

XI - CBSE CHEMISTRY

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NEET SYLLABUS

CHEMICAL THERMODYNAMICS : First law of thermodynamics-internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH , Hess's law of constant heat summation, enthalpy of : bond dissociation, combustion, formation, atomization, sublimation, phase transition, ionization, solution and dilution. Introduction of entropy as state function, Second law of thermodynamics, Gibbs energy change for spontaneous and non-spontaneous process, criteria for equilibrium and spontaneity. Third law of thermodynamics- Brief introduction.

OBJECTIVES

After studying this unit, we will be able to :

- *explain the terms : system and surroundings;*
- *discriminate between close, open and isolated systems;*
- *explain internal energy, work and heat;*
- *state first law of thermodynamics and express it mathematically;*
- *calculate energy changes as work and heat contributions in chemical systems;*
- *explain state functions: U , H .*
- *correlate ΔU and ΔH ;*
- *define standard states for ΔH ;*
- *calculate enthalpy changes for various types of reactions;*
- *state and apply Hess's law of constant heat summation;*
- *differentiate between extensive and intensive properties;*
- *define spontaneous and nonspontaneous processes;*
- *explain entropy as a thermodynamic state function and apply it for spontaneity;*
- *explain Gibbs energy change (ΔG);*
- *establish relationship between ΔG and spontaneity, ΔG and equilibrium constant.*

"Thermodynamics cannot be fathomed in all its profundity in a single pass"

Joseph Kestin

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Closed system : This type of systems can exchange energy, (in the form of heat, work or radiations) but not matter with its surroundings. The boundary is sealed but not insulated. Amount of the system will remain constant.

Eg.1 Coffee in closed vessel. Hot water in closed vessel.

Eg.2 Glowing bulb, tube light.

Eg.3 A satellite in orbit.

Isolated system : This type of system are perfectly insulated systems and cannot interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding. The boundary is sealed and insulated. Universe can be considered as an isolated system.

Eg.1 Coffee in thermosflask.

5.3 STATE OF THE SYSTEM :

- Properties which define state of any system are called its state variables or thermodynamic variables or thermodynamic quantities.
- The state of the system is defined by their measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

State Function :

- Those state variables which depend only upon initial and final state of the system but doesn't depend upon the path or mechanism followed by the system to achieve final state are called state function.
- State functions are denoted by capital letters.

Ex. E, H, S, G, T, P, V etc.

Path function :

- Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve final state are called path function.
- Path functions are denoted by small letters.

Eg. Work done (w), heat (q)

Thermodynamic properties :

- Intensive properties :** The properties of the system which are independent of matter (size and mass) present in system are called intensive properties.
- Extensive properties :** The properties of the system which are dependent on matter (size and mass) present in system are called extensive properties

Extensive Properties	Intensive Properties
Volume (V)	Molar volume (V_m)
Number of moles (n)	Density (d)
Mass (m)	Gibb's energy per mole (G_m)
Gibb's Energy (G)	Specific heat
Entropy (S)	Pressure (P)
Enthalpy (H)	Temperature (T)
Internal energy (E or U)	All concentration terms (M, N)
Heat capacity (C)	Boiling point, freezing point (T_b , T_f)
Force (F)	Cell potential (E_{cell})
Surface Area (A)	Specific conductance (κ)
	Refractive index
	Surface tension, Viscosity
	pH value
	Vapour pressure

Special Points :

- (i) The ratio of two extensive properties indicates the intensive property Eg. $d = \frac{\text{mass}}{\text{volume}}$
- (ii) An extensive property can be converted into intensive property when it is defined for unit amount of the substance.

Eg. Mass per unit volume = density; $\left(d = \frac{m}{V}\right)$

- (iii) Intensive properties of a substance are non-additive in nature while extensive properties are additive in nature.

	H₂O	H₂O	On adding
Vessel	A	B	
Mass	m_1	m_2	$m_1 + m_2$ (Total mass)
Moles	n_1	n_2	$n_1 + n_2$ (Total moles)
Volume	V_1	V_2	$V_1 + V_2$ (Total volume)
Density	d	d	Remains same (d)
Boiling point	T	T	Remains same (T)

5.4 TYPES OF THERMODYNAMIC PROCESSES :

When a system changes from one state to another, the operation is called a thermodynamic process.

Thermodynamic processes may be in form of expansion or compression.

(a) Isothermal Process ($n, T = \text{constant}$)

Isothermal processes are those processes in which

- (a) Temperature of system during entire process remains constant i.e. $\Delta T = 0$
- (b) Heat is exchanged with surroundings
- (c) Volume and pressure are variable
- For ideal gas in Isothermal process $\Delta E = 0$ and $\Delta H = 0$
 - All phase transitions are isothermal process but $\Delta E \neq 0$ and $\Delta H \neq 0$

(b) Isobaric Process ($n, P = \text{constant}$) :

Isobaric processes are those processes in which

- (a) Pressure of system during entire process remains const i.e. $\Delta P = 0$
- (b) Volume and temperature are variable.
- (c) Process in open system is isobaric in nature.

(c) Isochoric Process ($n, V = \text{constant}$) :

Isochoric processes are those processes in which

- (a) Volume remains constant i.e. $\Delta V = 0$
- (b) Pressure and temperature are variable
- (c) Work, $w = -P\Delta V$, $\therefore \Delta V = 0$, $\therefore w = 0$ (Zero)
- (d) Process in closed system is isochoric in nature.

(d) Adiabatic Process ($n = \text{constant}, q = 0$)

Adiabatic processes are those processes in which

- (a) No exchange of heat between system and surrounding takes place during entire process i.e. $q = 0$
- (b) The temperature pressure, volume of the system varies.
- (c) The system is thermally insulated by keeping the system in an insulated container.

(e) Cyclic Process :

When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

In cyclic process change in all state function will be zero. i.e. $\Delta E = 0$, $\Delta H = 0$, $\Delta P = 0$, $\Delta T = 0$

(f) Reversible Process (quasi-static) :

- (1) Process in which all changes occurring at any part of the system are exactly reversed when small changes in variables are carried out in opposite direction.
- (2) Driving force should be infinitesimally greater than opposing force.
- (3) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.
- (4) It is an ideal process.
- (5) Work obtained in expansion is maximum.
- (6) System is in virtual equilibrium at any state.
- (7) $P_{\text{ext}} = P_{\text{int}} \pm dP$; P_{ext} is variable.

Irreversible Process :

- (1) Process in which direction of change cannot be reversed by small changes in variables.
- (2) Driving force is much greater than opposing force.
- (3) It takes finite time and finite/usually single step.
- (4) Process takes place in short time
- (5) All natural processes are irreversible
- (6) System is in equilibrium only at initial and final state
- (7) $P_{\text{ext}} = P_{\text{int}} \pm \Delta P$; P_{ext} is constant.

5.5 WORK AND HEAT :

(A) Work : Product of force and displacement is known as work.

$$\text{work (w)} = \text{force (F)} \times \text{displacement (}\ell\text{)}$$

Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Suppose area of cross section of cylinder = A and pressure on the piston = P

Initial volume of the gas = V_1 and final volume of the gas = V_2

(By expansion) displacement of piston = ℓ

$$\text{work done by the gas (in expansion)} = w = F \cdot \ell$$

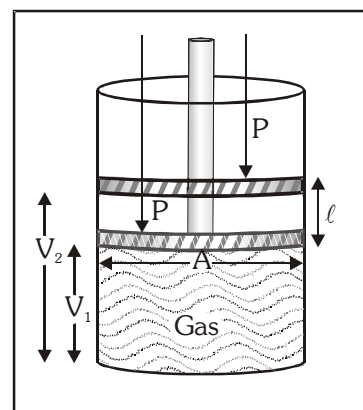
$$\therefore P = \frac{F}{A} \quad \therefore F = P \times A$$

$$w = P \times A \times \ell \text{ (change in volume} = A \times \ell = V_2 - V_1\text{)}$$

$$w = P \times (V_2 - V_1)$$

$$w = P\Delta V \text{ (According to Physics)}$$

$$\text{In general } \boxed{w = -P_{\text{external}} DV} \text{ (According to Chemistry)}$$



SIGN CONVENTIONS :

- According to latest sign conventions
 - Work done is taken negative if it is done by the system since energy of system is decreased.
Eg. Expansion of gas.
 $\therefore V_2 > V_1$; $\Delta V = \text{positive}$; $w = \text{negative}$
 - Work done is taken positive if it is done on the system, since energy of system is increased.
Eg. Compression work.
 $\therefore V_1 > V_2$; $\Delta V = \text{negative}$; $w = \text{positive}$

(B) Heat exchange (q) :

Heat is defined as the energy that flow in or out of a system because of a difference in temperature between the thermodynamic system and its surrounding. It is a path function.

According to IUPAC convention, heat given by the system is expressed with negative sign and heat given to the system is expressed with positive sign.

- Heat always flows from high temperature to low temperature.
- Heat flowing into the system $q = \text{positive}$
- Heat flowing out of the system $q = \text{negative}$

Units of heat & work :

Calorie : It is defined as the quantity of heat required to raise the temperature of 1 g of water by 1°C (14.5 to 15.5 $^\circ\text{C}$)

$$1 \text{ cal} = 4.184 \text{ J} \simeq 4.2 \text{ J}$$

$$1 \text{ L-atm} = 101.3 \text{ J} = 24,206 \text{ cal} = 101.3 \times 10^7 \text{ erg}$$

$$1 \text{ L-atm} > 1 \text{ Cal} > 1 \text{ J} > 1 \text{ erg}$$

GOLDEN KEY POINTS

- Molar properties like ΔH_m , ΔG_m , ΔS_m , ΔU_m are intensive properties.
- In cyclic process change in all state function will be equal to zero.
 $\Delta E = 0$; $\Delta H = 0$, $\Delta P = 0$, $\Delta T = 0$ etc.
- For ideal gases $\Delta E = 0$ (For isothermal process)
- All natural process are irreversible in nature.
- Both q and w are (+) **to** system.
- Both q and w are (–) **by** the system.

Illustrations

Illustration 1. Find the work done in each case :

- When one mol of ideal gas in 10 litre container at 1 atm is allowed to enter a **vacuum bulb** of capacity 100 litre.
- When 1 mol of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

Solution

(a) $W = -P\Delta V$ but since gas enters the vacuum bulb and pressure in vacuum is zero. This type of expansion is called **free expansion** and work done is zero.

Note :- Work done in free expansion is always zero.

(b) $W = -P\Delta V = -1(5 - 1) = -4 \text{ L-atm.}$

Illustration 2. A 5 litre cylinder contained 10 mol of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmosphere pressure is 1.0 atm. Calculate the work done by the gas ? ($R = 0.083 \text{ lit atm mol}^{-1} \text{ K}^{-1}$)

Solution

$$V_{\text{initial}} = 5 \text{ L}$$

$$T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$V_{\text{final}} = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 249 - 5 = 244 \text{ L}$$

$$W_{\text{exp}} = -P\Delta V = -1 \times 244 \text{ L-atm.} = -244 \text{ L-atm.}$$

BEGINNER'S BOX-1

- Which of the following open system
(1) Animals and plants (2) A fridge (3) A solar cooker (4) None of these
- One mole of gas occupying 3 litre volume is expanded against a constant external pressure of one atm to a volume of 15 litre. The work done by the system is :-
(1) $-1.215 \times 10^3 \text{ J}$ (2) $+12.15 \times 10^3 \text{ J}$ (3) $+121.5 \times 10^3 \text{ J}$ (4) $+1.215 \times 10^3 \text{ J}$
- The work done during the expansion of a gas from a volume of 4 dm³ to 6 dm³ against a constant external pressure of 3 atm is :-
(1) -608 J (2) +304 J (3) -304 J (4) -6 J
- The work done during the expansion of a gas from a volume of 14 dm³ to 16 dm³ against a constant external pressure of 2 atm is :-
(1) -405.2 J (2) +304 J (3) -304 J (4) -6 J

5.6 INTERNAL ENERGY (E/U) :

Internal energy of a system is defined as the sum of different energies associated with its atoms and molecules like Potential energy, Kinetic energy (due to translatory, rotatory and vibratory motion), electronic energy, nuclear energy etc.

$$E = E_{\text{PE}} + E_{\text{T}} + E_{\text{R}} + E_{\text{V}} + E_{\text{e}} + E_{\text{N}}$$

(i) Internal energy is an **extensive property**.

(ii) We can **never find out the absolute value** of internal energy (E) of system.

We can only calculate the change in internal energy of the system (ΔE) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.

(iii) Internal energy is a **state function**.

$$\Delta E = E_f - E_i$$

$$(\text{In reaction}) \quad \Delta E = E_p - E_R$$

$$\Delta E \text{ is } + \text{ ve if } E_f > E_i$$

$$\Delta E \text{ is } - \text{ ve if } E_f < E_i$$

5.7 LAWS OF THERMODYNAMICS :

GENERAL POINT :

Laws of thermodynamics are based on human experiences there is no formal proof for them.

FIRST LAW OF THERMODYNAMICS (FLOT) :

- This law is based on law of conservation of energy and was given by **Robert Mayer and Helmholtz**.
- Energy can neither be created nor destroyed but can be transformed from one form to another.
- The total energy of the universe is always constant. i.e. total energy of an isolated system is always conserved.
- The mathematical form of first law of thermodynamics can be expressed as follows

$$\boxed{\Delta E = q + w} : \text{where } q, w \text{ are path function and } E \text{ is state function.}$$

Here q is the energy given to the system and w is the work done on the system ; ΔE is change in internal energy.

Note :- Put the value of q and w with proper sign.

CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS :

(a) During isothermal process of an ideal gas :

During an isothermal process the temperature of the system remains constant and hence

$$\Delta E = 0$$

Therefore FLOT : $\Delta E = q + w$

$$\therefore \boxed{+q = -w} \text{ or } -q = +w$$

In isothermal process –

(I) Heat absorbed by the system is equal to work done by the system.

OR

(II) Heat evolved by the system is equal to work done on the system.

(b) During isochoric process :

At constant volume $V_1 = V_2$ i.e. $\Delta V = 0$

Hence $W = -P\Delta V = 0$ No work done at constant volume therefore,

$$\text{FLOT: } \Delta E = q + w \quad \boxed{\Delta E = q_v}$$

(i) In isochoric process

- At constant volume, heat absorbed by the system is equal to increase in internal energy of the system.

OR

- At constant volume, heat evolved by the system is equal to decrease in internal energy of the system.

(ii) Heat at constant volume (q_v) = ΔE

(iii) **In isochoric process heat is independent of path.**

(c) During adiabatic process :

During adiabatic process the system acts as an isolated system and hence $q = 0$ in such cases. Therefore

$$\text{FLOT : } \Delta E = q + w \quad \because q = 0 \quad \boxed{\Delta E = w}$$

- (i) Work done on the system is equal to increase in internal energy of the system i.e., when a gas is compressed adiabatically its internal energy increases.

OR

Work done by the system is equal to decrease in internal energy of the system, i.e., when a gas is expanded adiabatically its internal energy decreases.

- (ii) **In adiabatic process work is independent of path.**

(d) During Cyclic Process :

$$\Delta E = 0 \quad \text{FLOT ; } \Delta E = q + w \quad \boxed{+q = -w}$$

In cyclic process.

- (I) Work done by the system is equal to heat absorbed by the system.

OR

- (II) Work done on the system is equal to heat evolved by the system.

(e) During Isobaric process :

$P = \text{constant}$

$$\text{FLOT : } \Delta E = q + W$$

$$\Delta E = q + (-P\Delta V)$$

$$q_p = \Delta E + P\Delta V$$

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$q_p = (E_2 + PV_2) - (E_1 + PV_1)$$

$$\because \text{Enthalpy } H = E + PV$$

$$\therefore q_p = H_2 - H_1 \quad \boxed{q_p = \Delta H}$$

- (i) **In isobaric process :**

- At constant pressure, heat absorbed by the system is equal to increase in enthalpy of the system.

OR

- At constant pressure, heat evolved by the system is equal to decrease in enthalpy of the system.

- (ii) Heat at constant pressure (q_p) = ΔH

- (iii) **In isobaric process heat is independent of path.**

Illustrations

Illustration 3. 1g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere, the volume increases from 1 mL to 1671 mL. The heat of vaporisation at this pressure is 540 Cal/g. Find the increase in internal energy of water. (1 L atm = 101 J)

Solution Work done $w = -P\Delta V = -P(V_2 - V_1)$

$$= -1(1671 - 1) \times \frac{1}{1000} = \frac{-1670}{1000} \text{ L-atm}$$

$$= \frac{-1670}{1000} \times 101 \text{ J} = -168.67 \text{ J}$$

given that $q = 540 \text{ Cal} = 540 \times 4.2 \text{ J} = 2268 \text{ J}$

$\therefore \Delta E = q + w = 2268 - 168.67 = 2099.33 \text{ J}$

Illustration 4. A gas occupies 2 L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm. Calculate change in its internal energy.

Solution $w = -P\Delta V = -1 \times (2.5 - 2) = -0.5 \text{ L-atm}$ or $w = -0.5 \times 101.3 = -50.65 \text{ J}$.

$\Delta E = q + w = 300 + (-50.65)$

$\Delta E = 249.35 \text{ J}$

Illustration 5. A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2L to 12L. During the process, it absorbs 600 J of heat from the surroundings. Calculate the change in internal energy of the system.

Solution During the process,

$q = 600 \text{ J}$, $\Delta V = 12 - 2 = 10 \text{ L}$, $P = 1 \text{ atm}$

$w = -P\Delta V$

$= -1 \times 10 = -10 \text{ L atm}$

Now, $1 \text{ L atm} = 101.3 \text{ J}$

$\therefore w = -10 \times 101.3 = -1013 \text{ J}$

According to first law of thermodynamics,

$\Delta E = q + w = 600 - 1013 = -413 \text{ J}$

Illustration 6. Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half of its volume by a constant external pressure of 4 atm. Calculate q , w & ΔE . ($R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$)

Solution Work done on the system,

$w = -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i)$

$V_i = \frac{nRT}{P}$

$n = 2 \text{ mol}$ and $R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$,

$T = 273 + 27 = 300 \text{ K}$, $P = 2 \text{ atm}$

$V_i = \frac{2 \times 0.082 \times 300}{2} = 24.6 \text{ L}$ and $V_f = \frac{V_i}{2} = \frac{24.6}{2} = 12.3 \text{ L}$

$$w = -4 \text{ atm} \times (12.3 - 24.6) \text{ L} = 49.2 \text{ L atm} = 49.2 \times 101.3 \text{ J} = 4984 \text{ J}.$$

Since, it is isothermal compression, $\Delta E = 0$

Now, $\Delta E = q + w$

$$0 = q + 4984 \text{ J or } q = -4984 \text{ J}$$

Illustration 7 A system is provided with 100 J of heat. Work done on the system is 20 J. What is the change in internal energy.

Solution $q = 100 \text{ J}$ and $w = +20 \text{ J}$
 $\Delta E = q + w = 100 + 20 \text{ J} = 120 \text{ J}$

Illustration 8. An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T , while the other portion is a perfect Vacuum. If a hole is opened between the two portions, Calculate the –

(i) Change in internal energy of the gas (ii) Change in temperature of the gas

Solution For insulated system, $q = 0$

The gas is allowed to expand against vacuum, the process of free expansion and thus

$$w = -P\Delta V = 0 \text{ (for vacuum} = P_{\text{ext}} = 0)$$

$$\text{Thus from I law of thermodynamics, } \Delta E = q + w \text{ or } \Delta E = 0$$

i.e. internal energy change is zero or internal energy of gas remains constant during free expansion.

Also $E \propto T$ and thus temperature of the gas will also remains constant.

BEGINNER'S BOX-2

- A system absorb 300 cal of heat with the result of that, the volume of the system becomes double of its initial volume and temperature changes from 273K to 546K. The work done by the system on the surroundings is 200.0 Cal Calculate ΔE :-
 (1) 273 kCal (2) 500 Cal (3) 100 Cal (4) -500 Cal
- One mol of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The ΔE for the process is :- ($R = 2 \text{ Cal K}^{-1} \text{ mol}^{-1}$)
 (1) 163.7 Cal (2) 1381.1 Cal (3) 9 L-atm (4) Zero
- In an adiabatic process which of the following is true :-
 (1) $q = +w$ (2) $-\Delta E = -w$ (3) $P\Delta V = 0$ (4) $q = \Delta E$
- In an isochoric process, the increase in internal energy is :-
 (1) Equal to the heat absorbed (2) Equal to the heat evolved
 (3) Equal to the work done (4) Equal to zero

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The sum of internal energy and pressure volume (PV) energy is known as enthalpy.

- It is impossible to determine absolute value of enthalpy so we determine change in enthalpy (ΔH).

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

- $$\therefore H = E + PV$$

(when P, V and T are variables)

At constant volume : $\Delta H = \Delta E + V.\Delta P$...(iii)

For chemical reactions at constant temprature and pressure $\therefore P.\Delta V = \Delta n_g RT$

So from equation (i)

$\Delta H = \Delta E + \Delta n_g RT \dots (iv)$

where $\Delta H = q_p$; at constant P ; $\Delta E = q_v$; at constant V

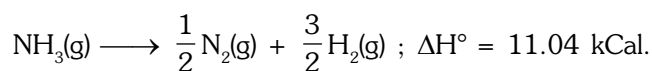
So equation (iv) can be also written as $\boxed{q_p = q_v + \Delta n_g RT} \dots (v)$

- If, $\Delta n_g = 0 \rightarrow \boxed{\Delta H = \Delta E}$ eg. $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- If, $\Delta n_g > 0 \rightarrow \boxed{\Delta H > \Delta E}$ eg. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- If, $\Delta n_g < 0 \rightarrow \boxed{\Delta H < \Delta E}$ eg. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Illustration 9. The heat of reaction for $\text{C}_{10}\text{H}_8(\text{s}) + 12\text{O}_2(\text{g}) \longrightarrow 10\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\ell)$ at constant volume is -1228.2 kCal at 25°C . Calculate the heat of reaction at constant pressure and at 25°C .

$$\begin{aligned}\Delta n_g &= [10] - [12] = -2 \\ \Delta H &= \Delta E + \Delta n_g RT \\ &= -1228.2 \times 10^3 + (-2)(2) \times 298 \\ &= -1229392 \text{ Cal} \\ \Delta H &= -1229.392 \text{ kCal}\end{aligned}$$

Illustration 10. For the reaction at 25°C



Calculate ΔE° of the reaction at the given temperature.

Solution

$$\Delta H^\circ = \Delta E^\circ + \Delta n_g RT$$

$$\Delta n_g = 2 - 1 = 1 \text{ mol}$$

$$\Delta E^\circ = \Delta H^\circ - \Delta n_g RT$$

$$= 11.04 \text{ Kcal} - 1 \text{ mol} \times \frac{2}{1000} \text{ kCal mol}^{-1} \text{K}^{-1} \times 298 \text{K}$$

$$= 11.04 - 0.596 = 10.44 \text{ kCal}$$

Illustration 11 At 27°C the internal energy change of reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$ is 2Cal. What is the enthalpy change of this reaction.

Solution

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta H = \Delta E + 0 \times RT$$

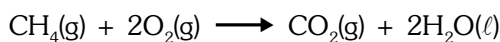
$$\Delta H = \Delta E$$

$$\Delta H = 2\text{Cal}$$

Illustration 12 The heat of combustion of gaseous methane (CH_4) at constant volume is measured in bomb calorimeter at 298K is found to be $-885.4 \text{ kJ mol}^{-1}$. Find the value of enthalpy change at the same temperature.

Solution

Combustion of methane gives $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ as



$$\Delta E = -885.4 \text{ kJ mol}^{-1} = -885400 \text{ J mol}^{-1}$$

$$\Delta n_g = 1 - (1 + 2) = -2 \text{ mol}$$

$$T = 298\text{K}, R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$$

$$\text{Now, } \Delta H = \Delta E + \Delta n_g RT$$

$$= -885400 + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{K}^{-1}) \times (298\text{K})$$

$$= -885400 - 4955$$

$$= -890355 = -890.355 \text{ kJ}$$

Illustration 13. The enthalpy change (ΔH) for the reaction : $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ is -92.38 kJ at 298 K. What is ΔE at 298 K ?

Solution

$$\Delta H \text{ and } \Delta E \text{ are related as } \Delta H = \Delta E + \Delta n_g RT$$

$$\text{for the reaction, } \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$$

$$\Delta n_g = 2 - (1 + 3) = -2 \text{ mol}, T = 298 \text{ K}$$

$$\Delta H = -92.38 \text{ kJ} = -92380 \text{ J}, R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$$

$$-92380 = \Delta E + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{K}^{-1}) \times (298 \text{ K})$$

$$-92380 = \Delta E - 4955$$

$$\Delta E = -92380 + 4955$$

$$= -87425 \text{ J} = -87.425 \text{ kJ.}$$

Illustration 14 The enthalpy change for the reaction $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ at 1000K is 176 kJ mol^{-1} . Calculate the change in internal energy.

Solution $\Delta H = \Delta E + \Delta n_g RT$
 $176 = \Delta E + (+1) \times 8.314 \times 10^{-3} \times 1000$
 $\Delta E = 167.686 \text{ kJ}$

BEGINNER'S BOX-3

- When a solid melts, there is :-
 (1) No increase in enthalpy (2) Increase in enthalpy
 (3) Decrease in enthalpy (4) Anything can happen
- For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ which of the following is valid :-
 (1) $\Delta H = \Delta E$ (2) $\Delta H < \Delta E$
 (3) $\Delta H > \Delta E$ (4) None of these
- Heat exchanged in a chemical reaction at constant pressure is called :-
 (1) Internal energy (2) Enthalpy
 (3) Entropy (4) Free energy
- Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is $10.0 \text{ kCal mol}^{-1}$. What will be the change in internal energy of 3 mol of liquid at same temperature and pressure
 (1) 13.0 kCal (2) -13.0 kCal
 (3) 27.0 kCal (4) -27.0 kCal
- What is the value of Δn_g if we consider the combustion of 1 mol of liquid ethanol if reactants and products are at 298 K :-
 (1) -1 (2) -2 (3) +1 (4) +2
- If a reaction involves only solids and liquids, which of the following is true
 (1) $\Delta H < \Delta E$ (2) $\Delta H = \Delta E$
 (3) $\Delta H > \Delta E$ (4) $\Delta H = \Delta E + RT\Delta n_g$
- The value of $\Delta H - \Delta E$ for the following reaction at 27°C will be, $2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$:-
 (1) $8.314 \times 273 \times (-2) \text{ J}$
 (2) $8.314 \times 300 \times (-2) \text{ J}$
 (3) $8.314 \times 27 \times (+2) \text{ J}$
 (4) $8.314 \times 300 \times (+2) \text{ J}$
- At constant temperature for the reaction $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\ell)$, $\Delta E - \Delta H$ is :-
 (1) +RT (2) -3RT (3) +3RT (4) -RT

5.9 HEAT CAPACITY / MOLAR HEAT CAPACITY / SPECIFIC HEAT CAPACITY :

- (i) **Heat capacity (C)** : Amount of heat required to raise the temperature of given amount of a substance by 1°C or 1K is called heat capacity.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temp.}}$$

$$C = \frac{dq}{dT}$$

Units :- JK⁻¹, Cal K⁻¹, J °C⁻¹, Cal °C⁻¹

- Heat capacity is extensive property.

- (ii) **Molar heat capacity (C_m)** : Amount of heat required to raise the temperature of 1 mole of substance by 1°C or 1 K is called as molar heat capacity.

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow C_m = \frac{C}{n}$$

Units :- Jmol⁻¹ K⁻¹, Cal mol⁻¹ K⁻¹, J mol⁻¹ °C⁻¹, Cal mol⁻¹ °C⁻¹

- Molar heat capacity is an intensive property.

- (iii) **Specific heat capacity (c)** : Amount of heat required to raise the temperature of 1 g of substance by 1°C or 1K is called as specific heat capacity.

$$c = \frac{C_m}{\text{molecular weight}}$$

Units :- Jg⁻¹ K⁻¹, Cal g⁻¹ K⁻¹, J g⁻¹ °C⁻¹, Cal g⁻¹ °C⁻¹

- Specific heat capacity is an intensive property.

- If heat is supplied at constant pressure, then $C_p = \left(\frac{dq}{dT} \right)_p = \frac{dH}{dT} \dots (i)$

- If heat is supplied at constant volume, then $C_v = \left(\frac{dq}{dT} \right)_v = \frac{dE}{dT} \dots (ii)$

From equation (i) and (ii) :

From equation (i)	Unit	From equation (ii)
ΔH = C_pdT [Here C_p is heat capacity at constant P]	JK ⁻¹	ΔE = C _v dT [Here C _v is heat capacity at constant V]
For n moles ΔH = nC_pdT [Here C_p is molar heat capacity at constant P]	J mol ⁻¹ K ⁻¹	ΔE = nC _v dT [Here C _v is molar heat capacity at constant V]
For m gram ΔH = mC_pdT [Here C_p is gram specific heat (specific heat capacity) at constant P]	J g ⁻¹ K ⁻¹	ΔE = mC _v dT [Here C _v is gram specific heat (specific heat capacity) at constant V]

Relation between C_p and C_v for 1 mole of an ideal gas :

$$\therefore H = E + PV$$

for ideal gas,

$$PV = nRT$$

$$PV = RT \quad \text{for 1 mole}$$

$$\therefore H = E + RT \text{ differentiate w.r.t. temperature}$$

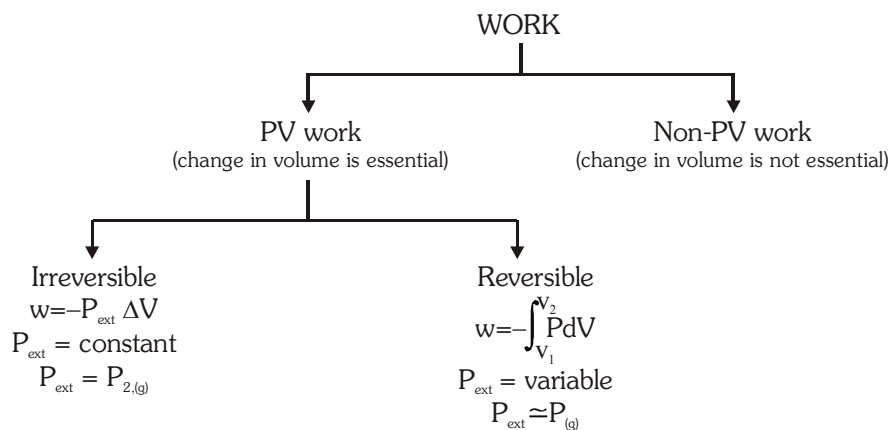
$$\left(\frac{dH}{dT}\right) = \left(\frac{dE}{dT}\right) + R$$

$$C_p = C_v + R$$

$$(i) \quad \boxed{C_p - C_v = R} \quad \text{Mayer's formula}$$

$$(ii) \quad \boxed{\frac{C_p}{C_v} = \gamma}, \quad \gamma = \text{Poisson's ratio}$$

5.10 WORK DONE IN DIFFERENT PROCESS :



Here $P_{2(g)}$ = Pressure of gas outside piston.

$P_{(g)}$ = Pressure of gas inside piston.

(a) Work done in reversible isothermal process :

$$P_{\text{external}} = \text{Variable}$$

For reversible process

$$P_{\text{ext}} = P_{\text{gas}} \pm dP$$

$$\therefore w_{\text{rev.}} = -\int_{V_1}^{V_2} P_{\text{ext.}} dV$$

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} (P_{\text{gas}} \pm dP) dV$$

Both dP and dV are very small so, $(dP \cdot dV)$ is negligible.

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} P_{\text{gas}} \cdot dV$$

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$w_{\text{rev.}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w_{\text{rev.}} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$\text{or, } \boxed{w_{\text{rev.}} = -2.303nRT \log_{10} \left(\frac{V_2}{V_1} \right)} \quad \dots(i)$$

according to Boyle's law at constant temperature $P \propto \frac{1}{V}$ or $PV = \text{constant}$

$$\therefore P_1 V_1 = P_2 V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\boxed{w_{\text{rev.}} = -2.303nRT \log \left(\frac{P_1}{P_2} \right)} \quad \dots(ii)$$

(b) Work done in reversible adiabatic process :

In adiabatic process $q = 0$

FLOT : $\Delta E = q + w$

$$\Rightarrow \boxed{w = \Delta E} \Rightarrow w = nC_v \Delta T$$

$$\boxed{w = nC_v (T_2 - T_1)} \quad \dots(i)$$

$$\therefore C_p - C_v = R$$

$$\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$$

$$\gamma - 1 = \frac{R}{C_v} \quad \left(\because \gamma = \frac{C_p}{C_v} \right) \Rightarrow C_v = \frac{R}{\gamma - 1} \quad \dots(ii)$$

$$\text{From equation (i) and (ii) } \boxed{w = \frac{nR}{\gamma - 1} (T_2 - T_1)} = \boxed{w = \frac{P_2 V_2 - P_1 V_1}{(\gamma - 1)}}$$

State equations of reversible adiabatic processes are :

$$PV^\gamma = \text{constant}$$

$$TV^{\gamma-1} = \text{constant}$$

$$T^\gamma P^{1-\gamma} = \text{constant}$$

GOLDEN KEY POINTS

- Work in closed vessel is zero because volume remains constant.
- Work during free expansion of an ideal gas in vacuum is zero, because P_{ext} is zero.
- Work in a chemical reaction $w = -P\Delta V = -\Delta n_g RT$

Illustrations

Illustration 15 5 moles of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas? The molar heat capacity of oxygen at constant pressure,

$$C_p = 7.03 \frac{\text{Cal}}{\text{molK}} \text{ and } R = 2 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

Solution We know mayer's relation is $C_p - C_v = R$

$$C_v = C_p - R = 7.03 - 2 = 5.03 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

$$\text{As we know } \Delta E = nC_v dT = 5 \times 5.03 \times 10 = 251.5 \text{ Cal}$$

Illustration 16 At 27°C, one mole of an ideal gas compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate ΔE and q in calorie.

Solution For isothermal process $\Delta E = 0$ and $w = -2.303 nRT \log_{10} \frac{P_1}{P_2}$

$$w = -2.303 \times 1 \times 2 \times 300 \times \log \frac{2}{10}$$

$$w = + 2.303 \times 600 \times \log 5$$

$$w = + 2.303 \times 600 \times 0.699$$

$$w = + 965.87 \text{ Cal}$$

$$\text{For isothermal process} \quad \therefore w = -q$$

$$\therefore q = -965.87 \text{ Cal}$$

Illustration 17 A gas expands from 3 dm³ to 5 dm³ against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mol of water of temperature 290 K. Calculate final temperature of water (if specific heat of water is 4.184 Jg⁻¹K⁻¹)

Solution Since work is done against constant P and thus, irreversible

$$\Delta V = 5 - 3 = 2 \text{ dm}^3 = 2 \text{ L}, P = 3 \text{ atm}$$

$$w = -P\Delta V = -3 \times 2 \text{ L atm} = -6 \times 101.3 \text{ J} = -607.8 \text{ Joule}$$

Now this work is used up in heating water

$$w = n \times C \times \Delta T$$

$$607.8 = 10 \times (4.184 \times 18) \times \Delta T$$

$$\Delta T = 0.81 = T_2 - T_1$$

$$\therefore \text{Final temperature} = T_1 + \Delta T = 290 + 0.81 = 290.81 \text{ K}$$

Illustration 18 A sample of 3 mol of an ideal gas at 200K and 2 atm is compressed reversibly and adiabatically until the temperature reaches 250K, given that molar heat capacity is $27.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at constant volume, calculate w .

Solution $C_v = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$

During reversible adiabatic process

$$w = nC_v (T_2 - T_1) = 3 \times 27.5 \times 50 = 4125 \text{ Joule}$$

Illustration 19 10 moles of an ideal gas at 27°C and 10 atm., pressure occupying a volume of 24.6 L undergoes the following changes.

(i) Isothermal & reversible expansion to 246 L

(ii) Isothermal and irreversible expansion to 246 L.

(iii) Isochoric heating to 177°C .

Calculate the work done in each transformation in kJ.

Solution (i) Work done in isothermal reversible expansion

$$w = -2.303 \times nRT \log \frac{V_2}{V_1} = -2.303 \times 10 \times 8.31 \times 300 \times \log \frac{246}{24.6}$$

$$= -57413.79 \text{ J} = -57.41 \text{ kJ}$$

(ii) Work done in isothermal irreversible expansion

$$w = -P (V_2 - V_1) = -1 (246 - 24.6) = -221.4 \text{ L-atm} = -221.4 \times 101.3 \text{ J} = -22.43 \text{ kJ}$$

(iii) Work done in isochoric change

$$\text{Since } \Delta V = 0 \quad \therefore w = 0$$

Illustration 20 Find the work done when 2 mol of a gas expands isothermally from 5dm^3 to 40dm^3 against a constant external pressure of 2 atm at 298K. Also calculate w_{rev} for the change.

Solution (i) $w = -P\Delta V$

$$w = -2 \times (40 - 5)$$

$$w = -70 \ell \text{ atm} = -70 \times 101.3 \text{ J}$$

$$w = -7091 \text{ J}$$

(ii) $w = -2.303 nRT \log \frac{V_2}{V_1}$

$$w = -2.303 \times 2 \times 8.314 \times 298 \log \frac{40}{5}$$

$$w = -10.3 \times 10^3 \text{ J}$$

BEGINNER'S BOX-4

1. Calculate w for the isothermal reversible expansion of 1mol of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K :-

- (1) -5227.2 J (2) $+5227.2 \text{ J}$ (3) -2257 J (4) $+2257 \text{ J}$

2. When 229 J of energy is supplied as heat at constant pressure to 3 mol Ar(g), the temperature of the sample is increased by 2.55K . Calculate the molar heat capacity at constant volume :-

- (1) $30 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (2) $30 \text{ J K}^{-1} \text{ mol}^{-1}$ (3) $21.7 \text{ J K}^{-1} \text{ mol}^{-1}$ (4) $21.7 \text{ kJ K}^{-1} \text{ mol}^{-1}$

Z:\NODE02\BOAI-BO\TARGET\CHEM\ENG\MODULE-1\5.THERMODYNAMICS\01-THERMO.P65

- The process which has a natural tendency to occur in a particular direction either of its own or after proper initiation under the given set of conditions.
- All natural processes are ir-reversible and spontaneous processes. The natural processes take place of their own in one direction only.

- The process which does not occur of its own in a particular direction i.e. a process which does not have a natural tendency to occur in a particular direction either of its own or after initiation is called as non-spontaneous process.
- Non-spontaneous process may be made to occur when energy from some external source is supplied continuously throughout the process.

Ex.1 Flow of water from high level to low level.
Flow of heat from hot body to cold body.
Flow of charge from high potential to low potential.
Flow of gas from high pressure to low pressure.

Dissolution of common salt in water.

$$\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

(ii) Tendency to attain maximum randomness (Entropy Factor)

(iii) The ratio of heat absorbed by the system in isothermal and reversible manner to the temperature at which heat is absorbed is equals to the change in entropy.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Unit : J K⁻¹ or Cal K⁻¹

$$(iv) \quad \Delta S = S_{\text{final}} - S_{\text{initial}}$$

If $S_{\text{final}} > S_{\text{initial}}$: Then $\Delta S = \text{positive}$

If $S_{\text{final}} < S_{\text{initial}}$: Then $\Delta S = \text{negative}$

(v) Entropy is an extensive property and state function.

(vi) Entropy change in a chemical reaction

$$\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$

(vii) Entropy change for a process : $\Delta S = \frac{q_{\text{rev}}}{T}$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\text{or } \Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Case I : For an ideal gas reversible isothermal process; : $T_2 = T_1$

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$$

$$\Delta S = 2.303nR \log \frac{V_2}{V_1} = 2.303nR \log \frac{P_1}{P_2}$$

Case II : For an isochoric process $V_2 = V_1$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} ; \quad \Delta S = 2.303 nC_v \log \frac{T_2}{T_1}$$

(viii) **For reversible adiabatic process :**

Entropy remains constant so process is also known as **isoentropic process**.

Factors affecting entropy of system :

(I) If $\Delta n_g > 0$ then $\Delta S > 0$

If $\Delta n_g < 0$ then $\Delta S < 0$

(II) Physical state : $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

(III) On increasing gaseous moles entropy increases.

(IV) On increasing temperature, S will increase.

Ex. $\text{Fe(s)} \rightarrow \text{Fe(s)}$: $\Delta S = \text{positive}$
 300K 400K

(V) On decreasing pressure, S increases.

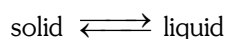
Ex. $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{g})$: $\Delta S = \text{positive}$
 5atm 2 atm

(VI) Mixture : $\left. \begin{array}{l} \text{Solid} + \text{solid} \\ \text{liquid} + \text{liquid} \\ \text{gas} + \text{gas} \end{array} \right\} S \uparrow$

Entropy change during phase transition :

(I) Entropy of fusion $[(\Delta S)_f]$ mole :

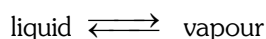
The entropy change, when 1 mol solid changes into liquid at its melting point temperature.



$$(\Delta S)_f = \frac{\Delta H_{\text{fusion}}}{T}$$

(II) Entropy of vapourisation $[(\Delta S)_{\text{vap}}]$ mole :

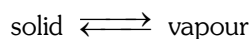
The entropy change, when 1 mol liquid changes into vapour at its boiling point temperature.



$$(\Delta S)_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

(III) Entropy of sublimation $[(\Delta S)_{\text{sub}}]$ mole :

The entropy change, when 1 mol solid changes into vapour at a particular temperature.



$$(\Delta S)_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

Some famous or extra ordinary examples of entropy change :

(i) Entropy of graphite > Entropy of diamond.

(ii) In rusting of iron entropy increases.

(iii) $\text{NH}_4\text{Cl(s)} + \text{aq} \longrightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

In this process NH_4^+ and Cl^- ions are free to move in solution where as they are not free to move in solid NH_4Cl . Hence ΔS is positive for this type of dissolution process.

(iv) On addition of HCl in the aqueous solution of Ag^+ ions entropy decreases due to precipitation of AgCl.

(v) **On boiling of egg :** Denaturation of proteins occur. Thus entropy increases.

(vi) **Stretching of rubber :** During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

Total entropy change in reversible process :

In reversible process, at every step system and surroundings remain in thermal equilibrium with each other.

Let a system, releases q heat to the surroundings at temperature T .

$$\Delta S_{\text{system}} = \frac{-q}{T}; \quad \Delta S_{\text{surroundings}} = \frac{+q}{T}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\Delta S_{\text{total}} = \frac{-q}{T} + \frac{q}{T} \Rightarrow \boxed{\Delta S_{\text{total}} = 0}$$

Total entropy change in irreversible process :

Let a system is at high temperature T_1 and surroundings are at low temperature T_2 .

Let q amount of heat is released by the system.

$$\Delta S_{\text{system}} = \frac{-q}{T_1}, \quad \Delta S_{\text{surroundings}} = \frac{+q}{T_2}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{-q}{T_1} + \frac{q}{T_2}$$

$$\therefore \boxed{\Delta S_{\text{total}} = +ve} \quad (\because T_1 > T_2)$$

Total entropy change for irreversible spontaneous process is always greater than zero.

Spontaneity of a process in terms of total entropy change :

If, $\Delta S_{\text{total}} = +ve \Rightarrow$ spontaneous process

If, $\Delta S_{\text{total}} = -ve \Rightarrow$ non spontaneous process

If, $\Delta S_{\text{total}} = 0 \Rightarrow$ process is at equilibrium

Illustrations

Illustration 21 The enthalpy change for transition of liquid water to steam is 40.8 kJ mol^{-1} at 373K . Calculate ΔS for the process.

Solution The entropy change for the vapourization of water is given by $\Delta S = \frac{\Delta H_{\text{vap.}}}{T}$

Given $\Delta H_{\text{vap.}} = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 1000 \text{ J mol}^{-1}$ and $T = 373 \text{ K}$

$$\Delta S = \frac{40.8 \times 1000 \text{ J mol}^{-1}}{373 \text{ K}} = 109.38 \text{ JK}^{-1} \text{ mol}^{-1}$$

Illustration 22 Calculate the change in entropy for the fusion of 1 mol of ice. The melting point of ice is 273K and molar enthalpy of fusion of ice = 6 kJ mol^{-1}

Solution $\Delta S_f = \frac{\Delta H_f}{T} = \frac{6 \times 10^3}{273} = 21.97 \text{ JK}^{-1} \text{ mol}^{-1}$

Illustration 23 The enthalpy of vapourisation of liquid diethyl ether $(\text{C}_2\text{H}_5)_2\text{O}$, is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS for conversion of :-

(i) Liquid to vapour and (ii) Vapour to liquid at 35°C

Solution (i) $\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T} = \frac{26 \times 10^3}{308} = 84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

(ii) $\Delta S_{\text{cond.}} = \frac{\Delta H_{\text{cond.}}}{T} = \frac{-26 \times 10^3}{308} = -84.41 \text{ JK}^{-1} \text{ mol}^{-1}$

5.14 GIBB'S ENERGY (G or F) :

- Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process.
- Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work or Gibb's energy is that part of the total energy of system which can be converted into useful work.
- The term Gibbs energy was introduced to explain criteria of spontaneity in terms of system.
 - Since ; energy = useful work + randomness energy

$$H = G + TS$$

$$\boxed{G = H - TS} \quad \dots(i)$$

So the function that takes both enthalpy and entropy of system into account is called Gibbs energy.

- Gibbs energy is an extensive property and state function.
- Absolute value of G can't be measured but change can be measured, So we discuss (ΔG)

$$\Delta G = G_{\text{final}} - G_{\text{initial}}$$

From eq. (i) $\boxed{\Delta G = \Delta H - T\Delta S}$

Where ΔG = Change in Gibb's energy

ΔH = Change in enthalpy

ΔS = Change in entropy

Relation between Gibb's energy change and non expansion work or useful work :

$$\text{FLOT : } \Delta E = q + W$$

If, work is done by the system, then, $\Delta E = q - W \quad \dots(i)$

According to Gibb's, system does both expansion and non expansion work.

$$\therefore W = W_{\text{expansion}} + W_{\text{non expansion}}$$

$$W = P\Delta V + W_{\text{non expansion}}$$

Put W in equation (i)

$$\Rightarrow \Delta E = q - (P\Delta V + W_{\text{non expansion}})$$

$$q = \Delta E + P\Delta V + W_{\text{non expansion}}$$

$$q = \Delta H + W_{\text{non expansion}} \quad (\because \Delta H = \Delta E + P\Delta V)$$

$$T\Delta S = \Delta H + W_{\text{non expansion}} \quad (\because \Delta S = q/T)$$

$$W_{\text{non expansion}} = T\Delta S - \Delta H \quad (\because \Delta G = \Delta H - T\Delta S)$$

$$\Rightarrow \boxed{W_{\text{non expansion}} = -\Delta G} \text{ or } \boxed{W_{\text{useful}} = -\Delta G}$$

The decrease in Gibb's energy of system is equal to the non expansion work or useful work.

Relation in between ΔG of system and ΔS_{total} or Gibb's energy change and spontaneity :

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Let system releases heat at constant temperature T and pressure P.

$$\therefore q = q_p = \Delta H$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$

$$\Rightarrow \Delta H_{\text{system}} = -\Delta H_{\text{surroundings}}$$

$$\Delta S_{\text{surr.}} = \frac{\Delta H_{\text{surr.}}}{T}$$

$$\Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{sys.}}}{T}$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{sys.}} + \left(\frac{-\Delta H_{\text{sys.}}}{T} \right)$$

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys.}} - \Delta H_{\text{sys.}}$$

$$T\Delta S_{\text{total}} = -(\Delta H_{\text{sys.}} - T\Delta S_{\text{sys.}})$$

$$T\Delta S_{\text{total}} = -\Delta G_{\text{sys.}}$$

or $\Delta G_{\text{sys.}} = -T\Delta S_{\text{total}}$

- (i) If, $\Delta S_{\text{total}} = +ve \Rightarrow \Delta G_{\text{system}} = -ve \Rightarrow$ spontaneous process
 (ii) If, $\Delta S_{\text{total}} = -ve \Rightarrow \Delta G_{\text{system}} = +ve \Rightarrow$ non spontaneous process
 (iii) If, $\Delta S_{\text{total}} = 0 \Rightarrow \Delta G_{\text{system}} = 0 \Rightarrow$ process is at equilibrium.

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description
-	+	-	Reaction spontaneous at all temperature
-	-	-	(at low T) Reaction spontaneous at low temperature
-	-	+	(at high T) Reaction nonspontaneous at high temperature
+	+	+	(at low T) Reaction nonspontaneous at low temperature
+	+	-	(at high T) Reaction spontaneous at high temperature
+	-	+	(at all T) Reaction nonspontaneous at all temperatures

Relationship between standard Gibbs energy change (ΔG°) and Equilibrium constant (K_{eq}) :-

For a reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium - $\Delta G = 0$ and $Q = K_{\text{eq}}$

$$0 = \Delta G^\circ + RT \ln K_{\text{eq}}$$

$$\therefore \Delta G^\circ = -RT \ln K_{\text{eq}} \quad \dots(i)$$

$$\text{or } \Delta G^\circ = -2.303RT \log_{10} K_{\text{eq}} \quad \dots(ii)$$

from equation (i)

$$\log K_{\text{eq}} = -\frac{\Delta G^\circ}{RT}$$

$$\therefore K_{\text{eq}} = e^{-\Delta G^\circ/RT} \quad \dots(iii)$$

Illustrations

Illustration 25. For a certain reaction the change in enthalpy and change in entropy are $40.63 \text{ kJ mol}^{-1}$ and 100 JK^{-1} . What is the value of ΔG at 27°C and indicate whether the reaction is possible or not?

Solution We know that :

$$\Delta G = \Delta H - T\Delta S$$

$$T = 27 + 273 = 300\text{K}$$

$$\Delta H = 40.63 \times 10^3 \text{ J mol}^{-1} = 40630 \text{ J mol}^{-1}$$

$$\Delta S = 100 \text{ JK}^{-1}$$

$$\Delta G = 40630 - 300 \times 100 = 40630 - 30000 = + 10630 \text{ J}$$

Positive value of ΔG indicates that the reaction is not possible.

Illustration 26 For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are $-11.7 \times 10^3 \text{ J mol}^{-1}$ and $-105 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. Find out whether this reaction is spontaneous or not.

Solution $\Delta G = \Delta H - T\Delta S$

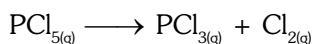
$$= -11700 - 298 \times (-105)$$

$$= +19590 \text{ J}$$

$\Delta G = +ve$, so reaction is non-spontaneous.

Illustration 27 Calculate the equilibrium constant for the reaction given below at 400K .

If $\Delta H^\circ = 77.2 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mol}^{-1}$



Solution $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 77200 - 400 \times 122 = 28400 \text{ J}$

$$\Delta G^\circ = -2.303 RT \log K_c$$

$$\text{or } 28400 = -2.303 \times 8.31 \times 400 \log K_c$$

$$\text{or } K_c = 1.958 \times 10^{-4}$$

Illustration 28 For the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$; $\Delta H = -95.4 \text{ kJ}$ and $\Delta S = -198.3 \text{ J K}^{-1}$. Calculate the temperature at which the reaction will proceed in forward direction.

Solution $\Delta G = \Delta H - T\Delta S$

$\therefore$ At equilibrium $\Delta G = 0$

$$\therefore \Delta H = T\Delta S \quad \text{so } T = \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ J K}^{-1}} = 481 \text{ K}$$

For this reaction ΔH is $-ve$ and ΔS is $-ve$, so it will be spontaneous at low temperature.

$\therefore$ Below 481K the reaction would be spontaneous.

Illustration 29 Enthalpy and entropy changes of a reaction are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Analyse the feasibility of the reaction at 27°C .

Solution $\Delta H = 40.63 \text{ kJ mol}^{-1} = 40630 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}$
 $T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$
 Now $\Delta G = \Delta H - T\Delta S$
 $= 40630 \text{ J mol}^{-1} - (300 \text{ K}) \times (108.8 \text{ J K}^{-1} \text{ mol}^{-1})$
 $\Delta G = 7990 \text{ J mol}^{-1}$.

Since ΔG is positive, the reaction is not feasible in the forward direction.

Illustration 30 For a certain reaction the change in enthalpy and change in entropy are $40.63 \text{ kJ mol}^{-1}$ and 100 JK^{-1} . Show that the reaction at 27°C is possible or not.

Solution $\Delta G = \Delta H - T\Delta S$
 $\Delta G = 40.63 - 300 \times 100 \times 10^{-3}$
 $\Delta G = + 10.630 \text{ kJ}$
 ΔG is positive so reaction is not possible.

Illustration 31 Zinc reacts with dilute hydrochloric acid to give hydrogen at 17°C . The enthalpy of the reaction is $-12.55 \text{ kJ mol}^{-1}$ and entropy change is $5 \text{ JK}^{-1} \text{ mol}^{-1}$ for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

Solution Given $\Delta H = -12.55 \text{ kJ mol}^{-1}$ and $\Delta S = 5 \text{ JK}^{-1} \text{ mol}^{-1}$
 $T = 17 + 273 = 290 \text{ K}$
 Applying $\Delta G = \Delta H - T \Delta S$

$$= -12.55 \frac{\text{kJ}}{\text{mol}} - 290\text{K} \times \frac{5}{1000} \frac{\text{kJ}}{\text{Kmol}}$$

$$= -12.55 - 1.45$$

$$= -14 \frac{\text{kJ}}{\text{mol}}$$

Since ΔG is negative, the reaction will be spontaneous

Illustration 32 For a reaction both ΔH and ΔS are positive under what condition will the reaction occur spontaneously.

Solution The reaction will occur spontaneously only when $T\Delta S > \Delta H$.
 $\Delta G = \Delta H - T\Delta S = (+) - T(+)$
 For ΔG to be negative, $T\Delta S$ must be $> \Delta H$

Illustration 33 Which of the following are state function ?

(i) q (ii) Entropy (iii) Specific heat capacity (iv) H (v) w

Solution **Ans.** (ii), (iii) and (iv)

BEGINNER'S BOX-6

1. If $\Delta G^\circ > 0$ for a reaction then :-
(1) $K_p > 1$ (2) $K_p < 1$ (3) $K_p = 1$ (4) None
2. For an endothermic reaction to be spontaneous :-
(1) ΔG must be +ve (2) ΔS must be > 0
(3) $T\Delta S$ must be -ve (4) $T\Delta S$ must be equal to ΔG
3. The value of ΔG for the process $\text{H}_2\text{O(s)} \longrightarrow \text{H}_2\text{O(l)}$ at 1 atm and 260 K is :-
(1) < 0 (2) $= 0$ (3) > 0 (4) Unpredictable
4. In a certain chemical reaction $\Delta H = 150 \text{ KJ}$ and $\Delta S = 10 \text{ JK}^{-1}$ at 300 K. The value of ΔG would be :-
(1) -2850 J (2) Zero
(3) $+2850 \text{ J}$ (4) 147 kJ
5. The standard Gibb's energy change for a gaseous reaction at 27°C is $X \text{ kCal}$. If equilibrium constant for a reaction is 100 and R is $2 \text{ Cal K}^{-1} \text{ mol}^{-1}$. Then X is :-
(1) -2.7636 (2) $+2.7636$ (3) $+ 807$ (4) $- 807$
6. The favourable conditions for a spontaneous reaction are :-
(1) $T\Delta S > \Delta H$, $\Delta H = +ve$, $\Delta S = +ve$ (2) $T\Delta S > \Delta H$, $\Delta H = +ve$, $\Delta S = -ve$
(3) $T\Delta S = \Delta H$, $\Delta H = -ve$, $\Delta S = -ve$ (4) $T\Delta S = \Delta H$, $\Delta H = +ve$, $\Delta S = +ve$

5.15 THIRD LAW OF THERMODYNAMICS (TLOT)

At zero kelvin (absolute zero temperature), the entropy of pure perfect crystalline solid is taken as zero.

Exceptions :

- (i) NO , N_2O (ii) CO , CO_2 (iii) Mixture of isotopes (iv) Ice

ENERGETICS

5.16 INTRODUCTION :

Thermochemistry is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system.

Depending upon the conditions under which the reaction is carried out, the quantity of heat transferred is related to energy or enthalpy change due to changes of states which occur in the system.

In this chapter we will introduced enthalpies of some specific reaction. Like, Enthalpy of formation (ΔH_f), Enthalpy of combustion (ΔH_{comb}), Bond dissociation enthalpy (ΔH_{BDE}) & Enthalpy of Neutralisation ($\Delta H_{\text{neutralization}}$)

THERMOCHEMICAL REACTION :

The balanced chemical reaction which give information about the physical states of reactants & products and heat change is called as thermo chemical reaction.



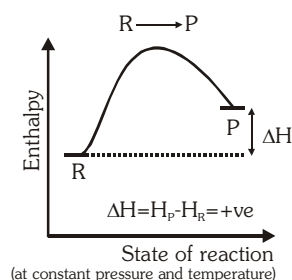
Thermo chemical reaction are of 2 types.

(i) Endothermic reaction :

The reaction which absorbs heat is called as endothermic reaction.

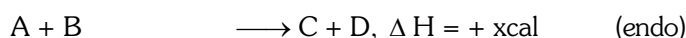
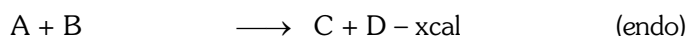
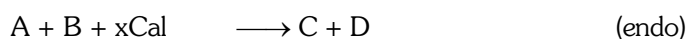
$$\Delta H = +ve$$

$$\Delta H = H_p - H_R = +ve \text{ i.e. } H_p > H_R$$



- (a) Stability of reactant > Stability of product because more heat is required to break the bonds of reactant.
- (b) The product formed in the endothermic reaction is called endothermic compound.
- (c) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

Representation of endothermic reaction :



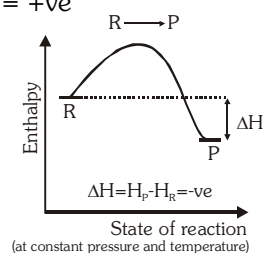
Examples :

- (I) Dissociation reactions (mostly)
- (II) Fusion reactions
- (III) Vaporization reactions
- (IV) Sublimation reactions
- (V) Photosynthesis $6\text{CO}_2 + 6\text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$, $\Delta H = +ve$

(ii) Exothermic reaction :

The reaction which evolves heat is called as exothermic reaction.

$$\Delta H = -ve \quad \Delta H = H_p - H_R = -ve \text{ i.e. } H_p < H_R$$



- (a) Stability of reactant < Stability of product because less heat is required to break the bonds of reactant.
- (b) The product formed in the exothermic reaction is called exothermic compound.
- (c) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

Representation of exothermic reaction.

