Reactivity 3.4 · Electron-pair sharing reactions

International Baccalaureate · IB Diploma · Chemistry · SL

Scope and prerequisites

This handout teaches Reactivity 3.4, Electron-pair sharing reactions, for the course first assessed in 2025.

Prerequisites: covalent and coordination bonds and electronegativity from Structure 2.2, functional groups and classes of compounds from Structure 3.2, and homolytic fission and radicals from Reactivity 3.3. At Higher Level you will also use rate expressions from Reactivity 2.2.

Nucleophiles and electrophiles

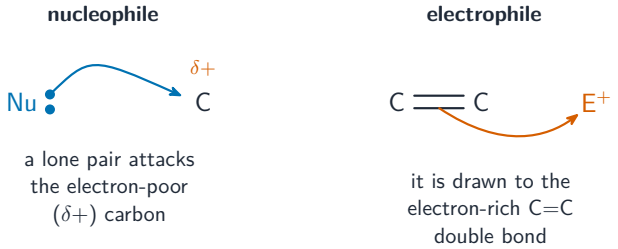
Why does bromoethane react with alkali, but ethane does not?

Shake bromoethane with warm sodium hydroxide solution and ethanol forms. Do the same with ethane and nothing happens. The difference is one polar bond. In Reactivity 3.3 a bond broke so that each atom took one electron. In this unit a whole electron pair moves, and a new bond forms from a pair that one particle gives to another.

Two kinds of reagent

- A **nucleophile** is a reactant that forms a new bond by giving both electrons of the bond. It has a lone pair, and it is neutral or negative: OH^-, H_2O, NH_3, CN^-, Cl^-.
- An **electrophile** is a reactant that forms a new bond by accepting both electrons of the bond. It is positive or has a partial positive charge: H^+, NO_2^+, Br_2 near a C=C bond, the H of HBr.

"Nucleophile" means "nucleus-loving": it is attracted to a positive centre. "Electrophile" means "electron-loving": it is attracted to a region of high electron density.



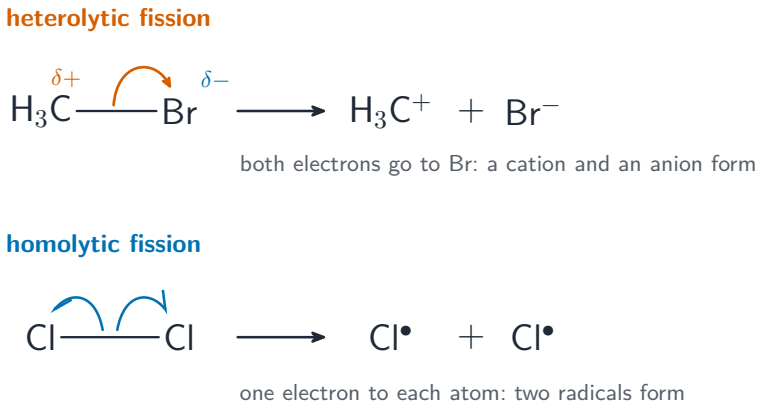
A nucleophile gives an electron pair; an electrophile takes one

Heterolytic fission and curly arrows

Breaking a bond unevenly

When a covalent bond breaks and **both** bonding electrons go to one atom, the break is **heterolytic fission** . The atom that takes the pair is usually the more electronegative one. Heterolytic fission makes ions, not radicals.

$$CH_3Br \rightarrow CH_3^+ + Br^-$$



A curly arrow moves an electron pair; a single-barbed arrow moves one electron

Drawing curly arrows

A **curly arrow** (with a full, double-barbed head) shows the movement of an electron PAIR.

- The tail starts where the pair is now: a lone pair, a bond, or a negative charge.
- The head points to where the pair goes: an atom (to form a new bond) or an atom that leaves with the pair.
- Every curly arrow must start at electrons. An arrow that starts at a nucleus or a positive charge loses the mark.

Nucleophilic substitution

Halogenoalkanes have a polar bond

In a **halogenoalkane** , such as bromoethane, the halogen is more electronegative than carbon (Br 3.0, C 2.6). The C–Br bond is polar, so the carbon is $\delta+$. A nucleophile attacks this $\delta+$ carbon.

