22.1 Electron-pair sharing: nucleophiles and electrophiles

Name: _____ Class: _____ Date: _____ **Total: 34 marks**

KEY WORDS nucleophile • electrophile • heterolytic fission • nucleophilic substitution • electrophilic addition • carbocation

Objective

Build the skills to answer exam questions on **electron-pair sharing reactions** : nucleophiles, electrophiles, substitution of halogenoalkanes and addition to alkenes.

You must be able to:

- define nucleophile and electrophile and identify them in reactions
- describe heterolytic fission
- write equations for nucleophilic substitution of halogenoalkanes and electrophilic addition to alkenes
- define Lewis acids and bases; describe S_N1 and S_N2 and electrophilic addition mechanisms; apply Markovnikov's rule

1 Key knowledge and worked examples

■ Nucleophiles and electrophiles

Heterolytic fission: a bond breaks and **one atom takes both electrons**, making ions: H–Br → H^+ + Br^-.

	nucleophile	**electrophile**
definition	electron-pair **donor**	electron-pair **acceptor**
attracted to	$\delta+$ atoms / positive centres	electron-rich regions (C=C)
examples	OH^-, H_2O, NH_3, CN^-	H^+, NO_2^+, Br_2 (polarized)

Nucleophilic substitution: in a halogenoalkane the C–X carbon is $\delta+$. CH_3CH_2Br + OH^- → CH_3CH_2OH + Br^- (warm, aqueous NaOH).

Electrophilic addition: alkenes have an electron-rich C=C. C_2H_4 + Br_2 → CH_2BrCH_2Br. **Test:** bromine water turns from orange to colourless.

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HL: a **Lewis acid** accepts an electron pair; a **Lewis base** donates one (forming a coordination bond). **S_N2** (primary): one step, rate = k[RX][OH^-]. **S_N1** (tertiary): carbocation first, rate = k[RX]. **Markovnikov:** H adds to the carbon that already has more H atoms, via the more stable carbocation.

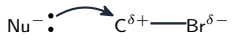
Worked example 1: identify. In NH_3 + CH_3Cl, NH_3 uses its lone pair: it is the **nucleophile**.

Worked example 2: product. Propene + Br_2 → **1,2-dibromopropane**, $CH_3CHBrCH_2Br$.

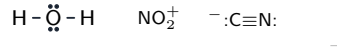
Answer shapes: "donates an electron pair to the $\delta+$ carbon"; name products with numbers.

2 Practice

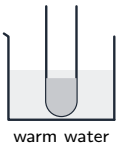
2.1 Define the terms nucleophile and electrophile. [2]



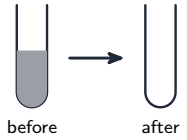
2.2 Classify each species as a nucleophile or an electrophile: H_2O, NO_2^+, CN^-. [3]



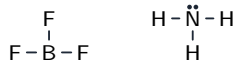
2.3 Bromoethane is warmed with aqueous sodium hydroxide. Write the equation, name the organic product and name the type of reaction. [3]



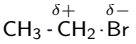
2.4 Bromine water is shaken with ethene. State what you see, write the equation, and name the type of reaction. [3]



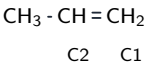
2.5 Boron trifluoride, BF_3, reacts with ammonia, NH_3. Identify the Lewis acid, and explain how the bond between them forms. [3]



2.6 Describe the S_N2 mechanism for the reaction of OH^- with bromoethane. [3]



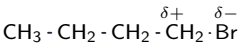
2.7 Hydrogen bromide adds to propene. Name the major product and explain why it forms, using Markovnikov's rule. [3]



3 Exam-style questions

3.1 1-bromobutane and 1-chlorobutane both react with aqueous hydroxide ions.

(a) Explain why the carbon bonded to the halogen is attacked by nucleophiles. [2]



(b) Predict which compound reacts faster, and explain. [2]

(c) Name the organic product formed from 1-bromobutane. [1]

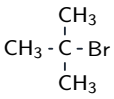
(d) Name the type of fission in which the C–Br bond breaks. [1]

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3.2 2-bromo-2-methylpropane, $(CH_3)_3CBr$, reacts with aqueous hydroxide ions by the S_N1 mechanism.

(a) Write the rate equation for this reaction. [1]

(b) Describe the two steps of the S_N1 mechanism. [3]



(c) Explain why tertiary halogenoalkanes react by S_N1, but primary ones by S_N2. [2]

(d) Explain why the C–Br bond breaks heterolytically, not homolytically. [2]

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Solutions

Marking: **M1** a correct method, **A1** the correct answer, **B1** an independent mark.

Each answer shows the steps, then the **result**.

2.1

nucleophile: an electron-pair donor; electrophile: an electron-pair acceptor

2.2

H_2O nucleophile; NO_2^+ electrophile; CN^- nucleophile

2.3

$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$; ethanol; nucleophilic substitution

2.4

orange to colourless; $C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$; electrophilic addition

2.5

BF_3 is the Lewis acid; N donates its lone pair to B; forming a coordination (dative) bond

2.6

OH^- lone pair attacks the $\delta+$ carbon opposite Br (curly arrow to C); transition state with partial C–O and C–Br bonds; C–Br breaks and Br^- leaves (arrow from bond to Br), in one step

2.7

2-bromopropane; H^+ adds to the end carbon, which has more H atoms; the secondary carbocation formed is more stable than a primary one

3.1

(a) the halogen is more electronegative, so the carbon is $\delta+$; it attracts the lone pair of the nucleophile

(b) 1-bromobutane; the C–Br bond is weaker than the C–Cl bond, so it breaks more easily

(c) butan-1-ol

(d) heterolytic

3.2

(a) rate = $k[(CH_3)_3CBr]$

(b) slow step: C–Br breaks heterolytically to a carbocation and Br^-; curly arrow from the C–Br bond to Br; fast step: OH^- donates a lone pair to the carbocation

(c) the tertiary carbocation is stabilized by three alkyl groups; the three methyl groups block attack from the back side (steric hindrance)

(d) Br is more electronegative, so the bond is polar; Br takes both bonding electrons and leaves as Br^-