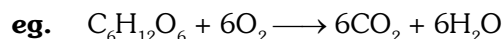


Examples :

(I) Combustion reactions

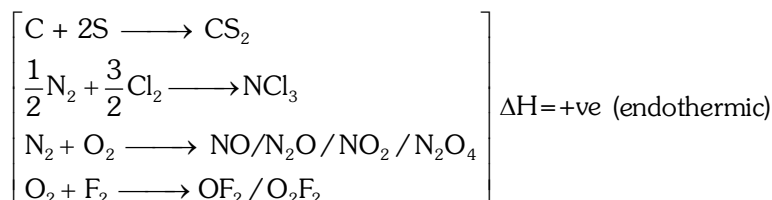
(II) Neutralisation reactions

(III) Respiration reaction



(IV) Formation reaction $\begin{cases} \nearrow \text{endo} \\ \searrow \text{exo (generally)} \end{cases}$

Exceptions of formation reaction :



GOLDEN KEY POINTS

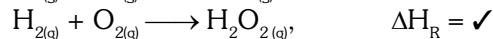
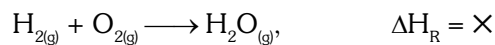
- (i) If conditions are not given then, ΔH is considered to be ΔH° .
- (ii) If thermochemical reaction is multiplied by a coefficient then, ΔH of reaction is also multiplied by that coefficient.
e.g. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta H = -285 \text{ kJ mol}^{-1}$
 $2\text{H}_2(\text{g}) + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}(\ell) \quad \Delta H = -2 \times 285 \text{ kJ}$
- (iii) If reaction is reversed then numerical value of ΔH remains same but sign is changed.
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta H = -285 \text{ kJ mol}^{-1}$
 $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = +285 \text{ kJ mol}^{-1}$

BEGINNER'S BOX-7

1. An endothermic reaction is one in which :
 (1) heat is converted into electricity
 (2) heat is absorbed
 (3) heat is evolved
 (4) heat is converted into mechanical work
2. If heat of reaction $A + 5B \longrightarrow 2C + 3D$, is -50 kJ . What is the heat of the reaction $2A + 10B \longrightarrow 4C + 6D$.
 (1) -50 kJ (2) -25 kJ (3) -100 kJ (4) $+100 \text{ kJ}$
3. The process $\text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^- + \text{H}^+$, should be :
 (1) exothermic (2) endothermic
 (3) neither exothermic nor endothermic (4) exothermic or endothermic depending upon temperature
4. For the given reaction :
 $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) ; \Delta H = 40 \text{ kJ}$
 The ΔH is specifically called
 (1) Heat of formation of CO (2) Heat of combustion
 (3) Heat of reaction (4) Heat of hydrogenation of C = O bond

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Example : $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(g)}, \quad \Delta H_{\text{R}} = \checkmark$



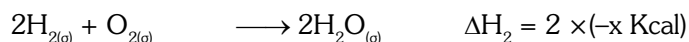
(i) Reaction condition :

- At constant pressure $q_p = \Delta H_{\text{reactin}}$

At constant volume $q_v = \Delta E_{\text{reaction}}$

$$\Delta H = \Delta E + \Delta n_g RT$$

Example : $\text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \longrightarrow \text{H}_2\text{O}_{(\text{g})} \quad \Delta H_1 = -x \text{ kCal mol}^{-1}$



(iii) Physical state of products and reactants :



Note : For $\text{H}_2\text{O}(\text{liq.})$, ΔH is more negative in comparison to the formation of $\text{H}_2\text{O}(\text{vap.})$ because when vapours convert into liquid then some heat is released.

$$\begin{array}{ll} \text{C}_{\text{graphite}} + \text{O}_2 \longrightarrow \text{CO}_2, & \Delta H_{\text{R}} = -393.5 \text{ kJ mole}^{-1} \\ \text{C}_{\text{diamond}} + \text{O}_2 \longrightarrow \text{CO}_2, & \Delta H_{\text{R}} = -399.5 \text{ kJ mole}^{-1} \end{array}$$


Effect of temperature on heat of reaction is given by **Kirchoff equation**

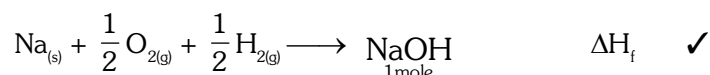
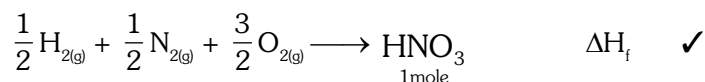
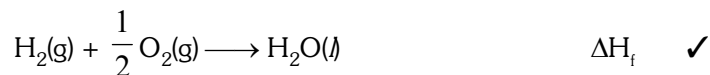
- (i) at constant pressure :
- $$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{Pm}$$
- $$\Delta C_{Pm} = \Sigma(C_{Pm})_P - \Sigma(C_{Pm})_R$$
- $$\Delta H_{T_1} = \text{Heat of reaction at } T_1 \text{ temperature}$$
- $$\Delta H_{T_2} = \text{Heat of reaction at } T_2 \text{ temperature}$$
- (ii) at constant volume :
- $$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{Vm}$$
- $$\Delta C_{Vm} = \Sigma(C_{Vm})_P - \Sigma(C_{Vm})_R$$

5.18 TYPES OF HEAT OF REACTION :

(A) Heat of formation, Enthalpy of formation (ΔH_f) or ($\Delta_f H$) :

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

The reference state of oxygen, carbon and sulphur are O_2 gas, C_{graphite} and S_{rhombic} , respectively some reactions with standard molar enthalpies of formation are :



APPLICATION OF ΔH_f :

Calculation of ΔH of any general reaction.

Let us considered a general reaction $aA + bB \rightarrow cC + dD$

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_{f(\text{products})} - \Sigma \Delta H_{f(\text{reactant})} = [c\Delta H_{f(C)} + d\Delta H_{f(D)}] - [a\Delta H_{f(A)} + b\Delta H_{f(B)}]$$

GOLDEN KEY POINTS

- Standard condition means, $P = 1 \text{ atm}$, $T = 25^\circ\text{C}$ or 298 K
Standard heat of formation is represent by ΔH_f° .
- If no condition is given then value of ΔH_f is considered as ΔH_f° .
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

Elements	Reference state
C	$C_{(\text{graphite})}$
S	$S_{8(\text{Rhombic})}$ (Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)
P	$P_{4(\text{white})}$
O	$O_{2(g)}$
H	$H_{2(g)}$
Br	$Br_{2(l)}$
Metal	$M_{(s)}$ [except $Hg_{(l)}$]

- The formation reaction may be exothermic or endothermic.

Illustrations

Illustration 34 Since enthalpy of elements in their natural state is taken as zero. The value of ΔH_f of compounds :

- | | |
|---------------------------------|------------------------|
| (1) is always negative | (2) is always positive |
| (3) may be positive or negative | (4) is zero |

Solution **Ans. (3)**

Illustration 35 The enthalpy of formation of ammonia at 298K is given as $\Delta H_f^\circ = -46.11 \text{ kJ per mol of } NH_3(g)$. To which of the following equation does this value apply ?

- | | |
|---|---|
| (1) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$ | (2) $N(g) + 3H(g) \longrightarrow NH_3(g)$ |
| (3) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ | (4) $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(l)$ |

Solution **Ans. (1)**

Illustration 36 Which of the following equation represents the standard heat of formation :

- (1) $\text{C(diamond)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$ (2) $\text{C(graphite)} + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$
 (3) $\text{C(diamond)} + 4\text{H}(\text{g}) \longrightarrow \text{CH}_4(\text{g})$ (4) $\text{C(graphite)} + 4\text{H}(\text{g}) \longrightarrow \text{CH}_4(\text{g})$

Solution **Ans. (2)**

Illustration 37 Which of the following reaction defines ΔH_f°

- (1) $\text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ (2) $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{F}_2(\text{g}) \longrightarrow \text{HF}(\text{g})$
 (3) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ (4) $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$

Solution **Ans. (2)**

Illustration 38 How much heat will be required at constant pressure to form 1.28 kg of CaC_2 from $\text{CaO}(\text{s})$ & $\text{C}(\text{s})$?

Given : $\Delta_f H^\circ (\text{CaO}, \text{s}) = -152 \text{ kCal mol}^{-1}$

$\Delta_f H^\circ (\text{CaC}_2, \text{s}) = -14 \text{ kCal mol}^{-1}$

$\Delta_f H^\circ (\text{CO}, \text{g}) = -26 \text{ kCal mol}^{-1}$

- (1) + 112 kCal (2) 224 kCal (3) 3840 kCal (4) 2240 kCal

Solution. $\text{CaO}(\text{s}) + 3\text{C}(\text{s}) \longrightarrow \text{CaC}_2(\text{s}) + \text{CO}(\text{g})$
 $\Delta_f H^\circ = (-14 - 26) - (-152) = +112 \text{ kCal mol}^{-1}$

$$\text{Total heat required} = \left(\frac{1280}{64} \right) \times 112 \Rightarrow 2240 \text{ kCal}$$

Illustration 39 The $\Delta_f H^\circ (\text{N}_2\text{O}_5, \text{g})$ in kJ mol^{-1} on the bases of the following data is :

$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ $\Delta_r H^\circ = -114 \text{ kJ mol}^{-1}$

$4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{N}_2\text{O}_5(\text{g})$ $\Delta_r H^\circ = -102.6 \text{ kJ mol}^{-1}$

$\Delta_f H^\circ (\text{NO}, \text{g}) = 90.2 \text{ kJ mol}^{-1}$

- (1) 15.1 (2) 30.2 (3) -36.2 (4) none of these

Solution $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{NO}(\text{g})$ $\Delta_f H^\circ = 90.2$
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$ $\Delta_r H^\circ = 90.2 \times 2$... (1)
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ $\Delta_r H^\circ = -114$... (2)
 $2\text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_5(\text{g})$ $\Delta_r H^\circ = \frac{-102.6}{2} = -51.3$... (3)

From Equations (1) + (2) + (3)

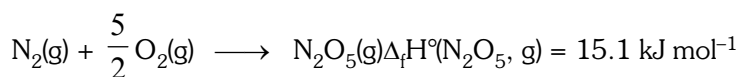
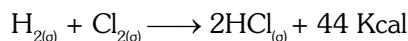


Illustration 40 Calculate ΔH° for $2\text{Al}_{(\text{s})} + \text{Fe}_2\text{O}_3 \longrightarrow 2\text{Fe}_{(\text{s})} + \text{Al}_2\text{O}_3$ given that standard enthalpy of Fe_2O_3 and Al_2O_3 are -196.5 and -399.1 kCal.

Solution $\Delta H_{\text{Reaction}}^0 = \Sigma \Delta H_{\text{P}}^0 - \Sigma \Delta H_{\text{R}}^0$
 $= [2 \times \Delta H_{\text{Fe}(\text{s})}^0 + \Delta H_{\text{Al}_2\text{O}_3}^0] - [2 \times \Delta H_{\text{Al}(\text{s})}^0 + \Delta H_{\text{Fe}_2\text{O}_3}^0] = 2 \times 0 + (-399.1) - [2 \times 0 + (-196.5)]$
 $\Delta H_{\text{Reaction}}^0 = -202.6 \text{ kCal}$

Illustration 41 The heat of formation of the compound in the following reaction is :



(1) $-44 \text{ kCal mol}^{-1}$ (2) $-22 \text{ kCal mol}^{-1}$ (3) $+11 \text{ kCal mol}^{-1}$ (4) $-88 \text{ kCal mol}^{-1}$

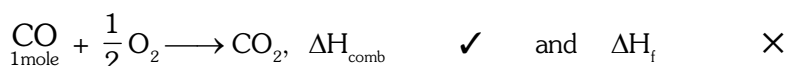
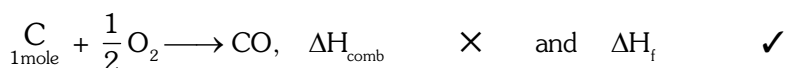
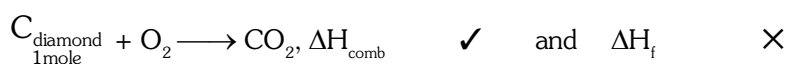
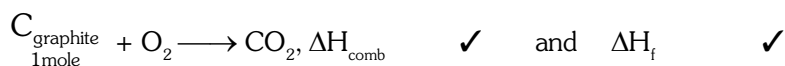
Solution **Ans. (2)**

For the formation of 1 mol of HCl from elements $\Delta H_f^\circ = -\frac{44}{2} = -22 \text{ Kcal}$

(B) Heat of combustion (ΔH_{comb}) :

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised) in excess of oxygen.

Example :



Note :

- (I) Heat of combustion reaction is always exothermic
- (II) If conditions are not given then ΔH_{comb} considered as $\Delta H_{\text{comb}}^\circ$.
- (III) If in a reaction heats of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\Delta H = \sum (\Delta H_{\text{comb}})_R - \sum (\Delta H_{\text{comb}})_P$$

APPLICATION OF HEAT OF COMBUSTION :

Calorific value or fuel value (C.V.) :

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\text{Calorific value} = \frac{\Delta H_{\text{comb}}}{\text{Molecular weight}}$$

Unit :- kJ g^{-1} or kCal g^{-1}

GOLDEN KEY POINTS

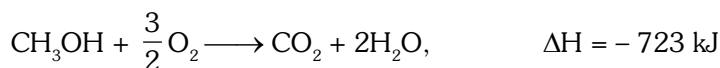
- Heat of combustion reaction is always exothermic
- If conditions are not given then ΔH_{comb} is considered as $\Delta H_{\text{comb}}^\circ$.
- Maximum value of calorific value = Maximum efficiency or best fuel
- H_2 has the highest calorific value (150 kJ/g) but it is not used as domestic or industrial fuel due to some technical problems.

Illustrations

Illustration 42 1 mole of methanol, when burnt in oxygen, gives out -723 kJ mol^{-1} heat. If 1 mole of oxygen is used what will be the amount of heat evolved?

- (1) 723 kJ (2) 964 kJ (3) 482 kJ (4) 241 kJ

Solution **Ans. (3)**



with 1 mole of O_2 , $\Delta H = -\frac{2}{3} \times 723 = -482 \text{ kJ}$

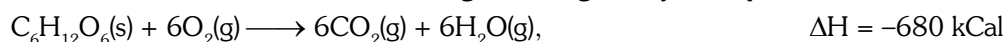
Illustration 43 Combustion of methane :

- (1) is an exothermic reaction (2) is an endothermic reaction
(3) requires a catalyst (4) gives H_2

Solution **Ans. (1)**

Combustion is always exothermic

Illustration 44 The heat evolved in the combustion of glucose is given by the equation



The wt. of $\text{CO}_2(\text{g})$ produced when 170 kCal of heat is evolved in the combustion of glucose is

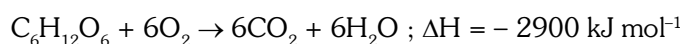
- (1) 264 g (2) 66 g (3) 11 g (4) 44 g

Solution **Ans. (2)**

Evolution of 680 Kcal is accompanied by $\text{CO}_2 = 6 \times 44 = 264 \text{ g}$

Evolution of 170 Kcal is accompanied by $\text{CO}_2 = \frac{264}{680} \times 170 = 66 \text{ g}$

Illustration 45 Find out the calorific value of Glucose



Solution $\therefore$ Heat evolved from 1 mol glucose = 2900 kJ

or Heat evolved from 180 gram glucose = 2900 kJ

$\therefore$ Heat evolved from 1 gram glucose = $\frac{2900}{180} = 16.11 \text{ kJ g}$

or another method $\text{C.V.} = \frac{\Delta H_{\text{comb}}}{M_w} = \frac{2900}{180} = 16.11 \text{ kJ g}$

Illustration 46 Enthalpy of combustion of a substance is always :

- (1) > 0 (2) ≥ 0 (3) ≤ 0 (4) < 0

Solution **Ans. (4)**

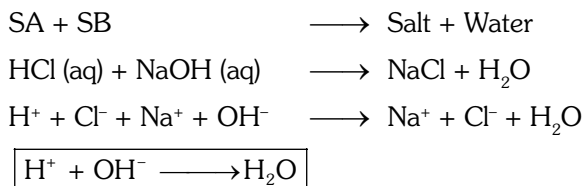
Illustration 47 The heat change for a reaction : $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2(\text{g})$ refers to

- (1) enthalpy of formation of carbon dioxide (2) enthalpy of combustion of carbon dioxide
(3) enthalpy of vapourisation (4) enthalpy of combustion of carbon monoxide

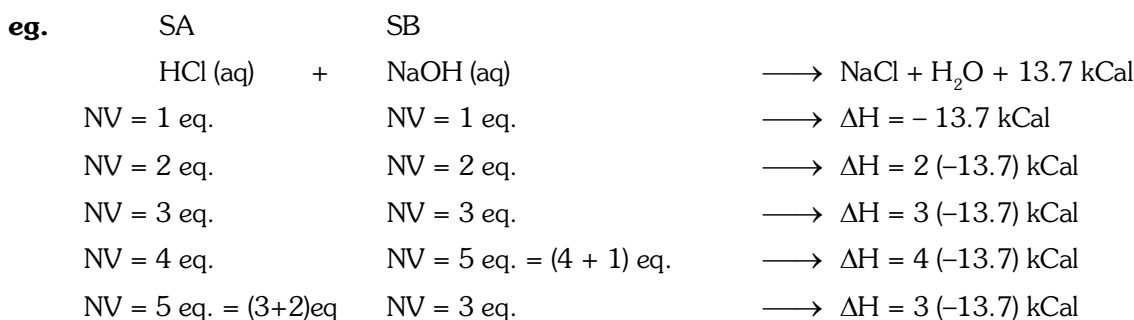
Solution **Ans. (4)**

(C) Heat of neutralisation (ΔH_{neut}) :

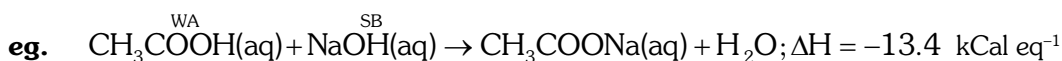
The heat evolved when one equivalent of an acid is completely neutralised by one equivalent of a base in dilute solution is called as heat of neutralisation.

**Note :**

- (i) When one equivalent of SA is neutralised by one equivalent of SB then evolve heat remain constant and its value is $-13.7 \text{ kCal/equivalent}$ or $-57.2 \text{ kJ equivalent}^{-1}$.



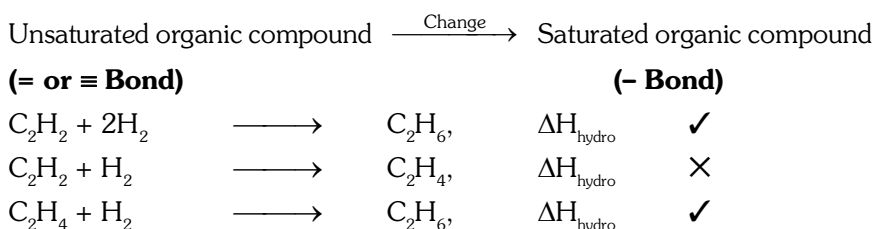
- (ii) If one of the acid or base or both are weak then heat of neutralization is usually less than $-13.7 \text{ KCal eq}^{-1}$ or -57.3 kJ eq^{-1} because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.

**Exception :**

For a reaction $\text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O}; \Delta H = -16.7 \text{ Kcal}$; this is because of hydration of F^- ion.

(D) Heat of hydrogenation ($\Delta H_{\text{Hydrogenation}}$) :

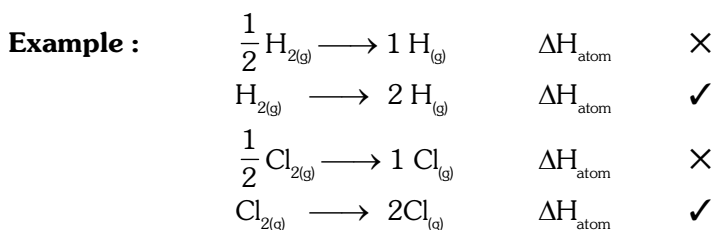
The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.



Note : Heat of hydrogenation is exothermic process.

(E) Heat of atomization (ΔH_{atom}) :

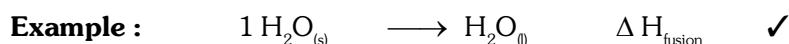
The amount of heat required to dissociate 1 mol substance into gaseous atoms is called as heat of atomization.



Note : It is an endothermic reaction.

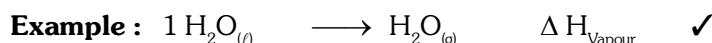
(F) HEAT OF TRANSFORMATION :

- (i) **Heat of fusion (ΔH_{fusion})**: The required amount of heat to convert 1 mole solid into liquid at its melting point is called as heat of fusion.



Note : Heat of fusion is always endothermic reaction i.e. ($\Delta H = +ve$)

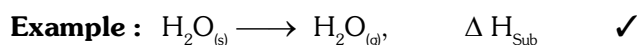
- (ii) **Heat of vapourization (ΔH_{vapour})**: The required amount of heat to convert 1 mole liquid into gas at its boiling point is called as heat of vapourization.



Note : Heat of vapourization is always endothermic reaction i.e. ($\Delta H = +ve$)

- (iii) **Heat of sublimation (ΔH_{sub})** :

The required amount of heat to convert 1 mole solid into gas at a certain temperature is called as heat of sublimation.



Note : Heat of sublimation is always endothermic reaction i.e. ($\Delta H = +ve$)

Illustrations

Illustration 48 Heat of neutralisation of an acid by a base is maximum when :

- (1) Both the acid and base are weak
- (2) Both the acid and base are strong
- (3) The acid is strong and the base is weak
- (4) The acid is weak and the base is strong

Solution

Ans. (2)

Heat of neutralisation is maximum (57.2 kJ eq^{-1} or $13.7 \text{ kCal eq}^{-1}$) when both acid and base are strong.

Illustration 49 The enthalpy change for the process $\text{C}_{(s)} \longrightarrow \text{C}_{(g)}$ corresponds to the enthalpy of

- (1) fusion
- (2) vapourization
- (3) combustion
- (4) sublimation

Solution

Ans. (4)

Solid $\longrightarrow$ gas, is sublimation.

Illustration 50 If $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} + 13.7 \text{ kCal}$, then heat of complete neutralisation of 1 gm mol of H_2SO_4 with base in excess will be :

- (1) -13.7 kCal
- (2) -27.4 kCal
- (3) -6.85 kCal
- (4) -3.425 kCal

Solution

Ans. (2)

Moles of $\text{H}_2\text{SO}_4 = 1 \text{ mol}$

g eq. of $\text{H}_2\text{SO}_4 = \text{moles} \times \text{V.F.} = 1 \times 2 = 2 \text{ g eq.}$

Heat evolve due to 2 g eq. = $-13.7 \times 2 = -27.4 \text{ kCal}$

Illustration 51 200 cm^3 of $0.1 \text{ M H}_2\text{SO}_4$ is mixed with 150 cm^3 of 0.2 M KOH . Find the value of evolved heat.

Solution

H_2SO_4

KOH

eq. = $NV = (0.1 \times 2) \times 0.2$

$(0.2 \times 1) \times (0.15)$

= 0.04

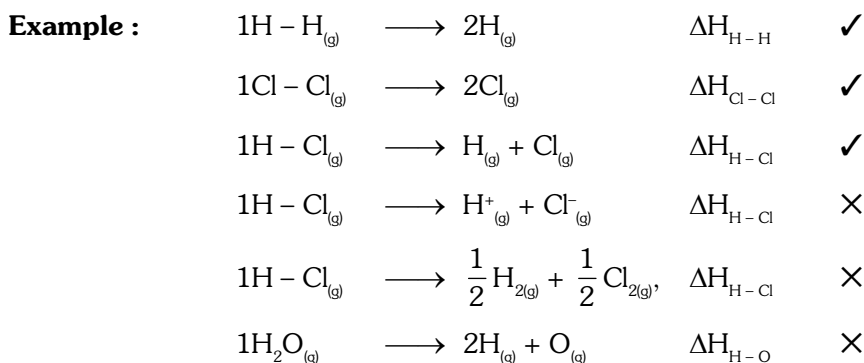
= 0.03

Heat liberated by 1 eq. = 57.2 kJ

So heat liberated by 0.03 eq. = $57.2 \times 0.03 = 1.7 \text{ kJ}$

(I) Bond energy / Bond dissociation energy :

The required amount of energy to dissociate **one mole gaseous bond** into separate **gaseous atoms** is called as **bond dissociation energy**.



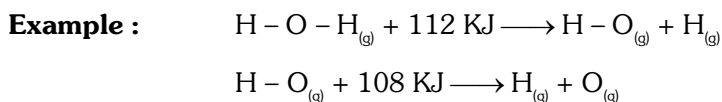
GOLDEN KEY POINTS

- The **bond energy** may be defined as the **average** amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.
- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then ΔH of that reaction can be calculate as follows.

$$\Delta H = \Sigma (\text{B.E.})_{\text{R}} - \Sigma (\text{B.E.})_{\text{P}}$$

- In the case of poly atomic molecule** we calculate the average bond energy.

$$(\text{BE})_{\text{av}} = \text{Average bond energy} = \frac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}$$



$$(\text{BE})_{\text{av}} = \text{Average bond energy} = \frac{112 + 108}{2} = 110 \text{ kJ mol}^{-1}$$

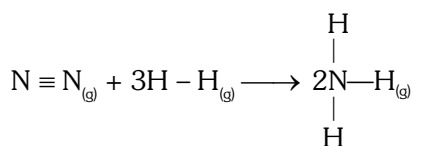
Illustrations

Illustration 52 Given the bond energy of $\text{N} \equiv \text{N}$, $\text{H} - \text{H}$ and $\text{N} - \text{H}$ bonds are 945, 436 and 391 kJ mol^{-1} respectively, the enthalpy of the reaction $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \longrightarrow 2\text{NH}_{3(\text{g})}$ is :

(1) - 93 kJ (2) 102 kJ (3) 90 kJ (4) 105 kJ

Solution

Ans. (1)



$$\begin{array}{ll} 945 + 3 \times 436 & 2 \times (3 \times 391) \\ = 2253 \text{ kJ} & = 2346 \text{ kJ} \end{array}$$

$$\Delta H = \Sigma (\text{B.E.})_{\text{R}} - \Sigma (\text{B.E.})_{\text{P}} = 2253 - 2346 = - 93 \text{ kJ}$$

Illustration 53 The enthalpy changes at 298 K in successive breaking of O – H bonds of H – O – H are

$$\text{H}_2\text{O}_{(g)} \longrightarrow \text{H}_{(g)} + \text{OH}_{(g)}, \quad \Delta H = 498 \text{ kJ mol}^{-1}$$

$$\text{OH}_{(g)} \longrightarrow \text{H}_{(g)} + \text{O}_{(g)}, \quad \Delta H = 428 \text{ kJ mol}^{-1}$$
The bond enthalpy of the O – H bond is
(1) 498 kJ mol⁻¹ (2) 463 kJ mol⁻¹ (3) 428 kJ mol⁻¹ (4) 70 kJ mol⁻¹

Solution **Ans. (2)**

$$(\text{B.E.})_{\text{av}} = \frac{498 + 428}{2} = 463 \text{ kJ}$$

Illustration 54 The required heat for dissociation of 1 mol H₂O into its atoms (H and oxygen) is ΔH_{Dis.}. Then calculate the bond energy of O – H bond.

Solution $\text{H}_2\text{O}_{(g)} \rightarrow \text{O}_{(g)} + 2\text{H}_{(g)}; \Delta H_{\text{Dissociation}}$
 $\text{H} - \text{O} - \text{H}_{(g)} \longrightarrow \text{O}_{(g)} + 2\text{H}_{(g)}; \Delta H_{\text{Dissociation}}$
 $\therefore$ required energy for breaking the 2 mol O – H bond = ΔH_{Dis.}
 $\therefore$ required energy for 1 mole = $\frac{\Delta H_{\text{Dis.}}}{2}$; $\Delta H_{\text{O-H}} = \frac{\Delta H_{\text{Dis.}}}{2}$

Illustration 55 Calculate the bond energy of C – H Bond in methane.

Solution $\text{CH}_{4(g)} \rightarrow \text{C}_{(g)} + 4\text{H}_{(g)}; \Delta H_{\text{Dis.}}$
or
$$\begin{array}{c} \text{H} \\ | \\ \text{H} - \text{C} - \text{H}_{(g)} \\ | \\ \text{H} \end{array} \longrightarrow \text{C}_{(g)} + 4\text{H}_{(g)}; \Delta H_{\text{Dis.}}$$

 $\therefore$ Bond energy of 4 mol C – H = ΔH_{Dis.}
 $\therefore$ Bond energy of 1 mol C – H bond = $\frac{\Delta H_{\text{Dis.}}}{4}$

Illustration 56 The energy change of reaction $\text{C}_2\text{H}_{6(g)} \longrightarrow 2\text{C}_{(g)} + 6\text{H}_{(g)}$ is X kJ. The bond energy of C – H bond is:

- (1) $\frac{X}{6} \text{ kJ mol}^{-1}$ (2) $\frac{X}{3} \text{ kJ mol}^{-1}$ (3) X kJ /mol⁻¹ (4) unpredictable from data

Solution **Ans. (4)**

Illustration 57 $\text{CuSO}_4(\ell) + 5\text{H}_2\text{O}(\text{s}) \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}); \Delta H = -x \text{ kJ}$

The value of ΔH represents :

- (1) enthalpy of solution of copper (II) sulphate
(2) enthalpy of hydration of copper (II) sulphate
(3) enthalpy of hydrolysis of copper (II) sulphate
(4) lattice energy of copper (II) sulphate

Solution **Ans. (2)**

Illustration 58 The bond energy of hydrogen is 103 kCal mol⁻¹. This means that :

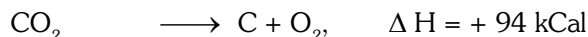
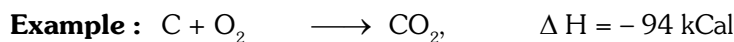
- (1) 103 kCal are required to break 6.023×10^{23} gaseous H₂ molecules into gaseous atoms
(2) 103 kCal are required to break the bonds in one gram of hydrogen
(3) 103 kCal are required to break one bond to form two atoms of hydrogen
(4) 103 kCal are required to break one mole of gaseous hydrogen molecules into ions.

Solution **Ans. (1)**

5.19 LAWS OF THERMOCHEMISTRY :

(I) LAVOISIER AND LAPLACE LAW :

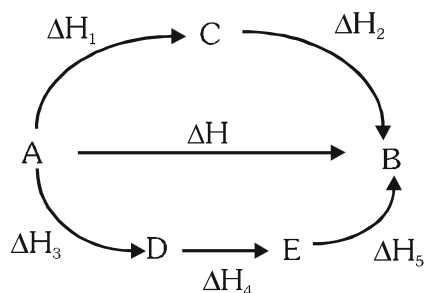
Enthalpy of formation of compound is **numerically equal** to the enthalpy of decomposition of that compound with **opposite sign**.



(II) HESS LAW OF CONSTANT HEAT SUMMATION :

The heat change in a complete chemical reaction always remain same whether reaction completes in one step or more.

Example - 1 :

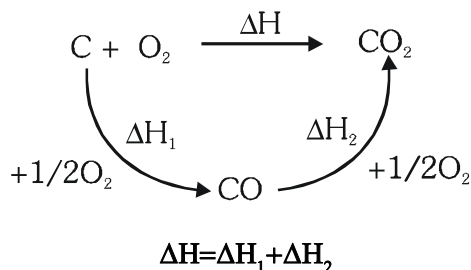


$$\Delta H = \Delta H_1 + \Delta H_2$$

or $\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$

or $\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$

Example - 2 :



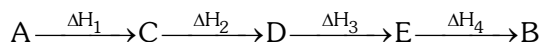
GOLDEN KEY POINTS

- Heat change of a reaction does not depend on the **number of steps** used in the reaction.
- Heat change of a reaction does not depend on **intermediate position**, it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on **time of reaction**.

Illustrations

Illustration 59 Single step reaction $\text{A} \rightarrow \text{B}$; $\Delta H = ?$

Multi step reaction to produce B from A is given

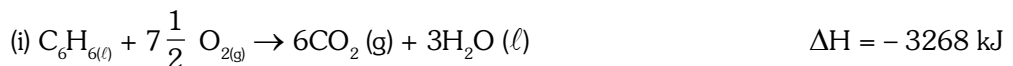


Solution

According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$

Illustration 60 Calculate the heat of formation of Benzene. The reaction is given below :
 $6\text{C(s)} + 3\text{H}_{2(\text{g})} \rightarrow \text{C}_6\text{H}_{6(\text{l})}$ and -3268 , -393.5 and $-285.8 \text{ kJ mol}^{-1}$ are the heats of combustion of benzene, heat of formation of CO_2 and heat of formation of $\text{H}_2\text{O}(\text{l})$ respectively.

Solution Target reaction $6\text{C}_{(\text{s})} + 3\text{H}_{2(\text{g})} \rightarrow \text{C}_6\text{H}_{6(\text{l})}$
 Given

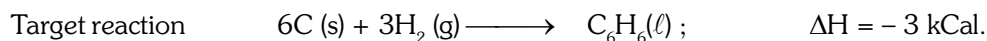
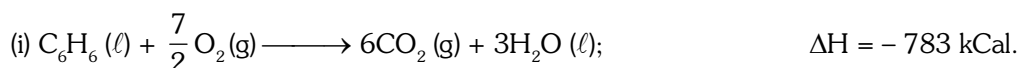


$$6 \times \text{eq. (ii)} + 3 \times \text{eq. (iii)} - \text{eq. (i)}$$

$$\Delta H = 6 \times -393.5 + 3 \times -285.8 - (-3268) = +49.6 \text{ kJ mol}^{-1}$$

Illustration 61 The heats of formation of $\text{CO}_{2(\text{g})}$ and $\text{H}_2\text{O}_{(\text{l})}$ are -97 and $-68 \text{ kcal mol}^{-1}$. The heat of combustion of benzene is $-783 \text{ kcal mol}^{-1}$. What will be the heat of formation of benzene ?

Solution Given :

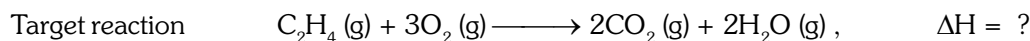
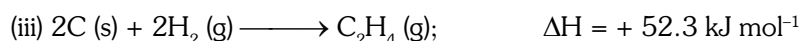
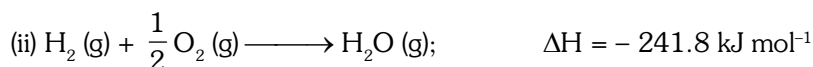


$$6 \times \text{eq. (ii)} + 3 \times \text{eq. (iii)} - \text{eq. (i)}$$

$$\Delta H = 6 \times -97 + 3 \times -68 - (-783) = -3 \text{ kcal mol}^{-1}$$

Illustration 62 Calculate the enthalpy of combustion of ethylene (gas) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of $\text{CO}_{2(\text{g})}$, $\text{H}_2\text{O}_{(\text{g})}$ and $\text{C}_2\text{H}_{4(\text{g})}$ are -393.7 , -241.8 , $+52.3 \text{ kJ per mol}$ respectively.

Solution We are given :



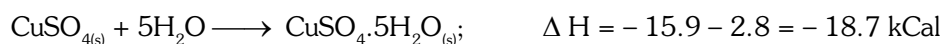
$2 \times \text{Equation (i)} + 2 \times \text{Equation (ii)} - \text{Equation (iii)}$ gives

$$\Delta H = 2(-393.7) + 2(-241.8) - (52.3) = -1323.3 \text{ kJ mol}^{-1}$$

Illustration 63 The heat of solution of anhydrous $\text{CuSO}_{4(\text{s})}$ is $-15.9 \text{ kcal mol}^{-1}$ and that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(\text{s})}$ is $2.8 \text{ kcal mol}^{-1}$. Calculate the heat of hydration of $\text{CuSO}_{4(\text{s})}$.

Solution Given $\text{CuSO}_{4(\text{s})} + \text{aq.} \longrightarrow \text{CuSO}_4(\text{aq}) \quad \Delta H = -15.9 \text{ kcal} \dots \text{(i)}$
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(\text{s})} + \text{aq.} \longrightarrow \text{CuSO}_4(\text{aq}) \quad \Delta H = +2.8 \text{ kcal} \dots \text{(ii)}$

Subtracting Eq. (ii) from Eq. (i)



Heat of hydration of $\text{CuSO}_4 = -18.7 \text{ kcal mol}^{-1}$

BEGINNER'S BOX-9

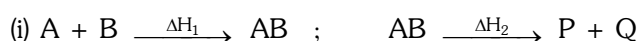
1. A hypothetical reaction, $X \longrightarrow 2Y$ proceeds by the following sequence of steps



The value of ΔH of reaction is :

- (1) $q_1 + q_2 + q_3$ (2) $2q_1 + 2q_2 + 3q_3$ (3) $2(q_1 + q_2 + 2q_3)$ (4) $2(q_1 + q_2 + q_3)$

2. Consider two paths of a certain reaction



(1) $(\Delta H_1 + \Delta H_2) > (\Delta H_3 + \Delta H_4)$

(2) $(\Delta H_1 + \Delta H_2) = (\Delta H_3 + \Delta H_4)$

(3) $(\Delta H_2 + \Delta H_3) = (\Delta H_1 + \Delta H_4)$

(4) $(\Delta H_1 + \Delta H_2) < (\Delta H_3 + \Delta H_4)$

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4						
	Ans.	1	1	1	1						
BEGINNER'S BOX-2	Que.	1	2	3	4						
	Ans.	3	4	2	1						
BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7	8		
	Ans.	2	2	2	3	1	2	4	3		
BEGINNER'S BOX-4	Que.	1	2								
	Ans.	1	3								
BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7			
	Ans.	2	3	4	3	3	1	2			
BEGINNER'S BOX-6	Que.	1	2	3	4	5	6				
	Ans.	2	2	3	4	1	1				
BEGINNER'S BOX-7	Que.	1	2	3	4						
	Ans.	2	3	2	3						
BEGINNER'S BOX-8	Que.	1	2	3	4	5					
	Ans.	3	2	4	4	2					
BEGINNER'S BOX-9	Que.	1	2								
	Ans.	3	2								

EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****INTRODUCTION**

- Thermodynamics is concerned with :-
 - (1) Total energy of a system
 - (2) Energy changes in a system
 - (3) Rate of a chemical change
 - (4) Mass changes in nuclear reactions
- A well stoppered thermos flask contains some ice cubes. This is an example of :-
 - (1) Closed system
 - (2) Open system
 - (3) Isolated system
 - (4) Non-thermodynamic system
- Identify the intensive quantity from the following -
 - (1) Enthalpy and temperature
 - (2) Volume and temperature
 - (3) Enthalpy and volume
 - (4) Temperature and refractive index
- Which of the following is an extensive property
 - (1) Mass
 - (2) Enthalpy
 - (3) Energy
 - (4) All of these
- For an adiabatic process which of the following relations is correct
 - (1) $\Delta E = 0$
 - (2) $P\Delta V = 0$
 - (3) $q = 0$
 - (4) $q = +W$
- In which of the following process work is independent of path :
 - (1) Isothermal
 - (2) Isochoric
 - (3) Adiabatic
 - (4) Isobaric
- When a gas is compressed adiabatically and reversibly, the final temperature is-
 - (1) Higher than the initial temperature
 - (2) Lower than the initial temperature
 - (3) The same as initial temperature
 - (4) Dependent upon the rate of compression
- Which one is dependent only on initial and final state ?
 - (1) Heat supplied at constant pressure
 - (2) Heat supplied at constant volume
 - (3) Enthalpy
 - (4) All of the above
- Out of boiling point (I), entropy (II), pH (III) and emf of a cell (IV), intensive properties are :
 - (1) I, III, IV
 - (2) I, II
 - (3) I, II, III
 - (4) All of these

- The work done by a weightless piston in causing an expansion ΔV (at constant temperature), when the opposing pressure P is variable, is given by :
 - (1) $W = - \int PdV$
 - (2) $W = 0$
 - (3) $W = -P\Delta V$
 - (4) None
- The work done by 100 calorie of heat in isothermal expansion of ideal gas is :-
 - (1) 418.4 J
 - (2) 4.184 J
 - (3) 41.84 J
 - (4) None
- Temperature and volume are not :-
 - (1) Extensive properties
 - (2) Intensive properties
 - (3) Intensive and extensive properties respectively
 - (4) Extensive and intensive properties respectively
- $q = -w$ is not true for :-
 - (1) Isothermal process
 - (2) Adiabatic process
 - (3) Cyclic process
 - (4) 1 and 3 both
- The temperature of an ideal gas increase in an -
 - (1) Adiabatic compression
 - (2) Adiabatic expansion
 - (3) Isothermal expansion
 - (4) Isothermal compression
- Enthalpy of 1 mole monoatomic ideal gas is equals to :-
 - (1) $\frac{3}{2}RT$
 - (2) $\frac{5}{2}RT$
 - (3) RT
 - (4) $2RT$
- Which statement is true for reversible process :-
 - (1) It takes place in single step
 - (2) Driving force is much greater than opposing force
 - (3) Work obtain is minimum
 - (4) None

FIRST LAW OF THERMODYNAMICS ($\Delta E = q + W$)

- Both q & w are _ _ _ _ function :-
 - (1) State
 - (2) State, Path
 - (3) Path, State
 - (4) Path
- If work done by the system is 300 joule when 100 cal. heat is supplied to it. The change in internal energy during the process is :-
 - (1) - 200 Joul
 - (2) 400 Joul
 - (3) 720 Joul
 - (4) 120 Joul

- 19.** A system has internal energy equal to E_1 , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -
 (1) $(E_1 + 150)$ (2) $(E_1 + 1050)$
 (3) $(E_1 - 150)$ (4) None of these
- 20.** The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :
 (1) 32 J (2) 40 J
 (3) 48 J (4) -32 J
- 21.** If a gas absorbs 100 J of heat and expands by 500cm^3 against a constant pressure of $2 \times 10^5 \text{Nm}^{-2}$, the change in internal energy is:-
 (1) - 300 J (2) - 100 J
 (3) + 100 J (4) None of these

ENTHALPY $[\Delta H = \Delta E + P\Delta V/\Delta H = \Delta E + \Delta n_g RT]$

- 22.** Internal energy change during a reversible isothermal expansion of an ideal gas is :-
 (1) Always negative
 (2) Always positive
 (3) Zero
 (4) May be positive or negative
- 23.** Under which of the following conditions is the relation, $\Delta H = \Delta E + P\Delta V$ valid for a system :-
 (1) Constant pressure
 (2) Constant temperature
 (3) Constant temperature and pressure
 (4) Constant temperature, pressure and composition
- 24.** The difference between heats of reaction at constant pressure and constant volume for the reaction $2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$ at 25°C in KJ is
 (1) + 7.43 (2) +3.72
 (3) - 7.43 (4) - 3.72
- 25.** For a gaseous reaction,
 $\text{A}(\text{g}) + 3\text{B}(\text{g}) \longrightarrow 3\text{C}(\text{g}) + 3\text{D}(\text{g})$
 ΔE is 17 kCal at 27°C assuming $R = 2 \text{Cal K}^{-1} \text{mol}^{-1}$, the value of ΔH for the above reaction is:
 (1) 15.8 Kcal (2) 18.2 Kcal
 (3) 20.0 Kcal (4) 16.4 Kcal
- 26.** Which of the following statements is correct for the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ at constant temperature and pressure
 (1) $\Delta H = \Delta E$ (2) $\Delta H < \Delta E$
 (3) $\Delta H > \Delta E$ (4) None of the above
- 27.** For the reaction $\text{Ag}_2\text{O}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$, which one of the following is true :
 (1) $\Delta H = \Delta E$ (2) $\Delta H = \frac{1}{2}\Delta E$
 (3) $\Delta H < \Delta E$ (4) $\Delta H > \Delta E$
- 28.** A mixture of 2 moles of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then :-
 (1) $\Delta H > \Delta E$ (2) $\Delta H < \Delta E$
 (3) $\Delta H = \Delta E$ (4) Not definite
- 29.** For the gaseous reaction involving the complete combustion of isobutane -
 (1) $\Delta H = \Delta E$ (2) $\Delta H > \Delta E$
 (3) $\Delta H = \Delta E = 0$ (4) $\Delta H < \Delta E$
- 30.** For the reversible isothermal expansion of one mole of an ideal gas at 300 K, from a volume of 10dm^3 to 20dm^3 , ΔH is -
 (1) 1.73 kJ (2) -1.73 kJ
 (3) 3.46 kJ (4) Zero
- 31.** For $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ at 977°C , $\Delta H = 174 \text{KJ/mol}$; then ΔE is :-
 (1) 160 kJ (2) 163.6 kJ
 (3) 186.4 kJ (4) 180 kJ
- 32.** Heat of reaction for , $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ at constant V is -67.71Kcal at 17°C . The heat of reaction at constant P at 17°C is :-
 (1) -68.0kCal (2) $+ 68.0 \text{kCal}$
 (3) $- 67.42 \text{kCal}$ (4) None
- 33.** The reaction :-

$$\text{NH}_2\text{CN}(\text{s}) + \frac{3}{2}\text{O}_{2(\text{g})} \rightarrow \text{N}_{2(\text{g})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})}$$

 was carried out in a bomb calorimeter. The heat released was 743kJ mol^{-1} . The value of $\Delta H_{300\text{K}}$ for this reaction would be :-
 (1) $- 740.5 \text{kJ mol}^{-1}$ (2) $- 741.75 \text{kJ mol}^{-1}$
 (3) $- 743.0 \text{kJ mol}^{-1}$ (4) $- 744.25 \text{kJ mol}^{-1}$
- 34.** The enthalpy of vaporisation of water at 100°C is 40.63kJ mol^{-1} . The value ΔE for this process would be:-
 (1) 37.53kJ mol^{-1} (2) 39.08kJ mol^{-1}
 (3) 42.19kJ mol^{-1} (4) 43.73kJ mol^{-1}
- 35.** For the system $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$:-
 (1) $\Delta H = \Delta E$ (2) $\Delta H > \Delta E$
 (3) $\Delta E > \Delta H$ (4) $\Delta H = 0$

36. For the reaction $\text{CO (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)}$

Which one of the statement is correct at constant T and P ?

- (1) $\Delta H = \Delta E$
 (2) $\Delta H < \Delta E$
 (3) $\Delta H > \Delta E$
 (4) ΔH is Independent of physical state of reactants
37. Which is true for the combustion of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) at 25°C :-
 (1) $\Delta H > \Delta E$ (2) $\Delta H < \Delta E$
 (3) $\Delta H = \Delta E$ (4) None

38. For which change $\Delta H \neq \Delta E$:-

- (1) $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$
 (2) $\text{HCl (l)} + \text{NaOH (l)} \rightarrow \text{NaCl (s)} + \text{H}_2\text{O (l)}$
 (3) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
 (4) $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$

39. The heat of combustion of ethanol determined in a bomb calorimeter is $-670.48 \text{ kCal mole}^{-1}$ at 27°C .

What is ΔH at 27°C for the reaction :-

- (1) -335.24 kCal (2) -671.08 kCal
 (3) -670.48 kCal (4) $+670.48 \text{ kCal}$

40. The difference in ΔH and ΔE for the combustion of methane at 25°C would be :-

- (1) Zero (2) $2 \times 298 \times -2 \text{ Cals.}$
 (3) $2 \times 298 \times -3 \text{ Cals.}$ (4) $2 \times 25 \times -3 \text{ Cals.}$

41. For which of the following reactions ΔH is less than ΔE :-

- (1) $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)} + 6\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}$
 (2) $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)}$
 (3) $\text{N}_2\text{O}_4\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$
 (4) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$

42. For a reaction $2\text{X(s)} + 2\text{Y(s)} \rightarrow 2\text{C(l)} + \text{D(g)}$

The q_p at 27°C is $-28 \text{ kCal mol}^{-1}$.

The q_v is ----- kCal mol^{-1} :-

- (1) -27.4 (2) $+27.4$
 (3) -28.6 (4) 28.6

WORK DONE IN DIFFERENT PROCESS

43. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25°C is :

- (1) $-2.303 \times 8.31 \times 10^7 \times 298 \log 2$
 (2) $-2.303 \times 0.0821 \times 298 \log 2$
 (3) $-2.303 \times 0.0821 \times 298 \log 0.5$
 (4) $-2.303 \times 2 \times 298 \log 2$

44. Two litre of N_2 at 0°C and 5 atm are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm. Assuming the gas to be ideal calculate work of expansion ?

- (1) -504.2 Joule (2) -405.2 Joule
 (3) $+810.4 \text{ Joule}$ (4) -810.4 Joule

45. Two moles of an ideal gas expand spontaneously into vacuum. The work done is :-

- (1) Zero (2) 2 J
 (3) 4 J (4) 8 J

46. One mole of a gas occupying 3 dm^3 expands against a constant external pressure of 1 atm to a volume of 13 lit. The workdone is :-

- (1) -10 atm dm^3 (2) -20 atm dm^3
 (3) -39 atm dm^3 (4) -48 atm dm^3

ENTROPY/SECOND LAW OF THERMODYNAMICS

47. For which reaction from the following, ΔS will be maximum ?

- (1) $\text{Ca(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CaO(s)}$
 (2) $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$
 (3) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2 \text{ (g)}$
 (4) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$

48. An adiabatic reversible process is one in which :-

- (1) Temperature of the system does not change
 (2) The system is not closed to heat transfer
 (3) There is no entropy change
 (4) None of these

49. Entropy means

- (1) Disorderliness (2) Randomness
 (3) Orderliness (4) both 1 & 2

50. ΔS for the reaction;

$\text{MgCO}_3\text{(s)} \rightarrow \text{MgO(s)} + \text{CO}_2\text{(g)}$ will be :

- (1) 0 (2) -ve (3) +ve (4) ∞

51. Change in entropy is negative for

- (1) Bromine (l) $\rightarrow$ Bromine (g)
 (2) $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{(g)}$
 (3) $\text{N}_2\text{(g, 10 atm)} \rightarrow \text{N}_2 \text{ (g, 1 atm)}$
 (4) $\text{Fe(at 400 K)} \rightarrow \text{Fe(at 300 K)}$

52. In which reaction ΔS is positive :-

- (1) $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (s)}$
 (2) $3\text{O}_2 \text{ (g)} \rightarrow 2\text{O}_3 \text{ (g)}$
 (3) $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)}$
 (4) $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3 \text{ (g)}$

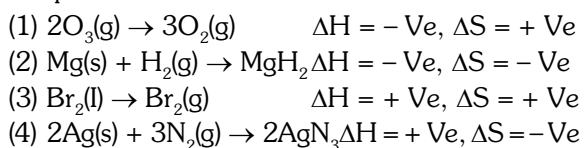
- 53.** When the egg is hard boiled, there is-
 (1) Increase in disorder
 (2) Decrease in disorder
 (3) No change in disorder
 (4) ΔG is negative
- 54.** If S° for H_2 , Cl_2 and HCl are 0.13, 0.22 and 0.19 $kJ K^{-1} mol^{-1}$ respectively. The total change in standard entropy for the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ is :
 (1) 30 $JK^{-1} mol^{-1}$ (2) 40 $JK^{-1} mol^{-1}$
 (3) 60 $JK^{-1} mol^{-1}$ (4) 20 $JK^{-1} mol^{-1}$
- 55.** Which has the least entropy :
 (1) Graphite (2) Diamond
 (3) $N_2(g)$ (4) $N_2O(g)$
- 56.** When two gases are mixed the entropy :-
 (1) Remains constant (2) Decreases
 (3) Increases (4) Becomes zero
- 57.** The enthalpy of vaporization for water is 186.5 $kJ mol^{-1}$, the entropy of its vaporization will be-
 (1) 0.5 $kJ K^{-1} mol^{-1}$ (2) 1.0 $kJ K^{-1} mole^{-1}$
 (3) 1.5 $kJ K^{-1} mole^{-1}$ (4) 2.0 $kJ K^{-1} mole^{-1}$
- 58.** The enthalpy of vaporisation of per mole of ethanol (b.p. = 79.5°C and $\Delta S = 109.8 JK^{-1} mol^{-1}$) is :-
 (1) 27.35 $kJ mol^{-1}$ (2) 32.19 $kJ mol^{-1}$
 (3) 38.70 $kJ mol^{-1}$ (4) 42.37 $kJ mol^{-1}$
- 59.** If 900J/g of heat is exchanged at boiling point of water, then what is increase in entropy?
 (1) 43.4 $JK^{-1}mole^{-1}$
 (2) 87.2 $JK^{-1}mole^{-1}$
 (3) 900 $JK^{-1}mole^{-1}$
 (4) Zero
- 60.** 5 mole of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C. The change in entropy is :-
 (1) 41.57 JK^{-1} (2) - 95.73 JK^{-1}
 (3) 95.73 JK^{-1} (4) - 41.57 JK^{-1}
- 61.** In a spontaneous irreversible process the total entropy of the system and surroundings
 (1) Remains constant (2) Increases
 (3) Decreases (4) Zero
- 62.** The total entropy change for a system & its surroundings increases if the process is :
 (1) Reversible (2) Irreversible
 (3) Exothermic (4) Endothermic
- 63.** Calculate the entropy of $Br_2(g)$ in the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, $\Delta S^\circ = 20.1 JK^{-1}$ given, entropy of H_2 and HBr is 130.6 and 198.5 $J mol^{-1} K^{-1}$:-
 (1) 246.3 JK^{-1} (2) 123.15 JK^{-1}
 (3) 24.63 JK^{-1} (4) 20 JK^{-1}
- 64.** Ammonium chloride when dissolved in water leads to cooling sensation. The dissolution of NH_4Cl at constant temperature is accompanied by :-
 (1) Increase in entropy
 (2) Decrease in entropy
 (3) No change in entropy
 (4) No change in enthalpy
- 65.** In which of the following case entropy decreases-
 (1) Solid changing to liquid
 (2) Expansion of a gas
 (3) Crystals dissolve
 (4) Polymerisation
- 66.** Which of the following state function is not zero at standard state :-
 (1) Enthalpy (2) Entropy
 (3) Free energy (4) Work
- 67.** Entropy of an adiabatic reversible process is:-
 (1) Positive (2) Zero
 (3) Negative (4) Constant

GIBBS FREE ENERGY

- 68.** A gas is allowed to expand under reversible adiabatic conditions then what is zero for such a process:-
 (1) $\Delta G = 0$ (2) $\Delta T = 0$
 (3) $\Delta S = 0$ (4) None of these
- 69.** For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are $-11.7 \times 10^3 Jmol^{-1}$ and $-105 J mol^{-1} K^{-1}$ respectively. The reaction is :
 (1) Spontaneous
 (2) Non spontaneous
 (3) At equilibrium
 (4) Can't say anything
- 70.** The spontaneous nature of a reaction is impossible if :
 (1) ΔH is +ve, ΔS is also +ve
 (2) ΔH is -ve; ΔS is also -ve
 (3) ΔH is -ve ; ΔS is +ve
 (4) ΔH is +ve; ΔS is -ve
- 71.** If $\Delta H > 0$ and $\Delta S > 0$, the reaction proceeds spontaneously when :-
 (1) $\Delta H > 0$ (2) $\Delta H < T \Delta S$
 (3) $\Delta H = T \Delta S$ (4) None

- 72.** The temperature at which the reaction $\text{Ag}_2\text{O(s)} \longrightarrow 2\text{Ag(s)} + \frac{1}{2}\text{O}_2\text{(g)}$ is at equilibrium is;
Given $\Delta H = 30.5 \text{ kJ mol}^{-1}$
and $\Delta S = 0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$:
(1) 462.12 K (2) 362.12 K
(3) 262.12 K (4) 562.12 K
- 73.** The enthalpy change for a given reaction at 298 K is $-x \text{ cal mol}^{-1}$. If the reaction occurs spontaneously at 298 K, the entropy change at that temperature
(1) Can be negative but numerically larger than $x/298 \text{ Cal K}^{-1} \text{ mol}^{-1}$
(2) Can be negative but numerically smaller than $x/298 \text{ Cal K}^{-1} \text{ mol}^{-1}$
(3) Cannot be negative
(4) Cannot be positive
- 74.** Which of the following is true for the reaction $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$ at 100°C and 1 atmosphere
(1) $\Delta S = 0$ (2) $\Delta H = 0$
(3) $\Delta H = \Delta E$ (4) $\Delta H = T\Delta S$
- 75.** For the reaction $\text{Ag}_2\text{O(s)} \longrightarrow 2\text{Ag(s)} + \frac{1}{2} \text{O}_2\text{(g)}$ the value of $\Delta H = 30.56 \text{ kJ mol}^{-1}$ and $\Delta S = 66 \text{ JK}^{-1} \text{ mol}^{-1}$. The temperature at which the free energy change for the reaction will be zero is :-
(1) 373 K (2) 413 K
(3) 463 K (4) 493 K
- 76.** For hypothetical reversible reaction $\frac{1}{2}\text{A}_2\text{(g)} + \frac{3}{2}\text{B}_2\text{(g)} \longrightarrow \text{AB}_3\text{(g)}$; $\Delta H = -20 \text{ kJ}$ if standard entropies of A_2 , B_2 and AB_3 are 60, 40 and $50 \text{ JK}^{-1} \text{ mole}^{-1}$ respectively. The above reaction will be in equilibrium at :-
(1) 400 K (2) 500 K
(3) 250 K (4) 200 K
- 77.** For the precipitation of AgCl by Ag^+ ions and HCl
(1) $\Delta H = 0$ (2) $\Delta G = 0$
(3) $\Delta G = -ve$ (4) $\Delta H = \Delta G$
- 78.** What is the sign of ΔG for the process of ice melting at 283 K ?
(1) $\Delta G > 0$ (2) $\Delta G = 0$
(3) $\Delta G < 0$ (4) None of these
- 79.** What is the free energy change ΔG , when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure :-
(1) 540 Cal (2) -9800 Cal
(3) 9800 Cal (4) 0 Cal
- 80.** A reaction $\text{A} + \text{B} \longrightarrow \text{C} + \text{D} + \text{q}$ is found to have a positive entropy change, the reaction will be -
(1) Possible at high temperature
(2) Possible only at low temperature
(3) Not possible at any temperature
(4) Possible at any temperature
- 81.** Equilibrium constant of a reaction is related to :
(1) Standard free energy change ΔG°
(2) Free energy change ΔG
(3) Entropy change
(4) None
- 82.** The Vant Hoff equation is :
(1) $\Delta G^\circ = RT \log_e K_p$ (2) $-\Delta G^\circ = RT \log_e K_p$
(3) $\Delta G^\circ = RT^2 \ln K_p$ (4) None
- 83.** If $\Delta G^\circ > 0$ for a reaction then :
(1) $K_p > 1$
(2) $K_p < 1$
(3) The products predominate in the equilibrium mixture
(4) None
- 84.** If the equilibrium constant for a reaction is 10, then the value of ΔG° will be
($R = 8 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$)
(1) $+ 5.527 \text{ kJ mol}^{-1}$
(2) $- 5.527 \text{ kJ mol}^{-1}$
(3) $+55.27 \text{ kJ mol}^{-1}$
(4) $- 55.27 \text{ kJ mol}^{-1}$
- 85.** The process of evaporation of a liquid is accompanied by :
(1) Increase in enthalpy
(2) Decrease in free energy
(3) Increase in entropy
(4) All
- 86.** For the process, $\text{CO}_2\text{(s)} \longrightarrow \text{CO}_2\text{(g)}$:
(1) Both ΔH and ΔS are +ve
(2) ΔH is negative and ΔS is +ve
(3) ΔH is +ve and ΔS is -ve
(4) Both ΔH and ΔS are -ve
- 87.** Which of the following provide exceptions to third law of thermodynamics
(1) CO (2) ice
(3) CO_2 (4) All the above
- 88.** The Gibbs free energy change of a reaction at 27°C is -26 kCal . and its entropy change is -60 Cals K . ΔH for the reaction is :-
(1) $- 44 \text{ kCals}$. (2) $- 18 \text{ kCals}$.
(3) 34 kals . (4) $- 24 \text{ kCals}$.

