

Haloalkanes NEET Notes – Part 1

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Haloalkanes and Haloarenes – Part 1: Haloalkanes

1. Introduction

- **Haloalkanes (alkyl halides):** Compounds of formula **R-X**, where R = alkyl group, X = F, Cl, Br, I.
- **Haloarenes (aryl halides):** Ar-X, where Ar is an aromatic ring (covered later).
- **C-X bond is polar** because X is more electronegative than C.
 - C gets partial + charge (δ^+), X gets partial – charge (δ^-).
 - Therefore carbon attached to halogen is **electrophilic**.

Classification of Alkyl Halides

1. Number of halogen atoms

- **Monohaloalkane:** one halogen
- **Dihaloalkane:** two halogens
- **Polyhaloalkane:** ≥ 3 halogens

2. Nature of carbon attached to X

- **Primary (1°):** C attached to one other C
- **Secondary (2°):** C attached to two C
- **Tertiary (3°):** C attached to three C

Examples (X = Cl for simplicity):

- 1°: $\text{CH}_3\text{-CH}_2\text{-Cl}$ (1-chloroethane)
 - 2°: $\text{CH}_3\text{-CH(Cl)-CH}_3$ (2-chloropropane)
 - 3°: $(\text{CH}_3)_3\text{C-Cl}$ (tert-butyl chloride)
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2. Structure and Bonding

- Carbon in R-X is **sp^3 hybridised**, roughly tetrahedral (bond angle $\sim 109.5^\circ$).
 - C-X bond length increases from **$\text{C-F} < \text{C-Cl} < \text{C-Br} < \text{C-I}$** .
 - Bond strength: **C-F strongest** (hardest to break), **C-I weakest** (easiest to break).
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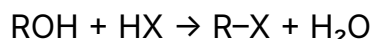
3. Methods of Preparation of Alkyl Halides

3.1 From Alcohols

General idea: Replace -OH group by halogen (X).

(A) Using Hydrogen Halides (HX)

Reaction:



Order of reactivity of alcohols:

$3^\circ > 2^\circ > 1^\circ$ (due to stability of carbocation intermediate).

Conditions:

- For **HI, HBr**: usually presence of **conc. H_2SO_4 / red P** or **H_3PO_4** .
- For **HCl**: less reactive, use **anhydrous ZnCl_2** as catalyst
→ **Lucas reagent** = conc. HCl + anhyd. ZnCl_2 .

Lucas test (visual)

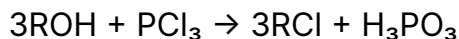
- 3° alcohol → turbidity **immediately**
- 2° alcohol → turbidity in a few **minutes**
- 1° alcohol → **no turbidity at room temp**

(B) Using Phosphorus Halides

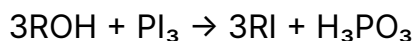
1. **PCl₅**:



2. **PCl₃ / PBr₃ (from red P + Cl₂ / Br₂ in situ)**:



3. **PI₃** (from P + I₂):



These give good yields of alkyl halides.

(C) Using Thionyl Chloride (SOCl₂)

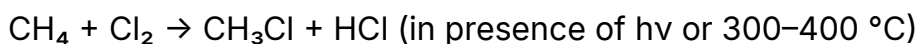


- Done in presence of **pyridine** (absorbs HCl).
 - Very clean because gaseous by-products escape → pure RCl.
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3.2 From Hydrocarbons

(A) Free Radical Halogenation of Alkanes

Example:

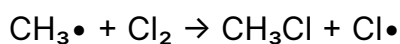
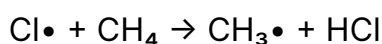


Mechanism (chain reaction):

1. **Initiation**

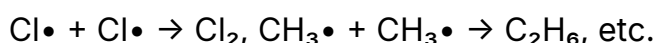


2. **Propagation**



3. **Termination**

Combination of radicals:



- Gives mixture of mono-, di-, tri-, tetra-halo products.
- Reactivity order of H abstraction: **3° > 2° > 1°**.

