Electron sharing reactions

Reactivity 3.3 · SL and HL

Why does sunlight matter?

> Light initiates radicals; **propagation** can amplify one **initiation** event.

- A room-temperature dark mixture can show little reaction.
- Suitable light absorbed by chlorine initiates a chain.
- Products depend on conditions, conversion and radical loss.

What a radical is

- The dot represents an **unpaired electron**, not a charge.
- These radicals are reactive intermediates; not every collision reacts.

Radical a particle with an unpaired electron, such as Cl•, $\bullet CH_3$ or •OH

Check: radical or ion?

Your turn

Which particle is a radical?

A. Cl^-
B. CH_4
C. $\bullet CH_3$
D. OH^-

Charge and radical character are independent

Species	Electron count	Classification
$Cl^{\bullet}$	17	neutral atomic radical
$NO^{\bullet}$	$7 + 8 = 15$	neutral molecular radical
$CH_4^{\bullet +}$	$6 + 4 - 1 = 9$	radical cation
$O_2^{\bullet -}$	$2(8) + 1 = 17$	radical anion

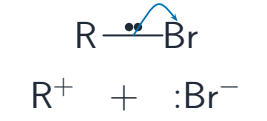
Homolytic or heterolytic fission

homolytic fission



one electron each
$\Rightarrow$ two **radicals**

heterolytic fission



both electrons to one
$\Rightarrow$ two **ions**

The curly arrow shows which

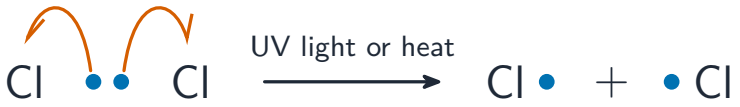
Radicals can be neutral or charged

$Cl^{\bullet}$	$NO^{\bullet}$	$CH_4^{\bullet+}$	$O_2^{\bullet-}$
charge 0	charge 0	charge $+1$	charge -1
17 electrons	15 electrons	9 electrons	17 electrons

an odd electron total needs an unpaired electron; a species can carry both a dot and a charge

A radical has an **unpaired electron**, whatever its charge

Homolytic fission



the shared pair splits:
one electron to each atom

two radicals, each with
one unpaired electron

For Cl–Cl homolysis, each atom receives one bonding electron.

Which bond breaks?

Bond	**Bond enthalpy / kJ mol^{-1}**
Br–Br	193
Cl–Cl	242
C–C	346
C–H	414

Use the evidence

Usual methane/chlorine photochemistry: light absorbed by Cl_2 makes 2Cl▪.

Trace each electron in homolysis

1. **Start.** Each fishhook starts at one electron in the shared bond.
2. **Finish.** One goes to each chlorine atom; write a dot on each product.
3. **Reverse.** Two Cl▪ combine: their unpaired electrons make one shared pair.

Decision

A fishhook moves one electron; a full curly arrow moves a pair.

Why alkanes are unreactive

Strong bonds

C–C 346 and C–H 414 kJ mol^{-1}.

Breaking them needs a lot of energy.

Almost non-polar

C–H has little polarity.

No strongly electron-rich or electron-poor functional-group centre.

Connect the four organic reaction types

Type	Bond change and example
Substitution	$CH_4 \rightarrow CH_3Cl$: replace C–H by C–Cl; Cl_2 and UV.
Addition	$CH_2{=}CH_2 \rightarrow CH_3CH_2OH$: add H/OH; steam and H_3PO_4.
Oxidation	$CH_3CH_2OH \rightarrow CH_3COOH$: excess acidified dichromate; reflux.
Polymerization	Ethene C=C bonds open to form a chain of $–CH_2–CH_2–$ units.

Keep conditions attached to each synthesis step

1. **Hydrate ethene.** $CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$; steam and phosphoric-acid catalyst.
2. **Oxidize ethanol.** $CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$; excess acidified dichromate, reflux.
3. **Check the route.** A **functional group** controls characteristic reactions; OH marks an alcohol, COOH an acid. Each molecule keeps two carbons.

The chain reaction

1. Initiation

$$Cl_2 \xrightarrow{UV} 2\,Cl^{\bullet}$$

Light absorbed by chlorine makes radicals.

2. Propagation

$$CH_4 + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + HCl$$

$$CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

One radical enters; another leaves each step.

3. Termination

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow C_2H_6$$

Each combination removes two radicals.

Propagation regenerates radicals; **termination** removes two.

Naming the stage

Radicals left	Radicals right	Stage
0	2	**initiation**
1	1	**propagation**
2	0	**termination**

A chain conserves material

1. **Given.** Invented model: 0.0020 mol Cl_2 initiates; 40 cycles per $Cl^{\bullet}$; ample reactants, no side products.
2. **Initiate.** $2 \times 0.0020 = 0.0040$ mol $Cl^{\bullet}$.
3. **Propagate.** $0.0040 \times 40 = 0.16$ mol CH_3Cl.
4. **Account. Propagation** also consumes 0.16 mol Cl_2 and 0.16 mol CH_4.

Decision

Radicals are regenerated; reactant molecules are still consumed.

Five reaction types

name the reaction type at each step

oxidation	loses electrons / gains O or loses H (e.g. alcohol → acid)
reduction	gains electrons / loses O or gains H
substitution	one atom or group swaps for another
addition	two molecules join; a C=C double bond opens
elimination	a small molecule is removed; a C=C forms

also give the **reagent** for each step, and watch for **by-products** (e.g. amines over-substitute)

> Name what happens to the molecule

Why a mixture forms

More CH_3Cl

Large excess of methane.

$Cl\bullet$ usually meets CH_4.

Improves selectivity; does not guarantee purity.

More CCl_4

Large excess of chlorine.

Substitution keeps going.