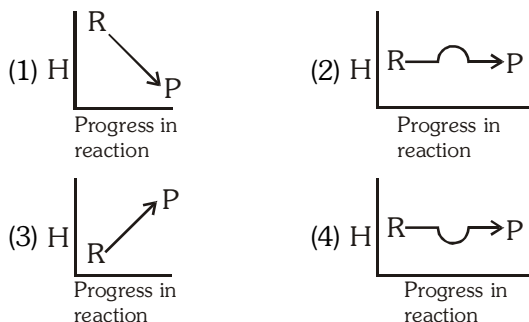
89. Which of the following reaction is expected never to be spontaneous :-



THERMOCHEMICAL REACTION

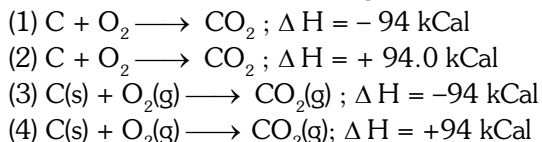
90. The formation of water from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is an exothermic process because :
 (1) The chemical energy of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is more than that of water
 (2) The chemical energy of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is less than that of water
 (3) The temperature of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is higher than that of water
 (4) The temperature of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is lower than that of water

91. Which plot represents for an exothermic reaction:



92. Which one of the following is not applicable for a thermochemical equation :
 (1) It tells about physical state of reactants and products
 (2) It tells whether the reaction is spontaneous
 (3) It tells whether the reaction is exothermic or endothermic
 (4) It tells about the allotropic form (if any) of the reactants

93. The correct thermochemical equation is :



94. The enthalpy changes of formation of the gaseous oxide of nitrogen (N_2O and NO) are positive because of :

- (1) The high bond energy of the nitrogen molecule
 (2) The high electron affinity of oxygen atoms
 (3) The high electron affinity of nitrogen atoms
 (4) The tendency of oxygen to form O^{2-}

95. ΔH for transition of carbon from diamond form to graphite form is -453.5 Cal . This suggests that :
 (1) Graphite is chemically different from diamond
 (2) Graphite is as stable as diamond
 (3) Graphite is more stable than diamond
 (4) Diamond is more stable than graphite

96. Which of the following values of heat of formation indicates that the product is least stable
 (1) -94 kCal (2) -231.6 kCal
 (3) $+21.4 \text{ kCal}$ (4) $+64.8 \text{ kCal}$

97. Heat of formation, ΔH_f° of an explosive compound like NCl_3 is -
 (1) Positive (2) Negative
 (3) Zero (4) Positive or negative

98. According to the following reaction
 $\text{C}(\text{s}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$, $\Delta H = -26.4 \text{ kCal}$
 (1) CO is an endothermic compound
 (2) CO is an exothermic compound
 (3) The reaction is endothermic
 (4) None of the above

99. Which of the following represents an exothermic reaction:-
 (1) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$, $\Delta H = 180.5 \text{ kJ}$
 (2) $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$, $\Delta E = 131.2 \text{ kJ}$
 (3) $2\text{HgO}(\text{s}) + 180.4 \text{ KJ} \rightarrow 2\text{Hg}(\text{l}) + \text{O}_2(\text{g})$
 (4) $2\text{Zn}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s})$, $\Delta E = -693.8 \text{ kJ}$

100. The heat change during the reaction 24g C and 128g S following the change $\text{C} + \text{S}_2 \rightarrow \text{CS}_2$; $\Delta H = 22 \text{ kCal}$
 (1) 22 kCal (2) 11 kCal
 (3) 44 kCal (4) 32 kCal

101. Consider the reaction $3\text{O}_2 \rightarrow 2\text{O}_3$; $\Delta H = +Ve$, from the reaction, we can say that :-
 (1) Ozone is more stable than oxygen
 (2) Ozone is less stable than oxygen and ozone decomposes forming oxygen readily
 (3) Oxygen is less stable than ozone and oxygen decomposes forming ozone readily
 (4) None of the above

102. From the reaction $\text{P}(\text{White}) \rightarrow \text{P}(\text{Red})$; $\Delta H = -18.4 \text{ kJ}$, it follows that :-
 (1) Red P is readily formed from white P
 (2) White P is readily formed from red P
 (3) White P can not be converted to red P
 (4) White P can be converted into red P and red P is more stable

FACTORS AFFECTING HEAT OF REACTION

- 103.** In Kirchoff's equation which factor affects the heat of reaction :
- (1) Pressure (2) Temperature
(3) Volume (4) Atomicity
- 104.** For the reaction; $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\ell)$, $\Delta C_p = 7.63 \text{ Cal deg}$; $\Delta H_{25^\circ\text{C}} = 68.3 \text{ kCal}$, what will be the value (in kCal) of ΔH at 100°C :
- (1) $7.63 \times (373 - 298) - 68.3$
(2) $7.63 \times 10^{-3} (373 - 298) - 68.3$
(3) $7.63 \times 10^{-3} (373 - 298) + 68.3$
(4) $7.63 \times (373 - 298) + 68.3$
- 105.** The enthalpy of a reaction at 273 K is -3.57 kJ . what will be the enthalpy of reaction at 373 K if $\Delta C_p = \text{zero}$:-
- (1) -3.57 (2) Zero
(3) $-3.57 \times \frac{373}{273}$ (4) -375
- 106.** For the reactions,
- (i) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}) + x\text{kJ}$
(ii) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\ell) + y\text{kJ}$
Which one of the following statement is correct :
- (1) $x > y$ (2) $x < y$
(3) $x = y$ (4) More data required

HEAT OF FORMATION

- 107.** Since the enthalpy of the elements in their standard states is taken to be zero. The heat of formation (ΔH_f) of compounds :
- (1) Is always negative
(2) Is always positive
(3) Is zero
(4) May be positive or negative
- 108.** Reaction $\text{H}_2(\text{s}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}$; $\Delta H = 12.40 \text{ kCal}$. According to this, heat of formation of HI will be -
- (1) 12.40 kCal (2) -12.40 kCal
(3) -6.20 kCal (4) 6.20 kCal
- 109.** At 300K the standard enthalpies of formation of $\text{C}_6\text{H}_5\text{COOH}(\text{s})$, $\text{CO}_{2(\text{g})}$ and $\text{H}_2\text{O}_{(\ell)}$ are -408 , -393 and -286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at constant volume :
- (1) $+3201 \text{ kJ}$
(2) $+3199.75 \text{ kJ}$
(3) -3201 kJ
(4) -3199.75 kJ

- 110.** Enthalpy of a compound is equal to its :- (When it is formed from constituent particles)
- (1) Heat of combustion
(2) Heat of formation
(3) Heat of reaction
(4) Heat of solution
- 111.** Which of the following equations represents standard heat of formation of CH_4 ?
- (1) $\text{C}_{(\text{diamond})} + 2\text{H}_{2(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
(2) $\text{C}_{(\text{graphite})} + 2\text{H}_{2(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
(3) $\text{C}_{(\text{diamond})} + 4\text{H}_{(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
(4) $\text{C}_{(\text{graphite})} + 4\text{H}_{(\text{g})} \longrightarrow \text{CH}_{4(\text{g})}$
- 112.** The enthalpy of formation of ammonia is $-46.0 \text{ kJ mol}^{-1}$. The enthalpy change for the reaction $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ is :
- (1) 46.0 kJ mol^{-1} (2) 92.0 kJ mol^{-1}
(3) $-23.0 \text{ kJ mol}^{-1}$ (4) $-92.0 \text{ kJ mol}^{-1}$
- 113.** Given enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{CaO}(\text{s})$ are -94.0 kJ and -152 kJ respectively and the enthalpy of the reaction : $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 42 kJ . The enthalpy of formation of $\text{CaCO}_3(\text{s})$ is
- (1) -42 KJ (2) -202 KJ
(3) $+202 \text{ KJ}$ (4) -288 KJ
- 114.** Given that standard heat enthalpy of CH_4 , C_2H_4 and C_3H_8 are -17.9 , 12.5 , $-24.8 \text{ kCal mol}^{-1}$. The ΔH for $\text{CH}_4 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_8$ is :
- (1) -55.2 kCal (2) -30.2 kCal
(3) 55.2 kCal (4) -19.4 kCal
- 115.** The standard molar heat of formation of ethane, CO_2 and water(ℓ) are respectively -21.1 , -94.1 and -68.3 kCal . The standard molar heat of combustion of ethane will be
- (1) -372 kCal (2) -162 kCal
(3) -240 kCal (4) -183.5 kCal
- 116.** Two atoms of hydrogen combine to form a molecule of hydrogen gas, the energy of the H_2 molecule is :
- (1) Greater than that of separate atoms
(2) Equal to that of separate atoms
(3) Lower than that of separate atoms
(4) Some times lower and some times higher
- 117.** The ΔH_f° for $\text{CO}_{2(\text{g})}$, $\text{CO}_{(\text{g})}$ and $\text{H}_2\text{O}_{(\text{g})}$ are -393.5 , -110.5 and $-241.8 \text{ kJ mol}^{-1}$ respectively the standard enthalpy change (in kJ) for the reaction $\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} \rightarrow \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$ is -
- (1) 524.1 (2) 41.2 (3) -262.5 (4) -41.2

- 118.** The enthalpies of combustion of carbon and carbon monoxide are -393.5 kJ and -283 kJ , respectively the enthalpy of formation of carbon monoxide is :
 (1) -676.5 kJ (2) -110.5 kJ
 (3) 110.5 kJ (4) 676.5 kJ

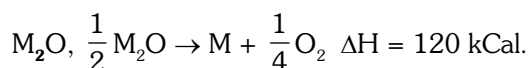
- 119.** The standard heat of formation of $\text{CS}_2(\ell)$ will be; given that the standard heat of combustion of carbon (s), sulphur(s) and $\text{CS}_2(\ell)$ are -393.3 , -293.72 and $-1108.76 \text{ kJ mol}^{-1}$ respectively is
 (1) $-128.02 \text{ kJ mole}^{-1}$
 (2) $+12.802 \text{ kJ mol}^{-1}$
 (3) $+128.02 \text{ kJ mol}^{-1}$
 (4) $-12.802 \text{ kJ mol}^{-1}$

- 120.** The heat of combustion of $\text{CH}_4(\text{g})$, $\text{C}(\text{s})$ and $\text{H}_2(\text{g})$ at 25°C are -212.4 K Cal , -94.0 K Cal and -68.4 K Cal respectively, the heat of formation of CH_4 will be -
 (1) $+54.4 \text{ K Cal}$ (2) -18.4 K Cal
 (3) -375.2 K Cal (4) $+212.8 \text{ K Cal}$

- 121.** Standard enthalpy of formation is zero for .
 (1) $\text{C}_{\text{diamond}}$ (2) $\text{Br}_{(\text{g})}$
 (3) $\text{C}_{\text{graphite}}$ (4) $\text{O}_{3(\text{g})}$

- 122.** The standard heats of formation of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are 8.0 and $2.0 \text{ kCal mol}^{-1}$ respectively the heat of dimerization of NO_2 in kCal is
 (1) 10.0 (2) -6.0 (3) -12.0 (4) -14.0

- 123.** M is a metal that forms an oxide



When a sample of metal M reacts with one mole of oxygen what will be the ΔH in that case

- (1) 240 kCal. (2) -240 kCal.
 (3) 480 kCal. (4) -480 kCal.

HEAT OF COMBUSTION

- 124.** According to equation,
 $\text{C}_6\text{H}_6(\ell) + 15/2 \text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell);$
 $\Delta H = -3264.4 \text{ kJ mol}^{-1}$ the energy evolved when 7.8 g benzene is burnt in air will be -
 (1) 163.22 kJ (2) 32.64 kJ
 (3) 3.264 kJ (4) 326.4 kJ
- 125.** Heat of combustion of CH_4 , C_2H_6 , C_2H_4 and C_2H_2 gases are -212.8 , -373.0 , -337.0 and -310.5 kCal respectively at the same temperature. The best fuel among these gases is :
 (1) CH_4 (2) C_2H_6 (3) C_2H_4 (4) C_2H_2

- 126.** Given standard enthalpy of formation of CO (-110 kJ mol^{-1}) and CO_2 (-394 kJ mol^{-1}). The heat of combustion when one mole of graphite burns is

- (1) -110 kJ (2) -284 kJ
 (3) -394 kJ (4) -504 kJ

- 127.** The enthalpy of formation for $\text{C}_2\text{H}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ at 25°C and 1 atm. pressure are 52 , -394 and $-286 \text{ kJ mole}^{-1}$ respectively. The enthalpy of combustion of C_2H_4 will be:-

- (1) $+1412 \text{ kJ mole}^{-1}$ (2) $-1412 \text{ kJ mole}^{-1}$
 (3) $+142.2 \text{ kJ mole}^{-1}$ (4) $-141.2 \text{ kJ mole}^{-1}$

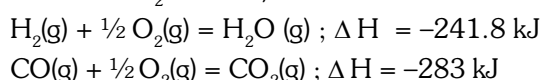
- 128.** The heat of combustion of carbon and carbon monoxide are -394 and -285 kJ mol^{-1} respectively. The heat of formation of CO in kJ mol^{-1} is:-

- (1) $+109$ (2) -109
 (3) $+218$ (4) -218

- 129.** If heat of combustion of ethylene is 1411 kJ when a certain amount of ethylene was burnt 6226 kJ heat was evolved. Then the volume of O_2 (at NTP) that entered into the reaction is :-

- (1) 296.5 ml (2) 296.5 litre
 (3) $6226 \times 22.4 \text{ litre}$ (4) 22.4 litre

- 130.** The heat evolved during the combustion of 112 litre of water gas at STP (mixture of equal volume of H_2 and CO) is : Given



- (1) 241.8 kJ (2) 283 kJ
 (3) 1312 kJ (4) 1586 kJ

- 131.** A person requires 2870 kCal of energy to lead normal daily life. If heat of combustion of cane sugar is -1349 kCal , then his daily consumption of sugar is :

- (1) 728 g (2) 0.728 g
 (3) 342 g (4) 0.342 g

- 132.** On complete combustion of 2 gm methane 26575 Cal heat is generated. The heat of formation of methane will be (given heat of formation of CO_2 and H_2O are -97000 and -68000 Cal respectively) :

- (1) $+20400 \text{ Cal}$ (2) $+20600 \text{ Cal}$
 (3) -20400 Cal (4) -2000 Cal

HEAT OF HYDROGENATION

- 149.** The heat of combustion of C_2H_4 , C_2H_6 and H_2 are -1409.5 kJ, -1558.3 kJ and -285.6 kJ. The heat of hydrogenation of ethene is -
 (1) -136.8 kJ (2) -13.68 kJ
 (3) 273.6 kJ (4) 1.368 kJ
- 150.** The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are respectively -3920 , -3800 and -241 kJ mol^{-1} . The heat of hydrogenation of cyclohexene is:-
 (1) -121 kJ mol^{-1} (2) 121 kJ mol^{-1}
 (3) -242 kJ mol^{-1} (4) 242 kJ mol^{-1}

BOND ENERGY/RESONANCE ENERGY

- 151.** Bond energy of a molecule :
 (1) Is always negative
 (2) Is always positive
 (3) Either positive or negative
 (4) Depends upon the physical state of the system
- 152.** Among the following for which reaction heat of reaction represents bond energy of HCl
 (1) $HCl(g) \longrightarrow H^+(g) + Cl^-(g)$
 (2) $HCl(g) \longrightarrow \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g)$
 (3) $2HCl(g) \longrightarrow H_2(g) + Cl_2(g)$
 (4) $HCl(g) \longrightarrow H(g) + Cl(g)$
- 153.** The bond energies of F_2 , Cl_2 , Br_2 and I_2 are 155.4 , 243.6 , 193.2 and 151.2 kJ mol^{-1} respectively. The strongest bond is :
 (1) $F - F$ (2) $Cl - Cl$
 (3) $Br - Br$ (4) $I - I$
- 154.** Energy required to dissociate 4g of gaseous hydrogen into free gaseous atoms is 208 kCal at $25^\circ C$. The bond energy of $H-H$ bond will be :
 (1) 1.04 kCal (2) 10.4 kCal
 (3) 104 kCal (4) 1040 kCal
- 155.** Heat evolved in the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ is 182 kJ. Bond energies of $H-H$ and $Cl-Cl$ are 430 and 242 kJ mol^{-1} respectively. The $H-Cl$ bond energy is :
 (1) 245 kJ mol^{-1}
 (2) 427 kJ mol^{-1}
 (3) 336 kJ mol^{-1}
 (4) 154 kJ mol^{-1}

- 156.** The enthalpy change for the reaction $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$ is..... . The bond energies are,
 $H - H = 103$, $C - H = 99$, $C - C = 80$ &
 $C = C = 145$ kCal mol^{-1}
 (1) -10 kCal mol^{-1} (2) $+10$ kCal mol^{-1}
 (3) -30 kCal mol^{-1} (4) $+30$ kCal mol^{-1}
- 157.** Bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are 436.0 kJ mol^{-1} and 941.8 kJ mol^{-1} respectively and enthalpy of formation of $NH_3(g)$ is -46 kJ mol^{-1} . What is enthalpy of atomization of $NH_3(g)$?
 (1) 390.3 kJ mol^{-1} (2) 1170.9 kJ mol^{-1}
 (3) 590 kJ mol^{-1} (4) 720 kJ mol^{-1}
- 158.** From the reactions :
 $C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H = -X$ Kcal
 $C(g) + 4H(g) \rightarrow CH_4(g)$, $\Delta H = -X_1$ Kcal
 $CH_4(g) \rightarrow CH_3(g) + H(g)$ $\Delta H = +Y$ (Kcal)
 Bond energy of $C-H$ bond is -
 (1) $\frac{X}{4}$ kCal mol^{-1}
 (2) Y kCal mol^{-1}
 (3) $\frac{X_1}{4}$ kCal mol^{-1}
 (4) X_1 kCal mol^{-1}
- 159.** The enthalpy changes at 298 K in successive breaking of $O-H$ bonds of water are
 $H_2O \longrightarrow H(g) + OH(g)$; $\Delta H = 498$ kJ mol^{-1}
 $OH(g) \longrightarrow H(g) + O(g)$; $\Delta H = 428$ kJ mol^{-1}
 the bond enthalpy of $O-H$ bond is
 (1) 498 kJ mol^{-1} (2) 428 kJ mol^{-1}
 (3) 70 kJ mol^{-1} (4) 463 kJ mol^{-1}
- 160.** If ΔH_f° of $ICl_{(g)}$, $Cl_{(g)}$, and $I_{(g)}$ is 17.57, 121.34 and 106.96 J mol^{-1} respectively. Then bond dissociation energy of ICl bond is -
 (1) 35.15 J mol^{-1} (2) 106.69 J mol^{-1}
 (3) 210.73 J mol^{-1} (4) 420.9 J mol^{-1}
- 161.** Heat of dissociation of benzene to elements is 5535 kJ mol^{-1} . The bond enthalpies of $C-C$, $C=C$ and $C-H$ are 347.3, 615.0 and 416.2 kJ respectively. Magnitude resonance energy of benzene is
 (1) 1.51 kJ (2) 15.1 kJ
 (3) 151 kJ (4) 1511 kJ

SOME OTHER HEAT OF REACTIONS

- 162.** The enthalpy change for the reaction $2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$ is called
 (1) Enthalpy of formation
 (2) Enthalpy of combustion
 (3) Enthalpy of hydrogenation
 (4) Enthalpy of vaporisation
- 163.** $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g})$, In this process value of ΔH will be -
 (1) Positive
 (2) Negative
 (3) Zero
 (4) Nothing can be predicted
- 164.** The magnitude of heat of solution on addition of solvent to solution
 (1) Decreases
 (2) Increases
 (3) Remains constant
 (4) Increases or decreases
- 165.** If $\text{H}_2(\text{g}) = 2\text{H}(\text{g})$; $\Delta H = 104 \text{ kCal}$, than heat of atomisation of hydrogen is :
 (1) 52 kCal (2) 104 kCal
 (3) 208 kCal (4) None of these
- 166.** $\text{S}_{(\text{rhombic})} + \text{O}_{2(\text{g})} \longrightarrow \text{SO}_{2(\text{g})}$; $\Delta H = -297.5 \text{ kJ}$
 $\text{S}_{(\text{monoclinic})} + \text{O}_{2(\text{g})} \longrightarrow \text{SO}_2$; $\Delta H = -300 \text{ kJ}$
 The data can predict that -
 (1) Rhombic sulphur is yellow in colour
 (2) Monoclinic sulphur has metallic lusture.
 (3) Monoclinic sulphur is more stable
 (4) ΔH transition of S_R to S_M is endothermic
- 167.** The heat of combustion of yellow phosphorous and red phosphorous are -9.91 kJ and -8.78 kJ respectively. The heat of transition of yellow phosphorous to red phosphorous is
 (1) -18.69 kJ (2) $+1.13 \text{ kJ}$
 (3) $+18.69 \text{ kJ}$ (4) -1.13 kJ
- 168.** For the change $\text{C}(\text{diamond}) \longrightarrow \text{C}(\text{graphite})$; $\Delta H = -1.89 \text{ KJ}$, if 6 g of diamond and 6g of graphite are seperately burnt to yield CO_2 the heat liberated in first case is :
 (1) Less than in the second case by 1.89 kJ
 (2) Less than in the second case by 11.34 kJ
 (3) Less than in the second case by 14.34 kJ
 (4) More than in the second case by 0.945 kJ

- 169.** $2\text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \longrightarrow 2\text{CO}_{2(\text{g})} + X \text{ kJ}$
 In the above equation X kJ refers to :
 (1) Heat of formation of CO_2
 (2) Heat of vapourisation
 (3) Heat of reaction
 (4) Heat of sublimation

- 170.** Which of the following reactions represents ΔH (hydration) :-
 (1) $\text{CuSO}_4(\text{s}) + (\text{aq}) \rightarrow \text{CuSO}_4(\text{aq})$; $\Delta H = -x \text{ kJ}$
 (2) $\text{BaCl}_2(\text{s}) + 2\text{H}_2\text{O}(\ell) \rightarrow \text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$;
 $\Delta H = -x' \text{ kJ}$
 (3) $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\ell) + (\text{aq}) \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{aq})$;
 $\Delta H = -y' \text{ kJ}$
 (4) None of the above

- 171.** ΔH for the reaction, $\text{I}_{(\text{g})} + \text{I}_{(\text{g})} \rightarrow \text{I}_{2(\text{g})}$ will be:-
 (1) Zero (2) -ve (3) +ve (4) ∞

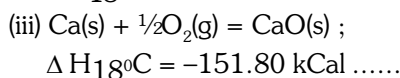
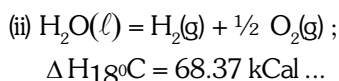
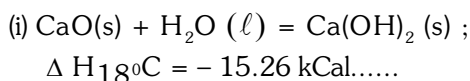
- 172.** Given that :
 $\text{A}(\text{s}) \rightarrow \text{A}(\ell)$; $\Delta H = x$, $\text{A}(\ell) \rightarrow \text{A}(\text{g}) - y$
 The heat of sublimation of A will be:-
 (1) $x + y$ (2) $x - y$
 (3) x or y (4) $-(x + y)$

HESS LAW

- 173.** The enthalpy change of a reaction does not depend on
 (1) State of reactants and products
 (2) Nature of reactants and products
 (3) Different intermediate reactions
 (4) Initial and final enthalpy change of reaction
- 174.** From the thermochemical reactions,
 $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}$; $\Delta H = -110.5 \text{ kJ}$
 $\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2$; $\Delta H = -283.2 \text{ kJ}$
 the heat of reaction of $\text{C}(\text{graphite}) + \text{O}_2 \longrightarrow \text{CO}_2$ is :
 (1) 393.7 kJ
 (2) -393.7 kJ
 (3) -172.7 kJ
 (4) $+172.7 \text{ kJ}$
- 175.** If $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$; $\Delta H = -68.39 \text{ kCal}$
 $\text{K} + \text{H}_2\text{O} + \text{water} \longrightarrow \text{KOH}(\text{aq}) + \frac{1}{2}\text{H}_2$;
 $\Delta H = -48.0 \text{ kCal}$
 $\text{KOH} + \text{water} \longrightarrow \text{KOH}(\text{aq})$ $\Delta H = -14.0 \text{ kCal}$
 the heat of formation of KOH is -
 (1) $-68.39 + 48 - 14.0$
 (2) $-68.39 - 48.0 + 14.0$
 (3) $+68.39 - 48.0 + 14.0$
 (4) $+68.39 + 48.0 - 14.0$

- 176.** Given $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 94.2 \text{ kCal}$
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) + 68.3 \text{ kCal}$
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 210.8 \text{ kCal}$
 The heat of formation of methane in Kcal will be
 (1) -45.9 (2) -47.8
 (3) -20.0 (4) -47.3

- 177.** From the following data, the heat of formation of $\text{Ca(OH)}_2(\text{s})$ at 18°C is kCal.



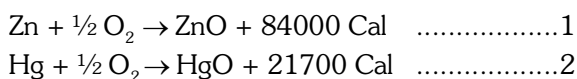
- (1) -98.69 (2) -235.43
 (3) 194.91 (4) 98.69

- 178.** If, $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl(g)} ; \Delta H^\circ = -44 \text{ kCal}$
 $2\text{Na(s)} + 2\text{HCl(g)} \longrightarrow 2\text{NaCl(s)} + \text{H}_2(\text{g})$;
 $\Delta H = -152 \text{ kCal}$
 Then, $\text{Na(s)} + 0.5 \text{ Cl}_2(\text{g}) \longrightarrow \text{NaCl(s)} ; \Delta H^\circ = ?$
 (1) 108 kCal (2) 196 kCal
 (3) -98 kCal (4) 54 kCal

- 179.** (i) $\text{S(s)} + \frac{3}{2}\text{O}_2(\text{g}) = \text{SO}_3(\text{g}) + 2x \text{ kCal}$
 (ii) $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{SO}_3(\text{g}) + y \text{ kCal}$
 Calculate the heat of formation of SO_2 :
 (1) $(2x + y)$ (2) $-(2x - y)$
 (3) $x + y$ (4) $2x / y$

- 180.** If $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2$; $\Delta H = -298.2$
 $\text{SO}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{SO}_3$; $\Delta H = -98.7$
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$; $\Delta H = -130.2$
 $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$; $\Delta H = -287.3$
 Then the enthalpy of formation of H_2SO_4 at 298 K is -
 (1) -814.4 kJ (2) -650.3 kJ
 (3) -320.5 kJ (4) -433.5 kJ

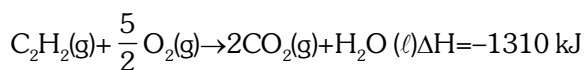
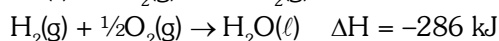
- 181.** Given that :



The heat of reaction (ΔH) for,
 $\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$ is :-

- (1) 105700 Cal
 (2) 62300 Cal
 (3) -105700 Cal
 (4) -62300 Cal

- 182.** Given that -

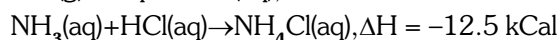
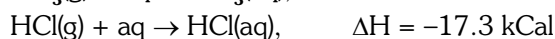
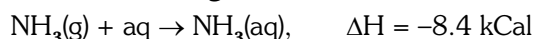


Heat of formation of acetylene is :-

- (1) + 1802 kJ (2) - 1802 kJ
 (3) - 800 kJ (4) + 237 kJ

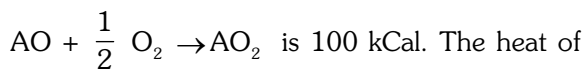
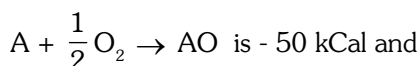
- 183.** Find the heat change in the reaction :
 $\text{NH}_3(\text{g}) + \text{HCl(g)} \rightarrow \text{NH}_4\text{Cl(s)}$

from the following data



- (1) -42.1 (2) -34.3
 (3) +34.3 (4) +42.1

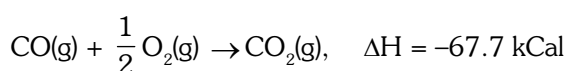
- 184.** The heat of reaction for



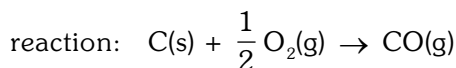
reaction for $\text{A} + \text{O}_2 \rightarrow \text{AO}_2$ is:-

- (1) -50 kCal (2) +50 kCal
 (3) 100 kCal (4) 150 kCal

- 185.** $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 94.0 \text{ kCal}$

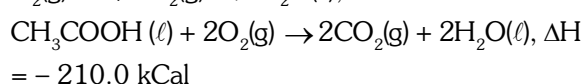
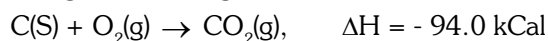


from the above reactions find how much heat (kCal mole^{-1}) would be produced in the following



- (1) 20.6 (2) 26.3
 (3) 44.2 (4) 161.6

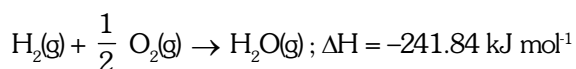
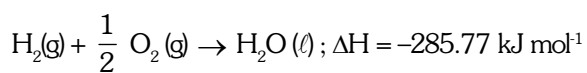
- 186.** Using the following thermochemical data:



The heat of formation of acetic acid is:-

- (1) 116.0 kCal (2) -116.0 kCal
 (3) -114.0 kCal (4) +114.0 kCal

187. The enthalpy of vapourisation of liquid water using the data:



(1) + 43.93 kJ mol⁻¹ (2) - 43.93 kJ mol⁻¹

(3) + 527.61 kJ mol⁻¹ (4) - 527.61 kJ mol⁻¹

188. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\ell); \Delta H_{298\text{K}} = -68.32 \text{ kCal}$. Heat of vapourisation of water at 1 atm and 25°C is 10.52 kCal. The standard heat of formation (in kCal) of 1 mole of water vapour at 25°C is

(1) 10.52 (2) -78.84

(3) +57.80 (4) -57.80

189. The heat of solution of anhydrous CuSO_4 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are - 15.89 and 2.80 kCal mol⁻¹ respectively. What will be the heat of hydration of anhydrous CuSO_4 ?

(1) -18.69 kCal (2) 18.69 kCal

(3) -28.96 kCal (4) 28.96 kCal

190. One mole of anhydrous salt AB dissolves in water and liberates 21.0 J mol⁻¹ of heat. The value of $\Delta H_{(\text{hydration})}$ of AB is -29.4 J mol⁻¹. The heat of dissolution of hydrated salt $\text{AB} \cdot 2\text{H}_2\text{O}(\text{s})$ is -

(1) 50.4 J mol⁻¹

(2) 8.4 J mol⁻¹

(3) -50.4 J mol⁻¹

(5) -8.4 J mol⁻¹

191. Which of the following expressions is true:-

(1) $H_f^0(\text{CO}, \text{g}) = \frac{1}{2} \Delta H_f^0(\text{CO}_2, \text{g})$

(2) $\Delta H_f^0(\text{CO}, \text{g}) = \Delta H_f^0(\text{C}, \text{graphite}) + \frac{1}{2} \Delta H_f^0(\text{O}_2, \text{g})$

(3) $\Delta H_f^0(\text{CO}, \text{g}) = \Delta H_f^0(\text{CO}_2, \text{g}) - \frac{1}{2} \Delta H_f^0(\text{O}_2, \text{g})$

(4) $\Delta H_f^0(\text{CO}, \text{g}) = \Delta H_{\text{comb}}^0(\text{C}, \text{graphite}) - \Delta H_{\text{comb}}^0(\text{CO}, \text{g})$

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	4	4	3	3	1	4	1	1	1	4	2	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	4	4	4	1	1	4	3	1	3	2	2	4	2	2	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	1	2	1	1	2	3	4	2	2	2	3	1	4	1
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	2	3	4	3	4	3	1	1	2	3	1	3	1	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	2	2	1	1	4	2	4	3	2	4	2	1	2	4	3
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	2	3	3	4	4	1	2	2	2	4	1	4	1	4	1
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
Ans.	1	2	3	1	3	4	1	2	4	3	2	4	2	3	1
Que.	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
Ans.	2	4	4	4	2	2	2	4	4	1	3	2	2	3	2
Que.	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135
Ans.	3	4	4	4	1	3	2	2	2	3	1	3	3	3	2
Que.	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150
Ans.	2	2	2	3	1	3	2	2	1	2	1	1	4	1	1
Que.	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165
Ans.	2	4	2	3	2	3	2	3	4	3	3	1	1	3	2
Que.	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180
Ans.	4	4	4	3	2	2	1	3	2	2	3	2	3	2	1
Que.	181	182	183	184	185	186	187	188	189	190	191				
Ans.	4	4	1	2	2	3	1	4	1	2	4				

AIPMT/NEET & AIIMS (2006-2018)

AIPMT 2006

1. Identify the correct statement for change of Gibbs energy for a system (ΔG_{system}) at constant temperature and pressure.
 - (1) If $\Delta G_{\text{system}} > 0$, the process is spontaneous.
 - (2) If $\Delta G_{\text{system}} = 0$, the system has attained equilibrium.
 - (3) If $\Delta G_{\text{system}} = 0$, the system is still moving in a particular direction.
 - (4) If $\Delta G_{\text{system}} < 0$, the process is not spontaneous.
2. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?
 - (1) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2 \text{HBr}(\text{g})$
 - (2) $\text{C}(\text{s}) + 2 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
 - (3) $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - (4) $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$
3. The enthalpy and entropy change for reaction $\text{Br}_2(\ell) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{BrCl}(\text{g})$ are 30 kJ mol^{-1} and $105 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is
 - (1) 285.7 K
 - (2) 273 K
 - (3) 450 K
 - (4) 300 K
4. The enthalpy of hydrogenation of cyclohexene is $-119.5 \text{ kJ mol}^{-1}$. If resonance energy of benzene is $-150.4 \text{ kJ mol}^{-1}$, its enthalpy of hydrogenation would be
 - (1) $-508.9 \text{ kJ mol}^{-1}$
 - (2) $-208.1 \text{ kJ mol}^{-1}$
 - (3) $-269.9 \text{ kJ mol}^{-1}$
 - (4) $-358.5 \text{ kJ mol}^{-1}$

AIIMS 2006

5. When you make ice cubes, the entropy of water
- (1) Does not change
 - (2) Increases
 - (3) Decreases
 - (4) May either increase or decrease depending on the process used
6. For a phase change $\text{H}_2\text{O}(\ell) \xrightleftharpoons{0^\circ\text{C } 1\text{ bar}} \text{H}_2\text{O}(\text{s})$
- (1) $\Delta G = 0$
 - (2) $\Delta S = 0$
 - (3) $\Delta H = 0$
 - (4) $\Delta U = 0$
7. For a spontaneous process the correct statement is –
- (1) Entropy of the system always increase
 - (2) Free energy of the system always increases
 - (3) Total entropy change is always negative
 - (4) Total entropy change is always positive

8. The enthalpy change (ΔH) for the reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ is -92.38 kJ at 298 K . The internal energy change ΔU at 298 K is
- (1) -92.38 kJ (2) -87.42 kJ
(3) -97.34 kJ (4) -89.9 kJ

AIPMT 2007

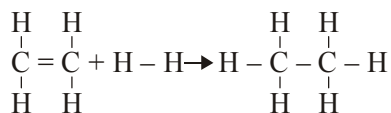
- 9.** Consider the following reactions :
- $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} = \text{H}_2\text{O}_{(\text{l})}, \Delta H = -X_1 \text{ kJ mol}^{-1}$
 - $\text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} = \text{H}_2\text{O}_{(\text{l})}, \Delta H = -X_2 \text{ kJ mol}^{-1}$
 - $\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} = \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})} - X_3 \text{ kJ mol}^{-1}$
 - $\text{C}_2\text{H}_{2(\text{g})} + \frac{5}{2} \text{O}_{2(\text{g})} = 2\text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})} + X_4 \text{ kJ mol}^{-1}$
- Enthalpy of formation of $\text{H}_2\text{O}_{(\text{l})}$ is :
- $+X_1 \text{ kJ mol}^{-1}$
 - $-X_2 \text{ kJ mol}^{-1}$
 - $+X_3 \text{ kJ mol}^{-1}$
 - $-X_4 \text{ kJ mol}^{-1}$
- 10.** Given that bond energies of H-H and Cl-Cl are $x \text{ kJ mol}^{-1}$ and 240 kJ mol^{-1} respectively and ΔH for HCl is -90 kJ mol^{-1} . Bond enthalpy of HCl is
- 245 kJ mol^{-1}
 - 290 kJ mol^{-1}
 - 380 kJ mol^{-1}
 - 425 kJ mol^{-1}

AIPMT 2008

- 11.** Bond dissociation enthalpy of H_2 , Cl_2 and HCl are 434, 242 and 431 kJmol^{-1} respectively. Enthalpy of formation of HCl is:-
- (1) -93 kJmol^{-1}
 - (2) 245 kJmol^{-1}
 - (3) 93 kJmol^{-1}
 - (4) -245 kJmol^{-1}
- 12.** For the gas phase reaction,
- $$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$
- Which of the following conditions are correct ?
- (1) $\Delta H < 0$ and $\Delta S < 0$
 - (2) $\Delta H > 0$ and $\Delta S < 0$
 - (3) $\Delta H = 0$ and $\Delta S < 0$
 - (4) $\Delta H > 0$ and $\Delta S > 0$
- 13.** Which of the following are not state functions ?
- | | |
|-------------|---------------|
| (I) $q + w$ | (II) q |
| (III) w | (IV) $H - TS$ |
- (1) (I), (II) and (III)
 - (2) (II) and (III)
 - (3) (I) and (IV)
 - (4) (II), (III) and (IV)

AIPMT 2009

14. From the following bond energies :-
 H – H bond energy : $431.37 \text{ kJ mol}^{-1}$
 C = C bond energy : $606.10 \text{ kJ mol}^{-1}$
 C – C bond energy : $336.49 \text{ kJ mol}^{-1}$
 C – H bond energy : $410.50 \text{ kJ mol}^{-1}$
 Enthalpy for the reaction,



will be :-

- (1) $553.0 \text{ kJ mol}^{-1}$ (2) $1523.6 \text{ kJ mol}^{-1}$
 (3) $-243.6 \text{ kJ mol}^{-1}$ (4) $-120.0 \text{ kJ mol}^{-1}$
15. The values of ΔH and ΔS for the reaction,
 $\text{C}_{(\text{graphite})} + \text{CO}_{2(\text{g})} \rightarrow 2\text{CO}_{(\text{g})}$ are 170 kJ and 170 JK^{-1} , respectively. This reaction will be spontaneous at :-
 (1) 510 K (2) 710 K
 (3) 910 K (4) 1110 K

AIPMT 2010

16. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ JK}^{-1}\text{mol}^{-1}$, respectively. The temperature when Gibbs energy change (ΔG) for this transformation will be zero, is :-
 (1) 393.4 K (2) 373.4 K
 (3) 293.4 K (4) 273.4 K
17. Three moles of an ideal gas expanded spontaneously into vacuum. The work done will be :-
 (1) 3 Joule (2) 9 Joule
 (3) Zero (4) Infinite
18. The following two reactions are known :
 $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$; $\Delta H = -26.8 \text{ kJ}$
 $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$; $\Delta H = -16.5 \text{ kJ}$
 Correct target equation is
 $\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \rightarrow 2\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$, $\Delta H = ?$
 (1) -43.3 kJ (2) -10.3 kJ
 (3) $+6.2 \text{ kJ}$ (4) $+10.3 \text{ kJ}$
19. Standard entropies of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ JK}^{-1}\text{mol}^{-1}$ respectively. For the reaction
 $\frac{1}{2}\text{X}_2 + \frac{3}{2}\text{Y}_2 \rightleftharpoons \text{XY}_3$, $\Delta H = -30 \text{ kJ}$ to be at equilibrium, the temperature should be :-
 (1) 500 K (2) 750 K
 (3) 1000 K (4) 1250 K

AIIMS 2010

20. Intensive property is :-
 (1) Moles (2) Volume
 (3) Enthalpy (4) Temperature
21. In which of following there is decrease in entropy :-
 (1) When temperature is raised from 30 K to 150 K .
 (2) When NaHCO_3 changes into $\text{Na}_2\text{CO}_3 (\text{s})$ and $\text{CO}_2(\text{g})$
 (3) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$
 (4) Liquid crystallises into a solid
22. Which of the following is not a state function:-
 (1) Pressure (2) Volume
 (3) Temperature (4) Heat

AIPMT Pre. 2011

23. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C , the entropy changes for the process would be:
 (1) $10 \text{ J mol}^{-1} \text{ K}^{-1}$
 (2) $1.0 \text{ J mol}^{-1} \text{ K}^{-1}$
 (3) $0.1 \text{ J mol}^{-1} \text{ K}^{-1}$
 (4) $100 \text{ J mol}^{-1} \text{ K}^{-1}$
24. Enthalpy change for the reaction,
 $4\text{H}_{(\text{g})} \rightarrow 2\text{H}_{2(\text{g})}$ is -869.6 kJ
 The dissociation energy of H–H bond is :
 (1) -434.8 kJ (2) 869.6 kJ
 (3) $+434.8 \text{ kJ}$ (4) $+217.4 \text{ kJ}$
25. Which of the following correct option for free expansion of an ideal gas under adiabatic condition ?
 (1) $q = 0$, $\Delta T \neq 0$, $w = 0$
 (2) $q \neq 0$, $\Delta T = 0$, $w = 0$
 (3) $q = 0$, $\Delta T = 0$, $w = 0$
 (4) $q = 0$, $\Delta T < 0$, $w \neq 0$

AIPMT Msins 2011

26. Consider the following processes :-
 $\Delta H(\text{kJ mol}^{-1})$
- | | |
|--|------|
| $\frac{1}{2} \text{A} \rightarrow \text{B}$ | +150 |
| $3\text{B} \rightarrow 2\text{C} + \text{D}$ | -125 |
| $\text{E} + \text{A} \rightarrow 2\text{D}$ | +350 |
- For $\text{B} + \text{D} \rightarrow \text{E} + 2\text{C}$, ΔH will be :
 (1) 325 kJ mol^{-1}
 (2) 525 kJ mol^{-1}
 (3) -175 kJ mol^{-1}
 (4) -325 kJ mol^{-1}

AIIMS 2011

- 27.** The enthalpy of formation of CO(g) , $\text{CO}_2\text{(g)}$, $\text{N}_2\text{O(g)}$ and $\text{N}_2\text{O}_4\text{(g)}$ is -110 , -393 , $+81$ and 10 kJ mol^{-1} respectively. For the reaction $\text{N}_2\text{O}_4\text{(g)} + 3\text{CO(g)} \rightarrow \text{N}_2\text{O(g)} + 3\text{CO}_2\text{(g)}$. ΔH_r is
- (1) -212 (2) $+212$
(3) $+778$ (4) -778
- 28.** For adiabatic process which is correct-
- (1) $\Delta T = 0$ (2) $w = 0$
(3) $q = 0$ (4) $\Delta U = 0$
- 29.** Which of the following is not thermodynamic function-
- (1) Internal energy (2) work done
(3) Enthalpy (4) Entropy
- 30.** Which of the following is intensive property-
- (1) Enthalpy (2) Entropy
(3) specific heat (4) volume

AIPMT Pre. 2012

- 31.** In which of the following reactions, standard reaction entropy change (ΔS°) is positive and standard Gibb's energy change (ΔG°) decreases sharply with increasing temperature?
- (1) $\text{Mg(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{MgO(s)}$
- (2) $\frac{1}{2} \text{C graphite} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \frac{1}{2} \text{CO}_2(\text{g})$
- (3) $\text{C graphite} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)}$
- (4) $\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- 32.** Standard enthalpy of vapourisation $\Delta_{\text{vap}}H^\circ$ for water at 100°C is 40.66 kJmol^{-1} . The internal energy of vaporisation of water at 100°C (in kJmol^{-1}) is
- (1) $+43.76$ (2) $+40.66$
(3) $+37.56$ (4) -43.76
- 33.** The enthalpy of fusion of water is $1.435 \text{ kCal mol}^{-1}$. The molar entropy change for the melting of ice at 0°C is:
- (1) $5.260 \text{ Cal mol}^{-1} \text{ K}^{-1}$
(2) $0.526 \text{ Cal mol}^{-1} \text{ K}^{-1}$
(3) $10.52 \text{ Cal mol}^{-1} \text{ K}^{-1}$
(4) $21.04 \text{ Cal mol}^{-1} \text{ K}^{-1}$

AIIMS 2012

- 34.** At equilibrium which is correct :-
- (1) $\Delta G = 0$ (2) $\Delta S = 0$
(3) $\Delta H = 0$ (4) $\Delta G^\circ = 0$
- 35.** Heat of atomisation of CH_4 is 360 kJ mol^{-1} and C_2H_6 has 620 kJ mol^{-1} . Then bond dissociation energy of C–C bond is :-
- (1) 170 kJ mol^{-1}
(2) 50 kJ mol^{-1}
(3) 80 kJ mol^{-1}
(4) 220 kJ mol^{-1}

AIIMS 2013

- 36.** Which thermodynamic parameter does not depend only on initial and final state ?
- (1) q at constant pressure
 - (2) q at constant volume
 - (3) w at adiabatic
 - (4) w at isothermal

AIPMT 2014

- 37.** For the reaction : $\text{X}_2\text{O}_4(\ell) \longrightarrow 2\text{XO}_2(\text{g})$
 $\Delta U = 2.1 \text{ kCal}$, $\Delta S = 20 \text{ cal K}^{-1}$ at 300 K
Hence ΔG is :-
(1) 2.7 kCal (2) -2.7 kCal
(3) 9.3 kCal (4) -9.3 kCal

AIIMS 2014

- 38.** $\Delta S_{\text{Total}} = -40 \text{ kJ mol}^{-1} \times \text{K}^{-1}$
 $\Delta H_{\text{sys}} = 2000 \text{ kJ mol}^{-1}$
 $T = 400 \text{ K}$
 Calculate value of ΔS_{system} ?
 (1) $-35 \text{ kJ mol}^{-1} \times \text{K}$
 (2) $-5 \text{ kJ mol}^{-1} \times \text{K}$
 (3) $-40 \text{ kJ mol}^{-1} \times \text{K}$
 (4) $+5 \text{ kJ mol}^{-1} \times \text{K}$

AIPMT 2015

- 39.** Which of the following statements is **correct** for a reversible process in a state of equilibrium ?
- (1) $\Delta G = 2.30 RT \log K$
 - (2) $\Delta G^\circ = -2.30 RT \log K$
 - (3) $\Delta G^\circ = 2.30 RT \log K$
 - (4) $\Delta G = -2.30 RT \log K$

Re-AIPMT 2015

- 40.** The heat of combustion of carbon to CO_2 is $-393.5 \text{ kJ mol}^{-1}$. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is:
- (1) -630 kJ (2) -3.15 kJ
(3) -315 kJ (4) $+315 \text{ kJ}$

AIIMS 2015

41. $A_{2(g)} \rightarrow 2A(g)$ and for this reaction on increasing T value of K_{eq} increases then for this reaction is
 (1) ΔH = positive; ΔS = positive
 (2) ΔH = negative; ΔS = negative
 (3) ΔH = positive; ΔS = negative
 (4) ΔH = negative ; ΔS = positive
42. For endothermic reaction when change in entropy is negative, then reaction is
 (1) not possible at any temperature
 (2) possible at low temperature
 (3) possible at all temperature
 (4) possible at high temperature
43. For the formation of CH_4 of $\Delta U^0 = -x \text{ kJ mol}^{-1}$ then what will be value of $\Delta H^0 \text{ kJ mol}^{-1}$.
 (1) $-x - RT$ (2) $-x + 2RT$
 (3) $-x + RT$ (4) $-2x - 4RT$

NEET-I 2016

44. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
 (1) $\Delta H > 0$ and $\Delta S > 0$
 (2) $\Delta H > 0$ and $\Delta S < 0$
 (3) $\Delta H < 0$ and $\Delta S > 0$
 (4) $\Delta H < 0$ and $\Delta S < 0$

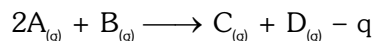
NEET-II 2016

45. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f , the entropy change is given by
 (1) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$ (2) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$
 (3) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$ (4) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$

AIIMS 2016

46. For a given reaction at 298K
 $2A_{(g)} + B_{(g)} \longrightarrow 2C_{(g)}$
 If $\Delta U^0 = -10 \text{ kJ mol}^{-1}$ $\Delta S^0 = -45 \text{ J K}^{-1} \text{ mol}^{-1}$
 Then what will be value of ΔG^0 for above reaction?
 (1) $+930 \text{ J mol}^{-1}$ (2) $-25890 \text{ J mol}^{-1}$
 (3) 2000 J mol^{-1} (4) 8500 J mol^{-1}
47. Calculate work done during isothermal reversible process when 5 mol ideal gas is expanded so that its volume is doubled at 400K?
 (1) -11.5 kJ (2) -344 kJ
 (3) 0 (4) -2.8 kJ

48. For a reaction



Where ΔS is -ve; then which of the following is correct?

- (1) reaction is possible only at low temperature
 (2) reaction is possible only at high temperature
 (3) reaction is never possible
 (4) reaction is possible at all temperature
49. If 400 kJ work is done by the system and 150 kJ heat is given to system then what will be effect on internal energy?
 (1) Increases by 250 kJ (2) Decreases by 250 kJ
 (3) Increases by 600 kJ (4) Decreases by 600 kJ
50. For gas 'A' in a calorimeter heat evolved is 250 kJ mol^{-1} . For 0.2 mol of A, temperature rise from 298 K to 300 K. Find out heat capacity of calorimeter:-
 (1) 12.5 kJ K^{-1} (2) 25 kJ K^{-1}
 (3) 50 kJ K^{-1} (4) 100 kJ K^{-1}

NEET(UG) 2017

51. For a given reaction, $\Delta H = 35.5 \text{ kJ mol}^{-1}$ and $\Delta S = 83.6 \text{ J K}^{-1} \text{ mol}^{-1}$. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with temperature)
 (1) $T > 425 \text{ K}$ (2) All temperatures
 (3) $T > 298 \text{ K}$ (4) $T < 425 \text{ K}$
52. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be:-
 (1) -500 J (2) -505 J
 (3) $+505 \text{ J}$ (4) 1136.25 J

AIIMS 2017

53. For an isolated system :-
 (1) $q = 0$ and $w = 0$
 (2) $q \neq 0$ and $w = 0$
 (3) $q = 0$ and $w \neq 0$
 (4) $q \neq 0$ and $w \neq 0$
54. An ideal gas is expanded against 42 Pascal external pressure by 10 m^3 . If 350 J heat is given to the system then ΔU of system (in J) will be :-
 (1) -50 J (2) -70 J
 (3) $+50 \text{ J}$ (4) $+70 \text{ J}$

55. The heat of combustion of C_4H_{10} is $-2878 \text{ kJ mol}^{-1}$. If the heats of formation of CO_2 and H_2O are $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ then the heat of formation of C_4H_{10} is :-
 (1) $-125.0 \text{ kJ mol}^{-1}$ (2) $126.75 \text{ kJ mol}^{-1}$
 (3) $-402.5 \text{ kJ mol}^{-1}$ (4) $402.5 \text{ kJ mol}^{-1}$
56. During adiabatic expansion of an ideal gas in vacuum :-
 (1) $q = 0$ and $\Delta U \neq 0$ (2) $q \neq 0$ and $\Delta U \neq 0$
 (3) $q \neq 0$ and $\Delta U \neq 0$ (4) $q = 0$ and $\Delta U = 0$

NEET(UG) 2018

57. The bond dissociation energies of X_2 , Y_2 and XY are in the ratio of $1 : 0.5 : 1$. ΔH for the formation of XY is -200 kJ mol^{-1} . The bond dissociation energy of X_2 will be
 (1) 200 kJ mol^{-1} (2) 100 kJ mol^{-1}
 (3) 800 kJ mol^{-1} (4) 400 kJ mol^{-1}

AIIMS 2018

58. Which of the following pair is an example of extensive property :-
 (1) P and T (2) C_p and E
 (3) E and V (4) T and V
59. An ideal gas expands from 2 L to 10 L adiabatically against a constant external pressure of 10 atm . Then find the change in internal energy:-
 (1) -80 L-atm (2) Zero
 (3) 80 L-atm (4) 40 L-atm
60. The correct set of intensive properties :-
 (1) P , T (2) V , T (3) P , V (4) V , E

61. Which of the following always increases for spontaneous process :-

(1) ΔH_{system} (2) ΔS_{system}

(3) $\Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$

(4) $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$

62. 1 mole of ideal gas (A) expands from 2 lit to 4 lit through reversible isothermal process. 3 mol of another ideal gas (B) expands from 2 lit to $x \text{ lit}$ and does the same amount of work as done by gas (A) the value of x is :- (Consider that both the gases temperature is same)

(1) 2 (2) 8 (3) $(8)^{1/3}$ (4) $(4)^{2/3}$

63. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ $\Delta H = -2220 \text{ kJ mol}^{-1}$
 $C_3H_6 + H_2 \rightarrow C_3H_8$ $\Delta H = -124 \text{ kJ mol}^{-1}$



Then find heat of combustion of C_3H_6

(1) $-2059 \text{ kJ mol}^{-1}$ (2) 2059 kJ mol^{-1}
 (3) $-4118 \text{ kJ mol}^{-1}$ (4) $+4118 \text{ kJ mol}^{-1}$

64. A rigid container contain 1 kg N_2 gas at 400 K if final temperature is 800 K then find change in entropy ($J K^{-1}$) [Given : $C_p = 29.099 \text{ joule}$]

(1) 512.86 (2) 1025.736
 (3) 256.43 (4) 170.9

65. Heat of formation of ethane $-20.2 \text{ kCal mol}^{-1}$ and heat of atomisation of C and H_2 are $179.2 \text{ kCal mol}^{-1}$ and $52.1 \text{ kCal mol}^{-1}$ respectively. If bond energy of $C-H$ bond is $73.3 \text{ kCal mol}^{-1}$. Then calculate approx. B.E. of $C-C$:-

(1) 96 kCal mol^{-1} (2) $230 \text{ kCal mol}^{-1}$
 (3) 88 kCal mol^{-1} (4) $540 \text{ kCal mol}^{-1}$

EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	1	1	2	3	1	4	2	2	4	1	4	2	4	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	3	3	2	4	4	4	4	3	3	3	4	3	2	3
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	1	1	3	4	2	1	2	3	1	1	1	3	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	1	1	3	2	2	1	2	1	2	1	4	3	3	1	1
Que.	61	62	63	64	65										
Ans.	3	4	1	1	1										

EXERCISE-III (Analytical Questions)

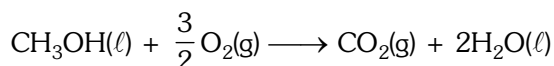
- For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w correspond to :-
 (1) $\Delta U < 0$, $w=0$ (2) $\Delta U < 0$, $w < 0$
 (3) $\Delta U > 0$, $w=0$ (4) $\Delta U > 0$, $w > 0$
- Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ?
 (1) $\Delta H < \Delta U$ (2) $\Delta H > \Delta U$
 (3) $\Delta H = 0$ (4) $\Delta H = \Delta U$
- For a reversible process at $T = 300K$, the volume is increased from $V_i = 1L$ to $V_f = 10L$. Calculate ΔH if the process is isothermal -
 (1) 11.47 kJ (2) 4.98 kJ
 (3) 0 (4) -11.47 kJ
- Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and $100^\circ C$, (Given : Molar enthalpy of vapourisation of water at 1 bar and $373 K = 41 kJ mol^{-1}$ and $R = 8.3 J mol^{-1} K^{-1}$ will be) :-
 (1) $4.100 kJ mol^{-1}$ (2) $3.7904 kJ mol^{-1}$
 (3) $37.904 kJ mol^{-1}$ (4) $41.00 kJ mol^{-1}$
- A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of $37.0^\circ C$. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :-
 ($R = 8.314 J mol^{-1} K^{-1}$) ($\ln 7.5 = 2.01$)
 (1) $q = + 208 J$, $w = - 208 J$
 (2) $q = - 208 J$, $w = - 208 J$
 (3) $q = - 208 J$, $w = + 208 J$
 (4) $q = + 208 J$, $w = + 208 J$
- The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of $10 dm^3$ to a volume of $100 dm^3$ at $27^\circ C$ is :-
 (1) $32.3 J mol^{-1} K^{-1}$ (2) $42.3 J mol^{-1} K^{-1}$
 (3) $38.3 J mol^{-1} K^{-1}$ (4) $35.8 J mol^{-1} K^{-1}$

Check Your Understanding

- The value of enthalpy change (ΔH) for the reaction $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ at $27^\circ C$ is $-1366.5 kJ mol^{-1}$. The value of internal energy change for the above reaction at this temperature will be :-
 (1) $-1371.5 kJ$ (2) $-1369.0 kJ$
 (3) $-1364.0 kJ$ (4) $-1361.5 kJ$
- For the process $H_2O_{(l)} (1 \text{ bar}, 373K) \rightarrow H_2O_{(g)} (1 \text{ bar}, 373K)$, the correct set of thermodynamic parameters is :
 (1) $\Delta G = 0$, $\Delta S = +ve$
 (2) $\Delta G = 0$, $\Delta S = -ve$
 (3) $\Delta G = +ve$, $\Delta S = 0$
 (4) $\Delta G = -ve$, $\Delta S = +ve$
- Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
 (1) endothermic and decreasing disorder
 (2) exothermic and increasing disorder
 (3) endothermic and increasing disorder
 (4) exothermic and decreasing disorder
- The conversion A to B is carried out by the following path :

$$\begin{array}{ccc} C & \longrightarrow & D \\ \uparrow & & \downarrow \\ A & & B \end{array}$$
 Given : $\Delta S_{(A \rightarrow C)} = 50 \text{ e.u.}$,
 $\Delta S_{(C \rightarrow D)} = 30 \text{ e.u.}$, $\Delta S_{(B \rightarrow D)} = 20 \text{ e.u.}$
 where e.u. is entropy unit then $\Delta S_{(A \rightarrow B)}$ is
 (1) $+ 100 \text{ e.u.}$
 (2) $+ 60 \text{ e.u.}$
 (3) $- 100 \text{ e.u.}$
 (4) $- 60 \text{ e.u.}$
- In conversion of lime-stone to lime,
 $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
 the values of ΔH° and ΔS° are $+179.1 kJ mol^{-1}$ and $160.2 J K^{-1}$ respectively at $298 K$ and 1 bar . Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-
 (1) $1008 K$
 (2) $1200 K$
 (3) $845 K$
 (4) $1118 K$

- 12.** In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

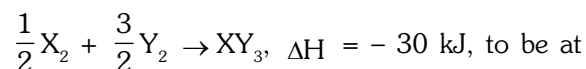


At 298 K standard Gibbs energies of formation for $\text{CH}_3\text{OH}(\ell)$, $\text{H}_2\text{O}(\ell)$ and $\text{CO}_2(\text{g})$ are -166.2 , -237.2 and $-394.4 \text{ kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be
(1) 90% (2) 97% (3) 80% (4) 87%

- 13.** Identify the correct statement regarding a spontaneous process :-

- (1) For a spontaneous process in an isolated system, the change in entropy is positive
(2) Endothermic processes are never spontaneous
(3) Exothermic processes are always spontaneous
(4) Lowering of energy in the reaction process is the only criterion for spontaneity

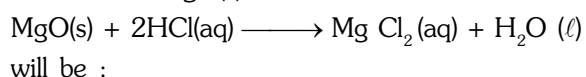
- 14.** Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. For the reaction,



equilibrium, the temperature will be

- (1) 1250 K (2) 500 K (3) 750 K (4) 1000 K

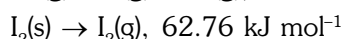
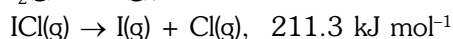
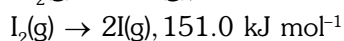
- 15.** The absolute enthalpy of neutralisation of the reaction for $\text{MgO}(\text{s})$:



will be :

- (1) $57.33 \text{ kJ mol}^{-1}$
(2) $-57.33 \text{ kJ mol}^{-1}$
(3) Greater than $-57.33 \text{ kJ mol}^{-1}$
(4) Less than $-57.33 \text{ kJ mol}^{-1}$

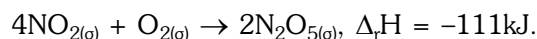
- 16.** The enthalpy changes for the following processes are listed below :



Given that the standard states for iodine and chlorine are $\text{I}_2(\text{s})$ and $\text{Cl}_2(\text{g})$, the standard enthalpy of formation for $\text{ICl}(\text{g})$ is :-

- (1) $-16.8 \text{ kJ mol}^{-1}$ (2) $+16.8 \text{ kJ mol}^{-1}$
(3) $+244.8 \text{ kJ mol}^{-1}$ (4) $-14.6 \text{ kJ mol}^{-1}$

- 17.** Consider the reaction :



If $\text{N}_2\text{O}_{5(\text{s})}$ is formed instead of $\text{N}_2\text{O}_{5(\text{g})}$ in the above reaction, the $\Delta_r H$ value will be :-

(given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1})

