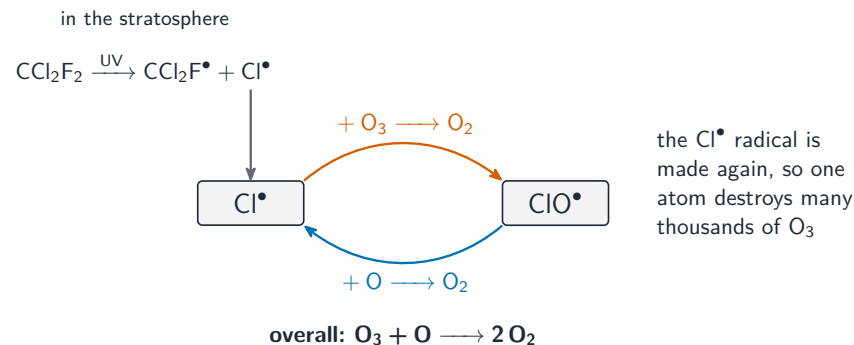
## Radicals in the atmosphere

### How CFCs destroy ozone

**Chlorofluorocarbons** (CFCs), such as  $\text{CCl}_2\text{F}_2$ , were used in fridges and spray cans. They are unreactive near the ground, so they drift up into the **stratosphere**. There, strong UV light breaks the C–Cl bond ( $324 \text{ kJ mol}^{-1}$ ), which is weaker than the C–F bond ( $492 \text{ kJ mol}^{-1}$ ):



The chlorine radical then destroys **ozone** in two propagation steps:



*The chlorine radical is made again at the end of each cycle*

Overall:  $\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2$ . The chlorine radical is made again, so one Cl atom can destroy many thousands of ozone molecules before a termination step removes it. This is why CFCs were banned by the Montreal Protocol (1987).

## Practice

- Which of these are radicals:  $\text{Cl}^-$ ,  $\text{Cl}\bullet$ ,  $\bullet\text{CH}_3$ ,  $\text{CH}_4$ ,  $\bullet\text{OH}$ ,  $\text{OH}^-$ ? Explain your choice.
- Write an equation for the homolytic fission of bromine. State the condition needed.
- Draw single-barbed arrows to show the homolytic fission of the C–Cl bond in  $\text{CH}_3\text{Cl}$ .
- Give two reasons why alkanes are unreactive with acids and alkalis.
- Ethane reacts with chlorine in UV light. Write equations for the initiation step, the two propagation steps and a termination step that forms butane.
- State whether each step is initiation, propagation or termination: (a)  $\bullet\text{CH}_3 + \text{Cl}\bullet \rightarrow \text{CH}_3\text{Cl}$  (b)  $\text{CH}_3\text{Cl} + \text{Cl}\bullet \rightarrow \bullet\text{CH}_2\text{Cl} + \text{HCl}$  (c)  $\text{Br}_2 \rightarrow 2\text{Br}\bullet$ .
- Explain why the reaction of methane with chlorine gives a mixture of products. Suggest how to make chloromethane the main product.
- Use bond enthalpies (C–H 414, H–Br 366, Br–Br 193, C–Br 285 kJ mol<sup>-1</sup>) to find  $\Delta H$  for each propagation step in the bromination of methane, and for the overall reaction.
- How many different monochloro products form when propane reacts with chlorine in UV light? Name them.
- Explain, with equations, how one chlorine atom from a CFC can destroy many ozone molecules.

### Answers.

- $\text{Cl}\bullet$ ,  $\bullet\text{CH}_3$  and  $\bullet\text{OH}$ : each has an unpaired electron.  $\text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{CH}_4$  have all electrons paired.

2.  $\text{Br}_2 \rightarrow 2\text{Br}\bullet$ , in UV light (or heat).
3. One single-barbed arrow from the bond to C and one from the bond to Cl, giving  $\bullet\text{CH}_3 + \text{Cl}\bullet$ .
4. C–C and C–H bonds are strong; the bonds are almost non-polar, so nothing attracts a charged or polar reagent.
5.  $\text{Cl}_2 \rightarrow 2\text{Cl}\bullet$ ;  $\text{C}_2\text{H}_6 + \text{Cl}\bullet \rightarrow \bullet\text{C}_2\text{H}_5 + \text{HCl}$ ;  $\bullet\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}\bullet$ ;  $2\bullet\text{C}_2\text{H}_5 \rightarrow \text{C}_4\text{H}_{10}$ .
6. (a) termination (b) propagation (c) initiation.
7. Chloromethane still has C–H bonds, so  $\text{Cl}\bullet$  substitutes it further to  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ ; termination adds ethane. Use a large excess of methane.
8. Step 1:  $414 - 366 = +48 \text{ kJ mol}^{-1}$ . Step 2:  $193 - 285 = -92 \text{ kJ mol}^{-1}$ . Overall:  $-44 \text{ kJ mol}^{-1}$ .
9. Two: 1-chloropropane and 2-chloropropane.
10. UV gives  $\text{Cl}\bullet$  from the CFC;  $\text{Cl}\bullet + \text{O}_3 \rightarrow \text{ClO}\bullet + \text{O}_2$ ;  $\text{ClO}\bullet + \text{O} \rightarrow \text{Cl}\bullet + \text{O}_2$ . The  $\text{Cl}\bullet$  is made again, so the cycle repeats thousands of times until termination.

## Exam tips

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- Always draw the dot on a radical, and put it on the atom that has the unpaired electron:  $\bullet\text{CH}_3$ , not  $\text{CH}_3\bullet$ .
- In the first propagation step the products are  $\bullet\text{CH}_3$  and  $\text{HCl}$ . Writing  $\bullet\text{H}$  loses the mark.
- A single-barbed arrow moves one electron; a double-barbed arrow moves a pair.
- Termination steps have two radicals on the left and none on the right.
- “Mixture of products” needs a reason: the product still has C–H bonds, and termination joins radicals.