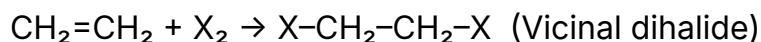
(B) Addition of HX to Alkenes

General:



- Follows **Markovnikov's rule**: "H goes to carbon already having more H".
- For **HBr in presence of peroxides** → **anti-Markovnikov (Kharasch effect)** via free radical mechanism.

(C) Halogenation of Alkenes



Mechanism: **electrophilic addition**.

(D) From Silver Salts of Carboxylic Acids (Hunsdiecker Reaction)



- Decreases chain length by one carbon (decarboxylation).
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4. Physical Properties of Alkyl Halides

4.1 Boiling Points and Melting Points

- For same alkyl group: **RI > RBr > RCl > RF**
(because size and mass of halogen ↑ → van der Waals forces ↑).
- For same X: boiling point ↑ as **chain length ↑**,
but **branching ↓ boiling point** (compact molecule → less surface area).
- **Isomeric dihaloarenes**: para-isomer often has higher m.p. due to better packing.

4.2 Density and Solubility

- Density: increases with **atomic weight of X** and **number of halogens**.
For given X: **RI most dense, RCl least**.
 - Alkyl halides are **practically insoluble in water**
(because they cannot form hydrogen bonds with water easily)
but **soluble in organic solvents** like ether, benzene.
 - Most are **heavier than water** (except some light chlorides).
-

5. Types of Reagents

5.1 Electrophiles

- Electron-deficient species, seek electrons.
- Examples: H^+ , Br^+ , NO^+ , SO_3 , PCl_5 .

5.2 Nucleophiles

- Species with **lone pair / negative charge** that seek positive centres.
- Examples: OH^- , OR^- , CN^- , NH_3 , RNH_2 , X^- (Cl^- , Br^- , I^-).

Nucleophilicity trends (very high yield NEET points):

1. In a given period (same row):

Nucleophilicity \propto basicity

- In gas phase or aprotic solvent: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
- For neutral bases: $\text{NH}_3 > \text{H}_2\text{O}$, etc.

2. Down a group in protic solvent (H_2O , ROH):

- $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

Because large anions are more polarizable and strongly solvated F^- becomes less available.

3. Bulky groups decrease nucleophilicity



5.3 Solvents

- **Protic solvents:** can donate H^+ / form H-bonds.
 - Examples: H_2O , ROH , NH_3 .
- **Aprotic polar solvents:** cannot donate H^+ but have high dielectric constant.
 - Examples: acetone, DMSO, DMF, acetonitrile.

Effect on nucleophilicity:

- In **protic**: large anions best ($\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$).
 - In **aprotic**: reverse order, basicity dominates ($\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$).
-

6. Leaving Group Ability

- Good leaving group = stable after departure.
 - **Weaker base = better leaving group.**
 - Order: $I^- > Br^- > Cl^- \gg F^-$ (F^- is very poor).
 - Tosylate, mesylate anions (sulfonate esters) are excellent leaving groups.
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7. Nucleophilic Substitution Reactions

Alkyl halides undergo **substitution** because C-X bond is polar.

Two main mechanisms: **S_n1** and **S_n2**.

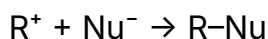
7.1 S_n1 Reaction (Unimolecular Nucleophilic Substitution)

Key features (visual picture):

1. **Step 1 (slow, RDS): ionisation → carbocation**



2. **Step 2 (fast): nucleophile attack**



- Rate law: **Rate = k[alkyl halide]** (depends only on substrate).
- Occurs via **planar carbocation** → nucleophile can attack from both sides → **racemisation** (mixture of enantiomers) with some retention.

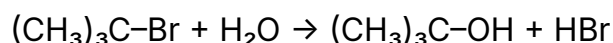
Favoured when:

- Substrate forms stable carbocation: **3° > 2° >> 1°**
- Polar protic solvent (water, alcohol).
- Weak or neutral nucleophile (H_2O , ROH).

Energy diagram:

Single big hump (for carbocation formation), then small hump for nucleophile attack.

Example:



7.2 S_n2 Reaction (Bimolecular Nucleophilic Substitution)

Key features (visual picture):

- **Single step, concerted** mechanism.
- Nucleophile attacks carbon **from backside** of C-X bond while X leaves.