- (1) -165 kJ (2) $+54 \text{ kJ}$
(3) $+219 \text{ kJ}$ (4) -219 kJ

- 18.** For complete combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} + 3\text{H}_2\text{O}(\ell)$, the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C . Assuming ideality the Enthalpy of combustion, $\Delta_c H$, for the reaction will be :- ($R = 8.314 \text{ kJ mol}^{-1}$)

- (1) $-1460.50 \text{ kJ mol}^{-1}$
(2) $-1350.50 \text{ kJ mol}^{-1}$
(3) $-1366.95 \text{ kJ mol}^{-1}$
(4) $-1361.95 \text{ kJ mol}^{-1}$

- 19.** If the bond dissociation energies of XY , X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is -200 kJ mol^{-1} . The bond dissociation energy of X_2 will be :-

- (1) 200 kJ mol^{-1} (2) 100 kJ mol^{-1}
(3) 800 kJ mol^{-1} (4) 300 kJ mol^{-1}

- 20.** The standard enthalpy of formation ($\Delta_f H^\circ$) at 298 K for methane, $\text{CH}_4(\text{g})$, is $-74.8 \text{ kJ mol}^{-1}$. The additional information required to determine the average energy for C-H bond formation would be:-

- (1) Latent heat of vapourization of methane
(2) The first four ionization energies of carbon and electron gain enthalpy of hydrogen
(3) The dissociation energy of hydrogen molecule H_2
(4) The dissociation energy of H_2 and enthalpy of sublimation of carbon

- 21.** The standard enthalpy of formation of NH_3 is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N-H bond in NH_3 is :-

- (1) $-1102 \text{ kJ mol}^{-1}$
(2) -964 kJ mol^{-1}
(3) $+352 \text{ kJ mol}^{-1}$
(4) $+1056 \text{ kJ mol}^{-1}$

22. The incorrect expression among the following is :-

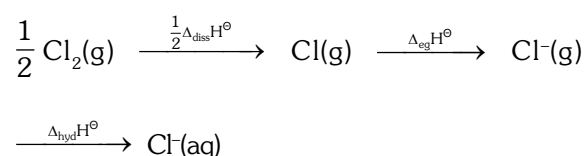
(1) $K = e^{-\Delta G^\circ/RT}$

(2) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

(3) In isothermal process, $W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$

(4) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

23. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:



The energy involved in the conversion of $\frac{1}{2} \text{Cl}_2(\text{g})$ to $\text{Cl}^-(\text{aq})$

(using the data $\Delta_{\text{diss}} H_{\text{Cl}_2}^\circ = 240 \text{ kJ mol}^{-1}$,

$\Delta_{\text{eg}} H_{\text{Cl}}^\circ = -349 \text{ kJ mol}^{-1}$, $\Delta_{\text{hyd}} H_{\text{Cl}^-}^\circ = -381 \text{ kJ mol}^{-1}$)

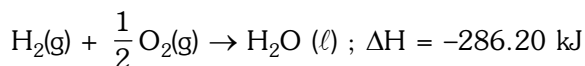
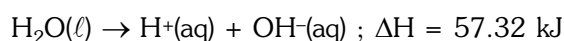
will be:-

(1) -610 kJ mol^{-1} (2) -850 kJ mol^{-1}

(3) $+120 \text{ kJ mol}^{-1}$ (4) $+152 \text{ kJ mol}^{-1}$

24. On the basis of the following thermochemical

data : $\left[\Delta H_f^\circ (H_{(\text{aq})}^+) = 0 \right]$



The value of enthalpy of formation of OH^- ion at 25°C is :-

(1) $+228.88 \text{ kJ}$ (2) -343.52 kJ

(3) -22.88 kJ (4) -228.88 kJ

EXERCISE-III (Analytical Questions)

ANSWER KEY

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

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** There is no reaction known for which ΔG is positive, yet it is spontaneous.
Reason :- For photochemical reactions, ΔG is negative.
 (1) A (2) B (3) C (4) D
- Assertion :-** Absolute value of enthalpy cannot be determined.
Reason :- Enthalpy is defined as $H=E+PV$, and value of internal energy cannot be determined absolutely therefore absolute value of enthalpy can not be determined.
 (1) A (2) B (3) C (4) D
- Assertion :-** When a rubber band is stretched entropy increases.
Reason :- During expansion entropy increases.
 (1) A (2) B (3) C (4) D
- Assertion :-** At constant pressure for the change $H_2O(s) \rightarrow H_2O(g)$ work done is negative.
Reason :- During phase transition work done is always negative.
 (1) A (2) B (3) C (4) D
- Assertion :-** Enthalpy of graphite is lower than that of diamond.
Reason :- Entropy of graphite is greater than that of diamond.
 (1) A (2) B (3) C (4) D
- Assertion :-** The enthalpy of formation of gaseous oxygen molecules at 298K and under a pressure of one atm. is zero.
Reason :- The entropy of formation of gaseous oxygen molecules under the same condition is zero.
 (1) A (2) B (3) C (4) D
- Assertion :-** Many endothermic reactions that are not spontaneous at room temp. becomes spontaneous at high temp.
Reason :- Entropy of the system increases with increase in temperature.
 (1) A (2) B (3) C (4) D
- Assertion :-** Mass, Volume and pressure are extensive properties.
Reason :- Extensive properties depend upon the amount of the substance.
 (1) A (2) B (3) C (4) D
- Assertion :-** For a particular reaction, heat of combustion at constant pressure (q_p) is always greater than that at constant volume (q_v).
Reason :- Combustion reactions are invariably accomplished by increase in no. of moles.
 (1) A (2) B (3) C (4) D
- Assertion :-** At constant temp 0°C and 1atm, the change $H_2O(s) \rightarrow H_2O(l)$ ΔH and ΔE both are zero.
Reason :- During isothermal process H and E both remains constant.
 (1) A (2) B (3) C (4) D
- Assertion :-** The change in internal energy (ΔE) for the vapourization of one mole of water at 1 atm and 373 K is zero.
Reason :- For all isothermal processes $\Delta E=0$
 (1) A (2) B (3) C (4) D
- Assertion:-** Water in liquid state is more stable than ice at room temperature.
Reason:- Water in liquid form has higher entropy than ice.
 (1) A (2) B (3) C (4) D
- Assertion:-** In an isolated system the entropy increases due to spontaneous process.
Reason:- The processes in an isolated system are isothermal.
 (1) A (2) B (3) C (4) D
- Assertion :-** Entropy is always constant for a closed system.
Reason :- Closed system is always reversible
 (1) A (2) B (3) C (4) D

15. **Assertion :-** For an isolated system q is zero.
Reason :- In an isolated system change in U is zero.
 (1) A (2) B (3) C (4) D
16. **Assertion :-** Entropy of system always increases for a spontaneous reaction.
Reason :- Enthalpy of reaction always decreases for spontaneous reaction.
 (1) A (2) B (3) C (4) D
17. **Assertion :-** Catalyst changes Gibbs free energy of system.
Reason :- Catalyst changes preexponential factor of a chemical reaction.
 (1) A (2) B (3) C (4) D
18. **Assertion :-** Entropy increases with increase in temperature of gas.
Reason :- If q_{rev} is same, then entropy of that system is higher for which temperature is higher.
 (1) A (2) B (3) C (4) D
19. **Assertion :-** The value of specific heat at constant pressure is more than that at constant volume.
Reason :- The energy required to raise temperature by a unit at constant pressure is greater because some amount of heat is used in doing work.
 (1) A (2) B (3) C (4) D
20. **Assertion :** Sum of two path functions is always path function.
Reason : Sum of path function depends on path followed.
 (1) A (2) B (3) C (4) D
21. **Assertion :-** Heat is not a state thermodynamic property.
Reason :- Heat given in a process depends on its type.
 (1) A (2) B (3) C (4) D
22. **Assertion :-** For ideal gas in a closed container with adiabatic walls, temperature decreases when work is done by the system.
Reason :- Internal energy is used in work done by the system.
 (1) A (2) B (3) C (4) D

23. **Assertion :-** Adiabatic free expansion of an ideal gas is irreversible.
Reason :- $PV = \text{constant}$ for reversible adiabatic expansion.
 (1) A (2) B (3) C (4) D
24. **Assertion :-** Internal energy at particular temperature does not depend on volume.
Reason :- State function does not depend on volume.
 (1) A (2) B (3) C (4) D
25. **Assertion :-** Graphite is thermodynamically most stable allotrope of carbon.
Reason :- Standard heat of formation of graphite is $+1.9 \text{ kJ/mol}$.
 (1) A (2) B (3) C (4) D
26. **Assertion :** A gas expands from (P_1, V_1, T_1) to (P_2, V_2, T_2) the work done in 2 steps will be more than, if the process is carried out in single step.
Reason : Work done is path dependent quantity.
 (1) A (2) B (3) C (4) D
27. **Assertion :** All spontaneous process in nature are irreversible.
Reason : All reversible process are quasistatic.
 (1) A (2) B (3) C (4) D
28. **Assertion :-** Sum of q and w is different in reversible and irreversible process.
Reason :- Sum of two path function can never state function.
 (1) A (2) B (3) C (4) D
29. **Assertion :** Internal energy of gas remain constant during adiabatic free expansion.
Reason : Work done is zero and heat exchange is zero.
 (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	1	4	3	2	3	2	4	4	4	4	2	1	4	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Ans.	4	4	3	1	4	1	1	3	3	3	1	2	4	1	

S. No.	CONTENTS	Page
1.	Format for IUPAC name	2
2.	Exercise-I (Conceptual Questions)	6
3.	Exercise-II (Previous Years Questions)	11
4.	Exercise-III (Analytical Questions)	14
5.	Exercise-IV (Assertion & Reason)	17

NEET SYLLABUS

General introduction, classification and IUPAC nomenclature of organic compounds :

OBJECTIVES

After studying this unit, we will be able to :

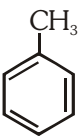
- *understand reasons for tetravalence of carbon and shapes of organic molecules;*
- *write structures of organic molecules in various ways;*
- *classify the organic compounds;*
- *name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names;*

*"Don't take rest after your first victory because if you fail in second,
more lips are waiting to say that your first victory was just luck."*

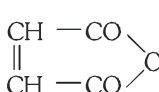
A.P.J. Abdul Kalam

CLASSIFICATION & NOMENCLATURE

BEGINNER'S BOX-1

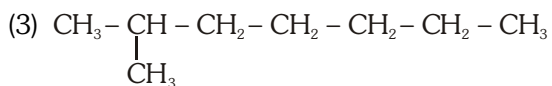
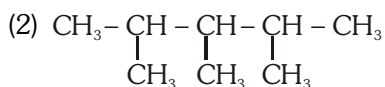
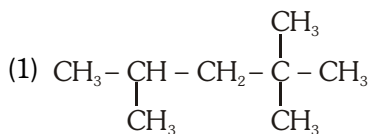
- How many 1° , 2° & 3° H atoms are present in  [Toluene] respectively :-
 (1) 3, 0, 5 (2) 3, 5, 0 (3) 4, 3, 0 (4) 0, 5, 3
- What is hybridisation of each carbon atom in following compound
 $\text{HC} \equiv \text{C} - \text{CH} = \text{CH} - \text{CH}_3$
 (1) sp , sp^2 , sp^2 , sp^2 , sp^3 (2) sp , sp , sp^2 , sp^2 , sp^3
 (3) sp , sp , sp^2 , sp^3 , sp^3 (4) sp , sp^2 , sp^2 , sp^3 , sp^3
- Which one is not correct for a homologous series -
 (1) All members have a general formula
 (2) All members have same chemical properties
 (3) All members have same physical properties
 (4) All members have same functional group

BEGINNER'S BOX-2

- How many carbon atom are present in third homologue of methyl ether.
 (1) 1 (2) 2 (3) 3 (4) 4
- Which of the following is not a hetero cyclic compound
 (1) Thiophene (2) Furane (3) Benzene (4) Pyridine
- In structure , how many hetero atoms are present ?
 (1) 1 (2) 2 (3) 3 (4) 4

BEGINNER'S BOX-3

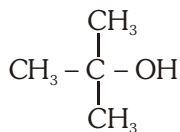
- Which of the followings is incorrect name :-
 (1) Isopropyl (2) Ter. butyl (3) Neo butyl (4) Neo pentyl
- Which of the followings is secondary radical :-
 (1) $\text{CH}_2=\text{CH}-$ (2) $(\text{CH}_3)_3\text{C}-$ (3) C_6H_5- (4) $\text{CH}_3-(\text{CH}_2)_2-\text{CH}_2-$
- Which of the followings is isooctane :-



(4) None

BEGINNER'S BOX-4

1. Common name of given compound is :-



- (1) Neobutyl alcohol (2) Isobutyl alcohol
 (3) Tertiary butyl alcohol (4) Secondary butyl alcohol
2. Which of the following is Crotonic acid ?
 (1) $\text{CH}_2 = \text{CH} - \text{COOH}$ (2) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CHO}$
 (3) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$ (4) $\text{CH}_3 - \text{CH} = \text{CH} - \text{COOH}$
3. What is derived name of Neopentyl alcohol :-
 (1) Isopropyl carbinol (2) n-Butyl carbinol
 (3) Tertiary butyl carbinol (4) Ethyl methyl carbinol

Format for IUPAC name :

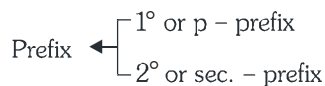
<u>s - prefix</u>	+	<u>p - prefix</u>	+	<u>word root</u>	+	<u>p - suffix</u>	+	<u>s - suffix</u>
Substituents with locants		cyclo		Alk word according to carbon in parent C chain		- ane - ene - yne		According to main functional group given in priority table

(a) **Locant** : Locants are separated by (,) comma.

- Locants and alphabets are separated by hyphen (-). [2, 3 - dimethyl pentane]
- di, tri, iso, neo and cyclo are neither separated by comma nor by hyphen

(b) **Prefix** :- According to substituents .

Prefix (es) are written in alphabetical order before root word.



Cyclo is 1° prefix and used for cyclic compound.

2° prefix is used for substituents and written before 1° prefix.

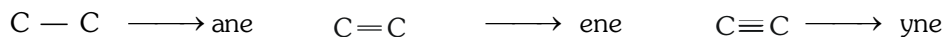
For acyclic compounds : 2° prefix + Root word + 1° suffix + 2° suffix.

Substituents	Prefix	Substituents	Prefix
— R	Alkyl group	— OR	Alkoxy
— X (F, Cl, Br, I)	Halo	— $\text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$	Nitro
— O — N=O	Nitrite	— N = O	Nitroso
— CH_2OH	Hydroxy methyl	— CH_2Cl	Chloro methyl
— NHC_2H_5	Ethyl amino		

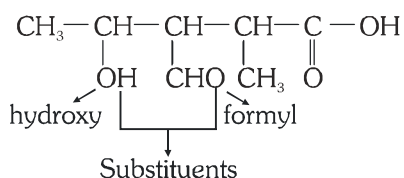
(c) **Word root** : According to number of carbons in parent C-chain.

Number of carbons	Root word	Number of carbons	Root word	Number of carbons	Root word
1	Meth	6	Hex	11	Undec
2	Eth	7	Hept	12	dodec
3	Prop	8	Oct	13	tridec
4	But	9	Non		
5	Pent	10	Dec		

(d) Primary suffix :- According to saturation and unsaturation.



(e) Secondary Suffix :- According to senior most of F. G.



3-Formyl-4-hydroxy-2-methyl pentanoic acid

S. NO.	Functional group	Prefix	Suffix
1.	— (C) OOH (carboxylic acid) — COOH	×	oic acid carboxylic acid
2.	— SO ₃ H (sulphonic acid)	sulpho	sulphonic acid
3.	$\begin{array}{c} \text{O} \\ \\ -(\text{C}) > \text{O} \\ \\ -(\text{C}) > \text{O} \\ \\ \text{O} \end{array}$ (anhydride)	×	oic anhydride
4.	— (C) OOR (ester) — COOR	×	alkyl ----- oate alkoxy carbonyl or carbalkoxy alkyl ----- carboxylate
5.	— (C) OX (acid halide) — COX	×	oyl halide carbonyl halide
6.	— (C) ONH ₂ (amide) — CONH ₂	×	amide carbamoyl carboxamide
7.	— (C) N (cyanide) — CN	×	Nitrile carbonitrile
8.	— N $\equiv$ C (isocyanide)	isocyano/carbyl amino	isonitrile/carbyl amine
9.	— (C) HO (aldehyde) — CHO	oxo formyl	al carbaldehyde
10.	— (C) — (Ketone) $\begin{array}{c} \text{O} \\ \\ -(\text{C}) - \end{array}$	keto/oxo	one
11.	— OH (alcohol)	hydroxy	ol
12.	— SH (thio alcohol)	mercapto	thiol
13.	— NH ₂ (amine)	amino	amine

Note : (C) atom written in brackets means that it has been included in the parent chain.

3. IUPAC name of $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ is :-

- (1) Acetic anhydride (2) Methanoic anhydride
(3) Ethanoic methanoic anhydride (4) Ethanoic anhydride

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3
	Ans.	2	2	3
BEGINNER'S BOX-2	Que.	1	2	3
	Ans.	4	3	1
BEGINNER'S BOX-3	Que.	1	2	3
	Ans.	3	3	1
BEGINNER'S BOX-4	Que.	1	2	3
	Ans.	3	4	3
BEGINNER'S BOX-5	Que.	1	2	3
	Ans.	4	4	1
BEGINNER'S BOX-6	Que.	1	2	3
	Ans.	4	3	4

EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****CLASSIFICATION**

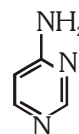
- The hybrid state of C-atoms which are attached to a single bond with each other in the following structure are : $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$
 (1) sp^2 , sp (2) sp^3 , sp
 (3) sp^2 , sp^2 (4) sp^2 , sp^3
- The third member of the homologous series of aliphatic aldehydes has the structure :-
 (1) $\text{CH}_3\text{CH}_2\text{CHO}$ (2) $\text{CH}_3(\text{CH}_2)_2\text{CHO}$
 (3) $\text{CH}_3\text{COCH}_2\text{CH}_3$ (4) CH_3COCH_3
- Molecular formula $\text{C}_4\text{H}_8\text{O}_2$ represents :-
 (1) An acid only
 (2) An ester only
 (3) An alcohol only
 (4) An acid and an ester also
- The higher homologue of dimethylamine ($\text{CH}_3-\text{NH}-\text{CH}_3$) has the structure :-
 (1) $\text{CH}_3-\text{N}(\text{CH}_3)_2$
 (2) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$
 (3) $\text{CH}_3-\text{NH}-\text{CH}_2-\text{CH}_3$
 (4) $\text{CH}_3-\text{CH}(\text{NH}_2)-\text{CH}_3$
- The third member of the family of alkenynes has the molecular formula :-
 (1) C_6H_6 (2) C_5H_6
 (3) C_6H_8 (4) C_4H_4
- The number of olefinic bonds in the given compound is/are :-
 $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}\equiv\text{N}$
 (1) 2 (2) 3
 (3) 1 (4) 4
- The number of acetylenic bonds in the given compound is/are :
 $\text{HC}\equiv\text{C}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}\equiv\text{N}$
 (1) 2 (2) 3
 (3) 1 (4) 4

- The number of C-atoms in second member of an ester is/are :
 (1) 2 (2) 3
 (3) 4 (4) 5

- Which of the following is an example of symmetrical or simple ether :

- $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$
- $\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_3$
- $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
- $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

- The number of hetero atoms present in the following compound is/are :



- (1) 2 (2) 3
(3) 1 (4) 4

- The minimum number of carbon atoms in an alkane having four primary carbon atoms are :-

- (1) 4 (2) 8
(3) 5 (4) 6

- Which of the following compound has sp -hybridised carbon atom :-

- (1) CH_3COOH (2) CH_3COCH_3
(3) $\text{CH}_3\text{CH}_2\text{CN}$ (4) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

- In compound $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$, the C_2-C_3 bond is the type of :-

- (1) $\text{sp} - \text{sp}^2$ (2) $\text{sp}^3 - \text{sp}^3$
(3) $\text{sp} - \text{sp}^3$ (4) $\text{sp}^2 - \text{sp}^2$

- Which of the following represents the given mode of hybridization $\text{sp}^2-\text{sp}^2-\text{sp}-\text{sp}$ from left to right :-

- (1) $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{CH}$ (2) $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$
(3) $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ (4) $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$

- Which of the following pair of compounds are homologues :-

- (1) 1-Propanol & 2-Propanol
(2) Ethanol & Propanal
(3) Acetone & Acetaldehyde
(4) Acetic acid & Butyric acid

16. Which of the following homologous series has incorrect general formula :-

- (1) Alkyne C_nH_{2n-2}
 (2) Alkanol $C_nH_{2n+2}O$
 (3) Alkanal $C_nH_{2n+1}O$
 (4) Carboxylic acid $C_nH_{2n}O_2$

17. The Cl – C – Cl bond angle in 1,1,2,2 – tetrachloro ethene and tetrachloro methane respectively are:-

- (1) 120° and 109.5° (2) 90° and 109.5°
 (3) 109.5° and 90° (4) 109.5° and 120°

18. Minimum number of carbon atoms present in an ester are :-

- (1) 2 (2) 1 (3) 4 (4) 3

19. Which of the following has general formula C_nH_{2n}

- (1) Only Alkyne
 (2) Only Alkane
 (3) Aromatic hydrocarbon
 (4) Alkene & cyclic Alkane

20. Which compound has alkyne group

- (1) C_7H_{14} (2) $C_{10}H_{22}$
 (3) C_9H_{16} (4) $C_{16}H_{32}$

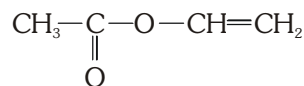
COMMON AND DERIVED NAME

21. Which of the following are tertiary radicals :-

- (a) $\begin{array}{c} CH_3 \\ | \\ CH_3-C- \\ | \\ CH_3 \end{array}$ (b) $\begin{array}{c} CH_3-CH- \\ | \\ CH_3 \end{array}$
 (c) $\begin{array}{c} CH_3 \\ | \\ CH_3-C-C_2H_5 \\ | \end{array}$ (d) $\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_2- \\ | \\ CH_3 \end{array}$

- (1) a and b (2) b and c
 (3) a and c (4) b and d

22. Common name of the given compound is :-



- (1) vinyl acetate (2) acryl acetate
 (3) methyl acrylate (4) Vinyl ethanoate

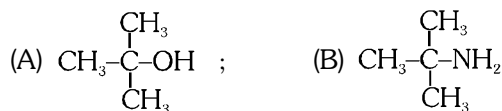
23. A primary amine has amino group ($-NH_2$) attached to:-

- (1) A primary carbon atom only
 (2) A secondary carbon atom only
 (3) A tertiary carbon atom only
 (4) A primary, secondary or tertiary carbon atom

24. Which of the following are secondary radicals :-

- (a) $CH_3-\overset{|}{CH}-C_2H_5$ (b) $CH_2=\overset{|}{C}-CH_3$
 (c) $CH_2=CH-$ (d) $(CH_3)_2CH-$
 (1) a, b, c (2) a, d, c
 (3) b, c, d (4) a, b, d

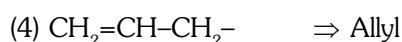
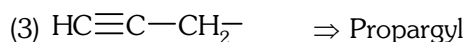
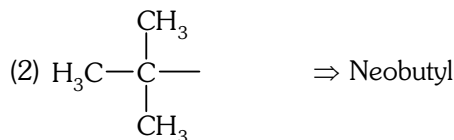
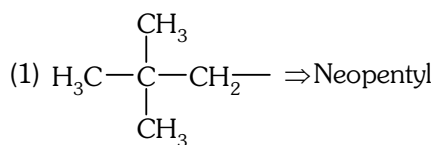
25. Examine the following structures :-



Which of the following statement is correct :-

- (1) A is tertiary alcohol while B is tertiary amine
 (2) A is primary alcohol while B is primary amine
 (3) A is tertiary alcohol while B is primary amine
 (4) A is primary alcohol while B is tertiary amine

26. Which of the following is not a correct match

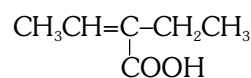


IUPAC NAME

27. The IUPAC name for isobutyl chloride is :-

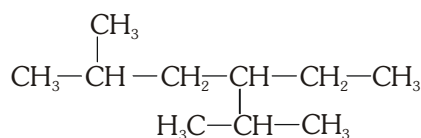
- (1) 2-Methyl-2-chloro butane
 (2) 2-Chloro-2-methyl butane
 (3) 1-Chloro-2-methyl propane
 (4) 2-Methyl-3-chloro propane

28. The IUPAC name of given compound is :-



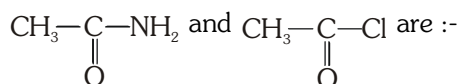
- (1) 3-Carboxy-2-pentene
 (2) 2-Ethylidene butanoic acid
 (3) 2-Ethyl-2-butenic acid
 (4) 3-Ethyl-2-buten-4-oic acid

29. The IUPAC name for the given structure is :-



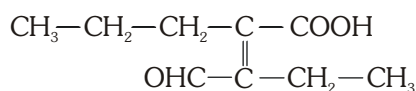
- (1) 3-Isopropyl-4-methylhexane
- (2) 4-Isopropyl-3-methylhexane
- (3) 3-Ethyl-2,5-dimethylhexane
- (4) 2-Ethyl-3-isopropylpentane

30. The IUPAC name for



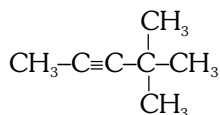
- (1) 1-Amino-1-oxo ethane, 1-chloro ethanal
- (2) 1-Amino ethanal, acetoxy chloride
- (3) 1-Oxoethanamine, ethanoyl chloride
- (4) Ethanamide, Ethanoyl chloride

31. The number of carbon atoms in the principle chain of the given compound are :-



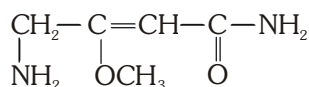
- (1) 7
- (2) 5
- (3) 4
- (4) 6

32. The IUPAC name of given compound is :-



- (1) Methyl tertiarybutyl acetylene
- (2) t-Butyl propyne
- (3) 4,4-Dimethyl-2-pentyne
- (4) 1,3,3,3-Tetramethyl ethyne

33. The IUPAC name of the compound is :-

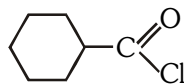


- (1) 4-Amino-2-methoxy-1-amino-2-butene
- (2) 4-Amino-3-methoxy-2-butenamide
- (3) 2-Methoxy-1,4-diamino-2-butenal
- (4) 1-Amino-2-methoxy-3-amino propene

34. The IUPAC name of $\text{CH}_3-\text{CH}_2-\text{NH}-\text{CH}_3$ is :-

- (1) Methyl ethyl amine
- (2) 1-methyl amino ethane
- (3) N-methyl ethan amine
- (4) N-ethyl methan amine

35. The IUPAC name for the compound is :-

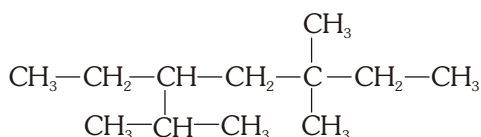


- (1) Cyclohexanoyl chloride
- (2) Cyclohexane carbonyl chloride
- (3) 1-Chloro cyclohexanal
- (4) Chloro cyclohexyl methanal

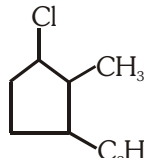
36. The IUPAC name of $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_3$ is

- (1) 3-Methyl-2-penten-4-yne
- (2) 3-Methyl-3-penten-1-yne
- (3) 3-Methyl-4-pentyn-1-ene
- (4) 3-Methyl pentenyne

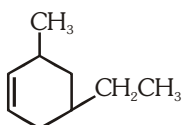
37. The IUPAC name of the structure is :-



- (1) 3-Isopropyl-5,5-dimethyl heptane
- (2) 5-Ethyl-3,3,6-trimethyl heptane
- (3) 3,3-Dimethyl-5-isopropyl heptane
- (4) 3-Ethyl-2,5,5-trimethyl heptane

38.  has the IUPAC name :-

- (1) 3-Chloro-1-ethyl-2-methyl cyclopentane
- (2) 1-Chloro-3-ethyl-2-methyl cyclopentane
- (3) 4-Chloro-1-ethyl-5-methyl cyclopentane
- (4) All are correct

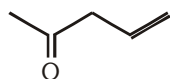
39. The IUPAC name of  is :-

- (1) 1-Methyl-5-ethyl cyclohex-2-ene
- (2) 5-Ethyl-3-methyl cyclohex-1-ene
- (3) 4-Ethyl-6-methyl cyclohex-1-ene
- (4) 1-Ethyl-5-methyl cyclohex-3-ene

40. $\text{H}-\text{C}(=\text{O})-\text{CN}$ in IUPAC called :-

- (1) Cyano methanal
- (2) 2-Oxo ethane nitrile
- (3) Cyano ethanal
- (4) Formonitrile

41. The IUPAC name for the compound is :-



- (1) 2-Acetyl prop-1-ene (2) Pent-1-en-4-one
(3) Pent-4-en-2-one (4) Formyl propene

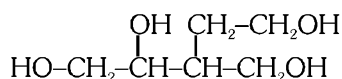
42. Which is incorrect IUPAC name :-

- (1) 3-Pentyne
(2) 3-Methyl-2-butanone
(3) 2-Ethyl-3-methyl-1-butene
(4) 3-Ethyl-2-methyl pentane

43. The IUPAC name of $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OCH}_3$ is :-

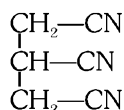
- (1) 1-Methoxy-4-amino benzene
(2) Aminophenyl methyl ether
(3) 4-Methoxy aniline
(4) None of the above

44. The IUPAC name of the given compound is :-



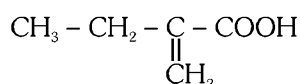
- (1) 3-Hydroxymethyl pentane-1,4,5-triol
(2) 3-Hydroxyethyl butane-1,2,4-triol
(3) 4-Hydroxyethyl-1,2,4-trihydroxy butane
(4) 3-Hydroxymethyl pentane-1,2,5-triol

45. The IUPAC name of the given compound is :-



- (1) 1,2,3-Tricarbonitrile propane
(2) Propane-1,1,1-tricarbylamine
(3) Propane-1,2,3-tricarbonitrile
(4) 3-Cyano pentane dicyanide

46. Number of carbon atoms in the principle carbon chain in the given compound are :-

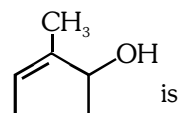


- (1) 4 (2) 3
(3) 2 (4) 5

47. Wrong IUPAC name is :-

- (1) $\text{CH}_3\text{CH}_2\text{CONH}_2$ Propanamide
(2) $\text{CH}_3\text{CH}_2\text{COOCH}_3$ Methyl propanoate
(3) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_3$ 2-Methyl pent-3-ene
(4) $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}(\text{CH}_2-\text{CH}_3)-\text{CH}_3$ 2-Ethoxy butane

48. The IUPAC name of the compound

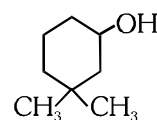


- (1) 2-Methyl cyclopent-1-en-2-ol
(2) 3-Methyl cyclopent-2-en-1-ol
(3) 2-Methyl cyclopent-2-en-1-ol
(4) 3-Methyl cyclopent-1-en-2-ol

49. The IUPAC name of $\text{CH}_3\text{COOCH}_2\text{COOH}$ is :-

- (1) Acetic anhydride
(2) Formyl ethanoate
(3) Butane-2,4-dione
(4) Ethanoic methanoic anhydride

50. The IUPAC name of given compound is :



- (1) 3,3-Dimethyl-1-hydroxy cyclohexane
(2) 1,1-Dimethyl-3-hydroxy cyclohexane
(3) 3,3-Dimethyl-1-cyclohexanol
(4) 1,1-Dimethyl-3-cyclohexanol

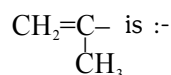
51. IUPAC name of $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ is :-

- (1) 2,2-Dimethyl butane (2) 2,3-Dimethyl butane
(3) 2,4-Dimethyl butane (4) 1-Methyl pentane

52. IUPAC name of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$ is :-

- (1) Allyl chloride
(2) 1-Chloro-3-propene
(3) 3-Chloro-1-propene
(4) Vinyl chloride

53. The IUPAC name of the following group

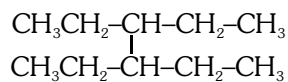


- (1) Isopropenyl (2) 1-Methylethenyl
(3) 2-Methylethynyl (4) None of the above

54. $\text{CH}_3-\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$ has IUPAC name :-

- (1) Pent-2-en-4-yne
(2) Pent-4-yn-2-ene
(3) Pent-1-yn-3-ene
(4) Pent-3-en-1-yne

55. The IUPAC name of the following compound



- (1) 3, 4 - Dimethyl octane
- (2) 3-sec pentyl pentane
- (3) 3, 4 - Diethyl hexane
- (4) 3, 4 - Dimethyl hexane

56. Correct IUPAC name is :-

- (1) 3-Methyl-2-ethylpentane
- (2) 2-Ethyl-3-methylpentane
- (3) 3-Ethyl-2-methylpentane
- (4) 2-Ethyl-2-methylpentane

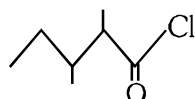
EXERCISE-I

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	1	4	3	3	1	3	2	4	1	3	3	3	1	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	1	1	4	3	3	1	4	4	3	2	3	3	3	4
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	2	3	2	2	4	2	2	2	3	1	3	4	3
Que.	46	47	48	49	50	51	52	53	54	55	56				
Ans.	2	3	3	4	3	2	3	2	4	3	3				

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT-2006**

1. The general molecular formula, which represents the homologous series of alkanols is
 (1) $C_nH_{2n}O_2$ (2) $C_nH_{2n}O$
 (3) $C_nH_{2n+1}O$ (4) $C_nH_{2n+2}O$

2. The IUPAC name of  is :-

- (1) 3,4-Dimethylpentanoyl chloride
 (2) 1-Chloro-1-oxo-2,3-dimethylpentane
 (3) 2-Ethyl-3-methylbutanoyl chloride
 (4) 2,3-Dimethylpentanoyl chloride

AIPMT-2008

3. In the hydrocarbon

$$\begin{array}{ccccccc} CH_3 & - & CH & = & CH & - & CH_2 & - & C \equiv & CH \\ 6 & & 5 & & 4 & & 3 & & 2 & 1 \end{array}$$
 The state of hybridization of carbons 1, 3 and 5 are in the following sequence :-
 (1) sp , sp^2 , sp^3 (2) sp^3 , sp^2 , sp
 (3) sp^2 , sp , sp^3 (4) sp , sp^3 , sp^2

AIPMT-2009

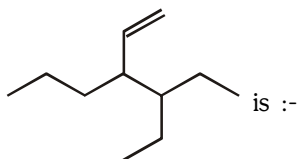
4. The IUPAC name of the compound having the formula $CH \equiv C - CH = CH_2$ is :-
 (1) 1-buten-3-yne (2) 3-buten-1-yne
 (3) 1-butyne-3-ene (4) but-1-yn-3-ene

AIPMT Mains-2010

5. The IUPAC name of the compound $CH_3CH=CHC \equiv CH$ is :-
 (1) Pent-3-en-1-yne (2) Pent-2-en-4-yne
 (3) Pent-1-yn-3-ene (4) Pent-4-yn-2-ene

AIPMT Pre.-2011

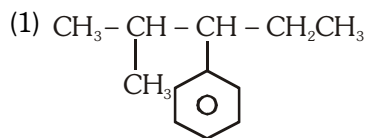
6. The correct IUPAC name of the compound



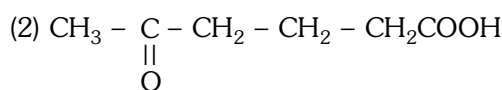
- (1) 4-Ethyl-3-propyl hex-1-ene
 (2) 3-Ethyl-4-ethenyl heptane
 (3) 3-Ethyl-4-propyl hex-5-ene
 (4) 3-(1-ethyl propyl) hex-1-ene

AIPMT Pre.-2012

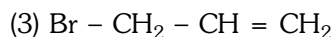
7. Which nomenclature is not according to IUPAC system?



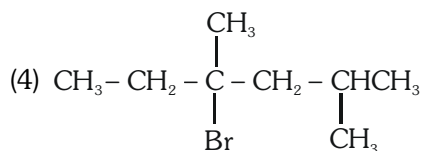
2-Methyl-3-phenylpentane



5-Oxohexanoic acid



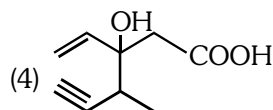
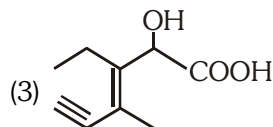
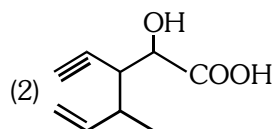
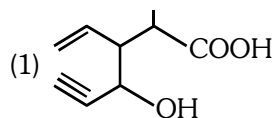
1-Bromo-prop-2-ene



4-Bromo,2,4-di-methylhexane

NEET UG-2013

8. Structure of the compound whose IUPAC name is 3-Ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is :-

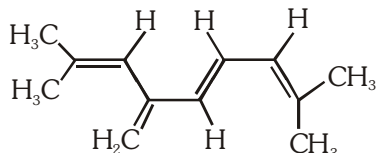


AIPMT-2014

9. Which of the following organic compounds has same hybridization as its combustion product CO_2 ?
- (1) Ethane (2) Ethyne
(3) Ethene (4) Ethanol

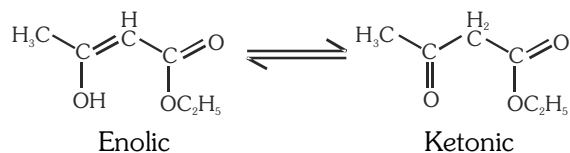
AIPMT-2015

10. The total number of π -bond electrons in the following structure is :-



- (1) 8 (2) 12 (3) 16 (4) 4

11. The enolic form of ethyl acetoacetate as below has:-



- (1) 16 sigma bonds and 1 pi - bond
(2) 9 sigma bonds and 2 pi - bonds
(3) 9 sigma bonds and 1 pi - bond
(4) 18 sigma bonds and 2 pi - bonds

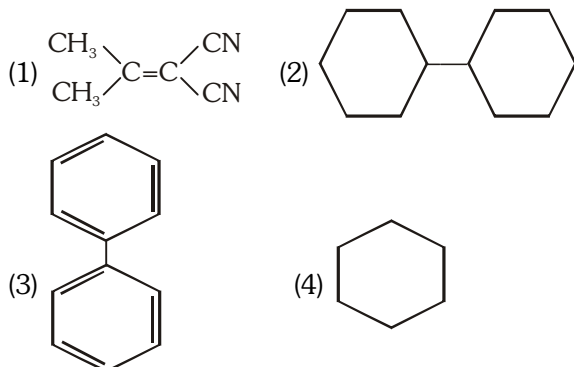
NEET-I 2016

12. The pair of electron in the given carbanion, $\text{CH}_3\text{C} \equiv \text{C}^\ominus$, is present in which of the following orbitals ?

- (1) 2p (2) sp^3
(3) sp^2 (4) sp

NEET-II 2016

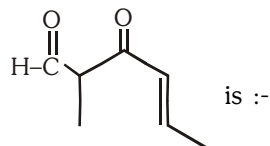
13. In which of the following molecules, all atoms are coplanar ?

**AIIMS 2016**

14. In which of the following multiple bond is absent:-
- (1) CH_3CN (2) HCOOH
(3) CH_2N_2 (4) C_3H_6

NEET(UG) 2017

15. The IUPAC name of the compound



- (1) 5-formylhex-2-en-3-one
(2) 5-methyl-4-oxohex-2-en-5-al
(3) 3-keto-2-methylhex-5-enal
(4) 3-keto-2-methylhex-4-enal

AIIMS 2017

16. IUPAC name for given compound is -

- (1) 2-Amino-4-ethyl-5-methyl hexan-1-ol
(2) 2-Amino-4-isopropyl-hexan-1-ol
(3) 5-Amino-3-ethyl-2-methyl hexan-6-ol
(4) 4-Ethyl-2-amino-5-methyl hexan-1-ol

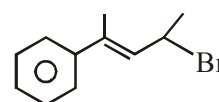
NEET(UG) 2018

17. Which of the following molecules represents the order of hybridisation sp^2 , sp^2 , sp, sp from left to right atoms ?

- (1) $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$
(2) $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$
(3) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
(4) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$

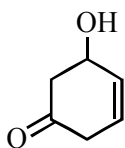
AIIMS 2018

18. IUPAC name of the compound



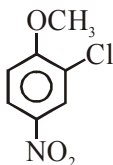
- (1) 2-Phenyl-4-bromopentane
(2) 4-Bromo-2-phenylpent-2-ene
(3) 2-Bromo-4-phenylpentene
(4) 4-Phenyl-2-bromopentane

19. IUPAC name of the given compound is



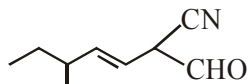
- (1) 3-Hydroxycyclohex-4-en-1-one
- (2) 5-Hydroxycyclohex-3-enone
- (3) 5-Ketocyclohex-2-enol
- (4) 3-Ketocyclohex-5-enol

20. IUPAC name of the given compound



- (1) 2-chloro-4-nitroanisole
- (2) 1-chloro-3-nitro-6-methoxybenzene
- (3) 3-chloro-1-nitro-4-methoxybenzene
- (4) 1-chloro-2-methoxy-5-nitrobenzene

21. Correct IUPAC name of the given compound



- (1) 2-cyano-5-methylhept-3-en-1-al
- (2) 2-Formyl-5-methylhept-3-ene-1-nitrile
- (3) 5-Ethyl-2-cyanohept-3-enal
- (4) 2-Cyano-5-ethylhex-3-enal

EXERCISE-II (Previous Year Questions)

ANSWER KEY

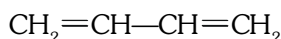
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	4	4	1	1	1	3	3	2	1	4	4	3	4	4
Que.	16	17	18	19	20	21									
Ans.	1	2	2	2	1	2									

EXERCISE-III (Analytical Questions)**Check Your Understanding**

1. The number of π bonds and σ bonds in the structure  respectively are :-

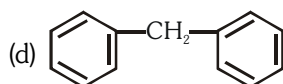
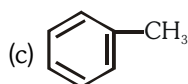
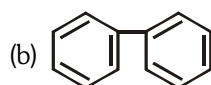
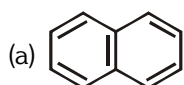
(1) 8, 5 (2) 8, 6
(3) 3, 8 (4) 5, 13

2. The geometry of the compound is :-



(1) Tetrahedral (2) Linear
(3) Planar (4) Pyramidal

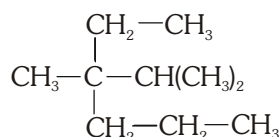
3. Which of the following have only 2° H-atom :



Correct code is :

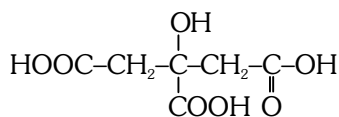
(1) a and b (2) a, b and d
(3) a, c and d (4) a, b, c and d

4. The IUPAC name of the given structure is :-



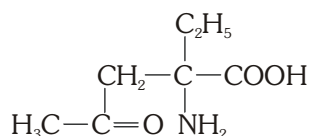
(1) 3-Methyl-3-isopropyl hexane
(2) 3-Isopropyl-3-methyl hexane
(3) 3-Ethyl-2,3-dimethyl hexane
(4) 2,3-Dimethyl-3-ethyl hexane

5. The IUPAC name of the given compound is :



(1) 3-Carboxy-3-hydroxy butane dioic acid
(2) 2-Hydroxy propane-1,2,3-tricarboxylic acid
(3) 3-Hydroxy butane dioic acid
(4) 2-Bis(carboxymethyl)-2-hydroxy ethanoic acid

6. The IUPAC name of given compound is :-



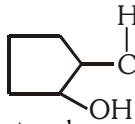
(1) 2-Oxo-4-amino-4-ethyl pentanoic acid
(2) 2-Amino-4-oxo-2-ethyl pentanoic acid
(3) 3-Amino-3-carboxy-5-hexanone
(4) 2-Amino-2-ethyl-4-oxo pentanoic acid

7. The IUPAC name from the incorrect name 4-Amino-3-hydroxy-2-butene is :-

(1) 1-Amino-2-hydroxy-2-butene
(2) 4-Amino-2-buten-3-ol
(3) 1-Amino-2-buten-2-ol
(4) 1-Amino-2-butenol

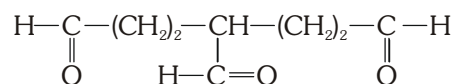
8. The correct IUPAC name of 2-chloro-3-butanol is :-

(1) 3-Chloro-2-hydroxy butane
(2) 3-Chloro-2-butanol
(3) 3-Hydroxy-2-chloro butane
(4) 2-Chloro-3-hydroxy butane

9. The IUPAC name for  is :-

(1) 2-Hydroxy cyclopentanal
(2) 2-Formyl-1-hydroxy cyclopentane
(3) 2-Hydroxy cyclopentane carbaldehyde
(4) Cyclopentane-2-ol-1-al

10. The IUPAC name of the compound is :-



(1) 1,4,7-Triheptanal
(2) 1,3,5-Triformyl pentane
(3) 3-Formyl heptane dial
(4) 1,3,5-Pentane tricarbaldehyde

11. $\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{COOH}$

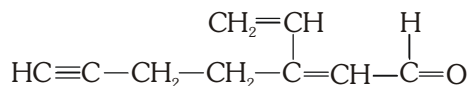
The IUPAC name of the above compound is :-

(1) 2-Acetoxy ethanoic acid
(2) 2-Methoxycarbonyl ethanoic acid
(3) 3-Methoxyformyl ethanoic acid
(4) 2-Methoxyformyl acetic acid

12. The IUPAC name of $\text{Cl}-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$ is :-

(1) Ethoxy formyl chloride
(2) Ethoxy methanoyl chloride
(3) Ethyl chloro methanoate
(4) Ethoxy carbonyl chloride

13. The IUPAC name of the compound is :-

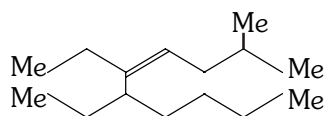


- (1) 3-(1-butynyl)-2,4-pentadienal
- (2) 5-Ethynyl-3-vinyl-2-pental
- (3) 3-Vinyl-2-hepten-6-ynal
- (4) 5-Acetyl-3-ethenyl-2-pental

14. The IUPAC name of $\text{CH}_3\text{CH}_2\text{NHCHO}$ is :

- (1) N-formyl ethanamine
- (2) Ethyl amino methanal
- (3) N-ethyl methanamide
- (4) N-ethyl methanol

15. The IUPAC name of the structure is :-



- (1) 2,4,5-Triethyl-3-nonene
- (2) 5,6-Diethyl-2-methyl-4-decene
- (3) 2,4,5-Triethyl-3-octene
- (4) 3-Ethyl-5-methyl-3-heptene

16. has the IUPAC name :

- (1) Ethyl-2-keto cyclopentane carboxylate
- (2) 2-Cyclopentanone-1-carbethoxy
- (3) 2-Ethylcarbonate cyclopentanone
- (4) 1-Keto-2-carbethoxy cyclopentanone

17. has the IUPAC name :-

- (1) 3,4-Dimethyl-1-penten-3-ol
- (2) Isopropyl-3-methyl vinyl carbinol
- (3) 2,3-Dimethyl-4-penten-3-ol
- (4) None of the above

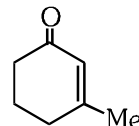
18. Which of the following has wrong IUPAC name

- (1) 5-Ethyl-1-methylcyclohexene
- (2) 5-Bromo-6-chloro-1-cyclohexen-3-yne
- (3) 1,2-Dimethylcyclopropane
- (4) 2-Methylcyclopent-4-en-1-ol

19. The IUPAC name of is :-

- (1) 3,4-Dihydroxy benzoic acid
- (2) 2,3-Dihydroxy benzoic acid
- (3) 4-Carboxy-2-hydroxy phenol
- (4) 4-Carboxy benzene-1,2-diol

20. The IUPAC name of the given compound is :-

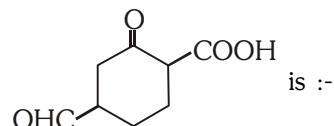


- (1) 3-Methyl-2-cyclohexenone
- (2) 2-Methyl-3-cyclohexenone
- (3) 1-Oxo-3-methyl cyclohexene
- (4) 2-Oxo-6-methyl cyclohexene

21. The IUPAC name of is :-

- (1) 2,3-Dimethyl hexane
- (2) 2-Ethyl-4-methyl pentane
- (3) 3-Ethyl -2-methyl pentane
- (4) 2,4-Dimethyl hexane

22. IUPAC name of



- (1) 6-Oxo-4-formyl cyclohexane carboxylic acid
- (2) 4-Formyl-2-oxo cyclohexane carboxylic acid
- (3) 4-Formyl-2-oxo cyclohexanoic acid
- (4) 1-Carboxy-4-formyl-2-oxo cyclohexane

23. Which is correct IUPAC name :-

- (1) $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_2-\text{Br}$ 1-Bromopropanone

- (2) 1,3,5-Cyclohexanetrione

- (3) 2-Ketocyclopentanecarbaldehyde

- (4) All are correct

24. Which of the following compounds has wrong IUPAC name ?

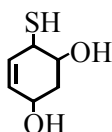
(1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 \rightarrow$ Ethylbutanoate

(2) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CHO} \rightarrow$ 3-Methylbutanal

(3) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3 \rightarrow$ 2-Methyl-3-butanol

(4) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_2-\text{CH}_3 \rightarrow$ 2-Methyl-3-Pentanone

25. Following compound is named as :-



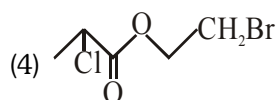
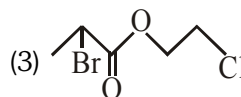
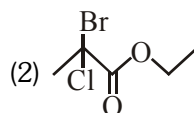
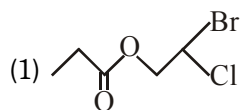
(1) 6-Mercaptocyclohex-4-ene-1,3-diol

(2) 1-Mercaptocyclohex-2-ene-4,6-diol

(3) 1-Mercaptocyclohex-5-ene-2,4-diol

(4) 4-Mercaptocyclohex-2-ene-1,5-diol

26. Structure of the compound Ethyl 2-bromo-2-chloropropanoate is :-



EXERCISE-III (Analytical Questions)

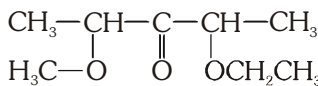
ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	3	2	3	2	4	3	2	3	4	2	3	3	3	2
Que.	16	17	18	19	20	21	22	23	24	25	26				
Ans.	1	1	4	1	1	4	2	4	3	1	2				

EXERCISE-IV (Assertion & Reason)**Target AIIMS****Directions for Assertion & Reason questions**

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion:-**  is called cyclohexanenitrile.
Reason :- It contains six carbon atoms in the ring and CN as substituent.
 (1) A (2) B (3) C (4) D
- Assertion :-** The IUPAC name of  is 2-ethoxy-4-methoxy pentan-3-one.
Reason :- Larger substituents are assigned lower locants.
 (1) A (2) B (3) C (4) D
- Assertion :-** The IUPAC name for $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$ is pent-4-en-1-yne.
Reason :- If there is a choice, a triple bond is always given a lower locant than a double bond.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzene is a carbocyclic compound.
Reason :- It has three π bonds in the cycle.
 (1) A (2) B (3) C (4) D
- Assertion :-** Number of bond angles of 120° and $109^\circ 28'$ in butenyne are 6 and 2 respectively.
Reason :- It's molecular formula is C_4H_6 .
 (1) A (2) B (3) C (4) D
- Assertion :-** Neopentane forms only one mono substituted compound.
Reason :- It has only one type of carbon atoms.
 (1) A (2) B (3) C (4) D
- Assertion :-** $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ is a planar compound.
Reason :- It has 9σ bonds and 2π bonds.
 (1) A (2) B (3) C (4) D
- Assertion :** Acetic acid is an unsaturated compound.
Reason : It has two double bonds.
 (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)**ANSWER KEY**

Que.	1	2	3	4	5	6	7	8
Ans.	4	3	4	2	4	3	2	4

IMPORTANT NOTES

S. No.	CONTENTS	Page
1.	Structural Isomerism	19
2.	Chain Isomerism	19
3.	Position Isomerism	19
4.	Ring-chain Isomerism	21
5.	Functional Isomerism	21
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7.	Geometrical Isomerism	23
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13.	Exercise-IV (Assertion & Reason)	43

NEET SYLLABUS

Isomerism (Conformational, Geometrical and Optical Isomerism) :

OBJECTIVES

After studying this unit, we will be able to :

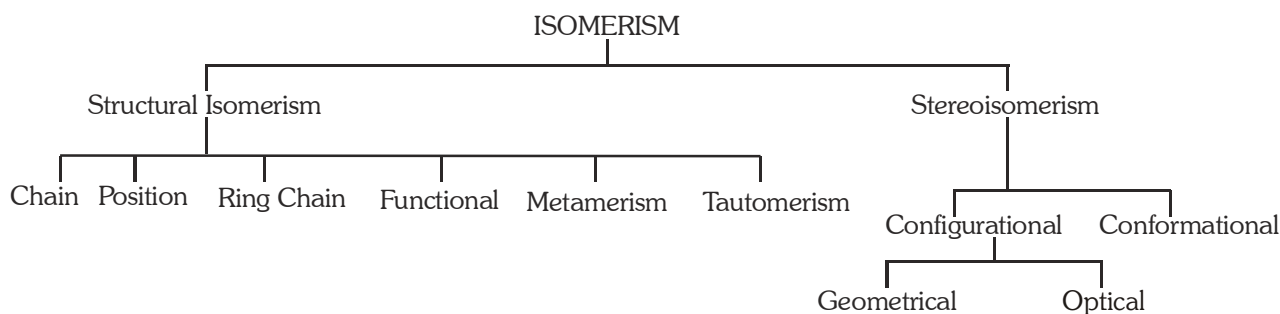
- recognise and write structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons;
- *understand the concept of molecular and structural formula;*
- draw and differentiate between various conformations of ethane;
- *understand the concept of restricted rotation and optical rotation;*

*"Dream is not that which you see while sleeping it is something that;
does not let you sleep."*

A.P.J. Abdul Kalam, Wings of Fire : An Autobiography

ISOMERISM

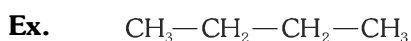
Two or more than two compounds having the same molecular formula but different physical/chemical or both properties are called isomers and the phenomenon is called isomerism.



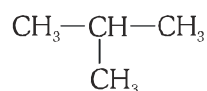
2.1 Structural Isomerism

2.1.1 Chain Isomerism (C.I.)

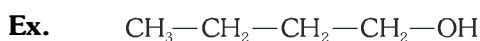
The compounds which have same molecular formula, same functional group but different arrangement of carbon chain (Parental or side chain) show chain isomerism.



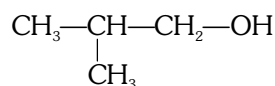
Butane (4C)



2-Methyl propane (3C)



1-Butanol (4C)



2-Methyl-1-propanol (3C)



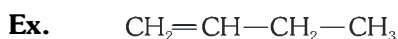
Methylcyclobutane



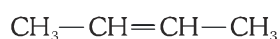
Cyclopentane

2.1.2 Position Isomerism (P.I.)

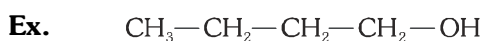
The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, show position isomerism.



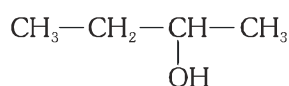
But-1-ene



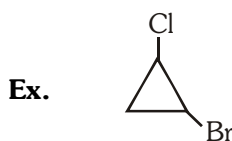
But-2-ene



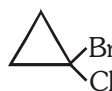
1-Butanol



2-Butanol



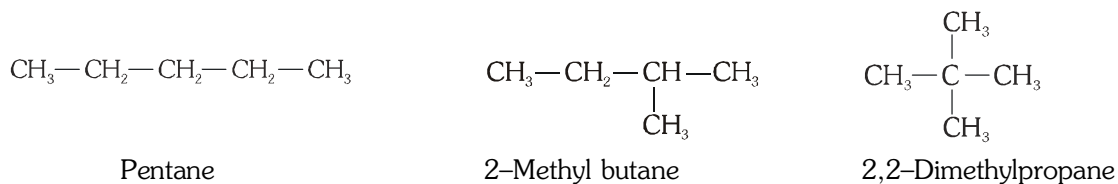
1-Bromo-2-chlorocyclopropane



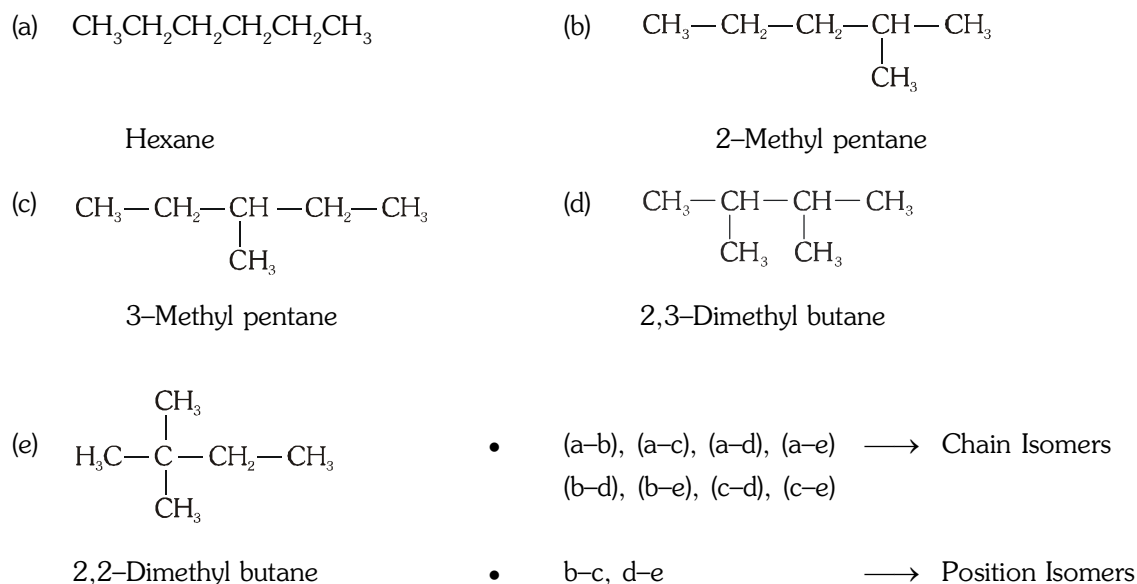
1-Bromo-1-chlorocyclopropane

Example of CI and PI :

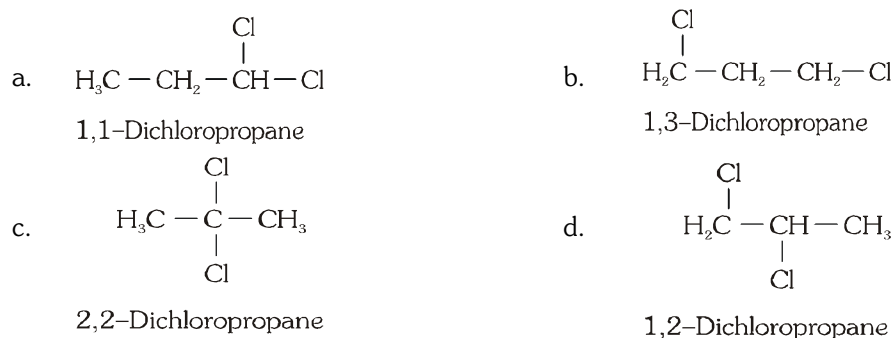
(i) C_5H_{12} has three structural isomers :



(ii) C_6H_{14} has 5 structural isomers

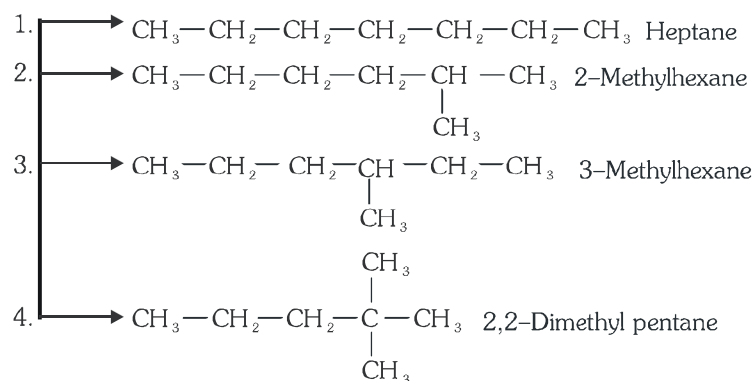


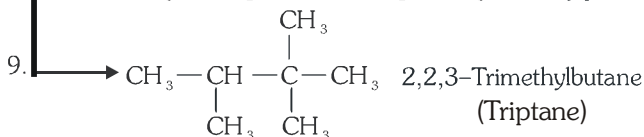
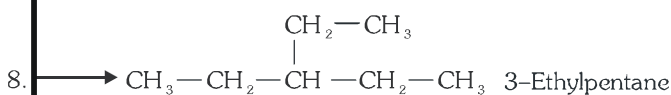
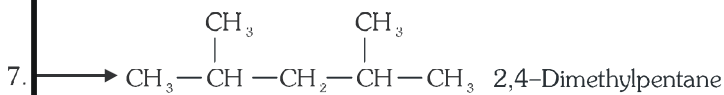
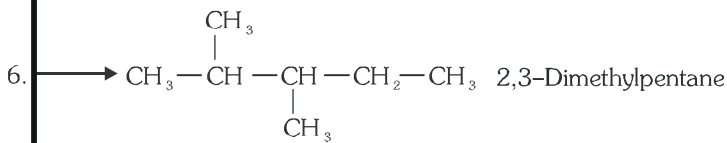
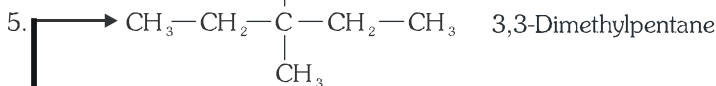
(iii) $C_3H_6Cl_2$ has 4 isomers : Position of chlorine atom is different in all the structure, so these are position Isomers.