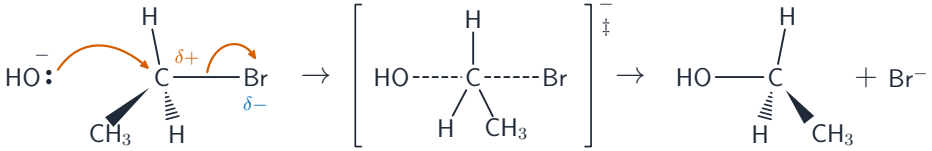
The reaction

In **nucleophilic substitution** , a nucleophile gives an electron pair to form a new bond as another bond breaks. The group that leaves with the old bonding pair is the **leaving group** .

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

Here OH^- is the nucleophile and Br^- is the leaving group. Conditions: warm, with aqueous sodium hydroxide.

S_N2 (primary, e.g. bromoethane): one step



lone pair on O attacks the $\delta+$ C from the side away from Br

transition state: O–C half-formed, C–Br half-broken

ethanol + bromide ion; the three groups have flipped

One curly arrow makes the new O–C bond; a second breaks C–Br

Two curly arrows describe the change:

1. From a lone pair on the O of OH^- to the $\delta+$ carbon: the new C–O bond forms.
2. From the C–Br bond to Br: the bonding pair leaves with Br as Br^-.

Other nucleophiles give other products: water gives an alcohol slowly, and ammonia gives an amine.

Electrophilic addition to alkenes

Why alkenes attract electrophiles

The C=C double bond in an alkene has four electrons between two carbon atoms: a region of high electron density. Electrophiles are attracted to it. In **electrophilic addition** the double bond opens and two new single bonds form, so one molecule adds across the C=C.

Three additions to learn

Reagent	Conditions	Example with ethene	Product
halogen, Br_2	room temperature	$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$	1,2-dibromoethane
hydrogen halide, HBr	room temperature	$C_2H_4 + HBr \rightarrow CH_3CH_2Br$	bromoethane
water (steam)	H_3PO_4 catalyst, about 300 °C	$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$	ethanol

The reaction with bromine is the test for an alkene: orange bromine water turns colourless. An alkane gives no colour change in the dark.

The addition of steam to ethene is how ethanol is made in industry.

Practice

1. Classify each species as a nucleophile or an electrophile: OH^-, NO_2^+, NH_3, H^+, CN^-.
2. Explain the difference between heterolytic and homolytic fission, and say what kind of arrow each uses.
3. Write an equation for the reaction of 1-bromopropane with aqueous sodium hydroxide. Identify the nucleophile and the leaving group.
4. Explain why the carbon atom in the C–Br bond of a halogenoalkane is attacked by nucleophiles.
5. Write equations for the reactions of propene with (a) bromine, (b) steam. Name the organic products.
6. Describe a test to tell cyclohexene from cyclohexane, with the result for each.

Answers.

1. Nucleophiles: OH^-, NH_3, CN^-. Electrophiles: NO_2^+, H^+.
2. Heterolytic: both bonding electrons go to one atom, giving ions; one curly arrow (double-barbed). Homolytic: one electron to each atom, giving radicals; two single-barbed arrows.
3. $CH_3CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2OH + Br^-$. Nucleophile OH^-; leaving group Br^-.
4. Br is more electronegative than C, so the C–Br bond is polar and C is $\delta+$; the lone pair of a nucleophile is attracted to it.
5. (a) $CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$, 1,2-dibromopropane. (b) $CH_3CH{=}CH_2 + H_2O \rightarrow CH_3CH(OH)CH_3$, propan-2-ol (major; some propan-1-ol).
6. Add bromine water and shake: cyclohexene turns it from orange to colourless; with cyclohexane it stays orange.

Exam tips

- Every curly arrow starts at a lone pair, a bond or a negative charge, never at an atom's nucleus or a positive charge.
- Show the lone pair on the nucleophile and the $\delta+/\delta-$ on the C–X bond.
- Bromine water decolourized means C=C; say "colourless", not "clear".