Mechanism:



Transition state: carbon simultaneously bonded partially to Nu and X

(visual: a trigonal bipyramidal arrangement).

Rate law:

$$\text{Rate} = k[\text{alkyl halide}][\text{nucleophile}]$$

Stereochemistry – Walden inversion

- For a chiral centre, backside attack gives **inversion of configuration** (like umbrella turning inside out).
- 100% inversion if only $\text{S}_\text{n}2$.

Favoured when:

- Substrate: $1^\circ > 2^\circ \gg 3^\circ$ (steric crowding reduces $\text{S}_\text{n}2$).
- Strong nucleophile (OH^- , OR^- , CN^-).
- Polar aprotic solvent (DMSO, DMF, acetone).

Reactivity order (typical example):

Methyl halide $> 1^\circ > 2^\circ \gg 3^\circ$ (almost no $\text{S}_\text{n}2$ on tertiary).

7.3 Factors Affecting $\text{S}_\text{n}1$ vs $\text{S}_\text{n}2$ (Very important for NEET)

1. Structure of alkyl halide

- $\text{S}_\text{n}1$: $3^\circ > 2^\circ > 1^\circ$ (carbocation stability).
- $\text{S}_\text{n}2$: methyl $> 1^\circ > 2^\circ \gg 3^\circ$ (steric hindrance).

2. Nature of nucleophile

- Strong, negatively charged nucleophile $\rightarrow \text{S}_\text{n}2$.
- Weak, neutral nucleophile $\rightarrow \text{S}_\text{n}1$.

3. Solvent

- Polar protic \rightarrow stabilise ions $\rightarrow \text{S}_\text{n}1$ favoured.

- Polar aprotic → stabilise cations but not anions, nucleophile free → S_n2 favoured.

4. Leaving group

- Better leaving group favours both S_n1 and S_n2, but S_n1 especially because it involves ionisation step.

8. Important Named Reactions and Applications

8.1 Finkelstein Reaction

- **Halogen exchange:** R-Cl / R-Br + NaI (in dry acetone) → R-I + NaCl / NaBr (ppt).
- Driving force: **NaCl/NaBr precipitate**, shifting equilibrium.
- Used to prepare **alkyl iodides** from cheaper chlorides/bromides.

8.2 Swarts Reaction

- For preparing **alkyl fluorides**:
$$\text{R-Cl} / \text{R-Br} + \text{AgF} / \text{Hg}_2\text{F}_2 / \text{CoF}_2 \rightarrow \text{R-F} + \text{AgCl} / \text{AgBr} \text{ etc.}$$

8.3 Hunsdiecker Reaction

Already above: silver salt of carboxylic acid + Br₂ → alkyl bromide (R-Br) with one C less.

8.4 Williamson Ether Synthesis

- From alkyl halide and alkoxide:
$$\text{R-X} + \text{R}'\text{O}^-\text{Na}^+ \rightarrow \text{R-O-R}' + \text{NaX} \text{ (S}_n\text{2 on primary alkyl halide)}$$

9. Typical NEET-Style Concepts & Tricks

1. Density order sample

For isomeric C₃H₇Br: density increases with mass of halogen same, so depends slightly on packing; often not heavily tested, but remember: **more substituted or multiple halogens → higher density**.

2. Boiling point vs branching

n-C₄H₉Cl > sec-C₄H₉Cl > tert-C₄H₉Cl.

3. Reactivity of alkyl halides towards S_n1

Benzyl > allyl > 3° > 2° > 1° > CH₃X

(benzyl and allyl have resonance-stabilised carbocations).

4. Reactivity towards S_n2

CH₃X > 1° > 2° (3° almost zero).

5. Order of leaving group ability

OTs⁻ (tosylate) ≈ OMs⁻ (mesylate) > I⁻ > Br⁻ > Cl⁻ >> F⁻.

6. Solvolysis

When solvent itself acts as nucleophile (e.g., water, alcohol) in S_n1.