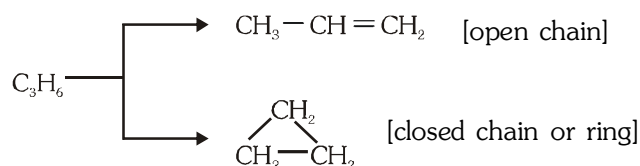
Ex. How many structural isomers of C_7H_{16} are possible ?

Ans. (9)





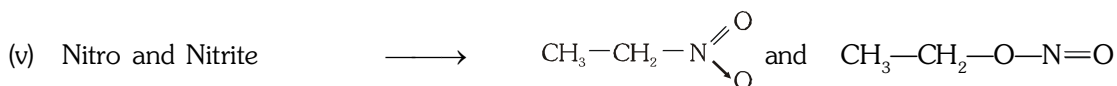
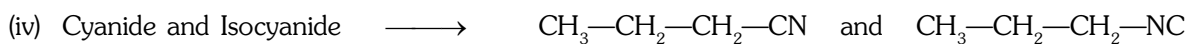
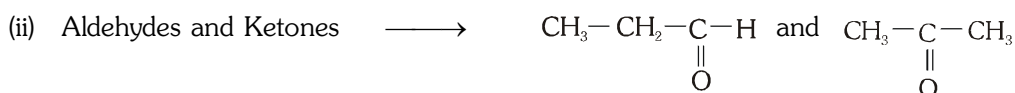
Same molecular formula but different mode of linking (open chain & closed chain) of carbon atoms.



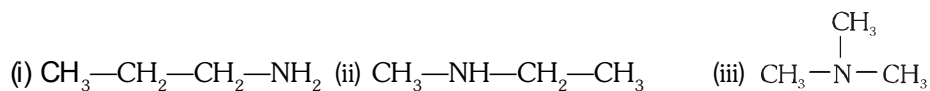
- Alkenes with cycloalkane and alkynes and alkadienes with cycloalkenes show Ring-chain Isomerism.
- Ring-chain Isomers are also Functional Isomers but priority must be given to Ring-chain Isomers.

Same molecular formula but different functional groups.

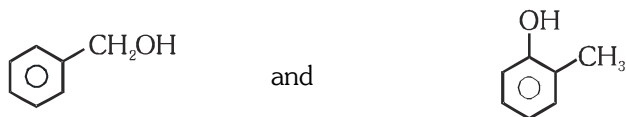
Following compounds show Functional isomerism, as they have same molecular formula and different functional group.



(vi) 1°, 2°, 3° Amines



(vii) Alcoholic and Phenolic compounds :



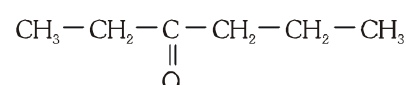
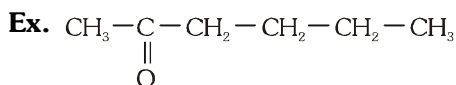
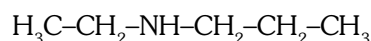
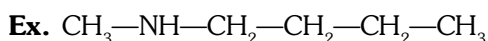
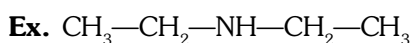
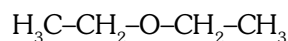
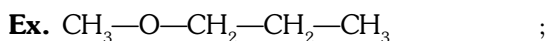
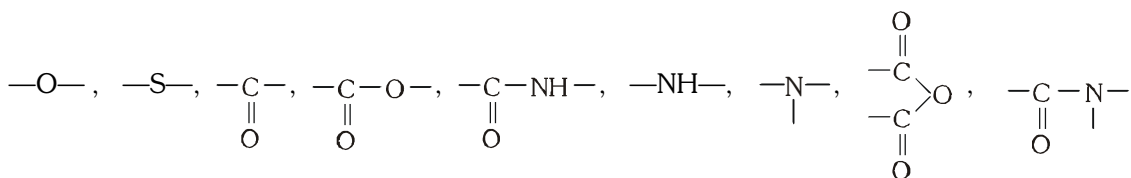
(viii) Alkyl halides do not show Functional isomerism.

(ix) $\text{CH}_3\text{—C}\equiv\text{CH}$ propyne and $\text{CH}_2=\text{CH}=\text{CH}_2$ allene

2.1.5 Metamerism

Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group.

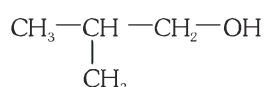
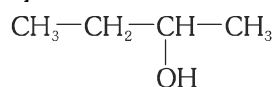
Polyvalent Functional group [Which have more than one valency] are :



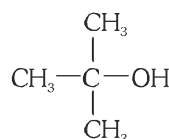
Examples Based on Structural Isomerism :-

Ex. 1 $\text{C}_4\text{H}_{10}\text{O}$ Structural isomers $\Rightarrow 7$ [4 alcohol and 3 ethers] total 7 structural isomers are possible.

Alcohol : $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$

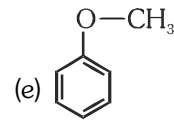
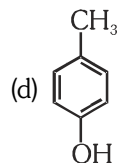
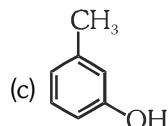
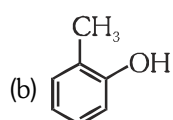
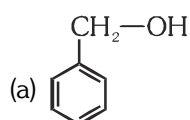


and



Ethers : $\text{CH}_3\text{—O—CH}_2\text{—CH}_2\text{—CH}_3$, $\text{C}_2\text{H}_5\text{—O—C}_2\text{H}_5$, $\text{CH}_3\text{—O—}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{—CH}_3$

Ex. 2 Aromatic isomers of $\text{C}_7\text{H}_8\text{O}$.



- a, b – Functional isomers
- c, d – Position isomers
- a, e – Functional isomers
- b, c – Position isomers
- a, d – Functional isomers
- a, c – Functional isomers

Note : Alcoholic and phenolic groups are Functional isomers.

1. Structures $\text{CH}_3\text{—CH}_2\text{—CH=CH}_2$ and $\text{CH}_3\text{—}\overset{\text{CH}_3}{\underset{|}{\text{C}}}\text{=CH}_2$ are :-

- (1) Chain isomers (2) Position isomers
(3) Both chain & position isomers (4) Not isomers

(1) 4, 5 (2) 3, 5 (3) 4, 6 (4) 4, 4

(1) 4, 5 (2) 3, 4 (3) 4, 4 (4) 5, 5

(1) 5, 4 (2) 5, 3 (3) 4, 6 (4) 4, 4

(1) Ring-chain Isomers (2) Chain Isomers (3) Functional Isomers (4) Position Isomers

(1) Position isomers (2) Functional isomers (3) Identical (4) Chain isomers

(1) Ring-chain Isomers (2) Chain Isomers (3) Functional Isomers (4) Identical

(1) Metamers (2) Chain Isomers (3) Identical (4) Position Isomers

Two or more than two compounds having same molecular formula, same structural formula but different arrangements of atoms or groups in space.

(a) Stereo isomer which cannot interconvert at room temperature due to restricted rotation known as Geometrical isomerism.

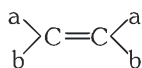
(B) Conformational Isomerism

(i) Alkenes ($>C=C<$), oximes ($>C=N-OH$) and azo compounds [$-N=N-$] etc., show G. I. due to restricted rotation about double bond and (ii) cycloalkanes show G. I. due to restricted rotation about single bond in ring.

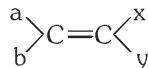
Reason : Restricted rotation about double bond :

Condition for Geometrical isomerism :

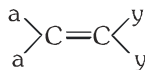
Only those alkenes show G. I. in which "Each sp^2 carbon individually have different atoms or groups"



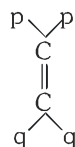
Geometrical isomerism
possible



Geometrical isomerism
possible



Geometrical isomerism
not possible

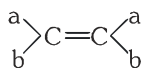


Geometrical isomerism
not possible

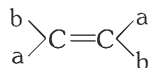
Nomenclature Systems of Geometrical isomers

(a) Cis-Trans System

If same groups are at same side then cis and if same groups are at different side then trans.

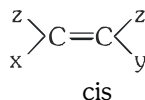
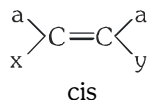


[Same groups, same side]
cis

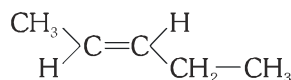


[Same groups different side]
trans

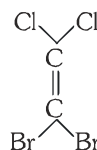
Ex.



Ex.



trans-2-pentene

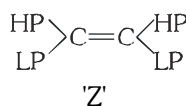
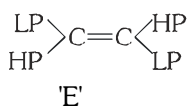


It does not show Geometrical isomers
So no cis-trans

(b) E - Z System :

E (Entgegen) : When high priority groups are at opposite side.

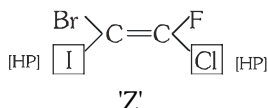
Z (Zusammen) : When high priority groups are at same side.



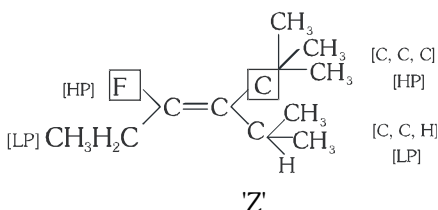
HP – High priority and LP – Low priority

Priority Rules [CIP Sequence Rule] :

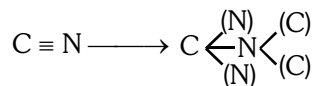
Rule I : Priority is proportional to atomic number of atom which is directly attached to sp^2 carbon.



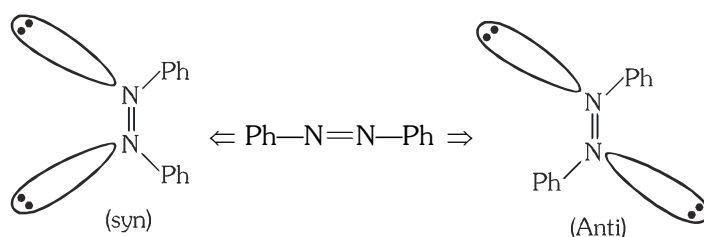
Rule II : If rule-I is failed then consider the atomic number of next atom and so on.



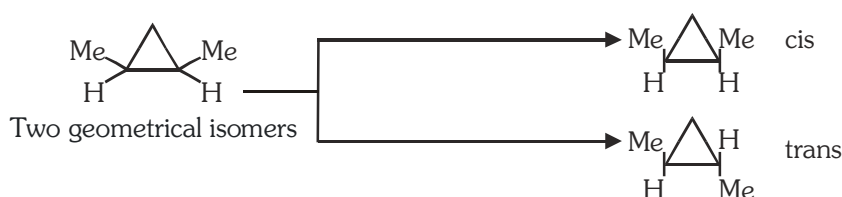
Z:\NODE02\B0A1-B0\TARGET\CHEM\ENG\MODULE-3\02 ISOMERISM\01-THEORY.P6.5



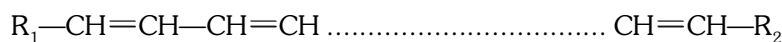
GEOMETRICAL ISOMERS IN AZO COMPOUNDS : ($-\ddot{\text{N}}=\ddot{\text{N}}-$)



GEOMETRICAL ISOMERS IN CYCLOALKANES : Cycloalkanes show Geometrical isomerism due to restricted rotation about single bond. Only those cyclo alkanes show Geometrical isomers in which atleast two different carbons have two different groups.



NUMBER OF GEOMETRICAL ISOMERS IN POLYENES :



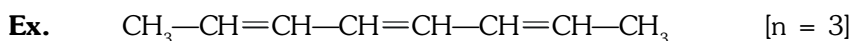
- (a) If $\text{R}_1 \neq \text{R}_2$ then number of Geometrical isomers = 2^n
 [n = number of double bonds which show G.I.]



As $n = 3$, number of Geometrical isomers = $2^3 = 8$

- (b) If $\text{R}_1 = \text{R}_2$ then number of Geometrical isomers = $2^{n-1} + 2^{p-1}$

where $p = \frac{n}{2}$ (when n is even) and $p = \frac{n+1}{2}$ (n is odd)

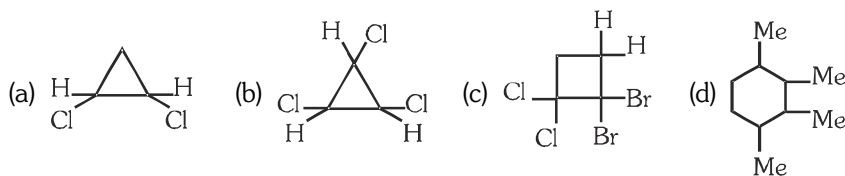


Number of Geometrical isomers = $2^2 + 2^1$
 $= 4 + 2 = 6$

BEGINNER'S BOX-3

- Which of the following shows Geometrical isomerism –
 - $\text{CH}_3-\text{CH}_2-\text{CH}=\text{N}-\text{OH}$
 - $\text{H}_2\text{C}=\text{N}-\text{OH}$
 - $\text{CH}_3-\text{C}(\text{N}=\text{OH})-\text{CH}_3$
 - $\text{CH}_3-\text{C}(\text{N}=\text{OH})-\text{CH}_2\text{CH}_3$
 - a, c
 - c, d
 - a, d
 - b, c
- Which of the following show Geometrical isomerism –
 - 1,1-Diphenyl-1-butene
 - 1,1-Diphenyl-2-butene
 - 2,3-Dimethyl-2-butene
 - 3-Phenyl-1-butene

3. Which of the following show Geometrical isomerism –



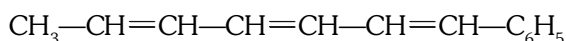
(1) a, b, d

(2) a, c, d

(3) a, b, c

(4) b, c, d

4. Calculate total number of geometrical isomers in the following compound



(1) 2

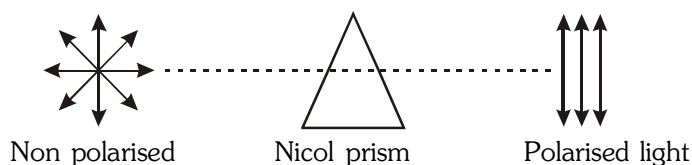
(2) 4

(3) 6

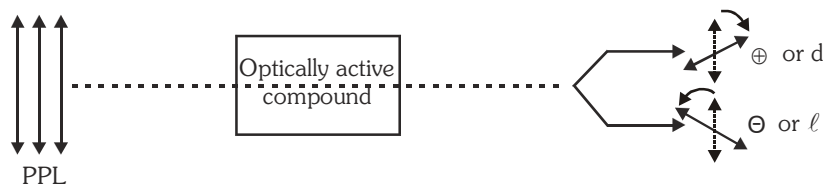
(4) 8

2.2.2 OPTICAL ISOMERISM :

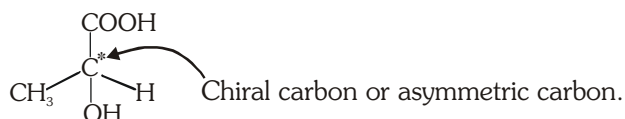
Optical isomers : Two or more than two compound have same molecular formula, same structural formula but different behaviour towards PPL (plane polarised light).



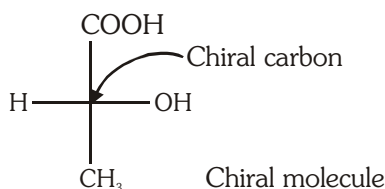
Optical activity : Tendency to rotate plane of PPL in a particular direction. If a compound rotates plane of PPL in clockwise direction then it will be dextrorotatory or d or (+) and if a compound rotates plane of PPL in anticlockwise direction then it will be levorotatory or ℓ or (–).



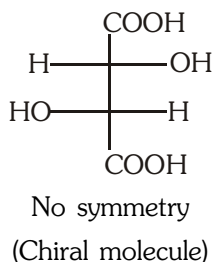
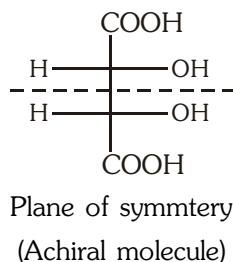
Chiral carbon : Carbon which is bonded to four different atoms or groups.



Chiral molecule : (i) A molecule having only one chiral centre then it will be always chiral. Except flipping



(ii) A molecule having atleast two chiral carbons and no symmetry then it will be chiral molecule.



Essential and sufficient condition for optical activity is :

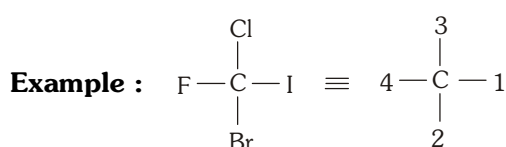
"Molecule should be **chiral**"
or
"Molecule should be **unsymmetrical**"
or
"**Nonsuperimposable** mirror images"

Absolute Configuration (R, S configuration) :

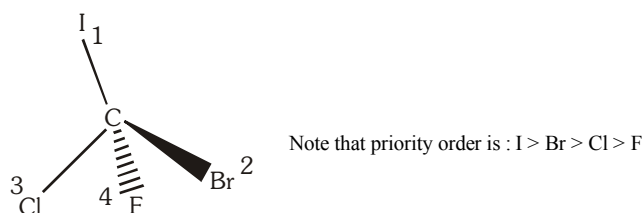
The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is termed as **absolute configuration**.

(R) (S) nomenclature is assigned as follows :

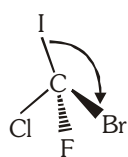
1. Each group attached to stereocentre is assigned a priority on the basis of CIP sequence rule.



2. After assigning priorities, the least priority group is written at remotest valency (going away).

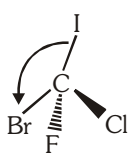


- ◆ Now the order from top priority to second priority and then to the third priority is determined. If it gives a clockwise direction then it is termed R configuration and if the anticlockwise direction is obtained then it is assigned S configuration. For example.



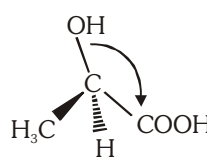
R-configuration

(clockwise from top priority)



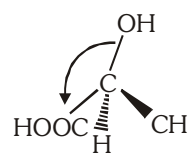
S-configuration

(Anti clockwise from top priority)



R-configuration

(clockwise from top priority)



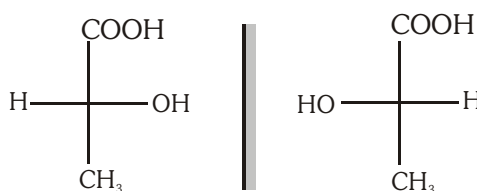
S-configuration

(Anti clockwise from top priority)

Enantiomers :

Stereoisomers which are mirror images to each other and not superimpose to each other.

Nonsuperimposable mirror images are called as enantiomers.



object (I) mirror image (II)

I and II are nonsuperimposable mirror images, so I and II are enantiomers.

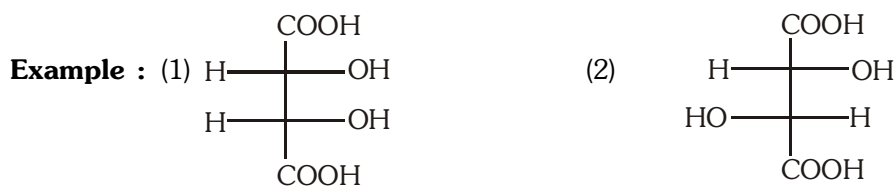
- (i) Enantiomers have chiral structures.
- (ii) Enantiomers are optically active substances. They rotate the plane polarized light in opposite directions but to the equal extent.

Diastereomers : Stereoisomers which are not mirror images of each others.



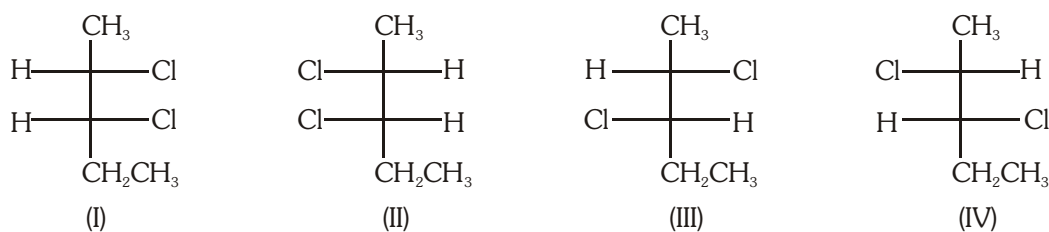
I and II are not mirror images, so I and II are diastereomers.

EXAMPLES OF OPTICAL ISOMERISM

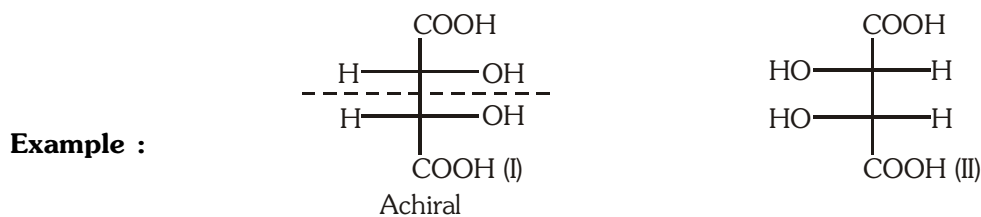


(1) and (2) are diastereomers.

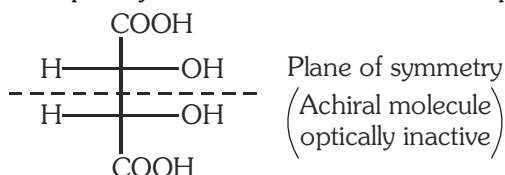
Example :



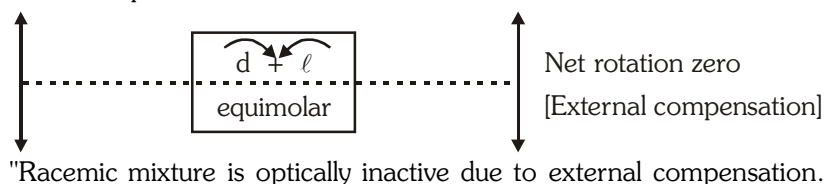
I, II	= Enantiomers,	III, IV	= Enantiomers
I, III	= Diastereomers,	II, IV	= Diastereomers
II, III	= Diastereomers,	I, IV	= Diastereomers



Meso compounds : Compounds having atleast two chiral carbons and plane of symmetry/cos/symmetry is called meso compounds. It is optically inactive due to internal compensation.



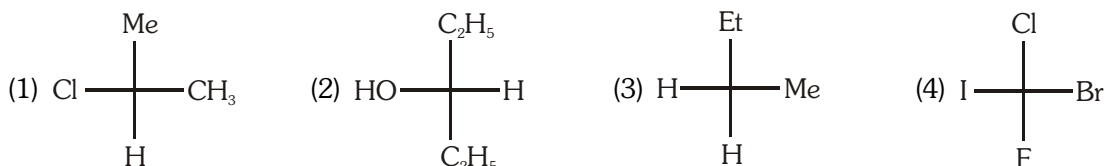
Racemic mixture : Equimolar mixture of d and ℓ enantiomers is called as racemic mixture. ($d\ell$ or $\pm$).



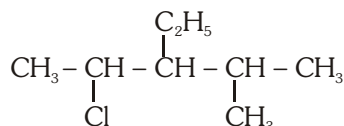
BEGINNER'S BOX-4

1. Which of the following molecule is chiral :-
 (1) Isobutane (2) Neopentane (3) Sec. butylchloride (4) All

2. Which of the following molecule has chiral carbon :-



3. How many chiral carbon atoms are present in following molecule :-

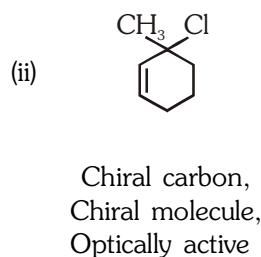
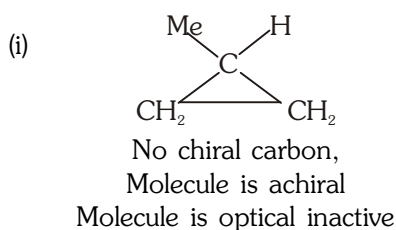


- (1) 1 (2) 2 (3) 3 (4) 4

Number of stereoisomers :

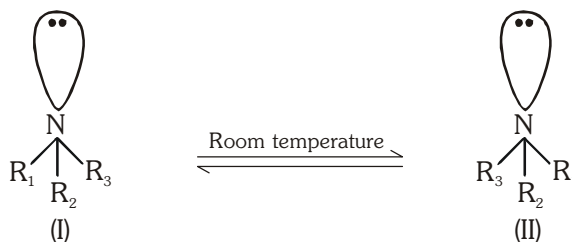
S.N.	Nature of compounds	No. of optically active isomers (a)	No. of meso compounds (m)	Total no. of Stereoisomer (a + m)
1	Compounds having dissimilar ends	2^n (n = No. of chiral centre)	0	$(2^n + 0)$
2	Compounds having similar ends with even chiral centres	2^{n-1}	$2^{\frac{n}{2}-1}$	$(2^{n-1} + 2^{\frac{n}{2}-1})$
3	Compounds having similar ends with odd chiral centres	$2^{n-1} - 2^{\frac{n-1}{2}}$	$2^{\frac{n-1}{2}}$	2^{n-1}

Optical Isomerism in cyclic compounds :

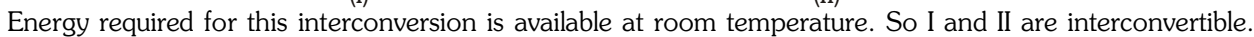


Special Point :

1. Chiral nitrogen containing/tertiary/open chain amine does not show optical isomerism
 Reason :- Rapid umbrella inversion.



Energy required for this interconversion is available at room temperature. So I and II are interconvertible.



Note :- Only 2nd period elements show flipping.

- $$\text{CH}_2=\text{C}=\text{CH}_2 \longrightarrow \begin{array}{c} \text{X} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Y} \end{array} = \text{C} = \text{C} = \begin{array}{c} \text{X} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Y} \end{array}$$

(No chiral C but molecule is chiral)

- Only those substituted allenes will be optically active in which "each sp^2 C have different atoms or group".



BEGINNER'S BOX-5

- $$\begin{array}{ccccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH} & - & \text{CH}_3 \\ & & | & & | & & \\ & & \text{OH} & & \text{OH} & & \end{array}$$

- Calculate total number of optical isomers in following compound :-



- (1)  (2)  (3)  (4) 

- (1) $\text{CH}_3\text{—CH}=\text{C}=\text{CH—CH}_3$

- (2) $\text{CH}_2=\text{C}=\text{CH}_2$

- (4) $\begin{array}{c} \text{Me} \\ \diagup \\ \text{C}=\text{C}=\text{C} \\ \diagdown \\ \text{Et} \end{array} \begin{array}{c} \text{Cl} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Br} \end{array}$

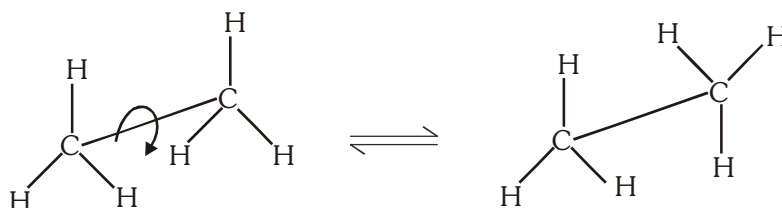
- $$(1) \begin{array}{c} \text{Et} \\ | \\ \text{H} - \text{C} - \text{F} \\ | \\ \text{Me} \end{array}$$

- (3)  CC[C@H](C)Cl

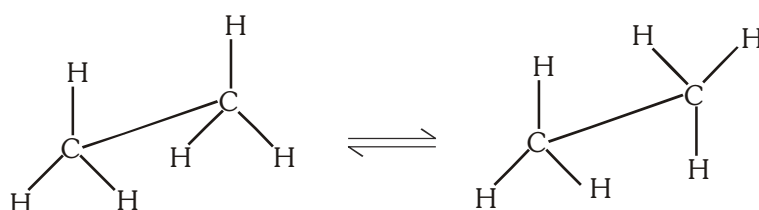
- 31

(B) Conformational Isomerism

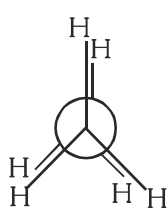
The different arrangement of atoms in space that result from the free rotation around single bond, are called conformations. The phenomenon is called conformational isomerism



Conformations of ethane [$\text{CH}_3\text{—CH}_3$] :

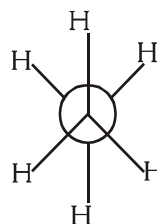


(Saw horse projection)



(III)

60°



(IV)

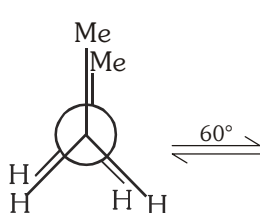
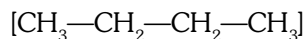
(Newman projection)

Stability order : Staggered > Eclipsed

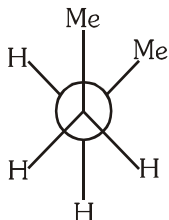
Dihedral Angle : Dihedral angle in eclipsed form of ethane is 0° .

Dihedral angle in staggered form of ethane is 60° .

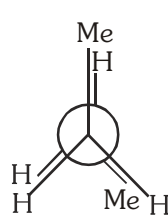
Conformation of Butane



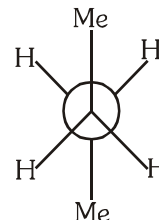
(I)



(II)



(III)



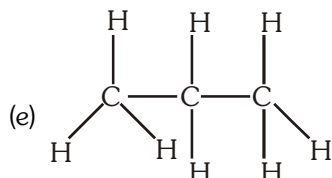
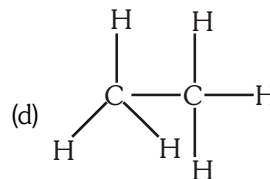
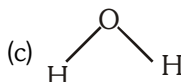
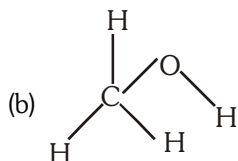
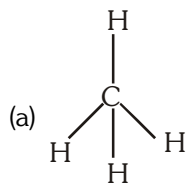
(IV)

I (Fully eclipsed form) : In this form distance between 2 methyl groups is minimum so maximum repulsion or minimum stable.

IV (Anti or staggered) : In this form distance between 2 methyl groups is maximum so minimum repulsion or maximum stable.

Stability order : IV > II > III > I

1. Which of the following shows conformational isomerism.



- (1) b, d, e (2) a, b, c, e (3) b, c, d (4) c, d, e
- 2.** Most stable conformation of butane is :-
- (1) Partial eclipsed (2) Full eclipsed (3) Staggered (4) Gauche
- 3.** Which of the following is not a pair of isomers :
- (1) Propyne and Cyclopropene (2) Propyne and Propadiene
- (3) Propene and Cyclopropene (4) 1-Propanol and Methoxy ethane
- 4.** What is dihedral angle in staggered form of ethane :-
- (1) 30° (2) 45° (3) 75° (4) 60°

BEGINNER'S BOX-1

Que.	1	2	3	4	5	6	7	8
Ans.	1	3	3	1	1	2	4	3

BEGINNER'S BOX-2

Que.	1	2	3	4
Ans.	Z	E	E	E

BEGINNER'S BOX-3

Que.	1	2	3	4
Ans.	3	2	1	4

BEGINNER'S BOX-4

Que.	1	2	3
Ans.	3	4	2

BEGINNER'S BOX-5

Que.	1	2	3	4	5
Ans.	2	2	3	2	3

BEGINNER'S BOX-6

Que.	1	2	3	4
Ans.	1	3	3	4

EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****STRUCTURAL ISOMERISM**

- $\text{CH}_3\text{CHOHCH}_2\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ constitute a pair of :-
 (1) Position isomers
 (2) Metamers
 (3) Optical isomers
 (4) Functional isomers
- The minimum number of carbon atoms present in an organic compound to show chain isomerism is
 (1) 2 (2) 3 (3) 5 (4) 4
- The minimum number of carbon atoms present in an organic compound to be able to show position isomerism is :-
 (1) 3 (2) 4 (3) 2 (4) 5
- Which of the following compound is isomeric with propanoic acid :-
 (1) $\text{CH}_3-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$
 (2) $\text{CH}_2(\text{OH})-\text{CH}_2-\text{C}(=\text{O})-\text{H}$
 (3) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_3$
 (4) $\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2\text{OH}$
- $\text{CH}_3-\text{NH}-\text{C}_2\text{H}_5$ and $(\text{CH}_3)_3\text{N}$ show which type of isomerism :-
 (1) Position (2) Functional
 (3) Chain (4) None
- $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2-\underset{\text{H}}{\text{C}}=\text{O}$ and
 $\text{CH}_3-\text{CH}_2-\text{CH}_2-\underset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{Cl}$
 are constitute a pair of :-
 (1) Position isomers
 (2) Metamers
 (3) Optical isomers
 (4) Functional group isomers
- The minimum number of carbon atoms in ketone to show position isomerism :-
 (1) 3 (2) 4 (3) 5 (4) 6

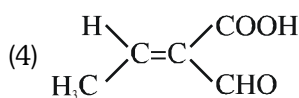
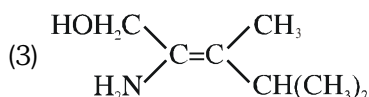
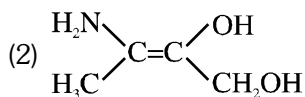
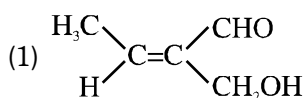
- Which are metamers :-
 (1) $\text{CH}_3-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$
 (2) $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (3) $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$, $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_3$
 (4) $\text{CH}_3-\underset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$, $\text{CH}_3-\text{CH}_2-\underset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{H}$
- Which similarity is necessary for isomerism-
 (1) Molecular formula
 (2) Structure formula
 (3) Physical formula
 (4) Chemical formula
- Number of structural isomers of C_6H_{14} is -
 (1) 3 (2) 4
 (3) 5 (4) 6

GEOMETRICAL AND OPTICAL ISOMERISM

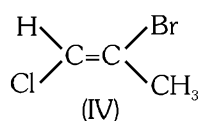
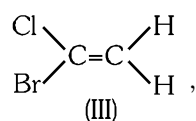
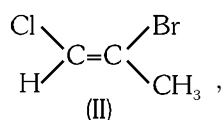
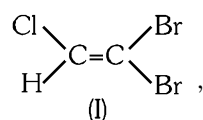
- $$\begin{array}{c} \text{H}_3\text{C} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H}_3\text{C} & & \text{H} \end{array} \quad \begin{array}{c} \text{H} \\ / \\ \text{C} \\ / \\ \text{COOH} \end{array}$$
 Exhibits :-
 (1) Tautomerism
 (2) Optical isomerism
 (3) Geometrical isomerism
 (4) Geometrical and optical isomerism
- The isomerism shown by Benzaldoxime

$$\left[\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{OH} \right]$$
 is :-
 (1) Optical (2) Geometrical
 (3) Metamerism (4) All of these
- Which of the following has Z-configuration :
 (1) $\text{H}_3\text{C}-\text{C}(\text{H})=\text{C}(\text{H})-\text{C}_2\text{H}_5$
 (2) $\text{HOCH}_2-\text{C}(\text{Br})=\text{C}(\text{CH}_2\text{CH}_3)-\text{CH}(\text{CH}_3)_2$
 (3) $\text{Cl}-\text{C}(\text{Br})=\text{C}(\text{H})-\text{D}$
 (4) All the above

14. Which of the following has E-configuration :-



15. Which is a pair of geometrical isomers :-



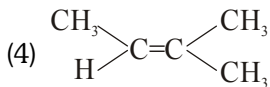
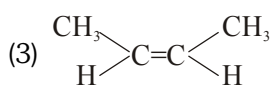
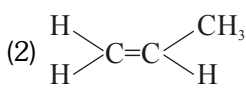
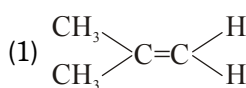
(1) I and II

(2) I and III

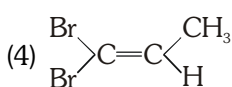
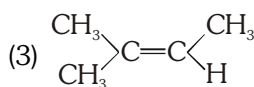
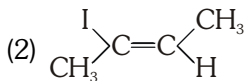
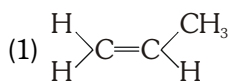
(3) II and IV

(4) III and IV

16. Which can show 'Geometrical isomerism' :-



17. Geometrical isomerism is shown by :



18. The simplest alkanol exhibiting optical activity is

(1) n-butyl alcohol

(2) Isobutyl alcohol

(3) s-butyl alcohol

(4) t-butyl alcohol

19. Meso-tartaric acid $\begin{bmatrix} \text{COOH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{COOH} \end{bmatrix}$ is optically

inactive due to the presence of :-

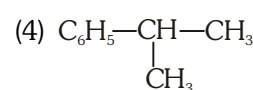
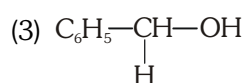
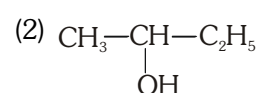
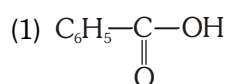
(1) Molecular symmetry

(2) Molecular asymmetry

(3) External compensation

(4) Two asymmetric carbon atoms

20. Which is optically active molecule :-



21. The number of stereo isomers of glucose (a six carbon sugar) is :-

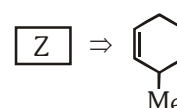
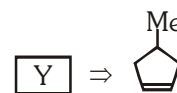
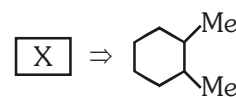
(1) 8

(2) 12

(3) 16

(4) 24

22. Number of chiral carbon atoms in the compound X, Y and Z respectively would be :



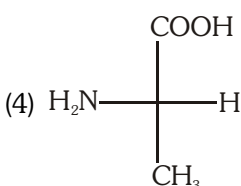
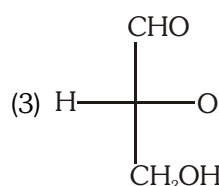
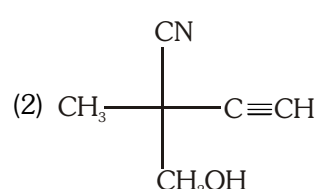
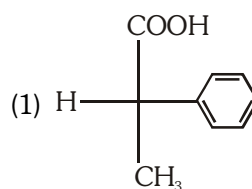
(1) 2, 1, 1

(2) 1, 1, 1

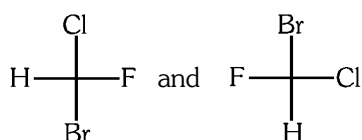
(3) 2, 0, 2

(4) 2, 0, 1

23. Identify R configuration :

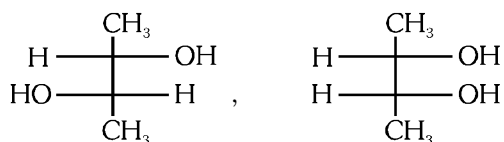


24. The following two compounds are



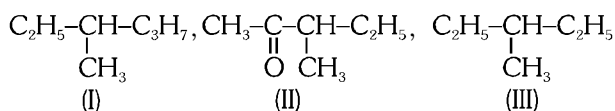
- (1) Enantiomers (2) Diastereomers
(3) Identical (4) Epimers

25. If optical rotation produced by the compound [A] is $+65^\circ$, then produced by the compound [B] is-



- [A] [B]
(1) $+65^\circ$ (2) -65°
(3) Zero (4) Unpredictable

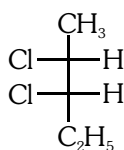
26. Among the following structure I to III



It is true that :-

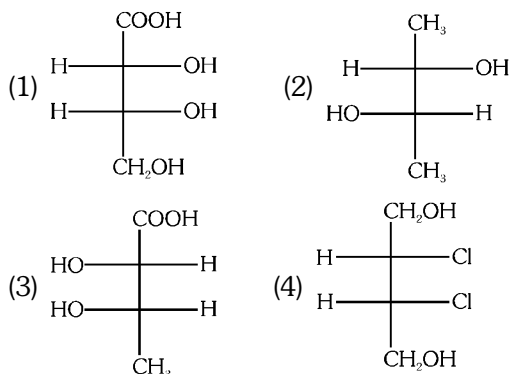
- (1) All three are chiral compounds
(2) Only I and II are chiral compounds
(3) Only II is chiral compound
(4) Only I and III are chiral compounds

27. The absolute configuration of the compound is :

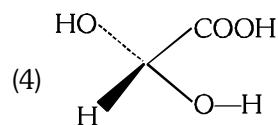
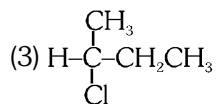
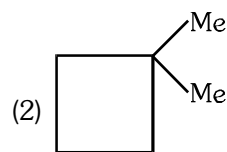
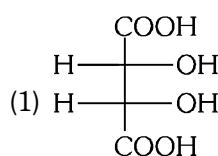


- (1) 2S, 3R (2) 2S, 3S
(3) 2R, 3S (4) 2R, 3R

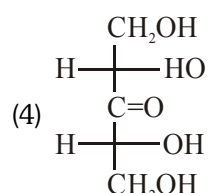
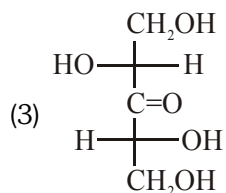
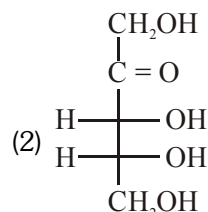
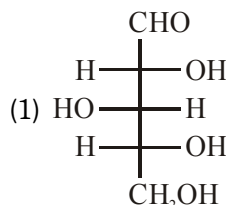
28. Which one of the following is a meso-compound.



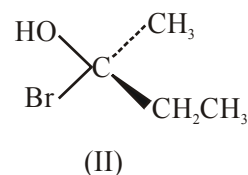
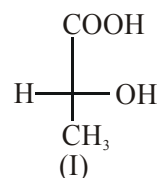
29. Which of the following is optically active :-



30. Amongst the following, which one could be the structure of an optically inactive monosaccharide having the molecular weight 150 :-

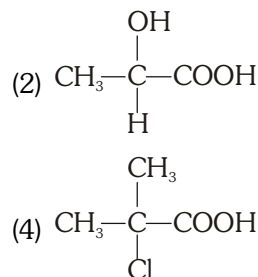
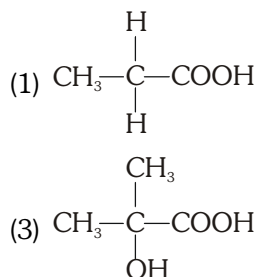


31. The correct configuration assigned for compounds (I) and (II) respectively are :-



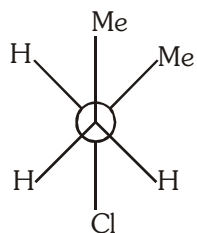
- (1) R, R (2) S, S
(3) R, S (4) S, R

32. Which compound is optical active -

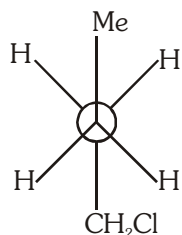


CONFORMATIONAL ISOMERISM

33. The pair of structures represents :-



- (1) Enantiomers
(3) Conformers



- (2) Position isomers
(4) None

34. Rotational angle required to get maximum stable conformer from minimum stable conformer in n-butane is :

- (1) 360° (2) 180°
(3) 120° (4) 240°

35. Which conformation of butane will have the minimum energy :-

- (1) Gauche
(2) Anti/staggered
(3) Eclipsed
(4) None

EXERCISE-I

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	4	3	2	2	4	3	1	1	3	2	2	4	4	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	2	3	1	2	3	4	3	1	3	2	3	4	3	4
Que.	31	32	33	34	35										
Ans.	1	2	2	2	2										

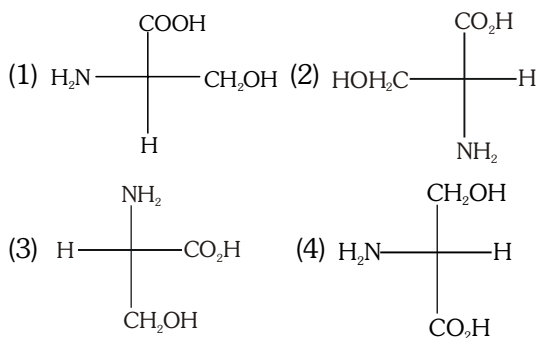
EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT-2006**

1. Which of the following is not chiral :-
 (1) 2-Butanol
 (2) 2,3-Dibromo pentane
 (3) 3-Bromo pentane
 (4) 2-Hydroxy propanoic acid

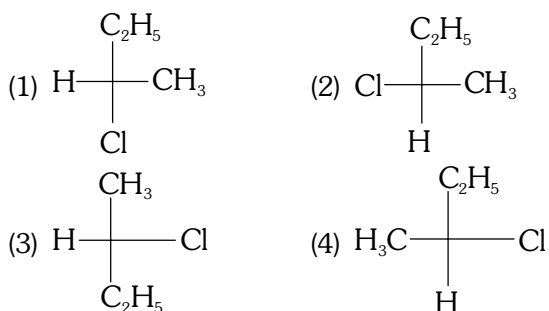
AIIMS-2006

2. Among the following which one can have a meso form -
 (1) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{Cl})\text{C}_2\text{H}_5$
 (2) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$
 (3) $\text{C}_2\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$
 (4) $\text{HOCH}_2\text{CH}(\text{Cl})\text{CH}_3$

3. Among the following L-serine is -

**AIPMT-2007**

4. $\text{CH}_3-\text{CHCl}-\text{CH}_2-\text{CH}_3$ has a chiral centre which one of the following represents its R configuration

**AIPMT-2008**

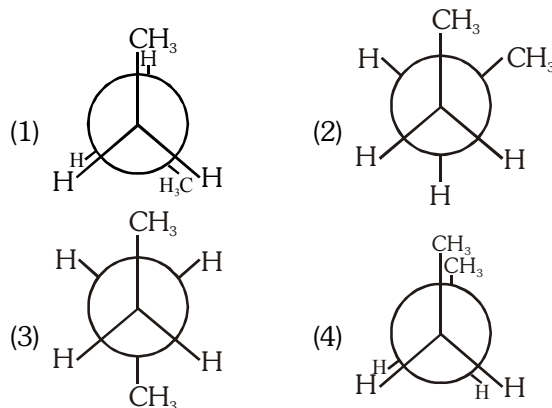
5. How many stereoisomer does this molecule have
 $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CHBrCH}_3$
 (1) 8 (2) 2
 (3) 4 (4) 6

AIPMT-2009

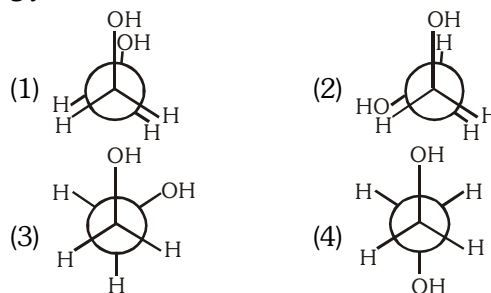
6. Which of the following compounds will exhibit cis-trans (geometrical) isomerism ?
 (1) 1-Butanol (2) 2-Butene
 (3) 2-Butanol (4) 2-Butyne

AIPMT-2010

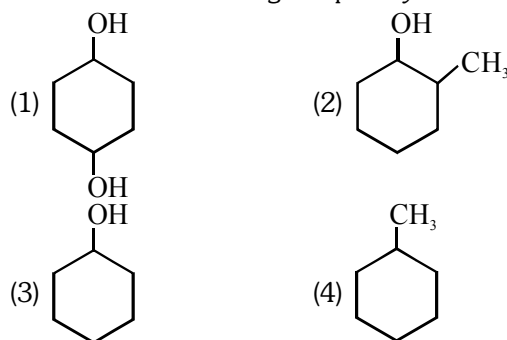
7. In the following the most stable conformation of n-butane is :-



8. Which of the following conformers for ethylene glycol is most stable :-

**AIIMS-2010**

9. Which of the following is optically active :-

**AIIMS-2011**

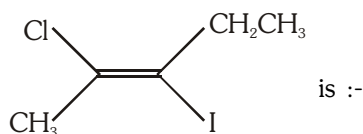
10. Find the number of stereo isomers of 1,2-dihydroxy cyclopentane:
 (1) 1 (2) 2
 (3) 3 (4) 4

AIPMT Pre.-2012

11. Which of the following acids does not exhibit optical isomerism?
 (1) Lactic acid (2) Tartaric acid
 (3) Maleic acid (4) α -amino acids

AIPMT Mains-2011

12. The IUPAC name of the following compound



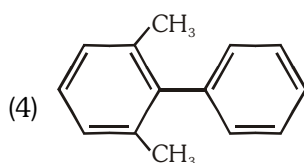
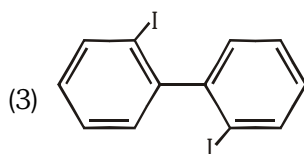
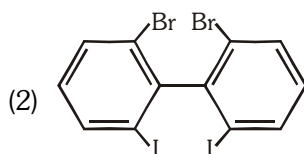
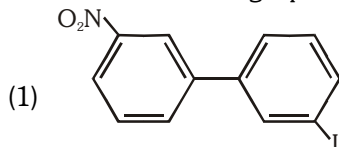
- (1) cis-2-chloro-3-iodo-2-pentene
(2) trans-2-chloro-3-iodo-2-pentene
(3) cis-3-iodo-4-chloro-3-pentene
(4) trans-3-iodo-4-chloro-3-pentene

Re-AIPMT-2015

13. Two possible stereo-structures of $\text{CH}_3\text{CHOH.COOH}$, which are optically active, are called :-
(1) Enantiomers
(2) Mesomers
(3) Diastereomers
(4) Atropisomers
14. The number of structural isomers possible from the molecular formula $\text{C}_3\text{H}_9\text{N}$ is :
(1) 2
(2) 3
(3) 4
(4) 5

NEET-I 2016

15. Which of the following biphenyls is optically active?

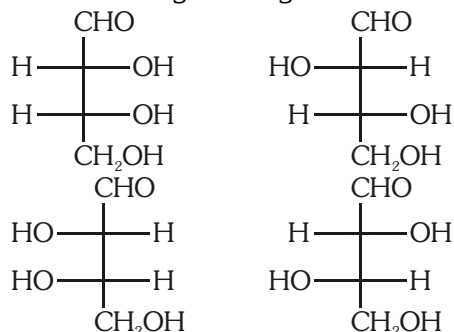


16. The **correct** statement regarding the comparison of staggered and eclipsed conformation of ethane, is :-

- (1) The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
(2) The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
(3) The eclipsed conformation of ethane is more stable than staggered conformation even through the eclipsed conformation has torsional strain
(4) The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.

NEET-II 2016

17. The **correct** corresponding order names of four aldoses with configuration given below

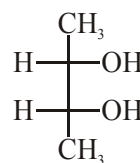


respectively, is :-

- (1) L-erythrose, L-threose, D-erythrose, D-threose
(2) D-erythrose, D-threose, L-erythrose, L-threose
(3) L-erythrose, L-threose, L-erythrose, D-threose
(4) D-threose, D-erythrose, L-threose, L-erythrose

AIIMS 2016

18. Give sawhorse representation for following compound



- (1)
- (2)
- (3)
- (4)



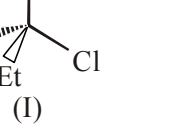
- (1) I and II are identical
- (2) II and III are identical
- (3) I and III are enantiomer
- (4) II and III are enantiomer

- (1) It is possible to separate eclipsed and staggered form of ethane at room temperature.
- (2) Eclipsed form has torsional strain.
- (3) Ethane has infinite number of conformer.
- (4) Energy difference between staggered form and eclipsed form of ethane is 12.5 kJ/mole.