Evidence for a chain

> Several observations support the model; one observation is not unique proof.

- Light dependence supports photochemical **initiation**.
- Many cycles per initiation explain chain amplification.
- Ethane is consistent with methyl-radical combination.

Two positions, not three drawings

Propane

Either end gives 1-chloropropane.

The middle gives 2-chloropropane.

Butane

Equivalent ends give 1-chlorobutane.

Equivalent middle positions give 2-chlorobutane.

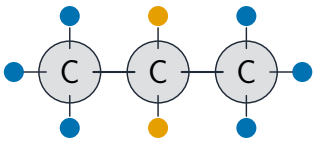
Invented selectivity model for propane

1. **Given.** Propane: six terminal H, two middle H; invented per-H relative reactivities 1 and 3.
2. **Weight.** Terminal: $6 \times 1 = 6$; middle: $2 \times 3 = 6$.
3. **Divide.** Each constitutional product: $6/(6 + 6) \times 100 = 50\%$.
4. **Limit.** Equal per-H reactivity instead gives 75% and 25%.

Decision

These are stated model assumptions, not universal measured percentages.

Two kinds of hydrogen in propane



- 6 terminal H $\longrightarrow$ 1-chloropropane
- 2 middle H $\longrightarrow$ 2-chloropropane

equal reactivity: $6 : 2 = 3 : 1$

invented per-H reactivity 1 : 3: $6(1) : 2(3) = 1 : 1$

Equal reactivity would give 3 : 1

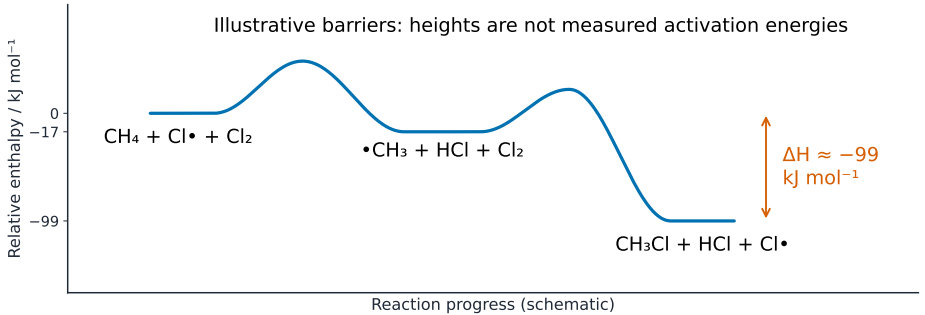
Energy of the propagation steps

1. **Step 1.** C–H broken, H–Cl formed: $414 - 431 = -17$ kJ mol^{-1}.
2. **Step 2.** Cl–Cl broken, C–Cl formed: $242 - 324 = -82$ kJ mol^{-1}.
3. **Add.** $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Decision

Estimated $\Delta H = -99$ kJ mol^{-1}; rate still depends on barriers and conditions.

Enthalpy change is not the barrier



A negative ΔH can coexist with a substantial activation barrier.

Slow until initiated, favourable once reacting

Kinetic resistance

A large **initiation** barrier can suppress a room-temperature reaction.

Suitable light or heat can open a faster route.

Thermodynamic change

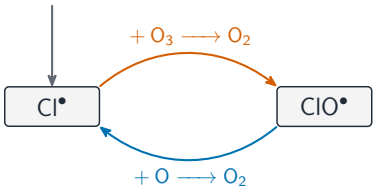
Combustion can favour lower-free-energy products.

This does not make every possible alkane reaction favourable.

How CFCs destroy ozone

in the stratosphere

$$CCl_2F_2 \xrightarrow{UV} CClF_2^{\bullet} + Cl^{\bullet}$$



the $Cl^{\bullet}$ radical is made again, so one atom destroys many thousands of O_3

overall: $\mathbf{O_3 + O \longrightarrow 2\,O_2}$

> $Cl^{\bullet}$ is regenerated; chain survival controls how much **ozone** is lost.

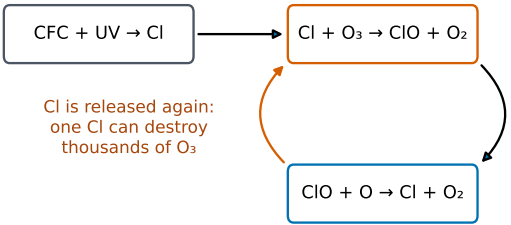
Add the ozone cycle carefully

1. **Given.** $Cl\blacksquare + O_3 \rightarrow ClO\blacksquare + O_2$; then $ClO\blacksquare + O \rightarrow Cl\blacksquare + O_2$.
2. **Cancel.** Remove regenerated $Cl\blacksquare$ and the $ClO\blacksquare$ intermediate.
3. **Net.** $O_3 + O \rightarrow 2O_2$, not $2O_3 \rightarrow 3O_2$ for this written pair.
4. **Limit.** Other atmospheric cycles and radical reservoirs also operate.

Decision

Regeneration explains amplification, not a fixed universal chain length.

How chlorine radicals destroy ozone



the Montreal Protocol phased out CFCs; the ozone layer is slowly recovering

> The chlorine is regenerated, so it acts as a catalyst

Exam tips

> A mixture forms because the product still has C–H bonds.

- Always draw the dot, on the atom with the **unpaired electron**.
- First **propagation** step gives $\bullet CH_3 + HCl$.
- Single barb, one electron; double barb, a pair.
- **Termination** has two radicals on the left, none on the right.

Check yourself

Try these

Write the homolytic fission of bromine and state the condition.

Write the mechanism for ethane + chlorine, with a termination step that forms butane.

Find ΔH for each propagation step in the bromination of methane.

Explain with equations how one Cl atom destroys many O_3 molecules.