10. Quick Revision Table

| Concept | S _n 1 | S _n 2 |
|--------------------|----------------------------------|-----------------------------|
| Steps | 2 (carbocation then attack) | 1 (concerted) |
| Rate law | k[substrate] | k[substrate][nucleophile] |
| Favoured substrate | 3° > 2° | CH ₃ > 1° > 2° |
| Nucleophile | weak / neutral | strong, negative |
| Solvent | polar protic | polar aprotic |
| Stereochemistry | racemisation (partial inversion) | complete inversion (Walden) |

NEET Mock Test – Haloalkanes (Part 1)

Section A: Single Correct MCQs (1–30)

Q1. In haloalkanes, the nature of the C–X bond is best described as:

- A. Non-polar due to equal electronegativity of C and X
- B. Polar with δ⁺ on halogen and δ⁻ on carbon
- C. Polar with δ⁺ on carbon and δ⁻ on halogen
- D. Non-polar due to tetrahedral geometry around carbon

Q2. Which of the following correctly represents the general formula for haloalkanes?

- A. Ar–X

- B. R-X
 - C. R-OH
 - D. Ar-OH
-

Q3. Which of the following statements about bond length and bond strength of C-X bonds is correct?

- A. Bond length: C-F > C-Cl > C-Br > C-I
 - B. Bond length: C-F < C-Cl < C-Br < C-I
 - C. Bond strength: C-I strongest, C-F weakest
 - D. Bond strength is independent of halogen size
-

Q4. Among the following haloalkanes, which represents a tertiary alkyl halide?

- A. CH₃CH₂Cl
 - B. CH₃CH(Cl)CH₃
 - C. (CH₃)₃CCl
 - D. CH₃Cl
-

Q5. Which of the following reagents is commonly known as Lucas reagent?

- A. Conc. HCl
 - B. Conc. HCl + anhydrous ZnCl₂
 - C. Conc. H₂SO₄ + NaCl
 - D. HCl gas in dry ether
-

Q6. In the Lucas test at room temperature, which of the following shows immediate turbidity?

- A. Primary alcohol
 - B. Secondary alcohol
 - C. Tertiary alcohol
 - D. All give turbidity at the same rate
-

Q7. Thionyl chloride (SOCl₂) is used to convert alcohols to alkyl chlorides because:

- A. The reaction is highly endothermic

- B. Only gaseous by-products are formed
 - C. The reaction does not require a catalyst
 - D. It produces a mixture of inorganic salts
-

Q8. Which of the following equations correctly represents the reaction of an alcohol with PCl_5 ?

- A. $\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{POCl}_3 + \text{HCl}$
 - B. $3\text{ROH} + \text{PCl}_5 \rightarrow 3\text{RCl} + \text{H}_3\text{PO}_4$
 - C. $\text{ROH} + \text{PCl}_5 \rightarrow \text{RCl} + \text{H}_3\text{PO}_3$
 - D. $3\text{ROH} + \text{PCl}_5 \rightarrow 3\text{RCl} + \text{POCl}_3$
-

Q9. The free radical chlorination of methane in the presence of UV light proceeds through:

- A. Ionic mechanism
 - B. Free radical chain mechanism
 - C. Pericyclic mechanism
 - D. Concerted nucleophilic substitution
-

Q10. During free radical halogenation of alkanes, the propagation step involves:

- A. Only formation of free radicals from non-radical species
 - B. Combination of free radicals to form stable molecules
 - C. Reaction of a free radical with a stable molecule to form a new radical
 - D. Photochemical cleavage of halogen
-

Q11. The addition of HBr to an unsymmetrical alkene in the presence of peroxides generally follows:

- A. Markovnikov's rule via ionic mechanism
 - B. Anti-Markovnikov's rule via free radical mechanism
 - C. Markovnikov's rule via free radical mechanism
 - D. Anti-Markovnikov's rule via ionic mechanism
-

Q12. The addition of Cl_2 to ethene gives:

- A. Geminal dichloride

- B. Vicinal dichloride
 - C. Allylic chloride
 - D. Benzylic chloride
-

Q13. In the Hunsdiecker reaction, the product obtained from silver salt of a carboxylic acid has:

- A. One carbon more than the acid
 - B. One carbon less than the acid
 - C. Same number of carbons as the acid
 - D. Two carbons less than the acid
-

Q14. Considering boiling points of isomeric C_4H_9Cl , the correct order is:

- A. tert-Butyl chloride > sec-Butyl chloride > n-Butyl chloride
 - B. n-Butyl chloride > sec-Butyl chloride > tert-Butyl chloride
 - C. sec-Butyl chloride > n-Butyl chloride > tert-Butyl chloride
 - D. All have the same boiling point
-

Q15. The low solubility of haloalkanes in water is mainly due to:

- A. Strong hydrogen bonding with water
 - B. Inability to form hydrogen bonds effectively with water
 - C. Strong covalent interactions with water
 - D. Their ionic nature in solution
-

Q16. Which of the following correctly represents the order of leaving group ability among halides?

- A. $F^- > Cl^- > Br^- > I^-$
 - B. $Cl^- > Br^- > I^- > F^-$
 - C. $I^- > Br^- > Cl^- \gg F^-$
 - D. $Br^- > I^- > Cl^- > F^-$
-

Q17. Which of the following is a good nucleophile but a poor base in protic solvent?

- A. F^-

- B. I^-
 - C. OH^-
 - D. NH_2^-
-

Q18. The correct order of nucleophilicity of halide ions in protic solvents is:

- A. $F^- > Cl^- > Br^- > I^-$
 - B. $Cl^- > F^- > Br^- > I^-$
 - C. $I^- > Br^- > Cl^- > F^-$
 - D. $Br^- > Cl^- > I^- > F^-$
-

Q19. The correct order of nucleophilicity of halide ions in aprotic polar solvents is:

- A. $F^- > Cl^- > Br^- > I^-$
 - B. $I^- > Br^- > Cl^- > F^-$
 - C. $Cl^- > F^- > Br^- > I^-$
 - D. $Br^- > I^- > Cl^- > F^-$
-

Q20. Which of the following best describes a polar protic solvent?

- A. Solvent capable of donating protons and forming hydrogen bonds
 - B. Solvent incapable of hydrogen bonding
 - C. Non-polar solvent with low dielectric constant
 - D. Solvent with no effect on nucleophilicity
-

Q21. In an S_N1 reaction, the rate of reaction depends on:

- A. Concentration of substrate only
 - B. Concentration of nucleophile only
 - C. Product concentration only
 - D. Concentration of both substrate and nucleophile
-

Q22. In an S_N2 reaction, the rate of reaction is:

- A. Independent of nucleophile concentration
- B. Directly proportional to concentration of substrate only
- C. Directly proportional to concentration of both substrate and nucleophile

D. Independent of substrate concentration

Q23. Which type of substrate is most reactive towards S_n1 reactions?

- A. Primary alkyl halide
 - B. Secondary alkyl halide
 - C. Tertiary alkyl halide
 - D. Methyl halide
-

Q24. Which type of substrate is most reactive towards S_n2 reactions?

- A. Tertiary alkyl halide
 - B. Secondary alkyl halide
 - C. Primary alkyl halide
 - D. Aryl halide
-

Q25. For an S_n2 reaction at a chiral carbon atom, the stereochemical outcome is:

- A. Retention of configuration
 - B. Inversion of configuration
 - C. Racemisation
 - D. No change in configuration
-

Q26. S_n1 reactions often lead to racemisation because:

- A. The transition state is tetrahedral
 - B. The carbocation intermediate is planar
 - C. The nucleophile attacks from only one fixed side
 - D. The leaving group remains attached during nucleophilic attack
-

Q27. The Finkelstein reaction is used for preparation of:

- A. Alkyl fluorides from alkyl bromides
 - B. Alkyl iodides from alkyl chlorides or bromides
 - C. Alkyl chlorides from alcohols
 - D. Aryl iodides from aryl chlorides
-

Q28. In the Finkelstein reaction, the commonly used solvent is:

- A. Water
 - B. Ethanol
 - C. Dry acetone
 - D. Benzene
-

Q29. The Swarts reaction is specifically used to prepare:

- A. Alkyl iodides
 - B. Alkyl bromides
 - C. Alkyl fluorides
 - D. Aryl chlorides
-

Q30. Williamson ether synthesis between an alkyl halide and an alkoxide ion generally proceeds by:

- A. S_N1 mechanism on a tertiary alkyl halide
 - B. S_N2 mechanism on a primary alkyl halide
 - C. Radical mechanism
 - D. Electrophilic addition mechanism
-

Section B: Assertion–Reason Type (31–35)

For Q31–Q35, choose:

- A: Both Assertion and Reason are true, and Reason is the correct explanation of Assertion
 - B: Both Assertion and Reason are true, but Reason is not the correct explanation of Assertion
 - C: Assertion is true, but Reason is false
 - D: Assertion is false, but Reason is true
-

Q31.