- (1) Bond angle changes but bond length remains same
- (2) Both bond angle and bond length change
- (3) Both bond angles and bond length remains same
- (4) Bond angle remains same but bond length changes

(1) 4 (2) 2 (3) 6 (4) 3

- (1) MP and dipolemoment of $b > a$
- (2) MP of $b > a$ but dipolemoment of $b < a$
- (3) MP and dipolemoment both of $b < a$
- (4) MP of $a > b$ but dipolemoment of $b > a$

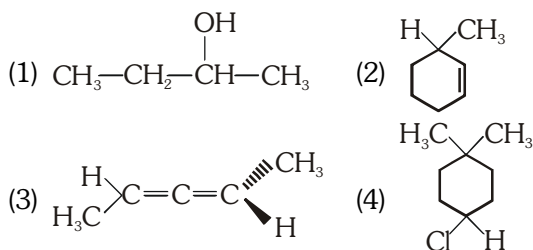


(1) I and III
 (2) II and III
 (3) I and II
 (4) I and IV

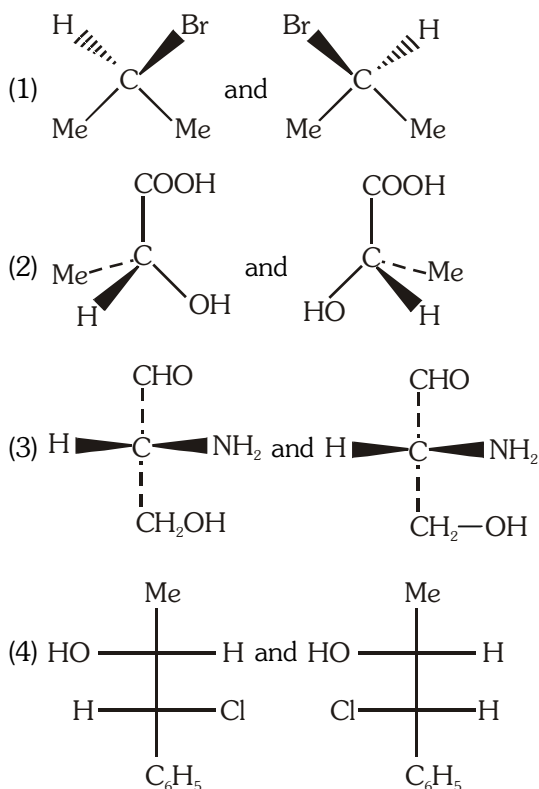
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	3	2	3	2	3	3	2	3	3	2	1	3	2
Que.	16	17	18	19	20	21	22	23	24						
Ans.	4	2	1	4	1	3	1	2	2						

EXERCISE-III (Analytical Questions)

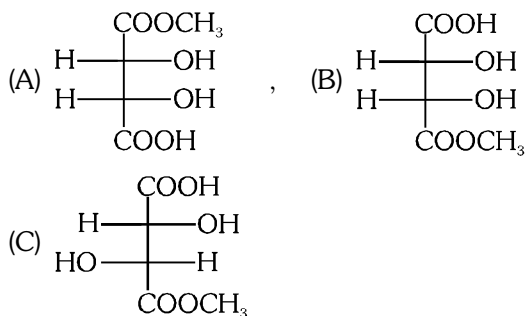
1. Which of the following compound is optically inactive:



2. Which of the following pairs are diastereomers :



3. The correct statement about the compound (A), (B) and (C) is :-

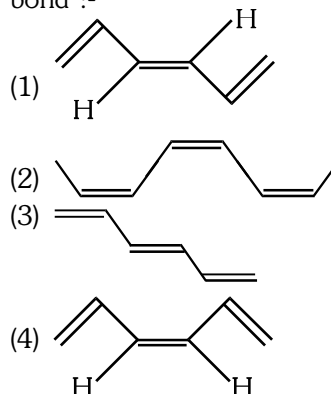


- (1) (A) and (B) are identical
(2) (A) and (B) are diastereomers
(3) (A) and (C) are enantiomers
(4) (A) and (B) are enantiomers

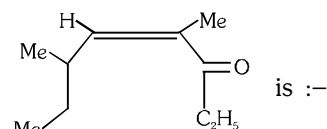
Check Your Understanding

4. Which of the following does not contain any asymmetric carbon but can show enantiomerism:-
(1) Lactic acid (2) 1,3-pentadiene
(3) Tartaric acid (4) 2,3-pentadiene

5. Which of the following represents the structure having cis arrangement around each double bond :-

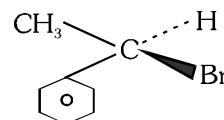


6. The IUPAC name of compound



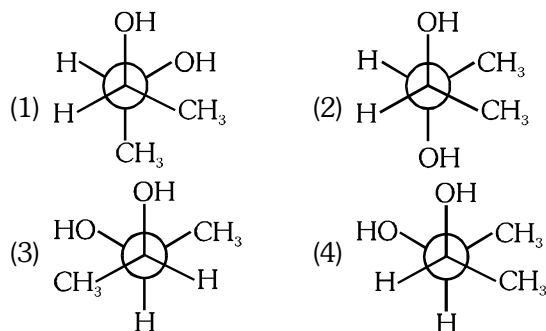
- (1) (Z)-4,6,7-Trimethyl hept-4-en-3-one
(2) (E)-4,6-Dimethyl oct-4-en-3-one
(3) (Z)-4,6-Dimethyl oct-4-en-3-one
(4) (E)-4,6-Dimethyl oct-4-en-6-one

7. The complete IUPAC name of the compound :-

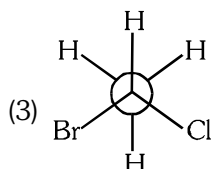
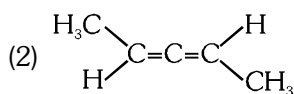
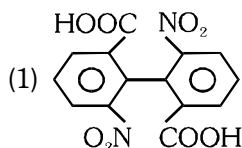


- (1) (R)-1-Bromo-1-phenyl ethane
(2) (S)-1-Bromo-1-phenyl ethane
(3) (E)-1-Bromo-1-phenyl ethane
(4) (Z)-1-Bromo-1-phenyl ethane

8. Which one of the following is the most stable conformation of 2, 3-butanediol :-



9. Which of the following shows optical isomerism:-



(4) All the above

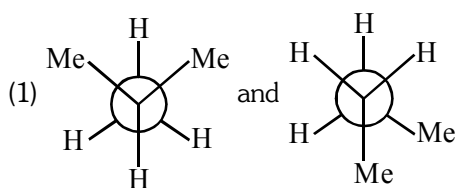
10. How many isomers of $C_5H_{11}OH$ will be primary alcohols (exclude stereoisomers) :-

(1) 2 (2) 3 (3) 4 (4) 6

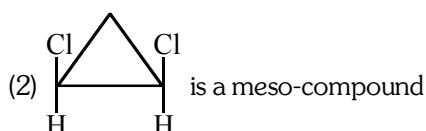
11. The minimum number of carbon atoms in ketone to show metamerism :-

(1) 3 (2) 4 (3) 5 (4) 6

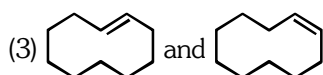
12. Which is incorrect statement :-



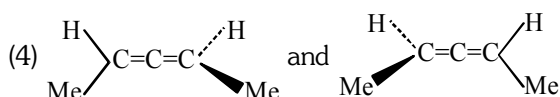
are conformations



is a meso-compound

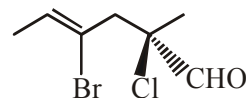


are Geometrical isomers



are Enantiomers

13. The IUPAC name of the given compound is :-



(1) (2R, 4Z)-4-bromo-2-chloro-2-methyl-4-hexenal

(2) (2R, 4E)-4-bromo-2-chloro-2-methyl-4-hexenal

(3) (2Z, 5R)-3-bromo-5-chloro-5-formyl-2-hexene

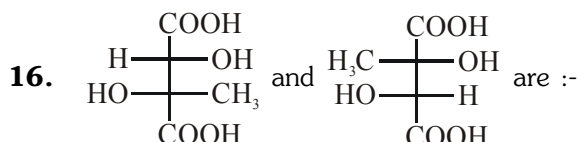
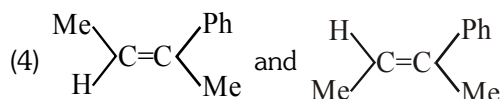
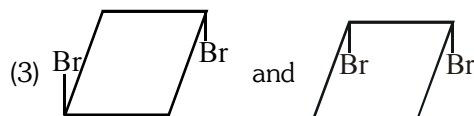
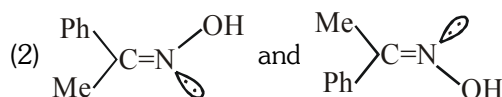
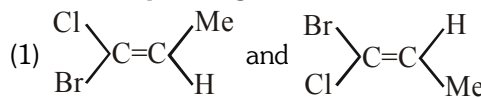
(4) (2S, 4E)-4-bromo-2-chloro-2-methyl-4-hexenal

14. The total number of configurational isomers of the given compound are :-



(1) 2 (2) 4 (3) 6 (4) 8

15. Which is a pair of geometrical isomers :-



(1) Enantiomers (2) Position isomers

(3) Geometrical isomers (4) Homomers

17. Which of the following is not a metamer of $C_4H_{10}O$

(1) Diethyl ether

(2) Methyl n-propyl ether

(3) 2-Methoxy propane

(4) Isobutyl alcohol

EXERCISE-III (Analytical Questions)

ANSWER KEY

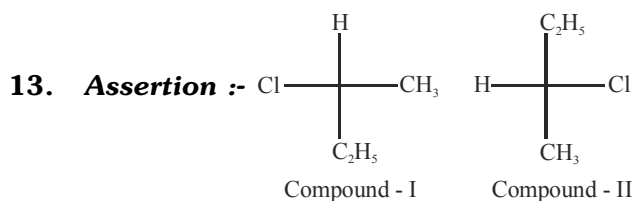
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	4	4	4	2	3	1	3	4	3	3	1	1	4	4
Que.	16	17													
Ans.	4	4													

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** The melting point of fumaric acid is higher than that of maleic acid.
Reason :- The molecules of fumaric acid are more symmetric than those of maleic acid and hence it gets closely arranged in the crystal lattice.
 (1) A (2) B (3) C (4) D
- Assertion :-** trans-1-chloro propene has higher dipole moment than cis-1-chloro propene.
Reason :- The resultant of two vectors in trans-1-chloropropene is more than in cis-1-chloro propene.
 (1) A (2) B (3) C (4) D
- Assertion :-** Trihydroxyglutaric acid (COOH—CHOH—CHOH—CHOH—COOH) exists in four stereoisomeric forms, two of which are optically active while the other two are meso-forms.
Reason :- It contains two asymmetric and one pseudo-asymmetric carbon atom.
 (1) A (2) B (3) C (4) D
- Assertion :-** All meso form of compound are optical isomer.
Reason :- Meso form is optically inactive.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzaldehyde forms two oximes on reacting with NH_2OH .
Reason :- The two oximes arise due to geometrical isomerism around $\text{C}=\text{N}$ bond.
 (1) A (2) B (3) C (4) D
- Assertion :-** The boiling point of cis 1, 2-dichloro ethene is higher than that of corresponding trans-isomer.
Reason :- Cis- 1,2-dichloro ethene has higher dipole moment as compared to that of the trans-isomer.
 (1) A (2) B (3) C (4) D
- Assertion :-** Meso tartaric acid is optically inactive.
Reason :- Its optically inactivity is due to external compensation.
 (1) A (2) B (3) C (4) D
- Assertion :-** 1,2-propadiene exhibits optical isomerism.
Reason :- Its mirror image is non-superimposable.
 (1) A (2) B (3) C (4) D
- Assertion :-** Ethanol cannot show position isomerism.
Reason :- Ethanol cannot show isomerism.
 (1) A (2) B (3) C (4) D
- Assertion :-** $\text{CH}_3\text{—CH}_2\text{—Br}$ and $\text{CH}_3\text{—CH}_2\text{—I}$ are Functional isomers.
Reason :- The above compounds are homologues.
 (1) A (2) B (3) C (4) D
- Assertion :-** Neopentyl bromide and 2-bromo-2-methyl butane are enantiomers.
Reason :- Both have same molecular formula as well as structure formula.
 (1) A (2) B (3) C (4) D
- Assertion :-** Organic compounds which do not contain chiral carbon atoms can be optically active.
Reason :- Presence of chiral carbon is an essential condition for optical activity.
 (1) A (2) B (3) C (4) D



Compound-I and II are enantiomers.

Reason :- Non superimposable mirror images are enantiomers.

(1) A (2) B (3) C (4) D

14. **Assertion :-** cis-3-bromopropenoic acid is more stable than its trans form.

Reason :- Dipole moment of cis form is greater than trans form

(1) A (2) B (3) C (4) D

15. **Assertion :-** All hydrogen atoms in $\text{CH}_2=\text{C}=\text{CH}_2$ lie in one plane.

Reason :- All the carbon atoms in it are sp^2 hybridised.

(1) A (2) B (3) C (4) D

16. **Assertion :-** 4-Methylhex-2-ene shows stereoisomerism.

Reason :- It can show Geometrical isomerism.

(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	1	1	2	1	1	3	4	3	4	4	3	1	4	4
Que.	16														
Ans.	2														

S. No.	CONTENTS	Page
1.	Concepts to Understand reaction mechanism	45
2.	Type of bond cleavage	45
3.	Type of attacking reagent	45
4.	Reaction Intermediate	46
5.	Electronic effect	47
6.	Inductive effect	47
7.	Resonance effect	51
8.	Hyperconjugation effect	62
9.	Electromeric effect	64
10.	Tautomerism	65
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12.	Exercise-II (Previous Years Questions)	74
13.	Exercise-III (Analytical Questions)	80
14.	Exercise-IV (Assertion & Reason)	83

NEET SYLLABUS

Electronic displacements in a covalent bond : inductive effect, electromeric effect, resonance and hyper conjugation. Homolytic and heterolytic fission of a covalent bond : free radicals, carbocations, carbanions; electrophiles and nucleophiles.

OBJECTIVES

After studying this unit, we will be able to :

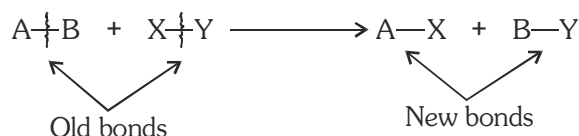
- *understand the concept of organic reaction mechanism;*
- *explain the influence of electronic displacements on structure and reactivity of organic compounds;*

*"When learning is purposeful, creativity blossoms. When creativity blossoms;
thinking emanates. When thinking emanates, knowledge is fully lit.
When knowledge is lit, economy flourishes."*

A.P.J. Abdul Kalam

REACTION MECHANISM : PART-I

- ❑ **Reaction :** Breaking of old bond and formation of new bond is known as chemical reaction



A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. Reactants are of two types substrate and reagent.

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

3.0 CONCEPTS TO UNDERSTAND REACTION MECHANISM :

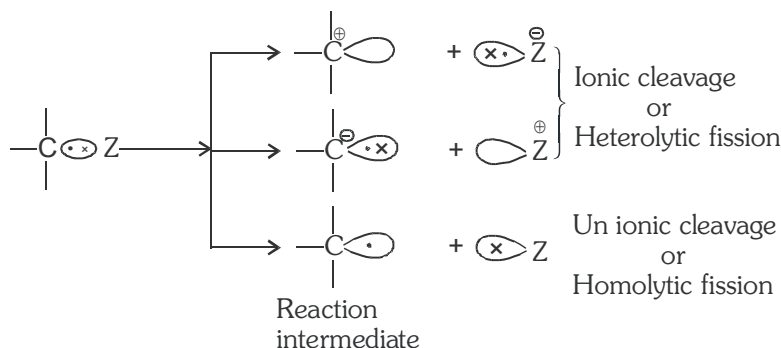
- (1) Bond cleavage (2) Attacking reagent (3) Reaction intermediate (4) Electronic effect

3.1 TYPE OF BOND CLEAVAGE :

(a) Heterolytical cleavage/fission : Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytical cleavage.

(b) Homolytical cleavage/fission : Cleavage in which equal distribution of e^- s takes place during the chemical reaction, is known as homolytical cleavage.

Due to equal distribution of electrons, without charge unpaired electron containing species are formed, which are known as free radicals and cleavage is known as unionic cleavage/homolytical fission.



3.2 TYPES OF ATTACKING REAGENTS

These are of two types :

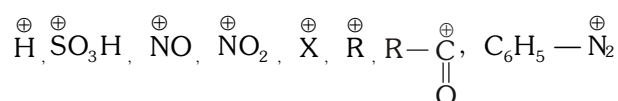
(a) Electrophilic reagent or electrophiles:

Electrophilic (electro + philic)
 (electron + loving)

The reagent which attacks on the negative part of the molecule or having attraction for electrons are called electrophiles.

Electrophiles may be positively charged or neutral.

(i) Positively charged electrophiles :



(ii) Neutral electrophiles :- central atom e^- deficient

(a) All Lewis acids as :

$\text{BF}_3, \text{AlCl}_3, \text{SO}_3, \text{ZnCl}_2, \text{BeCl}_2, \text{FeCl}_3, \text{SnCl}_2, \text{CO}_2, \text{SnCl}_4.$

(b) Free radicals, carbenes and nitrenes act as electrophiles.

(b) Nucleophilic reagent or nucleophiles

Which attacks on the positive site of the substrate or loves nucleus or having attraction towards nucleus.

Nucleophilic

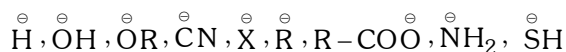
(Nucleo + philes)



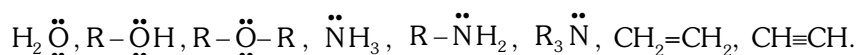
(Nucleus + loving)

Nucleophiles may be negatively charged ions or possess a lone pair of electron or πe^- .

(i) Negatively charged nucleophiles.



(ii) All Lewis base which contains lone pairs or πe^-



(iii) $\text{R}^* - \text{Mg} - \text{X}$, LiAlH_4^* , NaBH_4^*

The star (*) indicates the atom which donates electrons to the substrate.

Ambident nucleophile :- Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear a lone pair of electrons.

Examples :- $\text{K}^+\text{O}^--\text{N}=\text{O}$, $\ddot{\text{N}}\text{H}_2-\ddot{\text{O}}\text{H}$, $\text{Na}^+\text{C}^-\equiv\text{N}$

3.3 REACTION INTERMEDIATE

□ Carbocation :

Cation in which positive charge is present on carbon atom is called carbocation.

- ◆ Due to electron deficiency it acts as an electrophile and always attacks on electron richer site.
- ◆ It is incomplete octet species because it has six electrons in outermost shell.
- ◆ All electrons are paired.

□ Carbanions : Anion in which negative charge is present on carbon atom is called carbanion.

- ◆ It has eight electrons in outermost shell so it is complete octet species.
- ◆ It is an electron richer species because it has extra electron.
- ◆ Due to presence of non bonding electrons it acts as a nucleophile.

□ Free Radical :

- ◆ Electrically neutral species in which unpaired electron is present on carbon atom is known as carbon free radical.
- ◆ It has seven electrons or odd electron in outermost shell of unpaired electron containing carbon.
- ◆ It is electron deficient species due to incomplete octet.

□ Carbenes ($\text{CH}_2:$) :

Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atoms or groups and carries two nonbonded electrons.

- It behaves as an electrophile.
- It is neutral.
- $6 e^-$ in outermost shell.
- $4 e^-$ are bonded and two are nonbonded e^- .

□ Nitrenes ($-\ddot{\text{N}}:$)

Nitrenes are neutral nitrogen species in which the nitrogen is bonded to one monovalent atom or group and carries four non-bonded electrons.

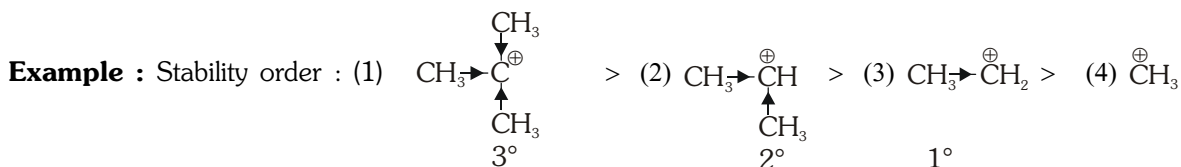
- It is monovalent radical.
- It is neutral.
- $6 e^-$ in outermost shell.
- Two are bonded and four are nonbonded electrons.

APPLICATION OF I-EFFECT

(1) Stability of carbocation :

$$\text{Energy} \propto \text{charge} \propto \frac{1}{\text{stability}}$$

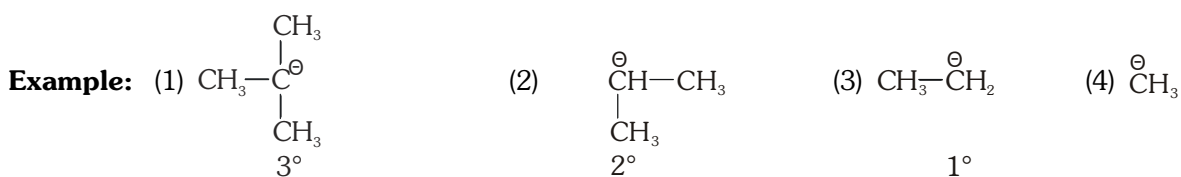
$$\text{Stability of carbocation} \propto \frac{+I \text{ effect}}{-I \text{ effect}}$$



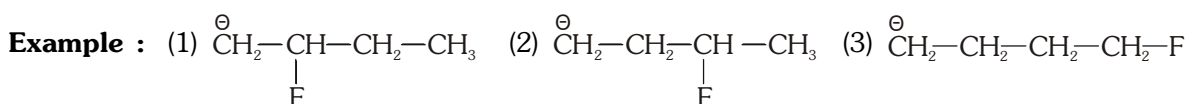
Reason : More no. of +I group.
more stable carbocation.
so stability order $1 > 2 > 3 > 4$.

(2) Stability of carbanion :

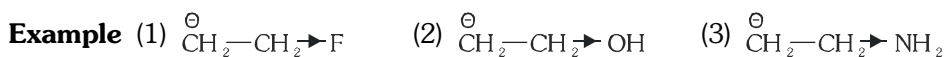
$$\text{Stability of Carbanion} \propto \frac{-I \text{ effect}}{+I \text{ effect}}$$



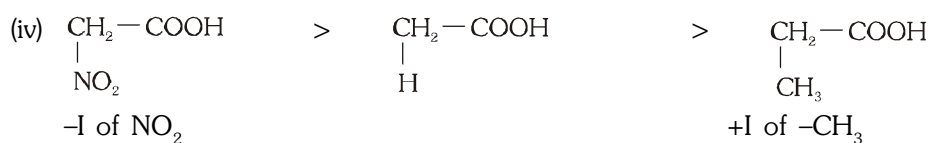
More No. of +I group.
Less stable carbanion.
So stability order $4 > 3 > 2 > 1$



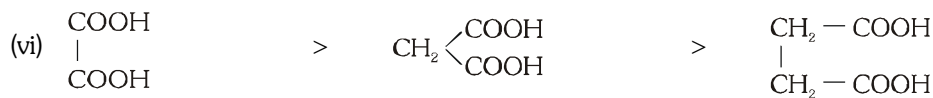
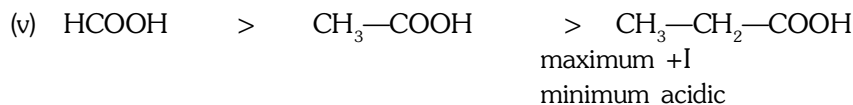
Minimum distance of -F.
Maximum -I of -F.
Minimum negative charge.
Maximum stable.
So stability order $1 > 2 > 3$



Maximum -I of F.
Negative charge will be minimum.
Maximum stable.
So stability order $1 > 2 > 3$



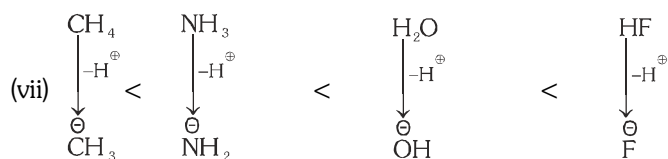
maximum acidic



minimum distance of $-\text{COOH}$ from other

maximum -I of $-\text{COOH}$ on other

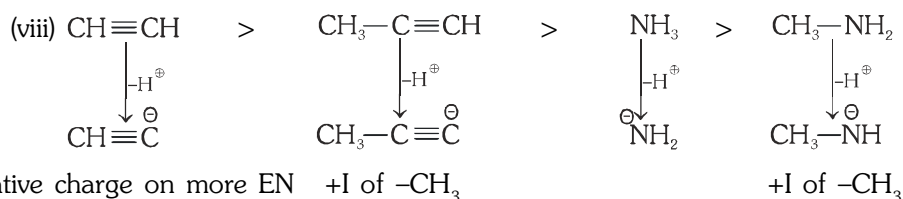
maximum acidic



Negative charge on maximum E.N.

Maximum stable anion

So corresponding acid is most acidic

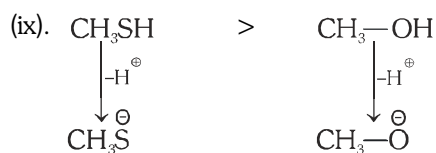


negative charge on more EN

atom and no +I

anion is maximum stable

so corresponding acid is most acidic

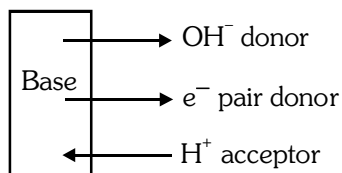


negative charge on big size atom

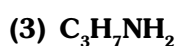
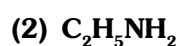
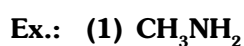
more stable anion

so corresponding acid is more acidic

◆ Basic strength :



$$\text{Basic strength} \propto +I \text{ effect} \propto \frac{1}{-I \text{ effect}}$$



Ans. 4 > 3 > 2 > 1

Maximum +I

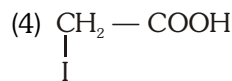
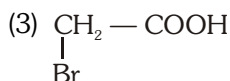
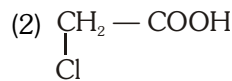
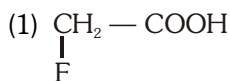
so maximum basic

BEGINNER'S BOX-3

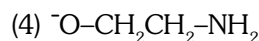
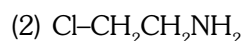
1. Which of the following is most acidic :

- (1) $\text{Cl}_3\text{C}-\text{COOH}$ (2) $\text{Cl}_2\text{CH}-\text{COOH}$ (3) $\text{ClCH}_2-\text{COOH}$ (4) CH_3COOH

2. Which of the following is most acidic :



3. Which is most basic among the following :

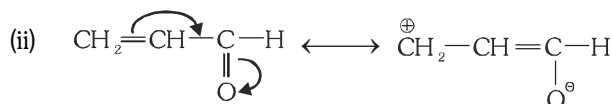
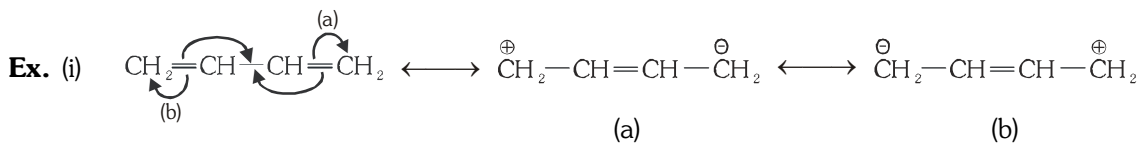


3.4.2 RESONANCE OR MESOMERIC EFFECT

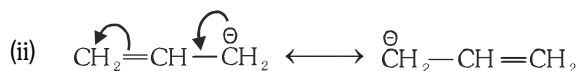
Delocalization of πe^- is called as resonance or complete transfer of πe^- from one shell to another shell is called as **Resonance**.

Conditions For Resonance

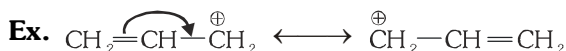
(1) If there are two π bonds in conjugation then e^- of one π bond are transferred towards another π bond.



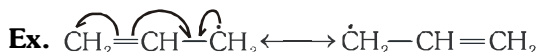
(2) If there is lone pair or a negative charge and π bond are in conjugation then lone pair of e^- or negative charge are transferred towards π bond.



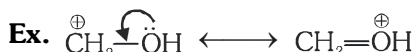
(3) If there is positive charge (vacant orbital) and π bond are in conjugation then e^- of π bond are transferred towards positive charge.



(4) If there is free e^- and π bond are in conjugation.



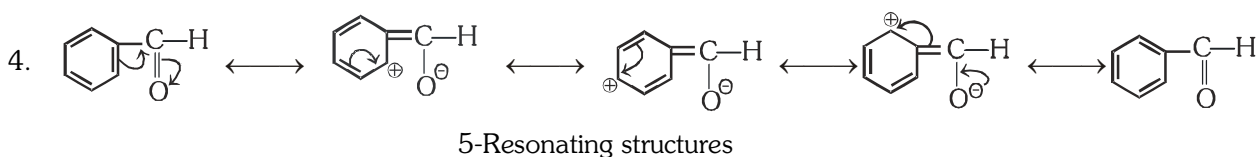
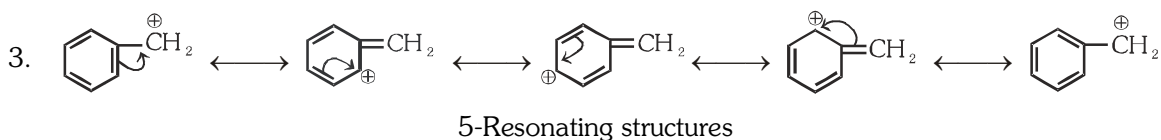
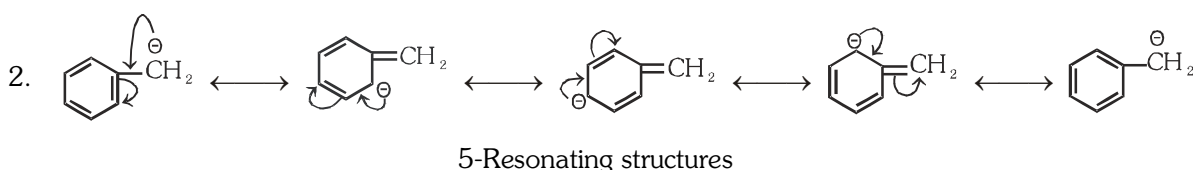
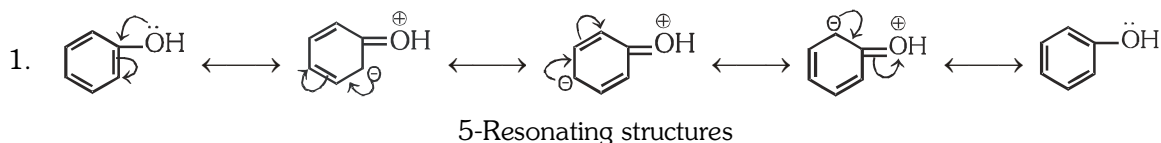
(5) If there is lone pair or negative charge and positive charge (vacant orbital) are in conjugation then e^- of lone pair or negative charge are transferred towards positive charge.



GOLDEN KEY POINTS

- In resonance only e^- are delocalised not atoms.
- The number of e^- or number of unpaired or paired e^- in all resonating structures should be same.
- It is permanent effect.
- All the resonating or canonical structures must follow the Lewis structures.

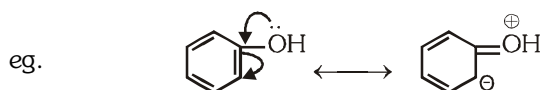
Draw resonating structures :



M-effect : Delocalisation of electron in conjugated system (due to presence of EWG or EDG) is known as 'M' effect.

(1) +M effect :- Group that donates the electron pair to conjugated system is known as +M effect exerting groups and the phenomena is known as +M effect.

+M group : Lone pair containing group like

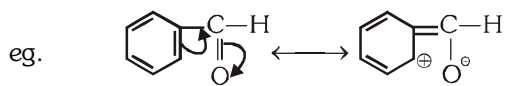


-OH group lone pair donor

So + M of -OH group

(2) -M effect :- Group, that withdraws electron pair from the conjugated system, is known as -M effect exerting groups and the phenomena is known as -M effect.

-M group : $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{COR}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{COX}$, $-\text{CONH}_2$, $-\text{SO}_3\text{H}$



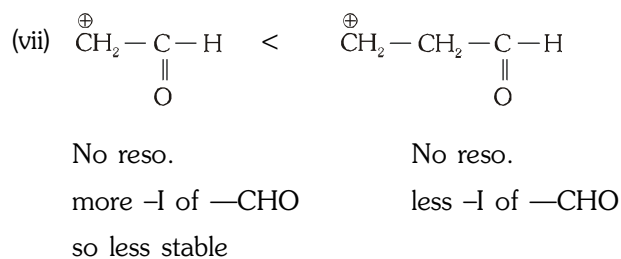
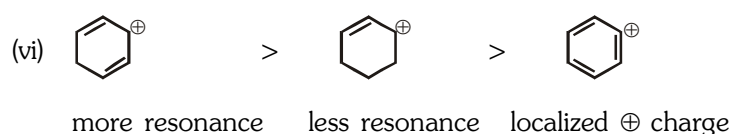
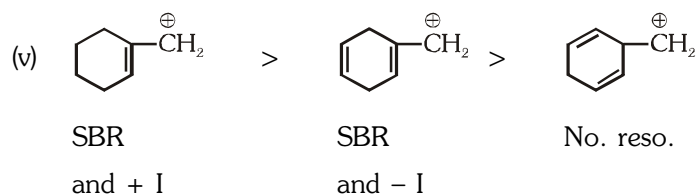
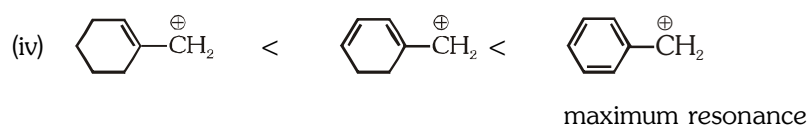
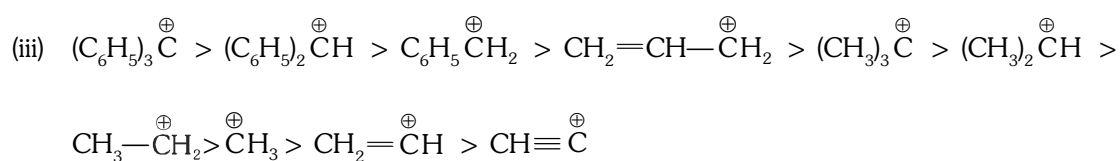
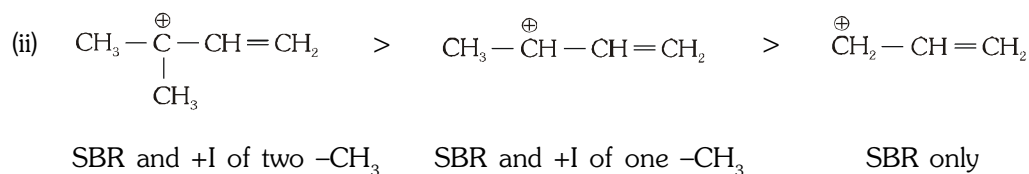
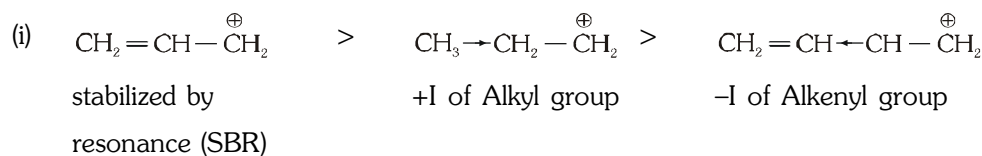
-CHO group withdrawing e^- .

So -CHO is -M group

APPLICATIONS OF RESONANCE EFFECT :

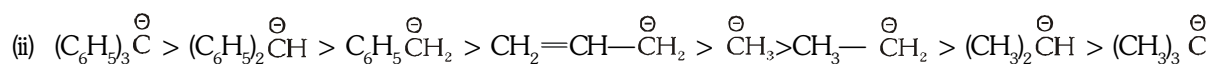
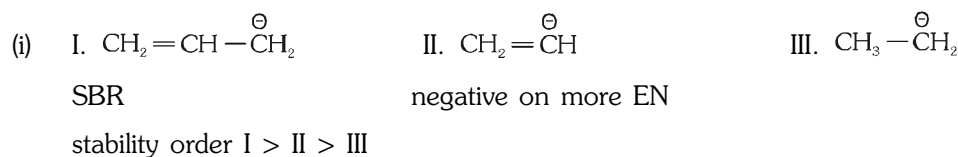
(1) Stability of carbocation.

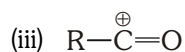
Ex. Give stability order for :-



(2) Stability of carbanion :

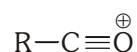
Ex. Give stability order of :



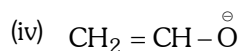


incomplete octet

<



complete octet



(negative charge on more EN)

>



(negative charge on less EN)

(5) Aromaticity (Huckel's rule) : Cyclic, planar and completely conjugated system with $(4n+2)\pi$ electrons (where $n = 0, 1, 2, 3, \dots$) is known as aromatic compounds, these compound gains extra stability which is known as aromaticity.

Note : $[4n + 2]$ π electrons. (Odd number of π electron pairs) means

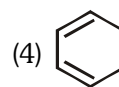
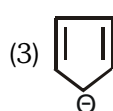
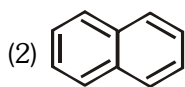
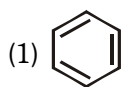
If $n = 0$	2π electrons	or 1 pair
$n = 1$	6π electrons	or 3 pairs
$n = 2$	10π electrons	or 5 pairs
$n = 3$	14π electrons	or 7 pairs

S.No	Compound	Cyclic	Planar	Cyclic Resonance	Huckel Rule $(4n+2) \pi e^-$	Aromatic Yes/No
1.		✓	✓	✓	$2\pi e^-$	Yes
2.		✓	✓	✓	$4\pi e^-$	No
3.		✓	✓	✓	$4\pi e^-$	No
4.		✓	✓	✓	$6\pi e^-$	Yes
5.		✓	✓	✓	$6\pi e^-$	Yes
6.		✓	✗	✗	$4\pi e^-$	No
7.		✓	✓	✓	$6\pi e^-$	Yes
8.		✓	✓	✓	$6\pi e^-$	Yes

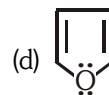
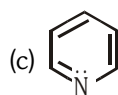
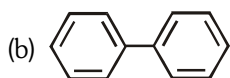
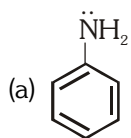
9.		✓	✓	✓	$6\pi e^-$	Yes
10.		✓	✓	✓	$6\pi e^-$	Yes
11.		✓	✓	✓	$6\pi e^-$	Yes
12.		✓	✓	✓	$10\pi e^-$	Yes
13.		✓	✓	✓	$14\pi e^-$	Yes
14.		✓	✓	✓	$6\pi e^-$	Yes
15.		✓	✗	✗	$6\pi e^-$	No
16.		✓	✓	✓	$6\pi e^- + 6\pi e^-$	Yes

BEGINNER'S BOX-4

1. Which of the following is nonaromatic



2. Which of the following compounds are aromatic in nature



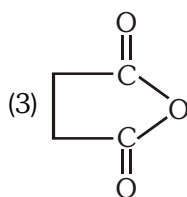
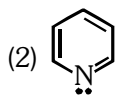
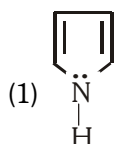
(1) Only a

(2) a and b

(3) a, b, d

(4) all of these

3. Which of the following is not aromatic compound



(4) All of these

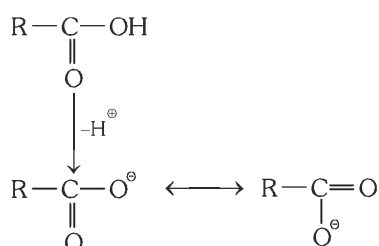
(6) Acidic and Basic strength :

(a) **Acidic strength :** $\left(\text{Acidic strength} \propto \text{stability of conjugate base (anion)} \propto \frac{-M, -I}{+M + I} \right)$

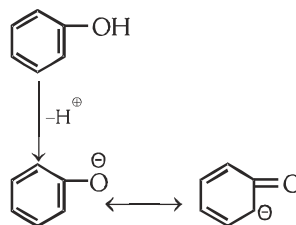
Illustrations

Illustration 1. Carboxylic acids are more acidic than phenols, why ?

Solution.



2, equal R.S. more stable anion
so corresponding acid is more acidic.
Here, carboxylate ion is more stable
than phenoxide ion.

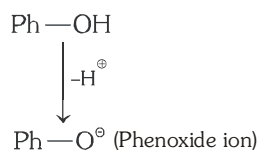


5, unequal R.S. less stable anion since -ve
charge is being shared by oxygen is less
electronegative carbon.

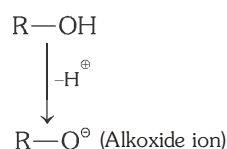
Note : The molecule having equivalent R.S. has more stability than the molecule having non equivalent R.S.

Illustration 2. Phenol is more acidic than alcohols why ?

Solution.



anion stable by resonance
So, corresponding acid is more acidic.



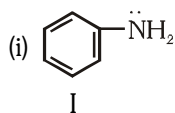
no resonance.
less stable anion

(b) Basic strength order :- Tendency to donate the electron pair by an atom or group is known as its basic strength. Compounds in which electron pair is delocalised will be less basic while, Those in which electron pair is localised will be more basic.

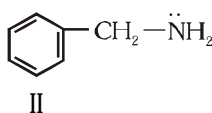
$$\left(\text{Basic strength} \propto \text{H}^+ \text{ accepting tendency} \propto \text{l.p. donating tendency} \propto \frac{+M, +I}{-M - I} \right)$$

Ex.

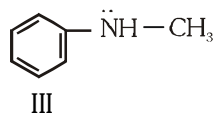
Give basic strength order :



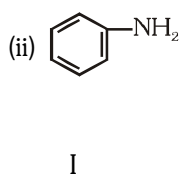
l.p. is stabilized by
resonance
basic order —



no reso. of l.p.
so maximum basic
II > III > I



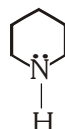
l.p. is stabilized by resonance
and +I of CH₃



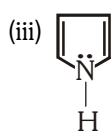
SBR
basic order —



localized l.p.
on more EN
III > II > I

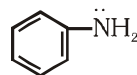


localized l.p.
on less EN

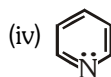


more resonance of l.p.
so less basic

<



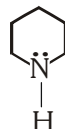
less resonance of l.p.
so more basic



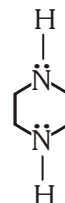
I
l.p. on
more EN
so minimum basic
So, basic order



II
more -I
of oxygen



III
+I

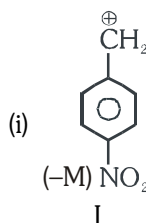


IV
less - I of
nitrogen

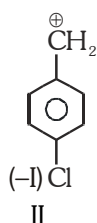
III > IV > II > I

Illustrations

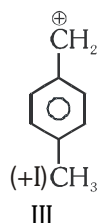
Illustration 3. Give stability order of :



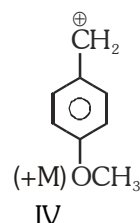
charge ↑
So stability order



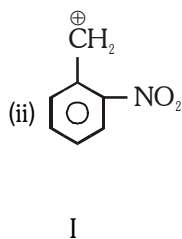
charge ↑
IV > III > II > I



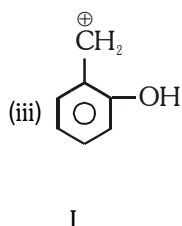
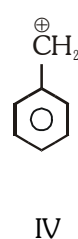
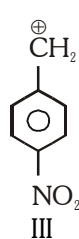
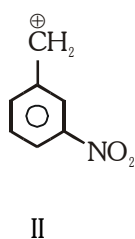
charge ↓



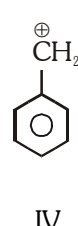
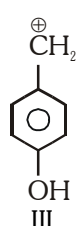
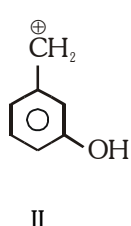
charge ↓



$-M_o = -M_p$ and $-M_m = 0$
but $-I_o > -I_m > -I_p$, $-M$ and $-I$ increases positive charge.
stability order is IV > II > III > I



$-OH$ group shows $+M$ effect
 $+M_o = +M_p$ and $+M_m = 0$ but $-I_o > -I_m > -I_p$ and $+M \gg -I$
So $+M$ stabilize the carbocation by decreasing positive charge
Stability order III > I > IV > II



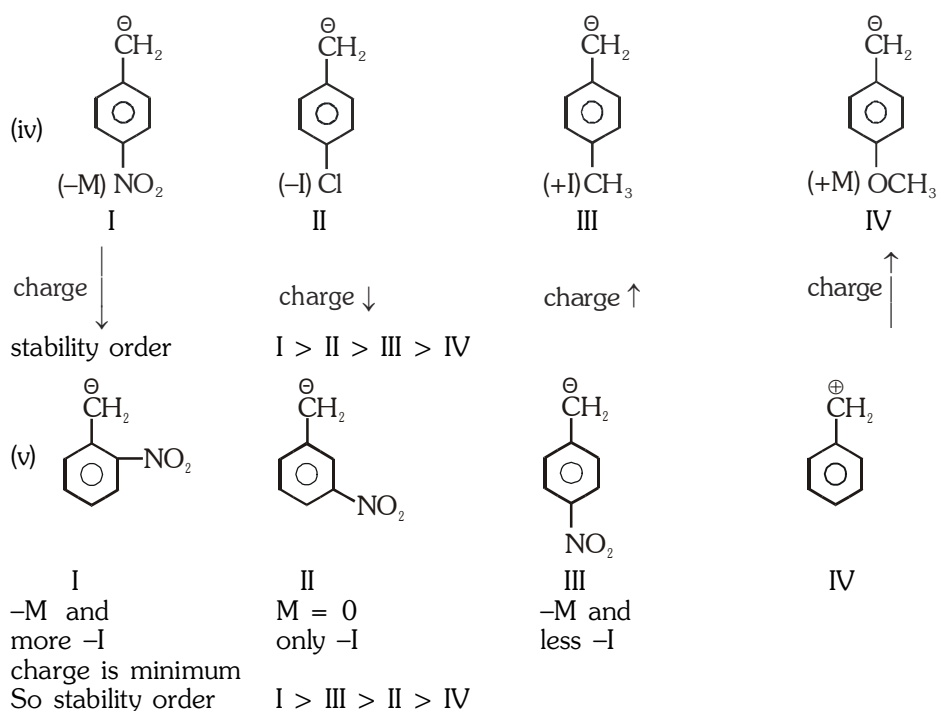
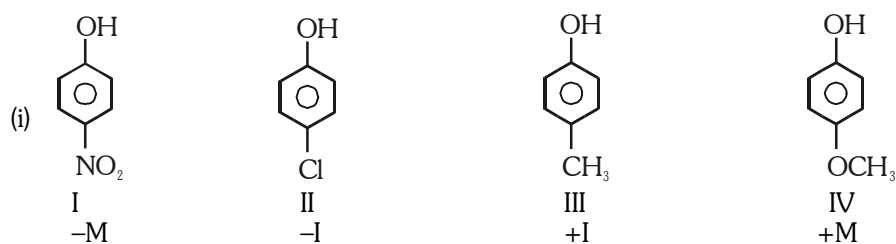
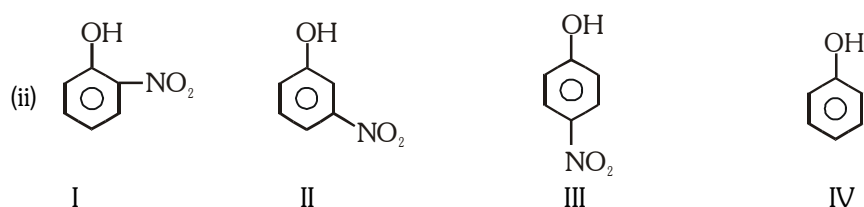


Illustration 4. Give acidic strength order for :



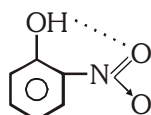
So acidic order is I > II > III > IV



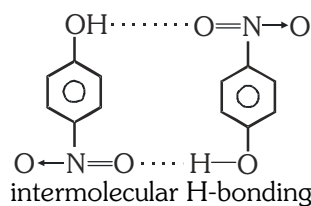
-M and more -I M = 0 only -I -M and less -I

Acidic order should be I > III > II > IV but correct order is III > I > II > IV

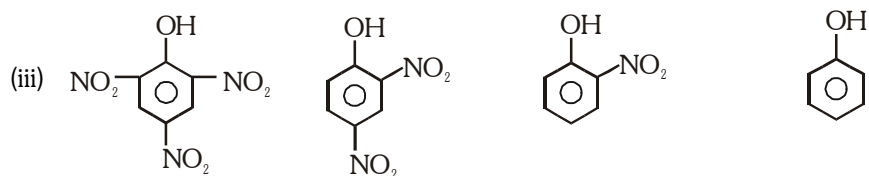
Reason : Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.



- intramolecular H-bonding
- less association
- less B.P.
- more volatile
- less acidic
- less soluble in water.



more association
more B.P.
less volatile
more acidic
more soluble in water.



I

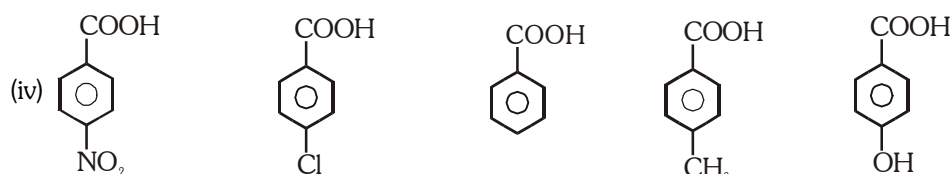
II

III

IV

maximum -M and
maximum -I effect
so maximum acidic

Acidic order $I > II > III > IV$



I

II

III

IV

V

-M

-I

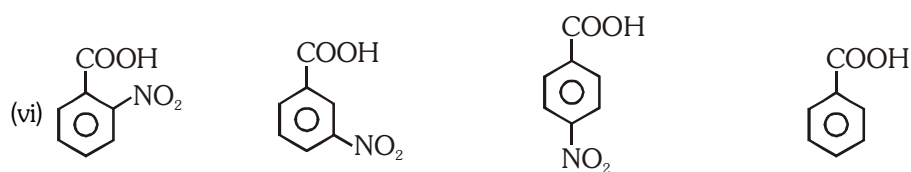
+I

+M

acidic order is $I > II > III > IV > V$



Acidic order is $I > III > II$

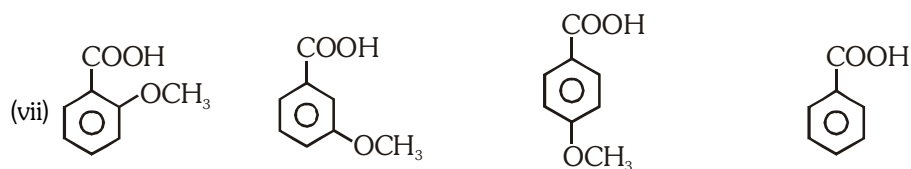


ortho effect

only -I

-I and -M

Acidic order is $\Rightarrow o > p > m > \text{benzoic acid}$

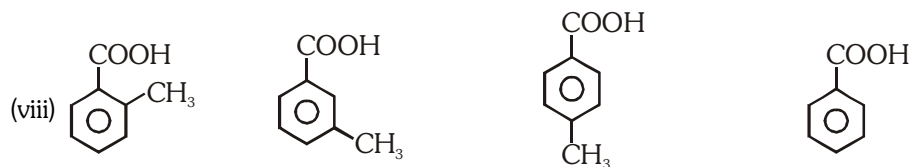


ortho effect

only -I

-I and +M

Acidic order is $\Rightarrow o > m > \text{benzoic acid} > p$

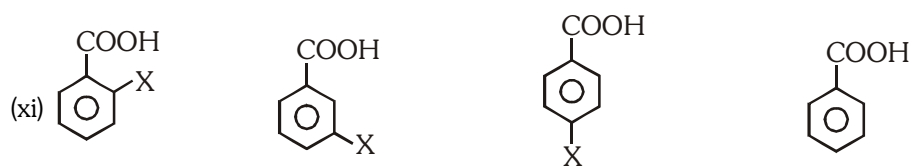


ortho effect

only +I

+I and +H

Acidic order is $\Rightarrow o > \text{benzoic acid} > m > p$



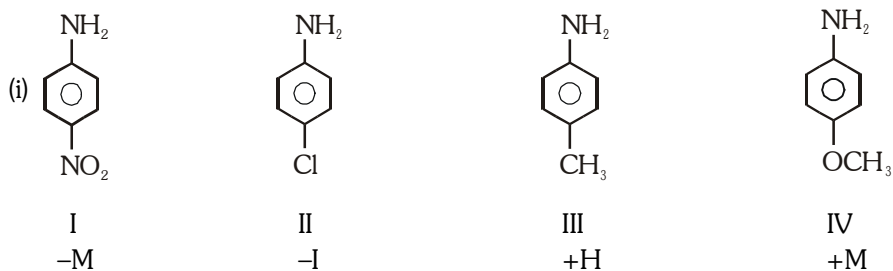
ortho effect

-I (more)

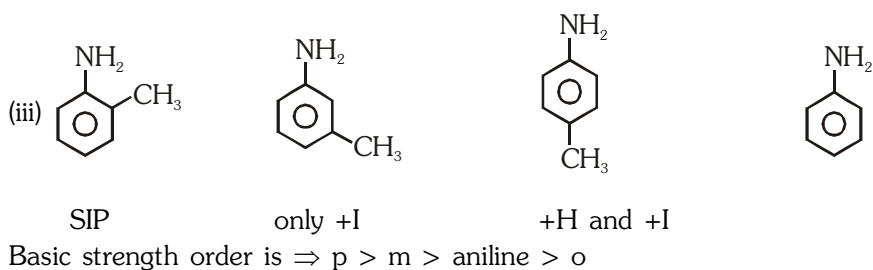
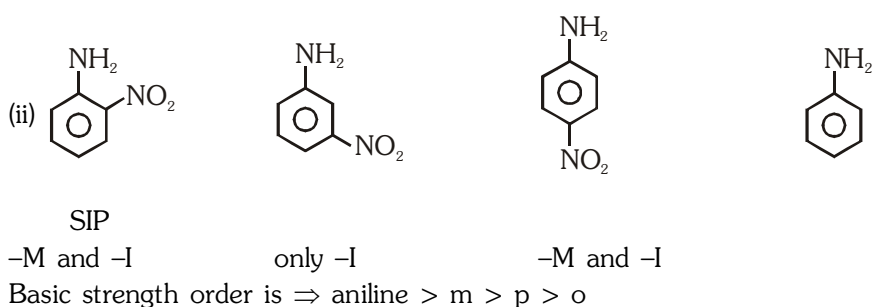
-I (less)

Acidic order is $\Rightarrow o > m > p > \text{benzoic acid}$

Illustration 5. Give basic strength order for :



Basic strength order $IV > III > II > I$

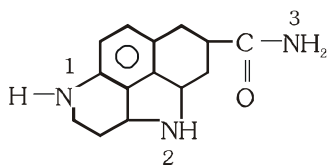


BEGINNER'S BOX-5

1. Most acidic among the following is :



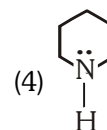
2. Which nitrogen is most basic :-



- | | | | |
|-------|-------|-------|---------------------------|
| (1) 1 | (2) 2 | (3) 3 | (4) All are equally basic |
|-------|-------|-------|---------------------------|

3. Which is strongest base ?

- | | | |
|-------------|-------------|--------------|
| (1) pyrrole | (2) Aniline | (3) Pyridine |
|-------------|-------------|--------------|



4. Which is weakest base :

- | | |
|------------------------|---------------------------|
| (1) $C_6H_5-CH_2-NH_2$ | (2) $C_6H_5-CH_2-NH-CH_3$ |
| (3) $O_2N-CH_2-NH_2$ | (4) $CH_3-NH-CHO$ |

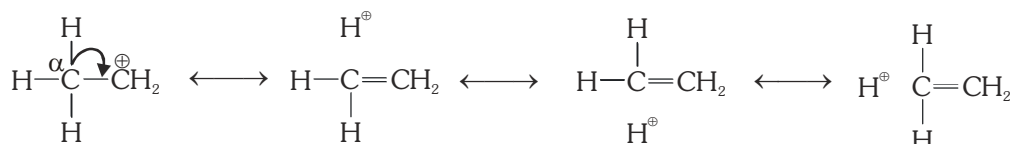
3.4.3 HYPERCONJUGATION EFFECT (H-EFFECT)

Complete transfer of e^- of C-H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as No bond resonance (given by Nathen and Baker).

□ CONDITIONS OF H-EFFECT :

1. If there is C-H σ bond and positive charge are in conjugation

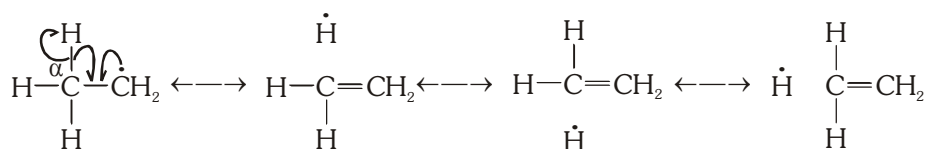
Carbon which is attached to positively charged carbon is called as α -C and H which is attached to α -C is called as α -H. So if number of α -H are more, then there will be more number of hyperconjugating structures, so more stable will be the carbocation.



all are called as hyperconjugating structures or canonical structures.

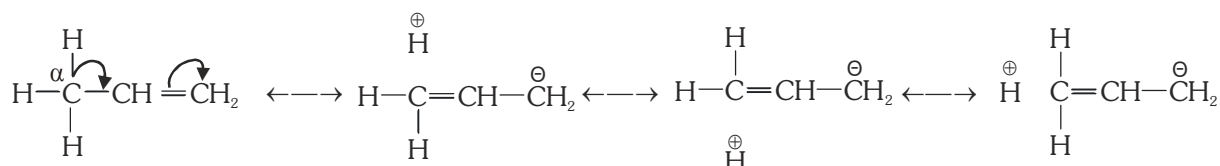
2. If there is C-H σ bond and free e^- are in conjugation then there will be H-effect.

Carbon, which is attached to C having unpaired e^- , is called as α -C and H which are attached to α -C are called as α -H.

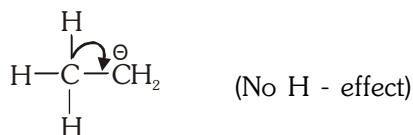


3. If there is C-H σ bond and π bond are in conjugation then there will be H-effect.

sp^3 carbon which is attached to double bonded C is called as α -C and H attached to α -C is called as α -H.



Note : If there is C-H σ bond and negative charge in conjugation then there will be no H-effect.



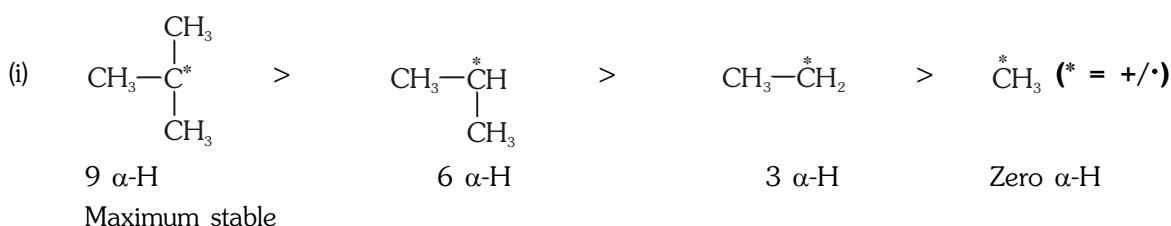
no shifting of C-H σ bond, because anion is having complete octet. ($8e^-$)

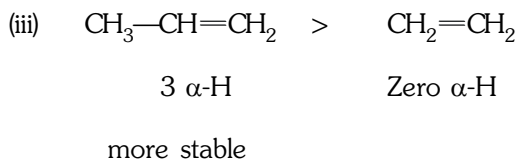
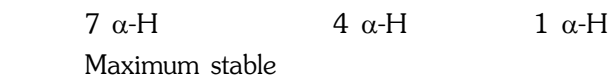
□ APPLICATION OF H-EFFECT

□ Stability of carbocation / Free Radical /Alkene

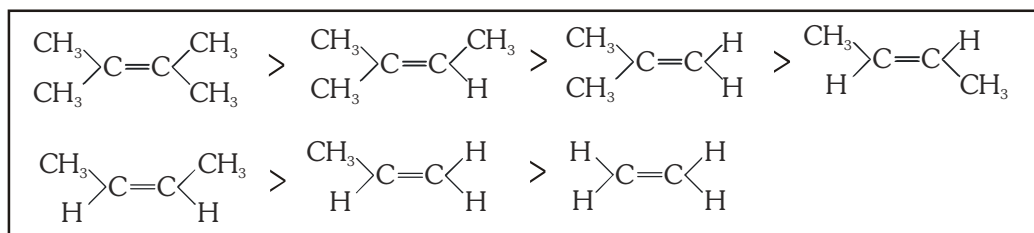
◆ Stability $\propto$ No. of canonical structures $\propto$ No. of α H.

Example : Give stability order for :-





(iv) Stability order of alkenes will be



GOLDEN KEY POINTS

$$\text{R}-\text{CH}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{R}-\text{CH}_2-\text{CH}_3 + \Delta\text{H (Heat of hydrogenation)}$$

Heat evolved when any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (ΔH)

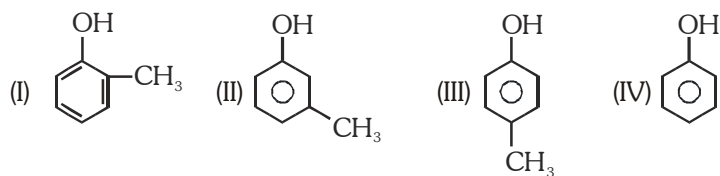
(If alkene is more reactive towards hydrogen then it will evolve more ΔH)

So, $\text{Heat of hydrogenation} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha\text{-H}}$

BEGINNER'S BOX-6

- Which of the following alkene is most stable ($R = CH_3$).
(1) $R_2C=CR_2$ (2) $R-CH=CR_2$ (3) $R-CH=CH-R$ (4) $R-CH=CH_2$
- Which of the following has minimum heat of hydrogenation.
(1) ethene (2) Propene (3) cis-2-butene (4) trans-2-butene
- Which of the following is most stable.
(1) Conjugated alkadiene ($CH_2=CH-CH=CH_2$)
(2) Isolated alkadiene ($CH_2=CH-CH_2-CH=CH_2$)
(3) Cumulated alkadiene ($CH_2=C=CH_2$)
(4) All are equal.

4. What is the order of acidic strength of given molecules



(1) $I > II > III > IV$

(2) $IV > III > II > I$

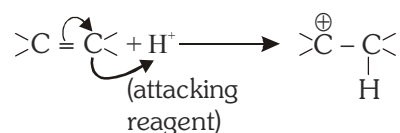
(3) $IV > II > III > I$

(4) $I > II > IV > III$

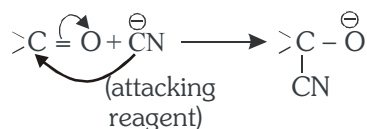
3.4.4 ELECTROMERIC EFFECT : (E Effect)

Complete transfer of a shared pair of π -electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

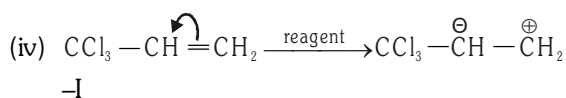
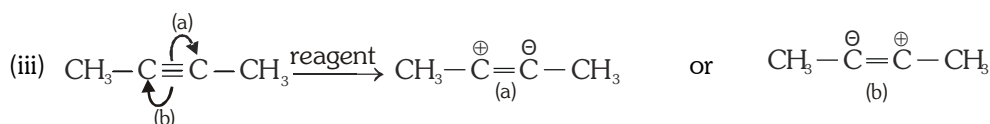
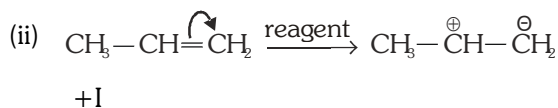
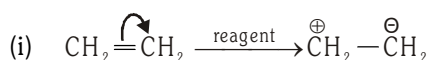
- (i) **Positive Electromeric Effect (+ E effect)** : In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



- (ii) **Negative Electromeric Effect (-E effect)** : In this effect the π -electrons of the multiple bond are transferred to that atom, to which the attacking reagent does not get attached. For example.

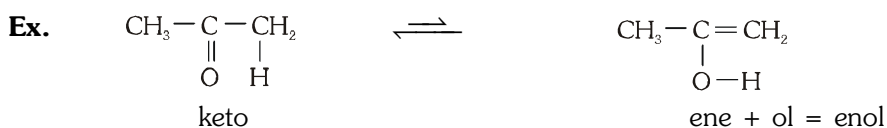
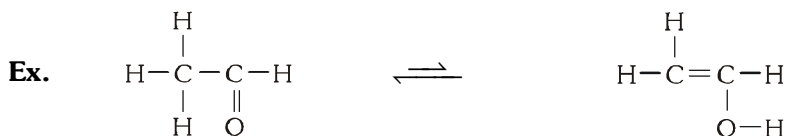
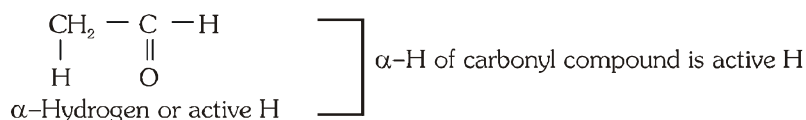


Shifting of π electrons :



3.5 TAUTOMERISM OR DESMOTROPISM

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This phenomena is known as tautomerism.
- Desmotropism means bond turning. [Desmos = Bond ; Tropos = Turn]



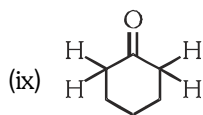
Note : (1) Tautomers exist in dynamic equilibrium.

(2) By shifting of H-atom, π bond also changes its position.

(I) Condition for Tautomerism :

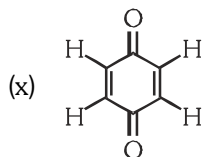
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α -H) show tautomerism

- | | | | |
|--------|--|----------------|----------------------------------|
| (i) | $ \begin{array}{c} \text{CH}_3 - \text{C} - \text{H} \\ \\ \text{O} \end{array} $ | 3 α H, | shows tautomerism. |
| (ii) | $ \begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{O} \end{array} $ | 6 α H, | shows tautomerism |
| (iii) | $ \begin{array}{c} \text{CH}_3 - \text{CH} - \text{C} - \text{H} \\ \quad \\ \text{CH}_3 \quad \text{O} \end{array} $ | 1 α H, | shows tautomerism |
| (iv) | $ \begin{array}{c} \text{H} - \text{C} - \text{H} \\ \\ \text{O} \end{array} $ | No α H, | No tautomerism |
| (v) | $ \begin{array}{c} \text{O} \\ \\ \text{C} - \text{H} \\ \\ \text{C}_6\text{H}_5 \end{array} $ | No α H, | No Tautomerism |
| (vi) | $ \begin{array}{c} \text{O} \\ \\ \text{C} - \text{CH}_3 \\ \\ \text{C}_6\text{H}_5 \end{array} \text{ (Acetophenone)} $ | 3 α H, | shows tautomerism (Acetophenone) |
| (vii) | $ \begin{array}{c} \text{O} \\ \\ \text{Ph} - \text{C} - \text{Ph} \text{ (Benzophenone)} \end{array} $ | No α H, | No tautomerism (Benzophenone) |
| (viii) | $ \begin{array}{c} \text{O} \quad \quad \text{O} \\ \quad \quad \\ \text{Ph} - \text{C} - \text{CH}_2 - \text{C} - \text{Ph} \end{array} $ | 2 α H, | shows tautomerism |



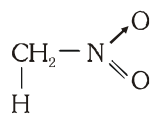
4 α H,

shows tautomerism

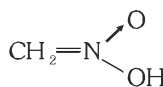


α -H, attached sp^2 carbon does not initiate in tautomerism

(b) For nitro compounds : Nitro compounds having at least one active-H (α - H) show tautomerism



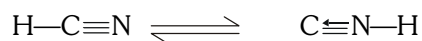
Nitro form



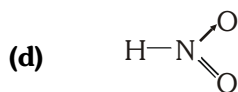
Acinitro form

(acidic form so soluble in base)

(c) $H-C\equiv N$ and $H-N\equiv C$ are tautomers [also Functional isomers] while $R-C\equiv N$ and $R-N\equiv C$ are only Functional isomers.



Active H

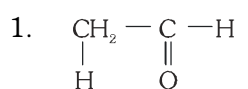


and

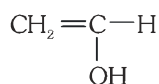
$H-O-N=O$ are tautomers.

Note : Nitro compounds with at least one α -H are soluble in NaOH.

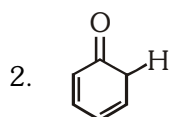
(II) Enol Content :



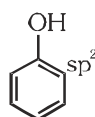
"keto" ($\approx 99\%$)



"enol" ($\approx 1\%$)



"keto" ($\approx 1\%$)

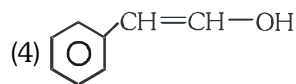
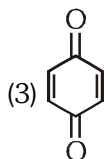
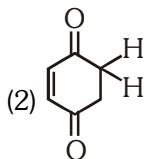
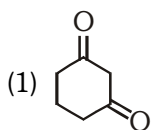


"enol" (stable by resonance and aromatic nature) ($\approx 99\%$)

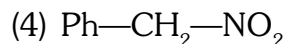
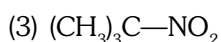
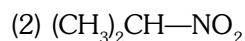
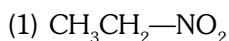
GOLDEN KEY POINTS

- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on (i) Resonance and (ii) H - Bond (iii) Aromaticity.

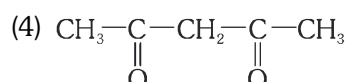
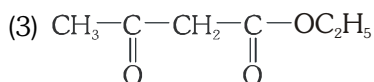
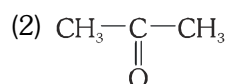
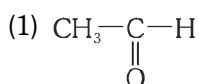
1. Which of the following does not show keto enol tautomerism.



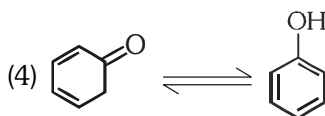
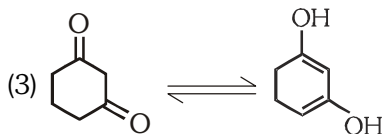
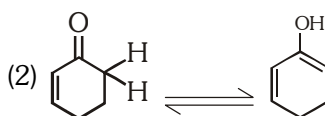
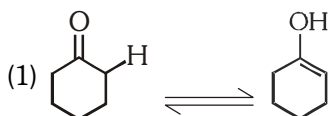
- 2.** Which of the following is not soluble in NaOH.



- 3.** Which of the following has highest enol content.



4. In which of the following reaction most stable enol is present.



BEGINNER'S BOX-1

Que.	1	2	3
Ans.	4	1	2

BEGINNER'S BOX-2

Que.	1	2	
Ans.	1	1	

BEGINNER'S BOX-3

Que.	1	2	3	
Ans.	1	1	4	

BEGINNER'S BOX-4

Que.	1	2	3	
Ans.	4	4	3	

BEGINNER'S BOX-5

Que.	1	2	3	4
Ans.	3	2	4	4

BEGINNER'S BOX-6

Que.	1	2	3	4
Ans.	1	4	1	3

BEGINNER'S BOX-7

Que.	1	2	3	4
Ans.	3	3	4	4

EXERCISE-I (Conceptual Questions)**Build Up Your Understanding****ATTACKING REAGENT**

- Which of the following species is an electrophile
(1) RNH_2 (2) SO_3
(3) NO_3^- (4) ROH
- Which of the following acts as a nucleophile?
(1) NO_2^+ (2) $:\text{CCl}_2$
(3) NH_2^- (4) $\cdot\text{CH}_3$

REACTION INTERMEDIATES

- Which of the following contains only three pair of electrons :
(1) Carbanion (2) Carbocation
(3) Carbon free radical (4) None
- Carbanion is a :-
(1) Base (2) Nucleophile
(3) Both the above (4) None

I-EFFECT

- CH_3^- is less stable than :-
(1) $\text{CH}_3-\text{CH}_2^-$ (2) $\text{CH}_3-\text{CH}^--\text{CH}_3$
(3) $\text{CH}_2^--\text{NO}_2$ (4) $\text{CH}_3-\text{CH}^--\text{C}_2\text{H}_5$
- Decreasing order of -I effect of the triad $[-\text{NO}_2, -\text{NH}_3^+, -\text{CN}]$ is :-
(1) $-\text{NH}_3^+ > -\text{NO}_2 > -\text{CN}$
(2) $-\text{NH}_3^+ > -\text{CN} > \text{NO}_2$
(3) $-\text{CN} > -\text{NO}_2 > -\text{NH}_3^+$
(4) $-\text{NO}_2 > -\text{CN} > -\text{NH}_3^+$
- Most stable carbanion is :-
(1) $\text{HC}\equiv\text{C}^-$ (2) $\text{H}_2\text{C}=\text{CH}^-$
(3) $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_2^-$ (4) $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}^-$

- The correct order of stability of given carbanions will be :-
 $\text{CH}_3-\text{CH}_2^-$ (I) $\text{CH}_2=\text{CH}^-$ (II) $\text{HC}\equiv\text{C}^-$ (III)
(1) $\text{I} > \text{II} > \text{III}$ (2) $\text{III} > \text{II} > \text{I}$
(3) $\text{I} > \text{III} > \text{II}$ (4) $\text{II} > \text{I} > \text{III}$

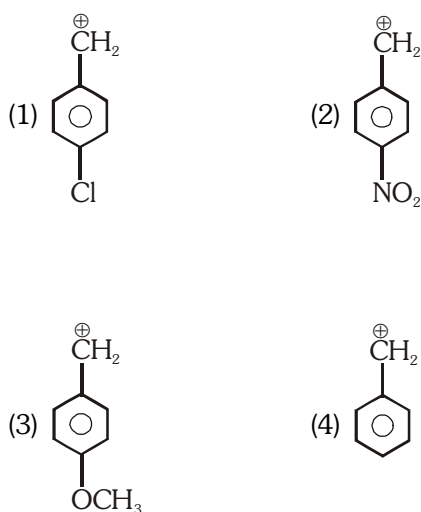
- Which is most basic among the following :-
(1) CH_3NH_2
(2) $\text{CH}_3\text{CH}_2\text{NH}_2$
(3) NH_3
(4) $(\text{CH}_3)_2\text{CHNH}_2$
- Which of the following has maximum pK_a :-
(1) CH_2FCOOH
(2) CH_2ClCOOH
(3) CH_3COOH
(4) HCOOH
- Which of the following is most acidic
(1) Methoxy acetic acid
(2) Acetic acid
(3) Chloro acetic acid
(4) Trifluoroacetic acid
- Which of the following show + I-effect :-
(1) -OH (2) -OCH₃ (3) -CH₃ (4) -Cl
- Among the following the most highly ionised in water is:
(1) $\text{CH}_3\text{CH}_2\text{CHClCOOH}$
(2) $\text{CH}_3\text{CH}_2\text{CCl}_2\text{COOH}$
(3) $\text{CH}_3\text{CHClCH}_2\text{COOH}$
(4) $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{COOH}$
- The strongest acid amongst the following compounds is ?
(1) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$
(2) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$
(3) CH_3COOH
(4) HCOOH
- Which of the following acids is stronger than acetic acid :-
(1) Propanoic acid (2) HCOOH
(3) Butyric acid (4) $(\text{CH}_3)_2\text{CHCOOH}$

16. Which of the following acids have the lowest pK_a value :-

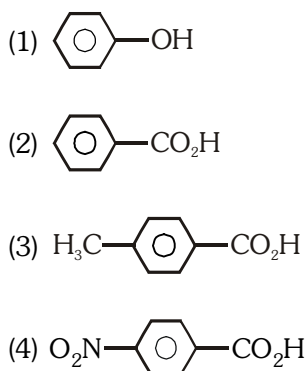
- (1) $\text{CH}_3-\overset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{COOH}$
 (2) $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COOH}$
 (3) CCl_3COOH
 (4) CHCl_2COOH

R- OR M-EFFECT

17. Most stable carbocation is :-



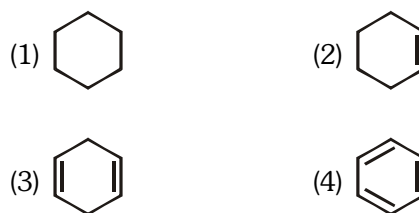
18. Most acidic compound is :-



19. Which resonating structure of vinyl chloride is least stable :-

- (1) $\text{CH}_2=\text{CH}-\ddot{\text{Cl}}:$
 (2) $\overset{\ominus}{\text{C}}\text{H}_2-\text{CH}=\overset{\oplus}{\text{C}}\text{Cl}$
 (3) $\overset{\ominus}{\text{C}}\text{H}_2-\overset{\oplus}{\text{C}}\text{H}-\text{Cl}$
 (4) All have equal stability

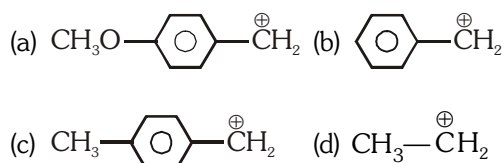
20. The stabilization due to resonance is maximum in



21. In which of the following compounds carbon-chlorine bond distance is minimum :-

- (1) CH_3-Cl
 (2) $\text{C}_6\text{H}_5-\text{CH}_2-\text{Cl}$
 (3) $\text{CH}_2=\text{CH}-\text{Cl}$
 (4) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$

22. Consider the following carbocations



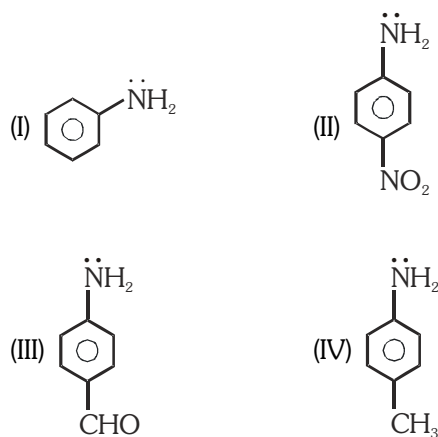
The relative stabilities of these carbocations are such that :-

- (1) $d < b < c < a$
 (2) $b < d < c < a$
 (3) $d < b < a < c$
 (4) $b < d < a < c$

23. Among the following, the strongest base is :-

- (1) $\text{C}_6\text{H}_5\text{NH}_2$
 (2) $p\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$
 (3) $m\text{-NO}_2\text{-C}_6\text{H}_4\text{NH}_2$
 (4) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

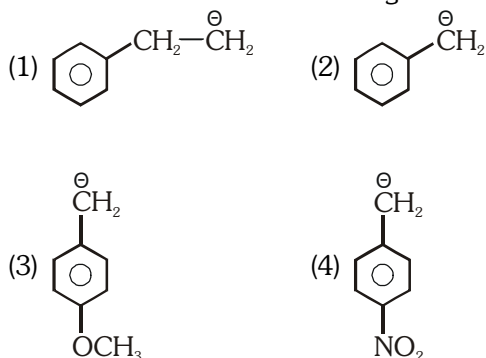
24. Arrange in decreasing order of basic strength :



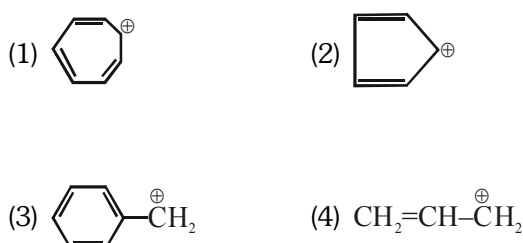
- (1) $\text{I} > \text{II} > \text{III} > \text{IV}$
 (3) $\text{IV} > \text{I} > \text{III} > \text{II}$

- (2) $\text{II} > \text{III} > \text{I} > \text{IV}$
 (4) $\text{IV} > \text{I} > \text{II} > \text{III}$

25. The most stable carbanion among the following is



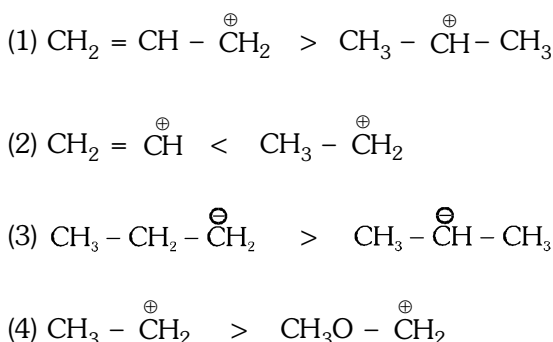
26. Which of the following is most stable carbocation:-



27. The oxygen atom in phenol -

- (1) exhibits only inductive effect
- (2) exhibits only resonance effect
- (3) has more dominating resonance effect than inductive effect
- (4) has more dominating inductive effect than resonance effect

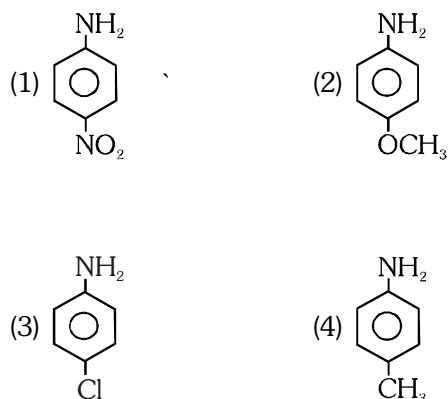
28. Which is incorrect stability order :-



29. Mesomeric effect is due to :-

- (1) Delocalization of σ e⁻
- (2) Delocalization of π e⁻
- (3) Migration of H - atom
- (4) Migration of proton

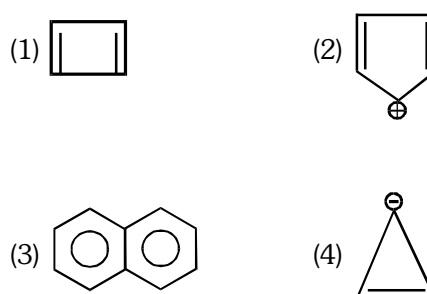
30. Which of the following is least basic :-



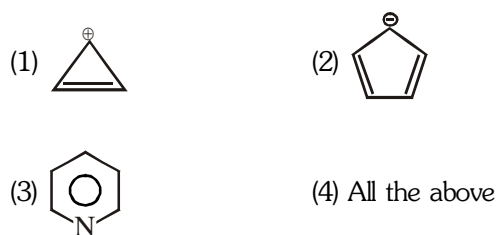
31. Among the following the pKa is minimum for :-

- (1) $\text{C}_6\text{H}_5\text{OH}$
- (2) HCOOH
- (3) $\text{C}_2\text{H}_5\text{OH}$
- (4) $\text{CH}_3\text{C}\equiv\text{CH}$

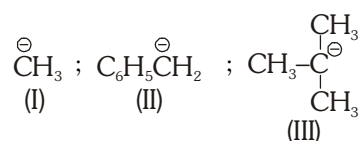
32. Among the following the aromatic compound is -



33. Which is aromatic compound among the following

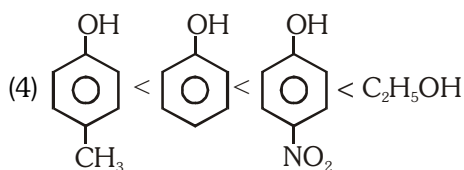
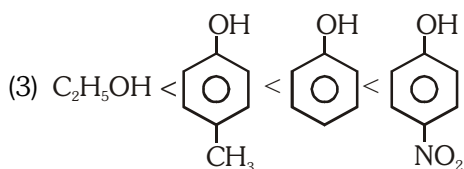
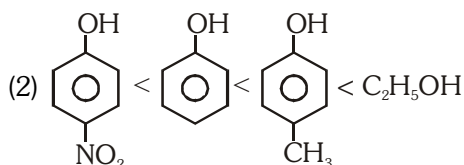
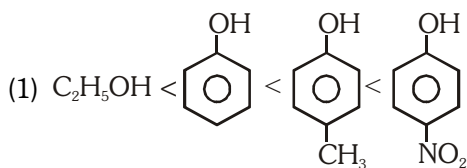


34. Select the correct option for stability of following carbanions :

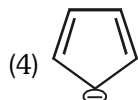
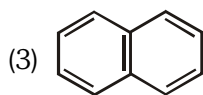
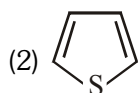
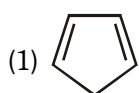


- (1) I > II > III
- (2) II > I > III
- (3) III > II > I
- (4) II > III > I

35. Correct increasing order of acidity of the following phenols is :-



36. The non aromatic compound among the following is :-



37. The correct order of acidic strength of the following compounds is :-

A. Phenol

B. p-Cresol

C. m-Nitrophenol

D. p- Nitrophenol

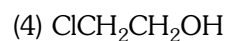
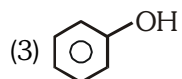
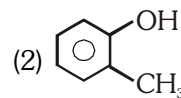
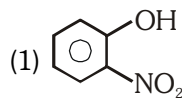
(1) $C > B > A > D$

(2) $D > C > A > B$

(3) $B > D > A > C$

(4) $A > B > D > C$

38. Which one of the following compounds is most acidic:-



39. Which of the following is most acidic :-

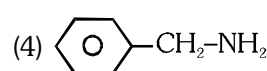
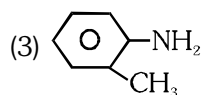
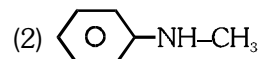
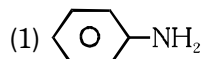
(1) phenol

(2) benzyl alcohol

(3) m-chloro phenol

(4) cyclohexanol

40. Which of the following is the strongest base :-



41. The dipole moment of vinyl chloride is lower than that of methyl chloride. This is due to :-

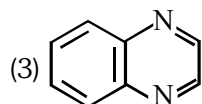
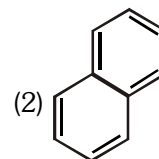
(1) Resonance effect

(2) Inductive effect

(3) Electromeric effect

(4) Hyperconjugation

42. Which is Aromatic compound :-

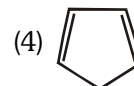


(4) 2 and 3 both

43. Which of the following is the most acidic compound :-

(1) $CH_2 = CH_2$

(2) $HC \equiv CH$



44. Among the following the strongest acid is :-

- (1) CH_3COOH
- (2) $\text{C}_6\text{H}_5\text{COOH}$
- (3) $m\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$
- (4) $p\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$

45. The least reactive chlorine is present in -

- (1) Methyl chloride
- (2) Allyl chloride
- (3) Ethyl chloride
- (4) Vinyl chloride

46. Which one of the following resonating structures of 1-methoxy-1,3-butadiene is least stable :-

- (1) $\overset{\ominus}{\text{C}}\text{H}_2\text{-CH=CH-CH}=\overset{\oplus}{\text{O}}\text{-CH}_3$
- (2) $\text{CH}_2=\text{CH}-\overset{\ominus}{\text{C}}\text{H-CH}=\overset{\oplus}{\text{O}}\text{-CH}_3$
- (3) $\overset{\ominus}{\text{C}}\text{H}_2-\overset{\oplus}{\text{C}}\text{H-CH=CH-O-CH}_3$
- (4) $\text{CH}_2=\text{CH-CH=CH-O-CH}_3$

47. Four structures are given in options (a) to (d). Examine them and select the aromatic structures.

- | | |
|-------------|-------------|
| (a) | (b) |
| (c) | (d) |
| (1) a and d | (2) b and c |
| (3) a and b | (4) a and c |

48. Order of acidic strength of the following compound will be :

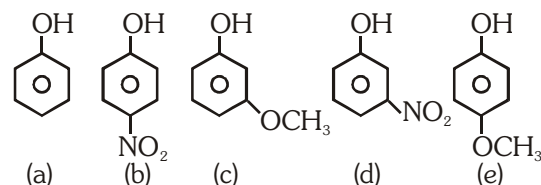
- | | |
|-----|-----|
| (A) | (B) |
| (C) | (D) |

- | | |
|---|---|
| (1) $\text{C} > \text{D} > \text{B} > \text{A}$ | (2) $\text{D} > \text{C} > \text{B} > \text{A}$ |
| (3) $\text{A} > \text{B} > \text{C} > \text{D}$ | (4) $\text{B} > \text{A} > \text{C} > \text{D}$ |

49. Phenol is less acidic than

- | | |
|--------------------|---------------------|
| (1) Ethanol | (2) o-Nitrophenol |
| (3) o-Methylphenol | (4) o-Methoxyphenol |

50. Mark the correct order of decreasing acid strength of the following compounds.



- | | |
|-------------------------|-------------------------|
| (1) $e > d > b > a > c$ | (2) $b > d > a > c > e$ |
| (3) $e > d > c > b > a$ | (4) $b > d > c > a > e$ |

HYPERCONJUGATION

51. Which of the following compounds exhibits hyperconjugation :

- | | |
|-------------|-------------|
| (1) Phenol | (2) Ethyne |
| (3) Ethanol | (4) Propene |

52. Which of the following is least stable :-

- (1) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$
- (2) $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{C}}\text{H}_2$
- (3) $\text{CH}_3-\overset{\oplus}{\text{C}}(\text{CH}_3)-\text{CH}_3$
- (4) $\text{CH}_3-\overset{\oplus}{\text{C}}(\text{CH}_3)_2-\text{CH}-\text{C}_6\text{H}_5$

53. Which of the following is most stable alkene :-

- (1) $\text{H} \diagup \text{C} = \text{C} \diagdown \text{H}$
 $\text{H} \diagdown \text{C} = \text{C} \diagup \text{H}$
- (2) $\text{CH}_3 \diagup \text{C} = \text{C} \diagdown \text{H}$
 $\text{H} \diagdown \text{C} = \text{C} \diagup \text{H}$
- (3) $\text{H}_5\text{C}_2 \diagup \text{C} = \text{C} \diagdown \text{H}$
 $\text{H} \diagdown \text{C} = \text{C} \diagup \text{H}$
- (4) $\text{CH}_3 \diagup \text{CH} \diagdown \text{C} = \text{C} \diagdown \text{H}$
 $\text{H} \diagdown \text{C} = \text{C} \diagup \text{H}$

58. Tautomerism is not observed in :—

- (1) $\text{CH}_3-\text{C}(\text{O})-\text{CH}_3$ (2) $\text{Ph}-\text{CH}=\text{CH}-\text{OH}$

- (3) $\text{CH}_3\text{-NO}_2$ (4) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{-C-CHO} \\ | \\ \text{CH}_2 \end{array}$

59. Which of the following is not soluble in NaOH solution :

- $$(1) \quad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \rangle \text{CH-NO}_2$$

- (2) 

- (3) $\text{CH}_3\text{CH}_2\text{-NO}_2$

- (1) $\text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-CH}_3$
- (2) $\text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-CH}_2\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-H}$
- (3) $\text{CH}_3\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-}\overset{\text{Br}}{\underset{|}{\text{CH}}}\text{-}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-CH}_3$

- $$(4) \text{ CH}_3\text{—CH}_2\text{—}\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{—NO}_2$$

- (4) 

60. Which of the following has highest enol content.

- (1) Chain (2) Position
(3) Geometrical (4) Tautomerism

- (1) 
- (2) 
- (3) 
- (4) 

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	3	2	3	3	1	1	2	4	3	4	3	2	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	4	3	4	3	1	4	3	4	1	3	4	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	4	2	3	1	2	1	3	4	1	4	4	3	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	3	4	1	2	4	4	2	2	3	3	4	4	4	2	2

EXERCISE-II (Previous Year Questions)**AIPMT 2006**

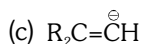
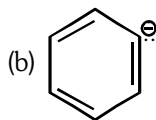
1. Which of the following is more basic than aniline
 (1) Diphenyl amine (2) Triphenyl amine
 (3) p-nitro aniline (4) Benzyl amine

AIPMT 2007

2. Which of the following presents the correct order of the acidity in the given compounds :
 (1) $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 (2) $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (3) $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 (4) $\text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$

AIPMT 2008

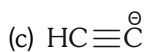
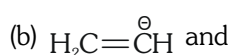
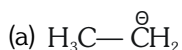
3. The stability of carbanions in the following:-



is in the order of:-

- (1) (d) > (b) > (c) > (a) (2) (a) > (c) > (b) > (d)
 (3) (a) > (b) > (c) > (d) (4) (b) > (c) > (d) > (a)

4. Basic strength of:-

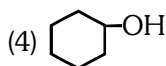
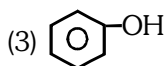
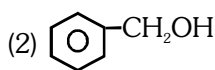
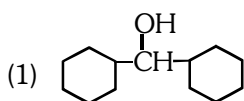


is in the order of:-

- (1) (a) > (c) > (b) (2) (a) > (b) > (c)
 (3) (b) > (a) > (c) (4) (c) > (b) > (a)

AIPMT 2010

5. Which one of the following compounds has the most acidic nature ?

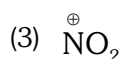
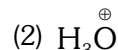
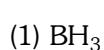
**AIPMT/NEET & AIIMS (2006-2018)**

6. Given are cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be :-
 (1) III > IV > II > I
 (2) III > II > IV > I
 (3) II > III > I > IV
 (4) II > III > IV > I

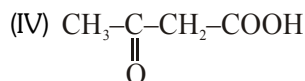
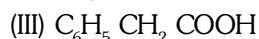
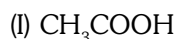
AIPMT Mains-2010

7. Among the following four compounds :-
 (a) phenol (b) methyl phenol
 (c) metanitrophenol (d) paranitrophenol,
 The acidity order is :
 (1) c > d > a > b (2) c > d > c > b
 (3) b > a > c > d (4) d > c > a > b

8. Which of the following species is not electrophilic in nature :-

**AIIMS 2010**

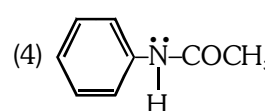
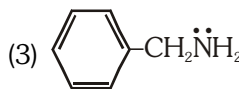
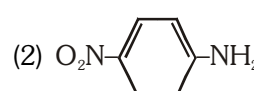
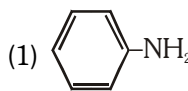
9. The correct order of pKa is



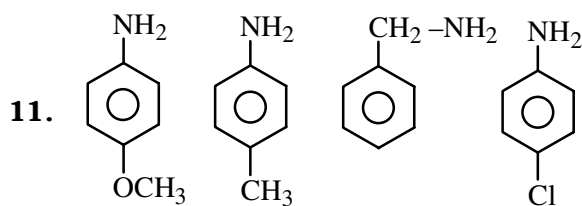
- (1) IV > III > II > I
 (2) III > IV > II > I
 (3) IV > II > III > I
 (4) II > I > III > IV

AIPMT Mains-2011

10. Which of the following compounds is most basic ?

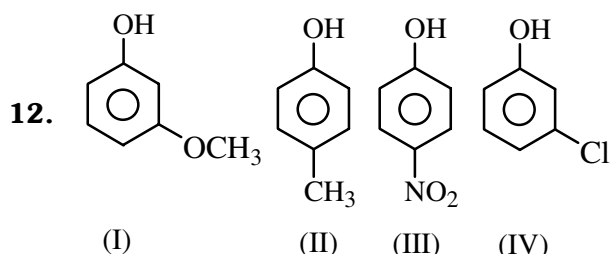


AIIMS 2011



The correct decreasing order of pK_b is:-

- (1) I > II > III > IV
(2) III > IV > II > I
(3) II > III > IV > I
(4) IV > II > I > III



The correct decreasing order of pK_a is:-

- (1) II > I > IV > III (2) IV > II > III > I
(3) III > II > IV > I (4) IV > I > II > III

AIPMT Pre.-2012

13. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is:

- (1) A > B > C > D (2) A > C > B > D
(3) B > A > D > C (4) B > D > C > A

AIIMS 2012

14. pK_a increases in benzoic acid, substituent "x" bonded at para position then "x" is :-

- (1) $-\text{COOH}$ (2) $-\text{NO}_2$
(3) $-\text{CN}$ (4) $-\text{OCH}_3$

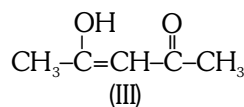
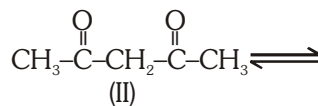
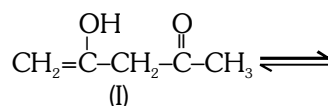
NEET-UG 2013

15. The radical, is aromatic because it

has :-

- (1) 6p-orbitals and 7 unpaired electrons
(2) 6p-orbitals and 6 unpaired electrons
(3) 7p-orbitals and 6 unpaired electrons
(4) 7p-orbitals and 7 unpaired electrons

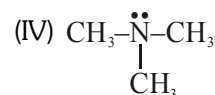
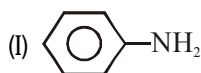
16. The order of stability of the following tautomeric compounds is :-



- (1) II > III > I (2) I > II > III
(3) III > II > I (4) II > I > III

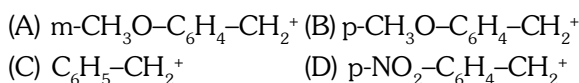
AIIMS 2014

17. Correct decreasing order of pK_b value of following compounds:-



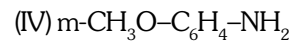
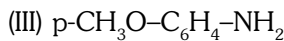
- (1) I > IV > II > III (2) I > II > IV > III
(3) IV > I > II > III (4) I > II > III > IV

18. Decreasing order of stability of following carbocations is :-



- (1) A > B > C > D (2) B > C > D > A
(3) C > B > A > D (4) B > C > A > D

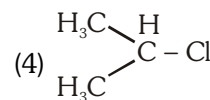
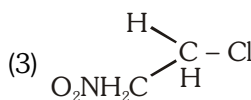
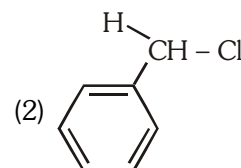
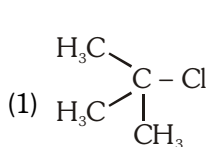
19. Decreasing order of basic strength is :-



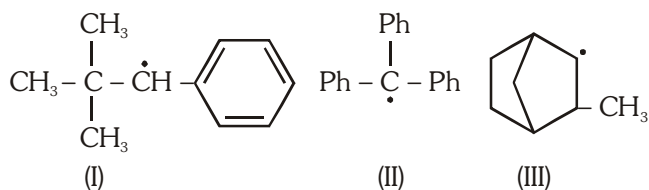
- (1) I > II > III > IV (2) II > IV > I > III
(3) II > IV > III > I (4) IV > I > II > III

AIPMT 2015

20. In which of the following compounds, C-Cl bond ionisation shall give most stable carbonium ion?



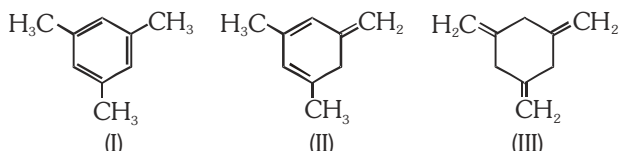
21. Consider the following compounds



Hyperconjugation occurs in :-

- (1) II only (2) III only (3) I and III (4) I only

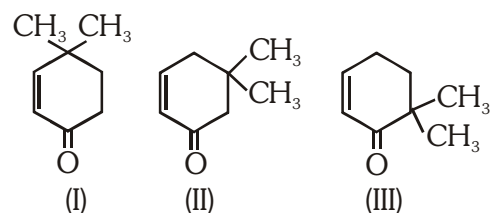
22. Given :-



The enthalpy of the hydrogenation of these compounds will be in the order as :-

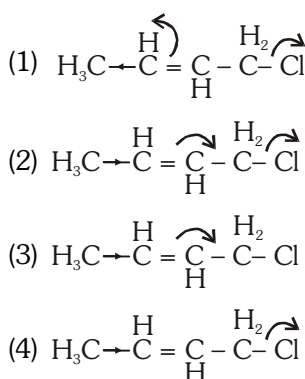
- (1) III > II > I (2) II > III > I
(3) II > I > III (4) I > II > III

23. Which of the given compounds can exhibit tautomerism?



- (1) I and III (2) II and III
(3) I, II and III (4) I and II

24. Which of the following is the most **correct** electron displacement for a nucleophilic reaction to take place?

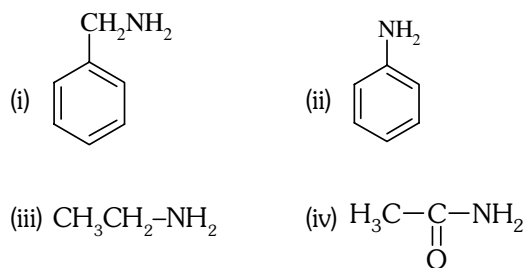


Re-AIPMT 2015

25. Which of the following statements is not correct for a nucleophile ?

- (1) Nucleophiles attack low e^- density sites
(2) Nucleophiles are not electron seeking
(3) Nucleophile is a Lewis acid
(4) Ammonia is a nucleophile

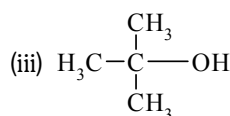
26. Correct order of K_b is



- (1) iv > iii > ii > i (2) iii > i > ii > iv
(3) i > ii > iii > iv (4) ii > iii > iv > i

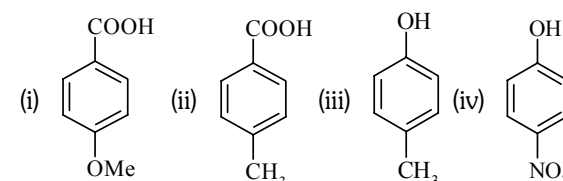
AIIMS 2015

27. Correct order of pK_a is



- (1) i > ii > iii (2) ii > i > iii
(3) iii > ii > i (4) ii > iii > i

28. Correct order of acidic strength is



- (1) i > ii > iv > iii (2) iii > iv > ii > i
(3) ii > i > iv > iii (4) iv > ii > iii > i

NEET-I 2016

29. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha carbon, is :-

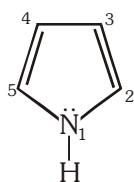
- (1) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.
(2) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.
(3) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.
(4) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.

30. The **correct** statement regarding the basicity of arylamines is :-

- (1) Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring π electron system.
- (2) Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring π electron system.
- (3) Arylamines are generally more basic than alkylamines because of aryl group.
- (4) Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is sp -hybridized.

NEET-II 2016

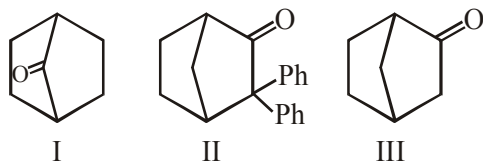
31. In pyrrole



The electron density is maximum on :-

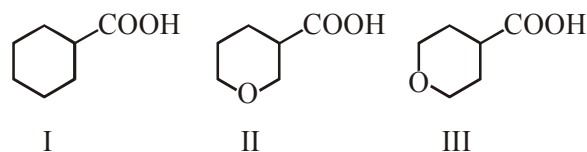
- (1) 2 and 4
- (2) 2 and 5
- (3) 2 and 3
- (4) 3 and 4

32. Which among the given molecules can exhibit tautomerism ?



- (1) Both I and II
- (2) Both II and III
- (3) III only
- (4) Both I and III

33. The **correct** order of strengths of the carboxylic acids



is

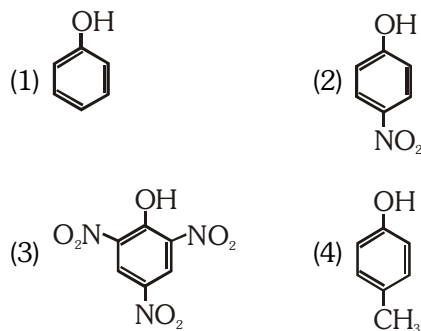
- (1) III > II > I
- (2) II > I > III
- (3) I > II > III
- (4) II > III > I

NEET(UG) 2017

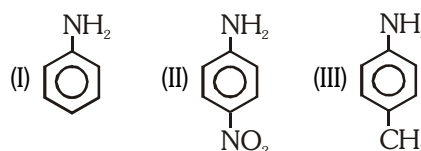
34. Which one is the correct order of acidity ?

- (1) $\text{CH} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$
- (2) $\text{CH} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_3 - \text{CH}_3$
- (3) $\text{CH}_3 - \text{CH}_3 > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH} \equiv \text{CH}$
- (4) $\text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH}_2 > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH} > \text{CH} \equiv \text{CH}$

35. Which one is the most acidic compound ?



36. The **correct** increasing order of basic strength for the following compounds is :



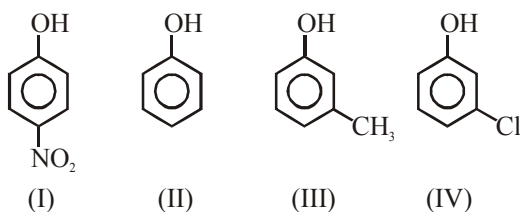
- (1) III < I < II
- (2) III < II < I
- (3) II < I < III
- (4) II < III < I

37. The **correct** statement regarding electrophile is :-

- (1) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
- (2) Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
- (3) Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile
- (4) Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile

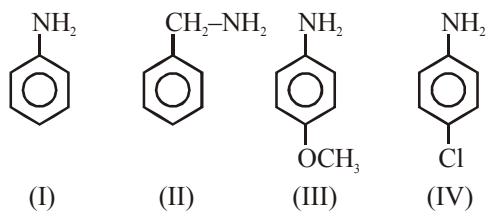
AIIMS 2017

38. Arrange followings in correct decreasing order of pK_a :-



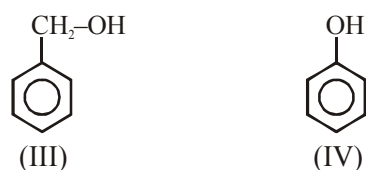
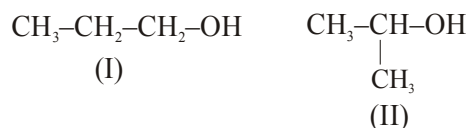
- | | |
|-----------------------|-----------------------|
| (1) I > II > IV > III | (2) III > IV > II > I |
| (3) III > II > IV > I | (4) III > I > II > IV |

39. Arrange followings in correct decreasing order of pK_b :-



- | | |
|-----------------------|-----------------------|
| (1) II > III > IV > I | (2) II > III > I > IV |
| (3) III > II > IV > I | (4) IV > I > III > II |

40. Arrange following in correct increasing order of pK_a



- | | |
|-----------------------|-----------------------|
| (1) IV < III < I < II | (2) IV < III < II < I |
| (3) I < II < III < IV | (4) II < III < IV < I |

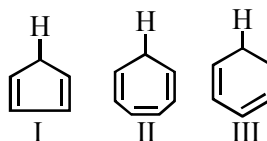
NEET(UG) 2018

41. Which of the following is correct with respect to -I effect of the substituents ? (R = alkyl)

- (1) $-\text{NH}_2 < -\text{OR} < -\text{F}$
- (2) $-\text{NR}_2 < -\text{OR} < -\text{F}$
- (3) $-\text{NH}_2 > -\text{OR} > -\text{F}$
- (4) $-\text{NR}_2 > -\text{OR} > -\text{F}$

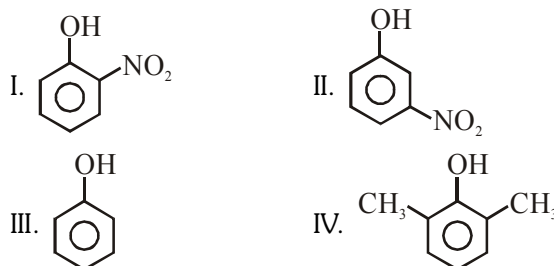
AIIMS 2018

42. Arrange the following compounds in their decreasing order of acidic strength



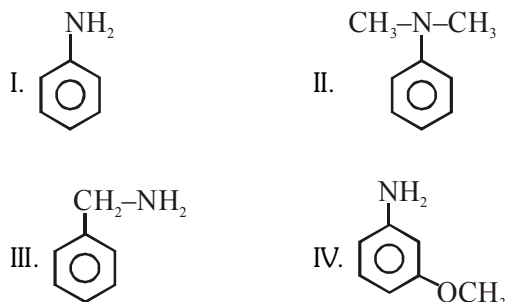
- (1) I > II > III
- (2) I > III > II
- (3) II > III > I
- (4) II > I > III

43. Arrange the following decreasing order of their acidic strength



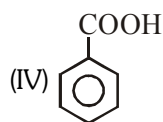
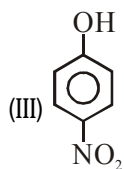
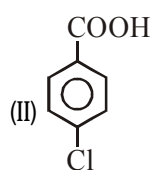
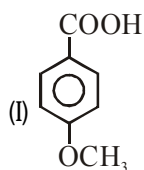
- (1) I > II > III > IV
- (2) I > II > IV > III
- (3) II > I > III > IV
- (4) IV > I > II > III

44. Arrange the following in decreasing order of basic strength



- (1) I > II > III > IV
- (2) III > II > IV > I
- (3) III > II > I > IV
- (4) IV > II > III > I

45. Arrange the following acids in decreasing order of their acidic strength :-



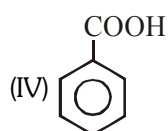
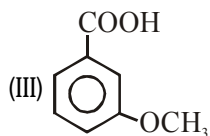
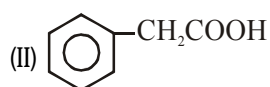
(1) III > II > IV > I

(2) II > IV > I > III

(3) I > III > II > IV

(4) IV > II > III > I

46. Compare the acidic strength of the given acids



(1) III > IV > II > I

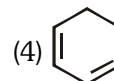
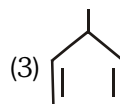
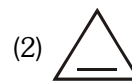
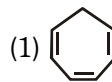
(2) IV > III > II > I

(3) III > IV > I > II

(4) II > IV > I > III

47. Which of the following molecule on reaction with

$\text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+$ gives aromatic species :-



EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	3	3	2	3	2	4	2	4	3	4	1	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	1	4	1	2	2	1	3	2	3	2	3	3	4	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	2	3	4	1	3	3	3	3	4	1	1	2	1	3	2
Que.	46	47													
Ans.	1	3													

EXERCISE-III (Analytical Questions)**Check Your Understanding**

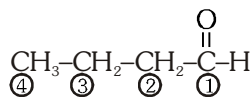
1. Consider the following statements :-

- (a) $\text{CH}_3\text{O}^+\text{CH}_2$ is more stable than CH_3CH_2^+
- (b) Me_2CH^+ is more stable than $\text{CH}_3\text{CH}_2\text{CH}_2^+$
- (c) $\text{CH}_2=\text{CH}-\text{CH}_2^+$ is more stable than $\text{CH}_3\text{CH}_2\text{CH}_2^+$
- (d) $\text{CH}_2=\text{CH}^+$ is more stable than CH_3CH_2^+

of these statements :-

- (1) a and b are correct
 (2) c and d are correct
 (3) a, b and c are correct
 (4) b, c and d are correct

2. Which of the following carbon has most acidic hydrogen.

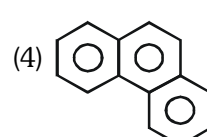
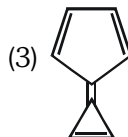
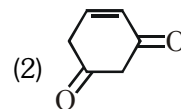
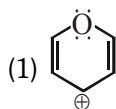


- (1) C_1-H (2) C_2-H
 (3) C_3-H (4) C_4-H

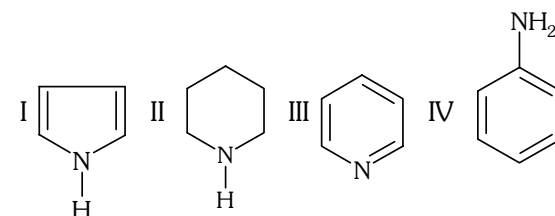
3. Which of the following has the most acidic proton:

- (1) $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$
- (2) $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{H}$
- (3) $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$
- (4) $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$

4. Which is not aromatic compound :-

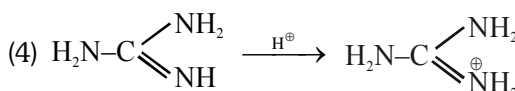
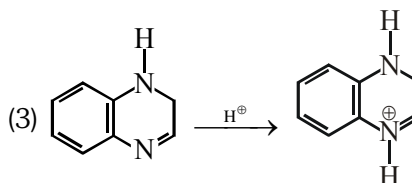
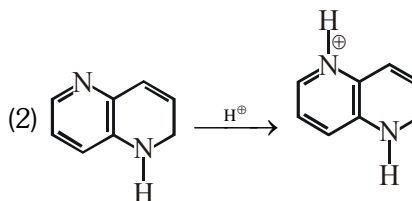
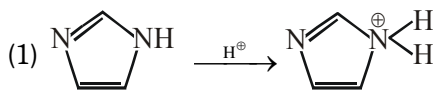


5. The correct order of decreasing basic strength is

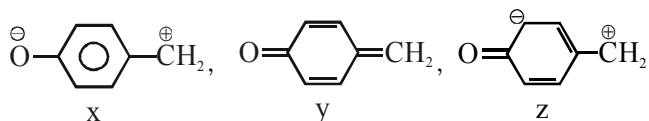


- (1) I > II > III > IV (2) II > III > I > IV
 (3) II > IV > I > III (4) II > III > IV > I

6. Which of the following acid-base reaction is not feasible :-



7. Select the correct option for stability of following resonance structures :-



- (1) $x > y > z$ (2) $z > y > x$
 (3) $y > x > z$ (4) $y > z > x$

8. (a) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
 (b) $\text{CH}_3-\text{CH}=\text{CH}_2$
 (c) CH_3-CH_3

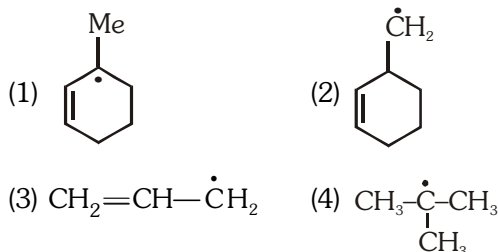
C—C single bond distance would be :-

- (1) $a < b < c$
 (2) $a > b < c$
 (3) $a < b > c$
 (4) $a < b > c$

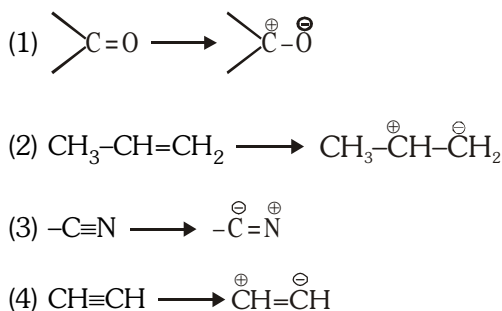
9. Hydrogen attached to sp^3 carbon in cyclopentadiene can be easily removed as what :-

- (1) Hydride ion
 (2) Hydrogen molecule
 (3) Proton
 (4) Hydrogen atom

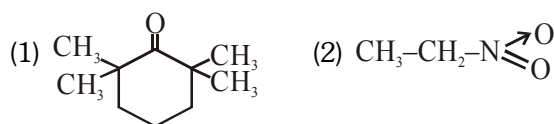
10. Which one is most stable free radical :



11. Which is wrong electromeric effect :



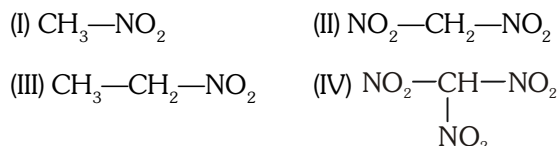
12. Tautomerism is exhibited by :-



13. Identify the compound that exhibits tautomerism :-

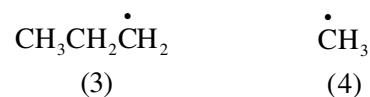
- (1) 2-Pentanone (2) Phenol
 (3) 2-Butene (4) Lactic acid

14. Arrange the following in correct order of acidic strength :



- (1) $\text{IV} > \text{II} > \text{I} > \text{III}$
 (2) $\text{IV} > \text{II} > \text{III} > \text{I}$
 (3) $\text{III} > \text{I} > \text{II} > \text{IV}$
 (4) $\text{III} > \text{I} > \text{IV} > \text{II}$

15. The correct order of stability of following carbon free radical is :-

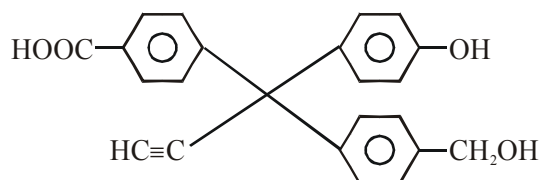


- (1) $1 > 2 > 3 > 4$
 (2) $4 > 3 > 2 > 1$
 (3) $2 > 3 > 1 > 4$
 (4) $2 > 1 > 3 > 4$

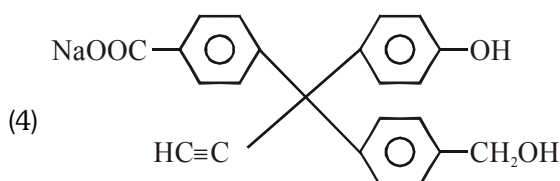
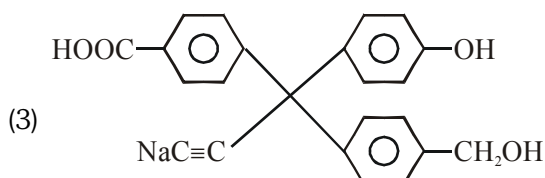
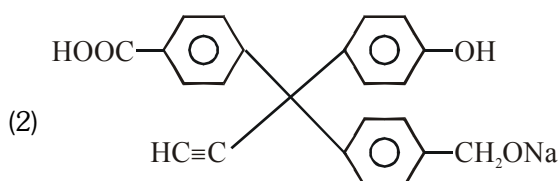
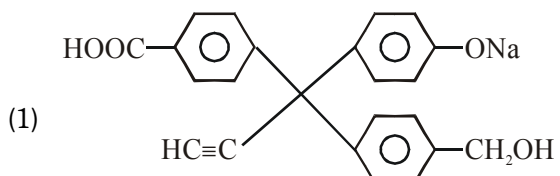
16. Which of the following is the strongest acid :-

- (1) Carbolic acid (2) Carbonic acid
 (3) Picric acid (4) Acetic acid

17.



$\xrightarrow[\text{(1mole)}]{\text{NaNH}_2}$ product is :-



18. The correct order of acidic strength is :-

- (1) $\text{CH}_3\text{COOH} < \text{HCN} < \text{H}_2\text{O} < \text{C}_2\text{H}_5\text{OH}$
- (2) $\text{CH}_3\text{COOH} > \text{HCN} > \text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH}$
- (3) $\text{HCN} > \text{CH}_3\text{COOH} > \text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH}$
- (4) $\text{CH}_3\text{COOH} > \text{HCN} > \text{C}_2\text{H}_5\text{OH} > \text{H}_2\text{O}$

19. Which of the following orders of acid strength is correct :-

- (1) $\text{RCOOH} > \text{ROH} > \text{HOH} > \text{HC}\equiv\text{CH}$
- (2) $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC}\equiv\text{CH}$
- (3) $\text{RCOOH} > \text{HOH} > \text{HC}\equiv\text{CH} > \text{ROH}$
- (4) $\text{RCOOH} > \text{HC}\equiv\text{CH} > \text{HOH} > \text{ROH}$

EXERCISE-III (Analytical Questions)**ANSWER KEY**

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	4	2	4	1	3	1	3	1	3	2	1,2	1	4
Que.	16	17	18	19											
Ans.	3	4	2	2											

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

- Assertion :-** Tertiary carbonium ions are generally formed more easily than primary carbonium ions.
Reason :- Hyperconjugative as well as inductive effect of additional alkyl groups stabilize tertiary carbonium ions.
 (1) A (2) B (3) C (4) D
- Assertion :-** Carbanions have ammonia like pyramidal shape.
Reason :- The carbon atom carrying negative charge has an octet of electrons.
 (1) A (2) B (3) C (4) D
- Assertion :-** Pyrrole is a weaker base than its hydrogenated product pyrrolidine.
Reason :- Lone pair of electrons on nitrogen is delocalized in pyrrole.
 (1) A (2) B (3) C (4) D
- Assertion :-** A mixture of o-nitrophenol and p-nitrophenol can be separated by steam distillation.
Reason :- o-nitrophenol is steam volatile but p-nitrophenol is not.
 (1) A (2) B (3) C (4) D
- Assertion :-** The carbocation $\text{CF}_3 - \overset{\oplus}{\text{CH}_2}$ is less stable than $\overset{\oplus}{\text{CF}_3}$.
Reason :- In case of $\text{CF}_3 - \overset{\oplus}{\text{CH}_2}$, the strongly electron withdrawing $-\text{CF}_3$ group intensifies the +ve charge but in case of $\overset{\oplus}{\text{CF}_3}$, the lone pairs of electrons on each of the three F-atoms overlap with the empty p-orbital of the carbocation carbon atom, thereby dispersing the +ve charge.
 (1) A (2) B (3) C (4) D
- Assertion :-** Acidity of the following compounds decreases in the order $\text{HC}\equiv\text{CH} > \text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}_3$
Reason :- Acidity of the compounds increase as the electronegativity of the carbon increases to which H is attached.
 (1) A (2) B (3) C (4) D
- Assertion :-** The acidity of alcohols follows the order : $1^\circ > 2^\circ > 3^\circ$.
Reason :- The + I effect of the additional alkyl groups favours the cleavage of O-H bond.
 (1) A (2) B (3) C (4) D
- Assertion :-** Phenol is less acidic than p-nitro phenol.
Reason :- Phenolate ion is more stable than p-nitro phenolate ion.
 (1) A (2) B (3) C (4) D
- Assertion :-** Pyrrole is more basic than pyridine.
Reason :- In pyrrole, nitrogen is sp^3 -hybridized.
 (1) A (2) B (3) C (4) D
- Assertion :-** Aniline is a weaker base than benzyl amine.
Reason :- In aniline, mesomeric interaction occurs between benzene ring and amino group.
 (1) A (2) B (3) C (4) D
- Assertion :** Cyclopentadienyl anion is much more stable than allyl anion.
Reason : Cyclopentadienyl anion is aromatic in character.
 (1) A (2) B (3) C (4) D
- Assertion :** Acetic acid is stronger acid than ethyl alcohol.
Reason : In acetate ion both C-O bond lengths are equal.
 (1) A (2) B (3) C (4) D

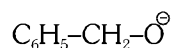
13. **Assertion :** Tropylium ion is more stable than benzyl cation.

Reason : Tropylium ion is anti-aromatic in nature.

(1) A (2) B (3) C (4) D

14. **Assertion :-** Phenol is more acidic than benzyl alcohol.

Reason :- $\text{C}_6\text{H}_5-\text{O}^\ominus$ is more stable than



(1) A (2) B (3) C (4) D

15. **Assertion :-** Picric acid is stronger acid than phenol.

Reason :- Picric acid has $-\text{COOH}$ group, while phenol has $-\text{OH}$ group.

(1) A (2) B (3) C (4) D

16. **Assertion :-** Pyridine is less basic than trimethyl amine.

Reason :- Nitrogen atom in pyridine is sp^2 hybridized, while in trimethylamine it is sp^3 .

(1) A (2) B (3) C (4) D

17. **Assertion :-** Enol form of cyclohexane-1,3,5-trione is more stable than its ketoform.

Reason :- It contains α -hydrogen atoms.

(1) A (2) B (3) C (4) D

18. **Assertion :-** $\text{C}_2\text{H}_5\text{NO}_2$ shows functional isomerism as well as tautomerism.

Reason :- Nitroethane shows tautomerism due to presence of α -hydrogens and functional isomerism with ethyl nitrite.

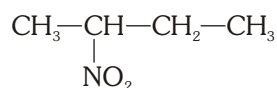
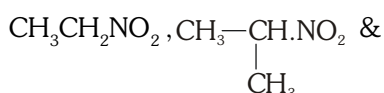
(1) A (2) B (3) C (4) D

19. **Assertion :** Tautomers have different functional group.

Reason : Tautomers have same molecular formula.

(1) A (2) B (3) C (4) D

20. **Assertion :-** The following compound are given below –



all three compounds are soluble in NaOH.

Reason :- All above compound have lower boiling than CH_3NO_2 .

(1) A (2) B (3) C (4) D

21. **Assertion :-** Phenol is stronger acid than alcohols.

Reason :- Phenol is stabilized by resonance whereas alcohols are not.

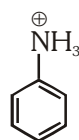
(1) A (2) B (3) C (4) D

22. **Assertion :-** Formic acid is a stronger acid than benzoic acid.

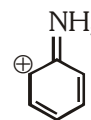
Reason :- pK_a of formic acid is higher than that of benzoic acid.

(1) A (2) B (3) C (4) D

23. **Assertion :-** Here two structures are given



I



II

I and II are not acceptable canonical structure.