Assertion (A): Tertiary alkyl halides react faster than secondary and primary alkyl halides in S_N1 reactions.

Reason (R): Tertiary carbocations are more stable due to inductive effect and hyperconjugation.

Q32.

Assertion (A): S_n2 reactions are highly sensitive to steric hindrance around the reacting carbon.

Reason (R): In S_n2 reactions, the nucleophile attacks from the side opposite to the leaving group in a single step.

Q33.

Assertion (A): In protic solvents, I^- is a better nucleophile than F^- .

Reason (R): Smaller anions are more strongly solvated in protic solvents, reducing their nucleophilicity.

Q34.

Assertion (A): Free radical halogenation of alkanes proceeds via a chain mechanism.

Reason (R): In the propagation step, radicals react with stable molecules to form new radicals.

Q35.

Assertion (A): Solvolysis of tertiary alkyl halides in water is generally faster than that of primary alkyl halides.

Reason (R): Tertiary carbocations formed in such reactions are more stable than primary carbocations.

Section C: Matching Type (36–40)

Q36. Match the reactions in Column I with their main features in Column II:

Column I

1. S_n1 reaction
2. S_n2 reaction
3. Free radical halogenation

Column II

- P. Involves carbocation intermediate
- Q. Involves backside attack and inversion
- R. Involves chain initiation, propagation, and termination

Options:

A. 1-P, 2-Q, 3-R

B. 1-Q, 2-P, 3-R

C. 1-R, 2-P, 3-Q

D. 1-P, 2-R, 3-Q

Q37. Match the reagents in Column I with their major use in Column II:

Column I

1. NaI in acetone
2. AgF
3. SOCl_2 / pyridine

Column II

- P. Clean conversion of alcohols to alkyl chlorides
- Q. Finkelstein reaction
- R. Swarts-type halide exchange to form alkyl fluorides

Options:

A. 1-Q, 2-R, 3-P

B. 1-R, 2-Q, 3-P

C. 1-Q, 2-P, 3-R

D. 1-P, 2-R, 3-Q

Q38. Match the following types of solvents in Column I with examples in Column II:

Column I

1. Protic solvent
2. Aprotic polar solvent

Column II

P. Water

Q. DMSO

Options:

- A. 1-P, 2-Q
 - B. 1-Q, 2-P
 - C. 1-P, 2-P
 - D. 1-Q, 2-Q
-

Q39. Match the following nucleophiles in Column I with their relative steric hindrance in Column II:

Column I

- 1. CH_3O^-
- 2. $(\text{CH}_3)_3\text{CO}^-$

Column II

- P. Less sterically hindered
- Q. More sterically hindered

Options:

- A. 1-P, 2-Q
 - B. 1-Q, 2-P
 - C. 1-P, 2-P
 - D. 1-Q, 2-Q
-

Q40. Match the following terms in Column I with definitions in Column II:

Column I

- 1. Electrophile
- 2. Nucleophile

Column II

- P. Electron-deficient species seeking electrons
- Q. Electron-rich species seeking positively charged centres

Options:

- A. 1-P, 2-Q
- B. 1-Q, 2-P
- C. 1-P, 2-P

Answer Key (for self-checking)

1. C
2. B
3. B
4. C
5. B
6. C
7. B
8. A
9. B
10. C
11. B
12. B
13. B
14. B
15. B
16. C
17. B
18. C
19. A
20. A
21. A
22. C
23. C
24. C
25. B

- 26. B
- 27. B
- 28. C
- 29. C
- 30. B
- 31. A
- 32. A
- 33. A
- 34. A
- 35. A
- 36. A
- 37. A
- 38. A
- 39. A
- 40. A