Reason :- Carbonium ions are less stable than ammonium ions.

(1) A (2) B (3) C (4) D

24. **Assertion :-** Benzene hexachloride is an aromatic compound.

Reason :- It contain 3π bonds in the ring.

(1) A (2) B (3) C (4) D

25. **Assertion :-** $\text{Cl}-\underset{\text{C}_2\text{H}_5}{\overset{\text{H}}{\text{C}}}-\text{CH}_3$ and $\text{H}-\underset{\text{CH}_3}{\overset{\text{C}_2\text{H}_5}{\text{C}}}-\text{Cl}$ are

enantiomers.

Reason :- Non-superimposable mirror images are known as enantiomers.

(1) A (2) B (3) C (4) D

26. **Assertion :-** Dimethyl amine has more basic strength than trimethyl amine.

Reason :- It is due to solvation effect.

(1) A (2) B (3) C (4) D

27. **Assertion :-** In $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}=\text{CH}_2$, the C-C-C bond

angles are different.

Reason :- The C has steric effect of $-\text{CH}_3$ group.

(1) A (2) B (3) C (4) D

28. Assertion :- Benzyl amine is more basic than ethyl amine.

Reason :- Phenyl group has +I effect.

(1) A (2) B (3) C (4) D

29. Assertion :- o-nitrophenol is more acidic than m-nitrophenol.

Reason :- At o-position, -I effect of $-\text{NO}_2$ is more than at m-position.

(1) A (2) B (3) C (4) D

30. Assertion :- N, N-diethylethane is more basic than N, N-dimethyl methane.

Reason :- +I of ethyl is more than methyl group.

(1) A (2) B (3) C (4) D

31. Assertion :- Dimethyl amine has more basic strength than trimethyl amine.

Reason :- It is due to solvation effect.

(1) A (2) B (3) C (4) D

32. Assertion :- In $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$, the C-C-C bond

angles are different.

Reason :- The C has steric effect of $-\text{CH}_3$ group.

(1) A (2) B (3) C (4) D

33. Assertion :- Benzyl amine is more basic than ethyl amine.

Reason :- Phenyl group has +I effect.

(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	2	1	1	1	1	3	3	4	1	1	2	3	1	3
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	1	2	3	2	3	2	4	1	1	1	4	2	1
Que.	31	32	33												
Ans.	1	1	4												

IMPORTANT NOTES

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3.	Substitution reactions	98
4.	Elimination reactions	113
5.	Exercise-I (Conceptual Questions)	118
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8.	Exercise-IV (Assertion & Reason)	142

NEET SYLLABUS

Types of organic reaction (free radical reaction of Alkane, addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect) in alkene and alkyne, mechanism of electrophilic substitution - Nitration sulphonation, halogenation, Friedel Craft's alkylation and acylation; directive influence of functional group in mono-substituted benzene, mechanism of substitution reactions, mechanism of nucleophilic addition)

OBJECTIVES

After studying this unit, we will be able to :

- *recognise the types of organic reactions;*
- *predict the formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism;*
- *understand mechanism of electrophilic substitution reactions of benzene;*

*"Thinking should become your capital asset, no matter whatever ups and downs;
you come across in your life."*

A.P.J. Abdul Kalam

REACTION MECHANISM : PART-II

4.0 TYPE OF REACTIONS :

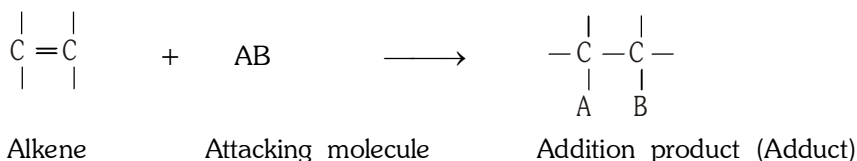
Reactions are of mainly four types :

1. Addition reactions.
2. Substitution reactions.
3. Elimination reactions.
4. Isomerisation reactions

4.1 ADDITION REACTIONS : It is also of three types :

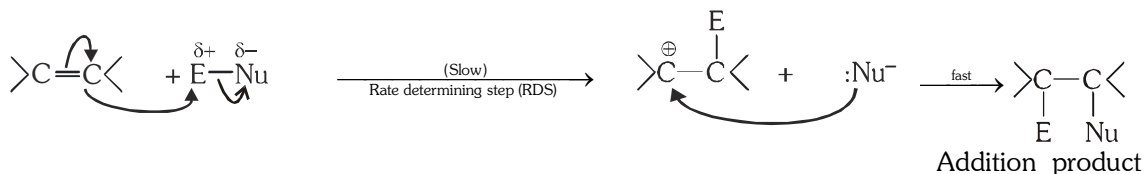
- (A) Electrophilic addition reactions
- (B) Free radical addition reactions
- (C) Nucleophilic addition reactions

(A) Electrophilic addition reaction :- Because of the presence of $>C=C<$ bond in molecules, alkenes generally take part in the **addition reactions**.



From mechanism point of view, the addition in alkenes is generally **electrophilic in nature** which means that attacking reagent which carries the initial attack is an electrophile (E^+). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds in two steps.

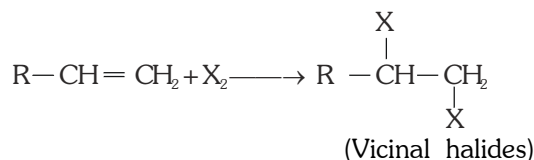
Step I : The π -electron cloud of the double bond causes the polarisation of the attacking molecule ($E-Nu$) which cleaves to release the electrophile (E^+) for the attack. The double bond simultaneously undergoes electromeric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a **carbocation** intermediate.



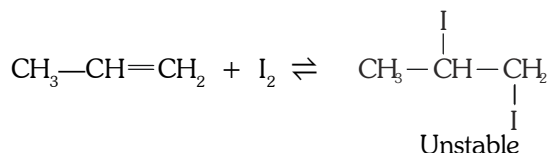
Step II : The nucleophile ($:Nu^-$) released in the slow step combines with the carbocation to give the desired addition product in the fast step.

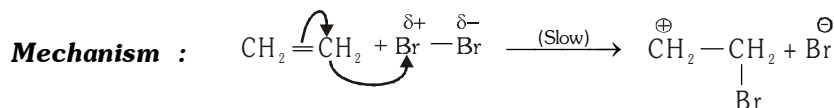
Reactivity for Electrophilic addition reaction $\propto$ stability of carbocation formed in RDS

(1) Addition of Halogen : It is a electrophilic addition reaction.

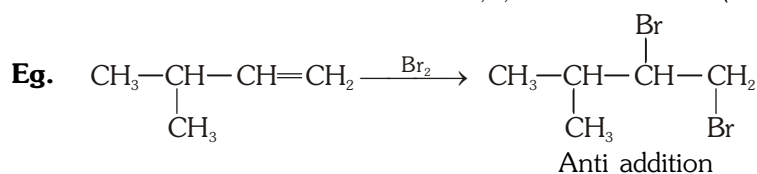
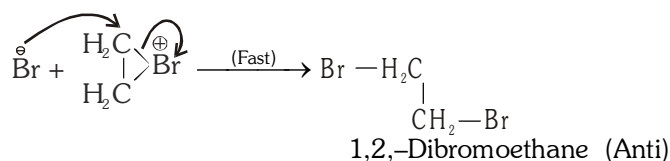
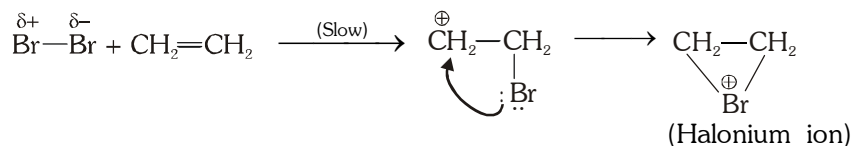


- (a) The addition of Br_2 on alkenes provides a useful test for unsaturation in molecule. The brown colour of the bromine being rapidly discharged. Thus decolorization of 5% Br_2 in CCl_4 by a compound suggest unsaturation in it. Colourless dibromo compound is formed.
- (b) I_2 reacts with alkenes to form Vicinal di-iodides which are unstable and I_2 gets eliminated to give original alkene.



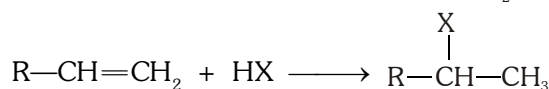
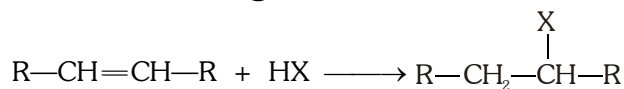


It is interesting to note that product which is mainly formed as a result of addition is **trans** in nature whereas the cis isomer is obtained in relatively smaller proportions. Since carbocation intermediate is planar (sp^2 hybridised), both cis and trans addition products must be formed almost in equal proportions. The trans product can be justified in case a cyclic halonium ion is formed by the initial electrophile attack.



No carbocation rearrangement and anti addition product.

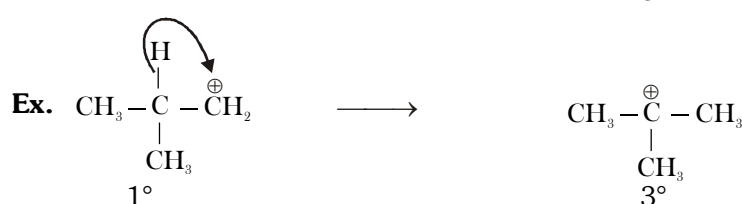
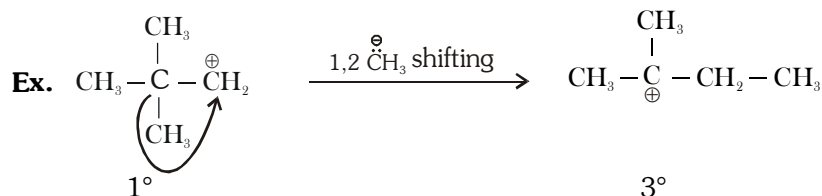
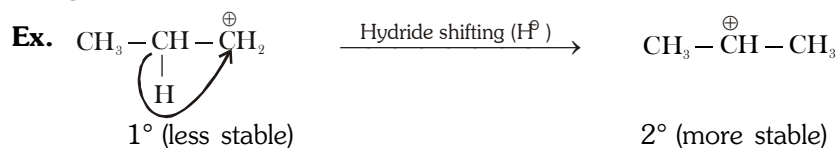
(2) Addition of halogen acid :

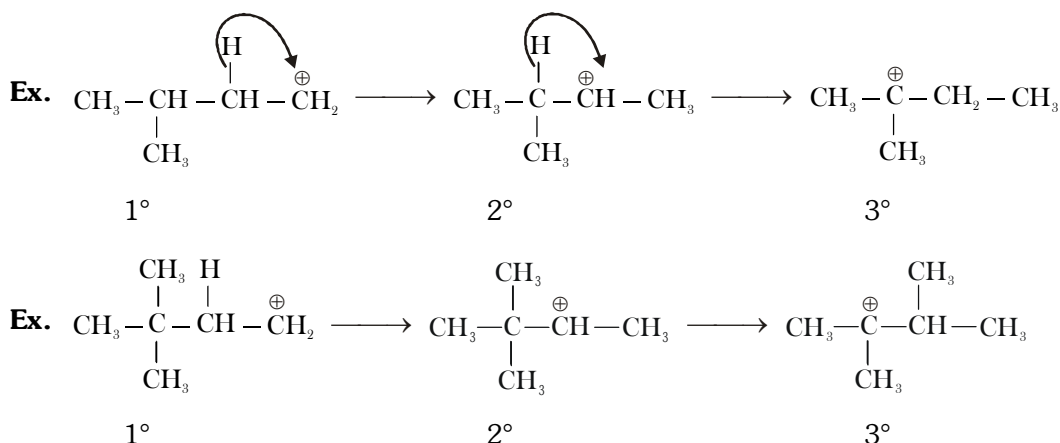


GOLDEN KEY POINTS

- The order of reactivity of hydrogen halide is : **HI > HBr > HCl**
- Addition on alkene proceeds via the formation of more stable carbonium ion.
- Addition of HX on unsymmetrical alkenes ($\text{R}-\text{CH}=\text{CH}_2$) takes place according to Markovnikov's rule. Carbocation rearrangement is observed in the reaction.

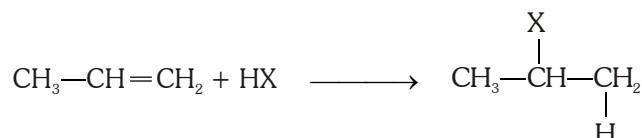
Rearrangement in carbocation



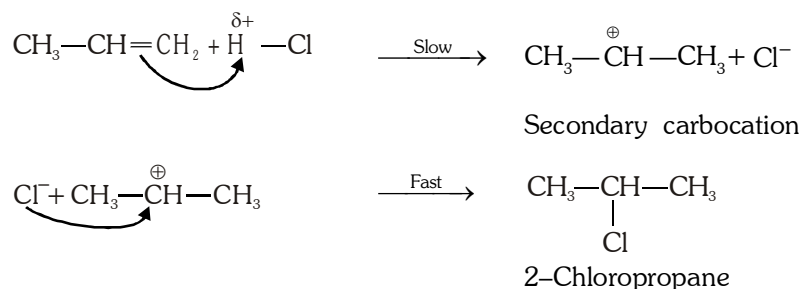


Markovnikov's Rule States :

- (a) **First Rule** : When molecule of HX add up on unsymmetrical unsaturated hydrocarbon, the electrophile (H^+) goes to the unsaturated carbon atom bearing more number of hydrogen atoms.



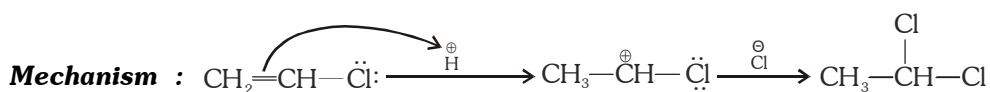
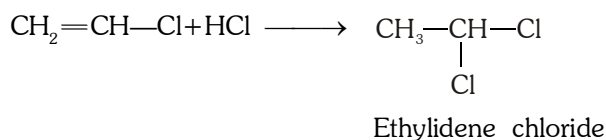
Mechanism : It is electrophilic addition and is illustrated by the action of HCl to propene.



Primary carbocation ($\text{CH}_3-\text{CH}_2-\text{CH}_2^+$) is also formed but only in very small proportion since it is less stable than the secondary carbocation. Markovnikov's rule is based on stability of carbocation.

Note ; The electrophilic addition of HX to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

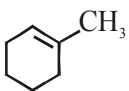
- (b) **Second Rule** : In the addition of HX to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.



All polar reagents of the general structure $\overset{\oplus}{\text{Y}}-\overset{\ominus}{\text{Z}}$ (such as $\overset{\oplus}{\text{H}}-\overset{\ominus}{\text{X}}$, $\overset{\oplus}{\text{H}}-\overset{\ominus}{\text{OH}}$, $\overset{\oplus}{\text{H}}-\overset{\ominus}{\text{SO}_3\text{H}}$, $\overset{\oplus}{\text{X}}-\overset{\ominus}{\text{OH}}$) add on unsymmetrical unsaturated compound in accordance with Markovnikov's rules. Such additions are called normal Markovnikov's rule, where as additions in the opposite manner are referred to as abnormal or **anti Markovnikov's additions**.

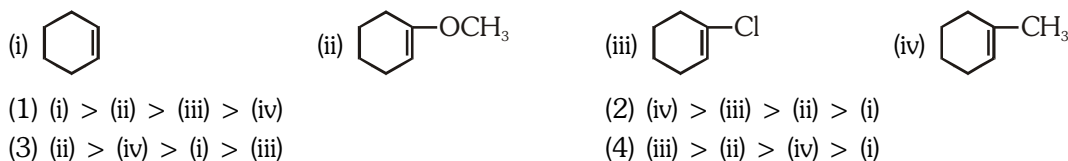
BEGINNER'S BOX-1

1. The intermediate in the Electrophilic addition-reaction is :-
 (1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

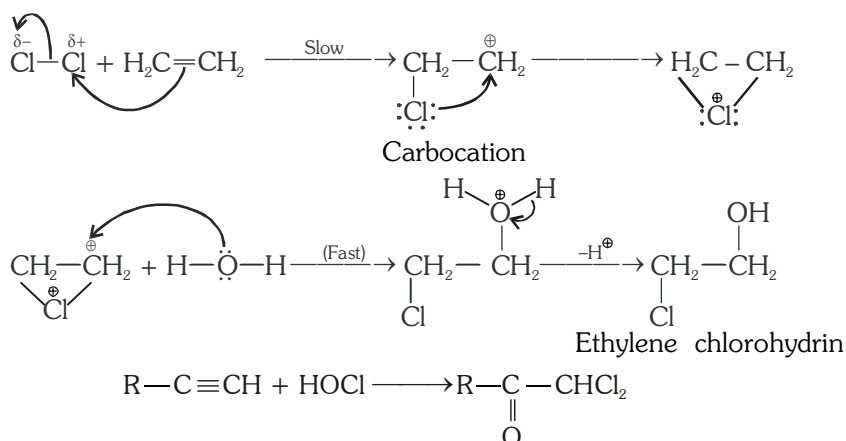
2.  + HI $\longrightarrow$ major product is



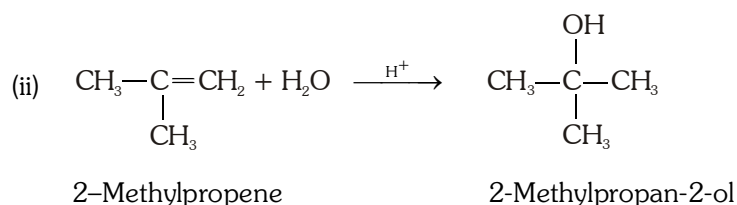
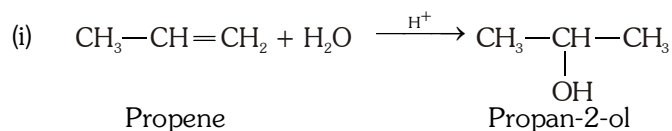
3. Give reactivity order towards EAR.



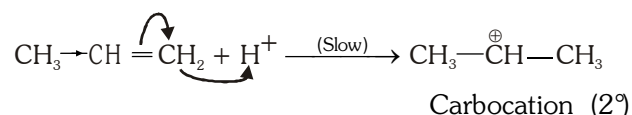
(3) Addition of Hypohalous acid (or X_2/H_2O , or HOX) : It is a electrophilic addition and follows Markovnikov's rule, and anti addition.

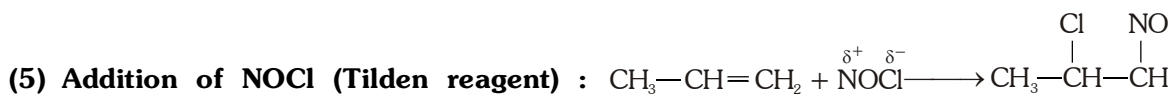
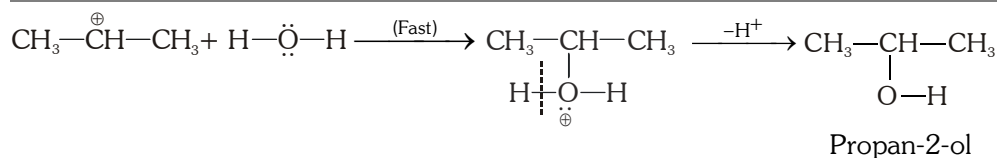


(4) Addition of water (Hydration of alkenes) : Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as acidic **hydration reaction**. Intermediate in this reaction is carbocation, so rearrangement may take place.



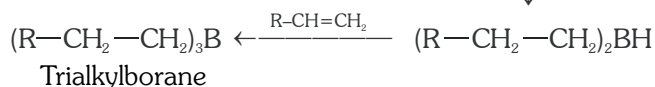
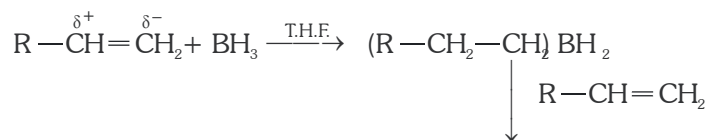
Mechanism :



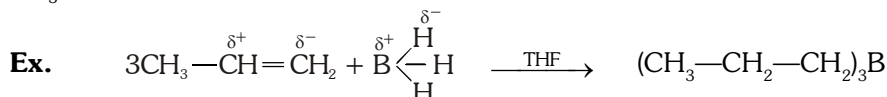


Propylene nitroschloride

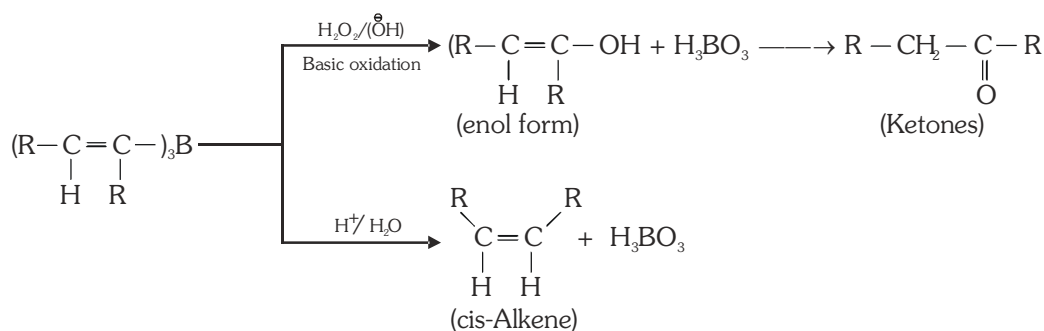
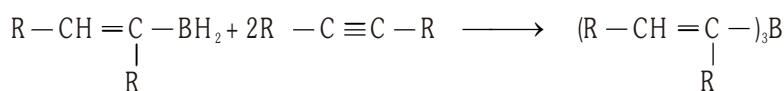
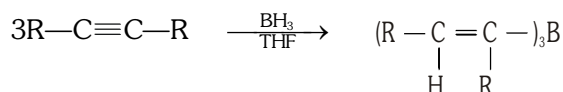
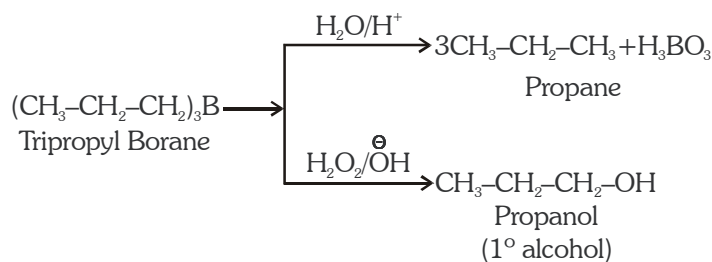
(6) Hydroboration Oxidation : Borane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.



BH_3 does not exist freely as monomer so a solvent THF (tetra hydro furane) is used to stabilised it.

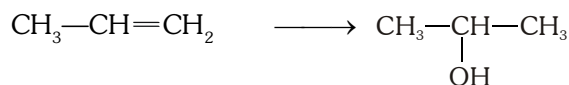


BHR_2 also can be taken.



Note : The overall process appears to be addition of water according to anti Markovnikov's rule and involves syn. addition.

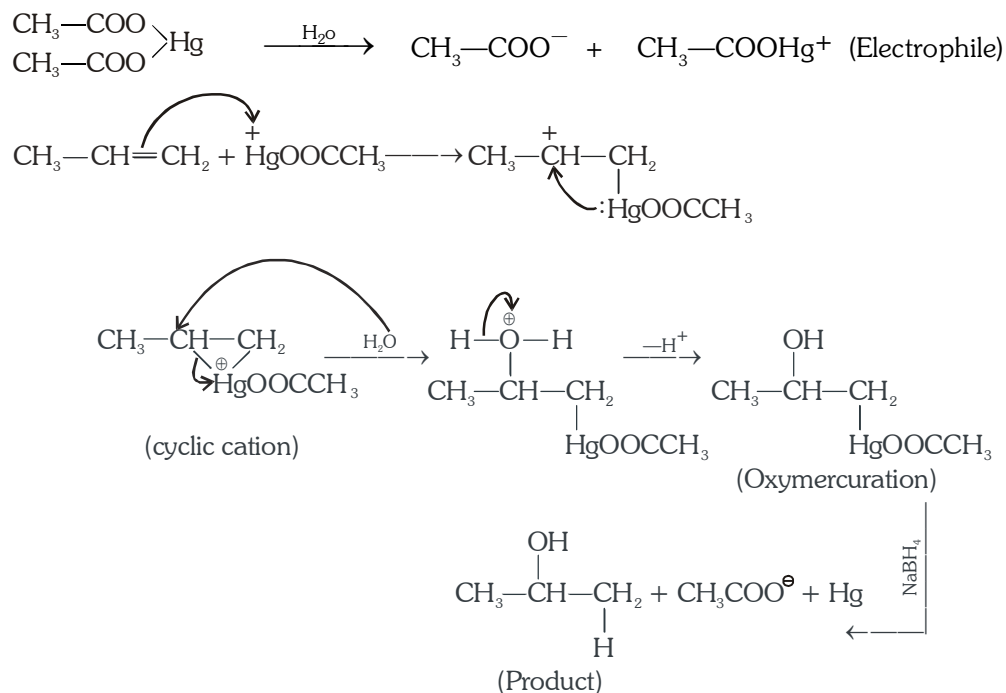
(7) Oxymercuration – demercuration : Mercuric acetate in water is treated with an alkene. The addition product on reduction with sodium Boro hydride in aqueous NaOH Solution gives alcohol. It follows the Markovnikov's rule.



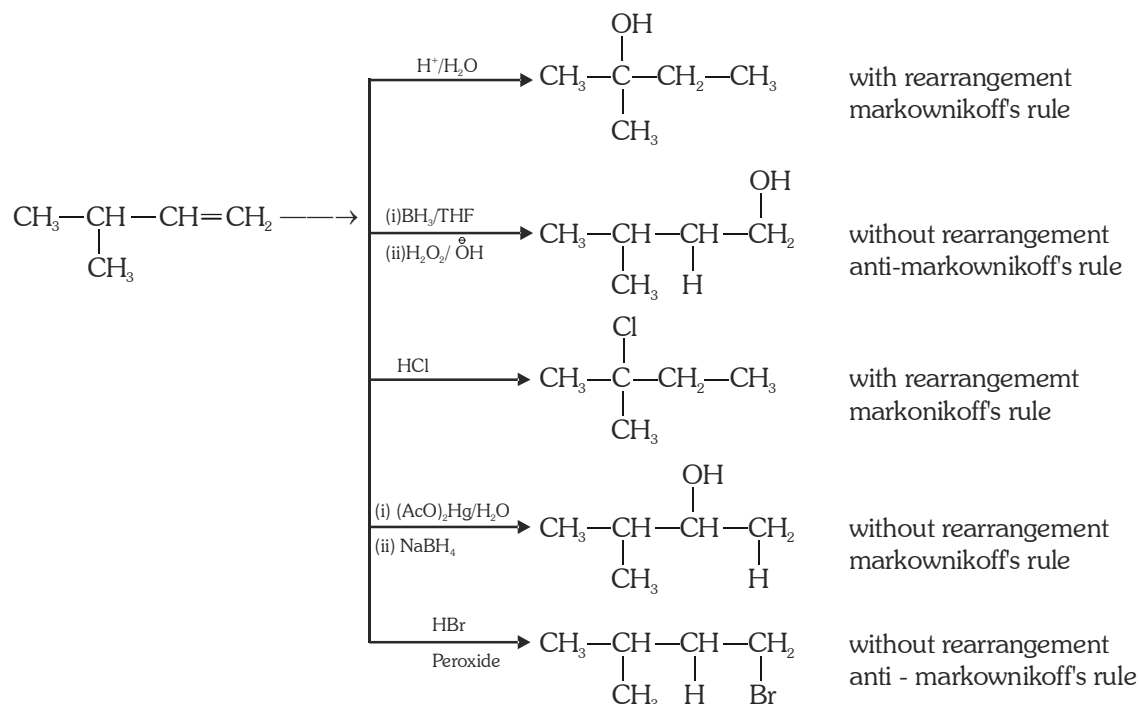
(i) $(\text{AcO})_2\text{Hg}/\text{H}_2\text{O}$ (Mercuric acetate) or $(\text{CH}_3\text{COO})_2\text{Hg}/\text{H}_2\text{O}$

(ii) NaBH_4

Mechanism :



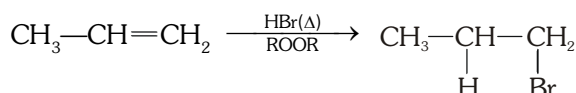
Note : Intermediate is cyclic cation so there is no rearrangement.



BEGINNER'S BOX-2

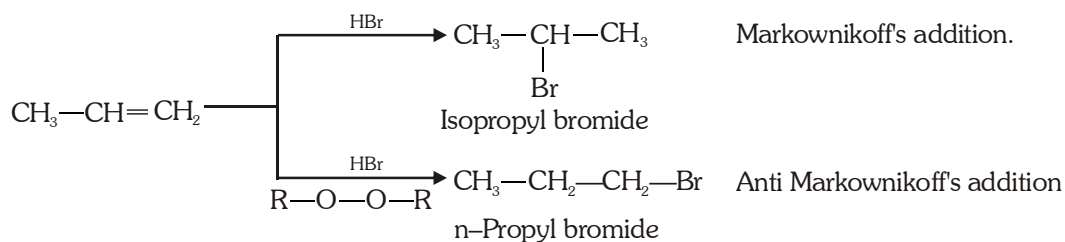
- (1) $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2 \xrightarrow[\text{(2) H}_2\text{O}_2/\text{OH}^-]{\text{(1) BH}_3, \text{THF}}$
- (2) $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2 \xrightarrow{\text{dil. H}_2\text{SO}_4}$
- (3) $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2 \xrightarrow[\text{(2) NaBH}_4]{\text{(1) (CH}_3\text{COO)}_2\text{Hg, H}_2\text{O}}$
- (4) 2 & 3 both

(B) Free radical addition reactions :- Addition of HBr on alkene or alkyne in presence of peroxide.



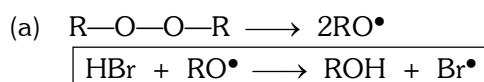
Anti Markovnikov's rule or peroxide effect or Kharasch rule

- (i) In the presence of peroxides the addition of HBr on unsaturated unsymmetrical compound takes place contrary to Markovnikov's rule. This is called peroxide effect and is due to the difference in the mechanism of the addition.
- (ii) In the normal Markovnikov's addition the mechanism is ionic.
- (iii) In the presence of peroxide the addition of HBr takes place via free radicals.
- (iv) Peroxide effect is not observed in case of H-F, HCl and HI. Reactions follows electrophilic addition mechanism.

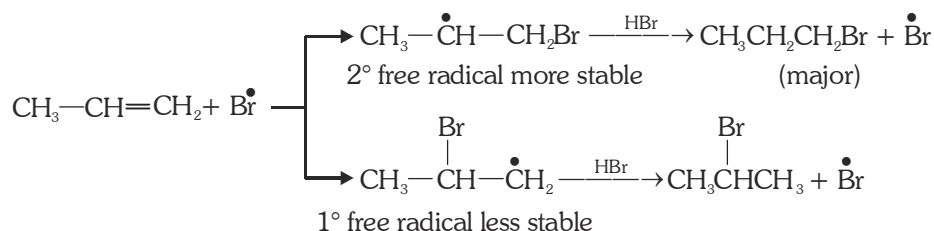


Mechanism :

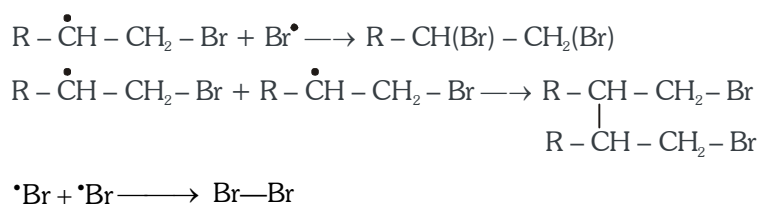
(i) Chain initiation -

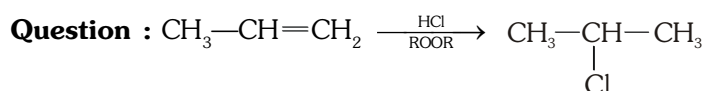


(ii) Chain propagation



(iii) Chain termination :



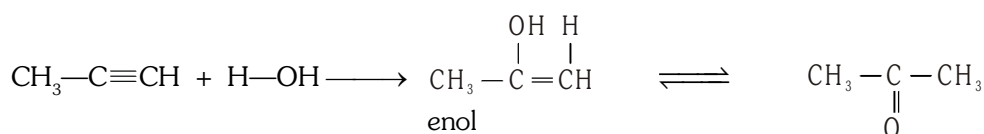
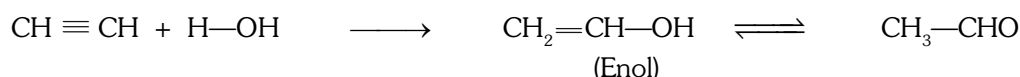


Ans. no effect simple EAR

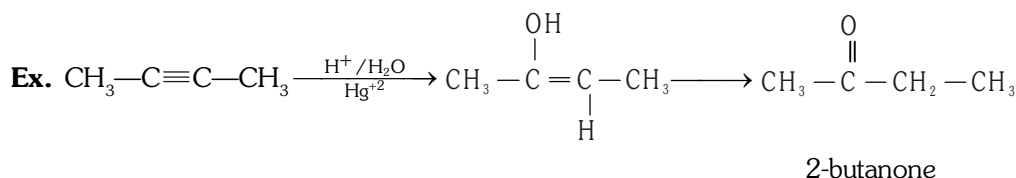
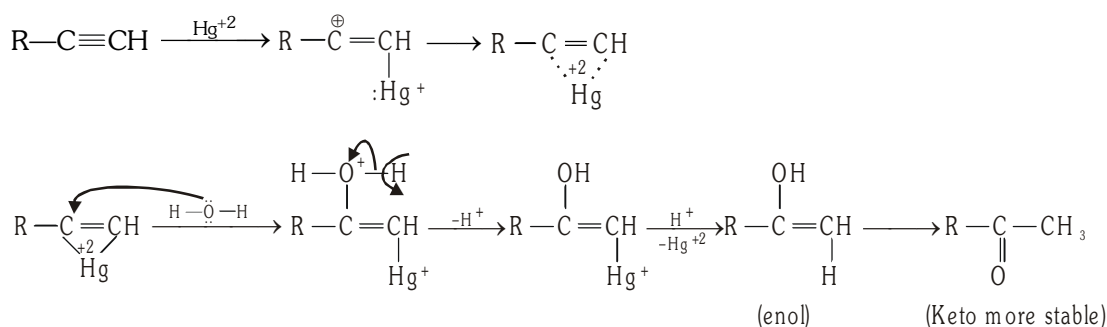
(C) Nucleophilic Addition Reaction :-

(C₁) NAR in Alkyne : In these reactions some heavy metal cation like Hg^{+2} , Pb^{+2} , Ba^{+2} are used. These cation attracts the π e^- of alkynes and decrease the e^- density and hence a nucleophile can attack an alkynes.

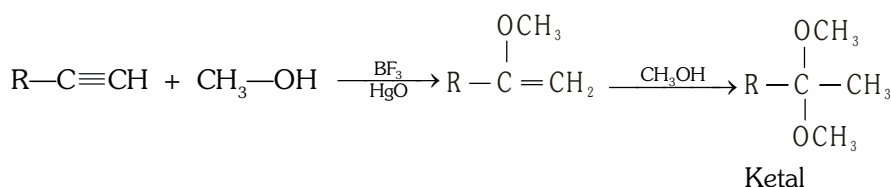
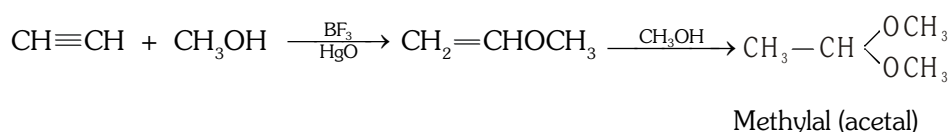
(1) Addition of dil. H_2SO_4 (Hydration) : The addition of water takes place in the presence of Hg^{+2} and H_2SO_4 [1% HgSO_4 + 40% H_2SO_4].



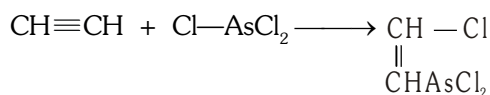
Mechanism :



(2) Addition of alcohols : In presence of BF_3 and HgO alkynes react with alcohols and form acetal and ketal



(3) Addition of AsCl_3 : In presence of AlCl_3 or HgCl_2 acetylene combines with AsCl_3 to yield Lewisite gas. It is four times poisonous than mustard gas.



2-Chlorovinyl dichloro arsine (Lewisite gas)

E Z:\NODE02\B0AI-B0\TARGET\CHEM\ENG\MODULE-3\04 GOC-II\01-THEORY.P65

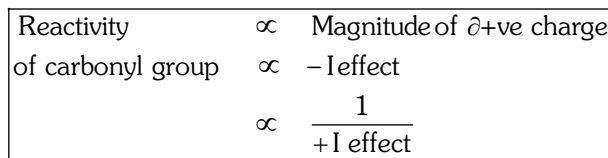
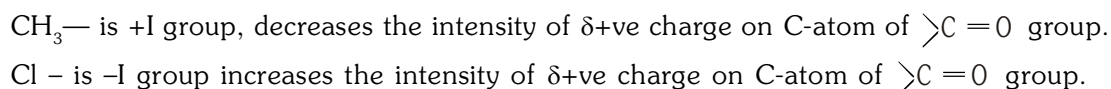


Illustration 1. Arrange the following for reactivity in decreasing order

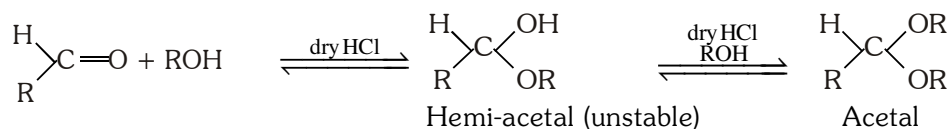

$$\begin{array}{l}
 \text{CH}_3\text{C}(=\text{O})\text{H} + \text{HCN} \longrightarrow \text{CH}_3\text{C}^*(\text{OH})(\text{CN})\text{H} \\
 \text{Acetaldehyde Cyanohydrin} \\
 \text{* (Racemic mixture)}
 \end{array}$$

$$\begin{array}{ll}
 \xrightarrow[\text{Partial hydrolysis}]{\text{HO/OH}} & \text{CH}_3\text{C}(\text{OH})(\text{CONH}_2)\text{H} \\
 & \text{Lactamide (2-Hydroxy propanamide)} \\
 \xrightarrow[\text{Complete hydrolysis}]{2\text{H}_2\text{O/H}^+} & \text{CH}_3\text{C}(\text{OH})(\text{COOH})\text{H} \\
 & \text{Lactic acid (2-Hydroxy propanoic acid)} \\
 \xrightarrow[\text{Reduction}]{\text{LiAlH}_4} & \text{CH}_3\text{C}(\text{OH})(\text{CH}_2\text{NH}_2)\text{H} \\
 & \text{1-Amino - 2-Propanol}
 \end{array}$$

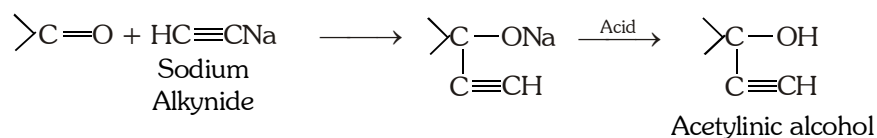
(2) Addition of NaHSO₃ : This reaction is utilized for the separation of carbonyl compounds from non-carbonyl compounds.



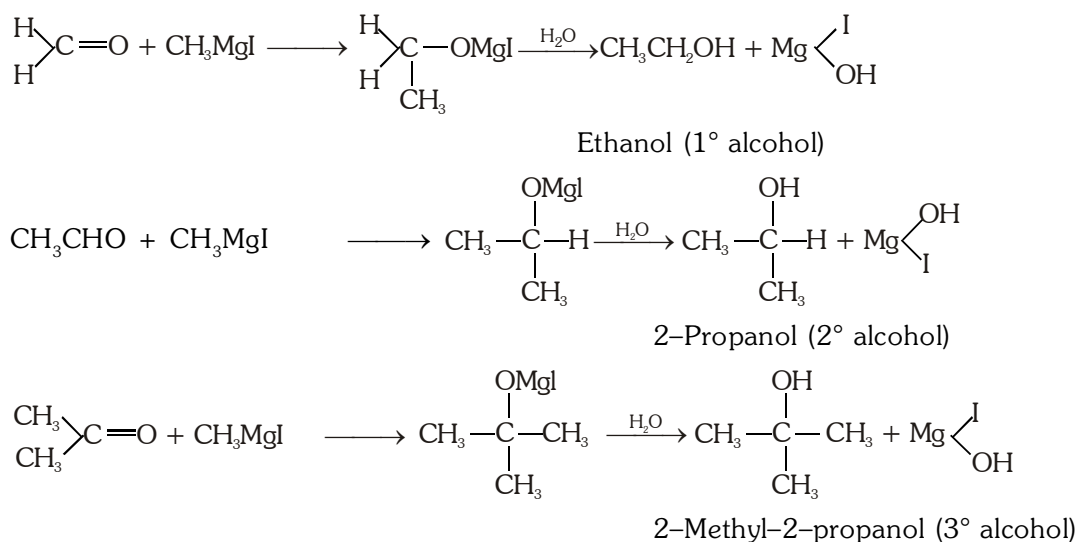
(3) With Alcohol :



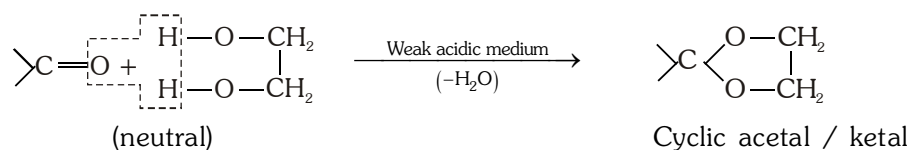
(4) Reaction with sodium alkynide :



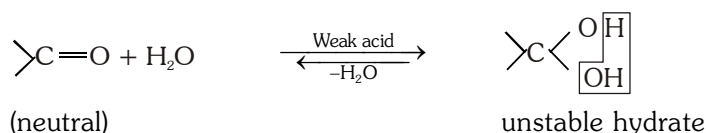
(5) Reaction with Grignard reagent :



(6) Reaction with glycol :

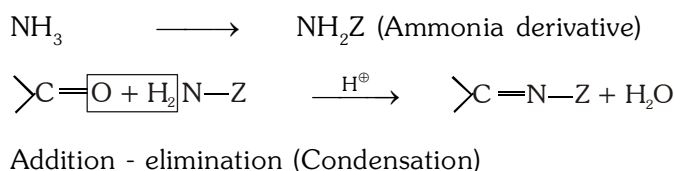


(7) Reaction with H₂O : It is a reversible reaction.



Note : Chloral (Cl₃C-CH=O) forms stable hydrate [CCl₃ - CH(OH)₂] (chloral hydrate)

(8) Reaction with ammonia derivatives : These are condensation or addition elimination reaction. These proceeds well in weakly acidic medium.



4.2 SUBSTITUTION REACTIONS : Reactions in which one atom or a group of substrate is replaced by other atom or group are called as substitution reactions.

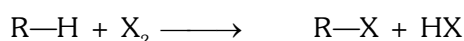
On the basis of reaction conditions and attacking species, substitution reaction is also of three types :

- (A) Free radical substitution reactions
- (B) Electrophilic substitution reactions
- (C) Nucleophilic substitution reactions

(A) Free radical substitution reactions : Substitution reaction in alkanes show free radical mechanism.

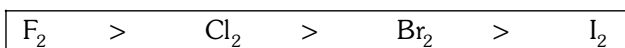
They give following substitution reaction.

(a) Halogenation : Replacement of H-atom by halogen atom

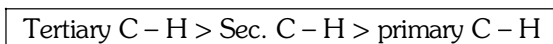


Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temp.

The reactivity order for halogens shows the order.

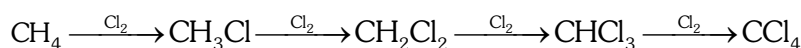


Reactivity order of hydrogen atom in alkane is



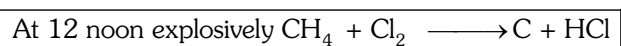
(i) **Fluorination :** Reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F_2 diluted with an inert gas like N_2 .

(ii) **Chlorination :**



The monochloro derivative of alkane is obtained as major product by taking alkane in large excess.

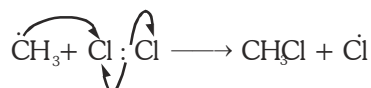
When chlorine is in excess then perchloro derivative is obtained as major product.



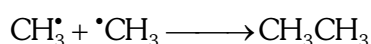
Mechanism for $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$

Step I **Chain initiation step :** $Cl:Cl \xrightarrow[or \Delta]{UV} Cl^\bullet + Cl^\bullet$

Step II **Chain propagation step :** $Cl^\bullet + H:\underset{\text{Methane}}{CH_3} \longrightarrow H:Cl + \underset{\text{Methyl radical}}{\cdot CH_3}$



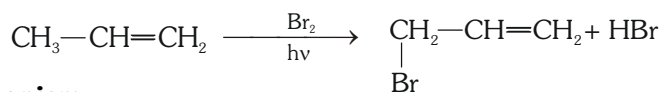
Step III **Chain termination step :** $Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$, $CH_3^\bullet + \cdot Cl \longrightarrow CH_3Cl$,



(iii) **Bromination :** Br_2 reacts with alkanes in a similar manner but less vigorously.

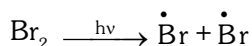
GOLDEN KEY POINTS

Allylic or benzylic substitution by Br₂ (low concentration)/hν or NBS/hν

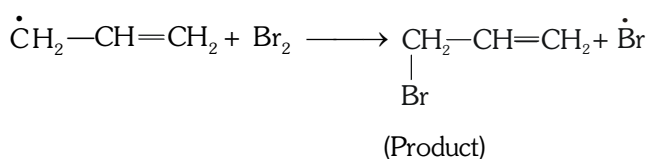
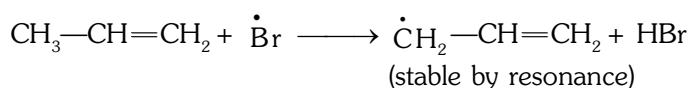


Mechanism :

I Chain initiation step :

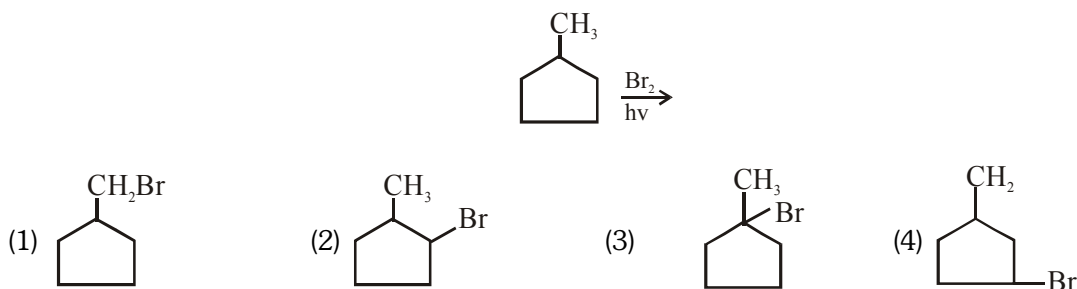


II Chain propagation step :



BEGINNER'S BOX-4

1. In the following reaction, the major product is :-



2. The bond dissociation energy at the C-H bond for the compound :-

(I) CH₃H (II) CH₃-CH₂-H (III) CH₂=CH-CH₂-H (IV) C₆H₅-H

(1) I > II > III > IV

(2) IV > III > II > I

(3) IV > I > II > III

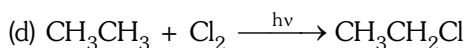
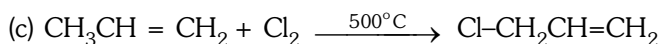
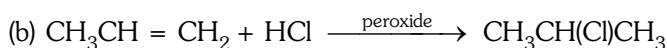
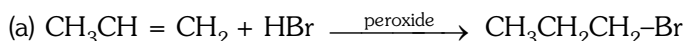
(4) II > I > IV > III

3. Arrange the following in correct order of reactivity towards Cl₂/hν -

(A) CH₄ (B) CH₃CH₃ (C) CH₃CH₂CH₃ (D) 

(1) A > B > C > D (2) D > C > B > A (3) B > C > A > D (4) C > B > D > A

4. Which of the following are free radical reactions:-



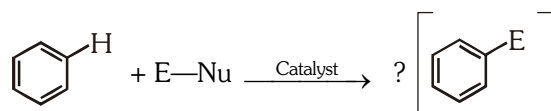
(1) Only d

(2) a, c

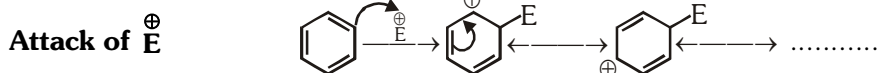
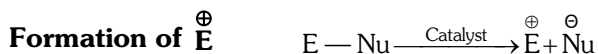
(3) a, b, d

(4) a, c, d

(B) Electrophilic substitution reaction [ESR] : Characteristic reaction of arenes is ESR

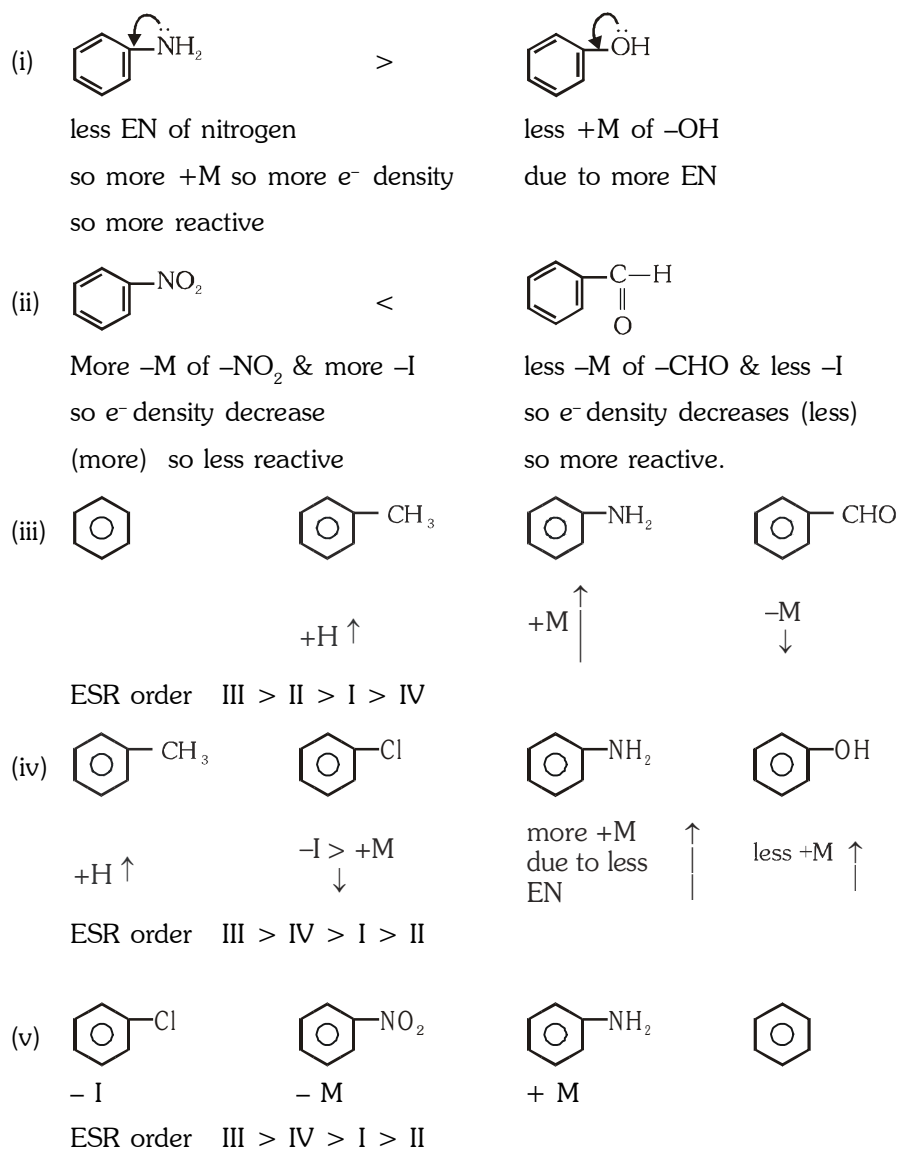


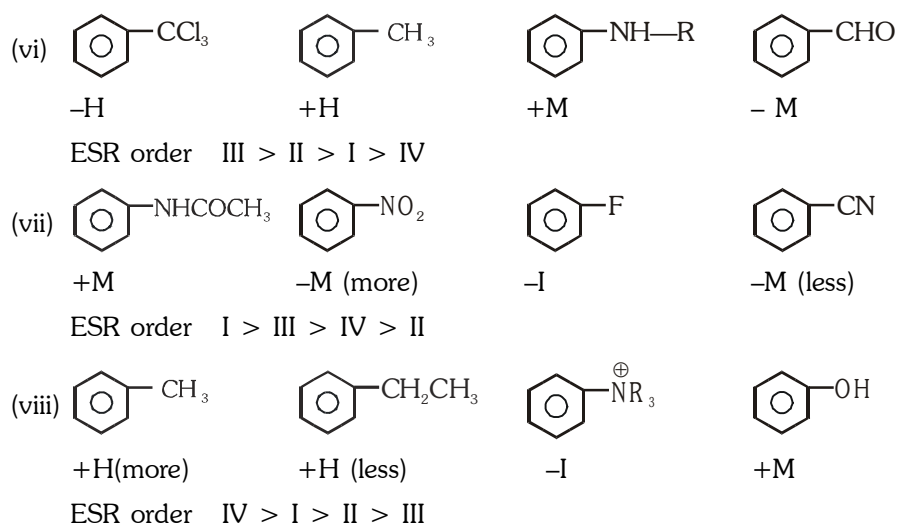
Mechanism :



Illustrations

Illustration 2. Give reactivity order for electrophilic substitution reaction.



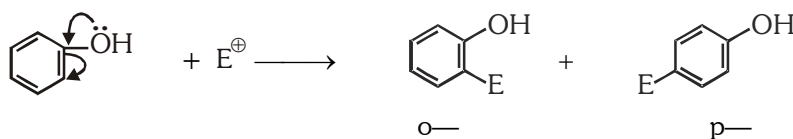
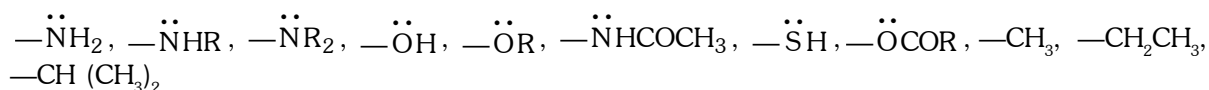


Note:

(1) ortho/para directing group or activating group : Group which direct electrophile on ortho and para position is called as o/p directing group.

These group increases electron density or increases reactivity of benzene ring so are called activating group.

These groups are :

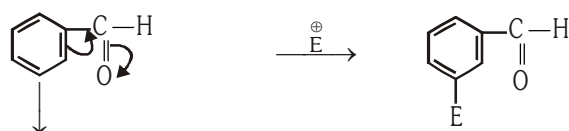


due to +M/+H of these groups electron density at ortho and para position is increased so electrophile easily attack on ortho/para position.

(2) Meta directing or deactivating group : Due to -M/-H of groups electron density at ortho and para position is less but more at meta position so electrophile attack on meta position. So, groups which direct electrophile on meta position are called as meta directing groups.

These groups decrease electron density in benzene ring and decrease reactivity of benzene ring so are called as deactivating group.

These groups are :

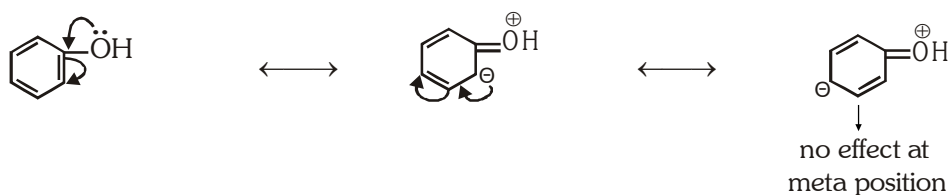


More e^- density at meta position

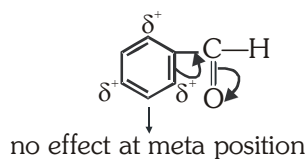
(3) Halogens are o/p directing group due to +M effect but are deactivating group due to -I > +M.

(4) M and H effect does not depend on distance while I-effect depends on distance In given example

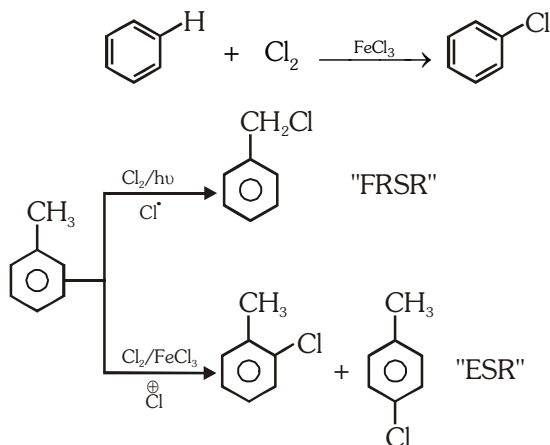
(5) M-effect at meta position is considered zero.



Similarly :

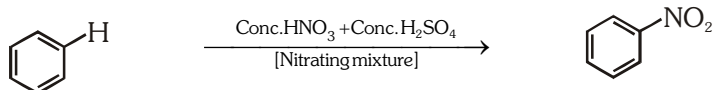


(i) Halogenation :

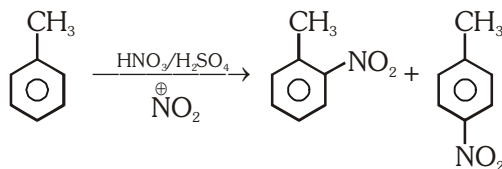
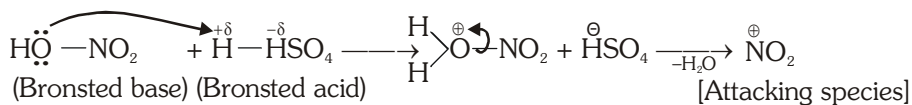


Note: CH_3 group in toluene is o/p directing and activating group.

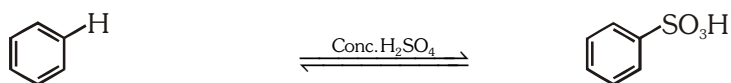
(ii) Nitration :



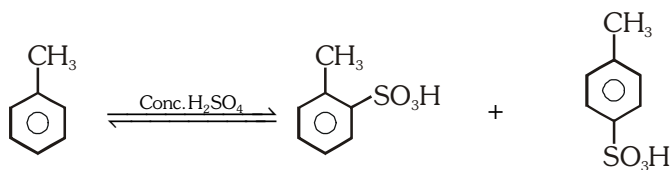
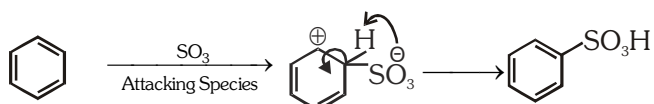
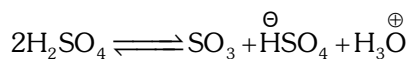
Formation of $\text{E}^{\oplus}$



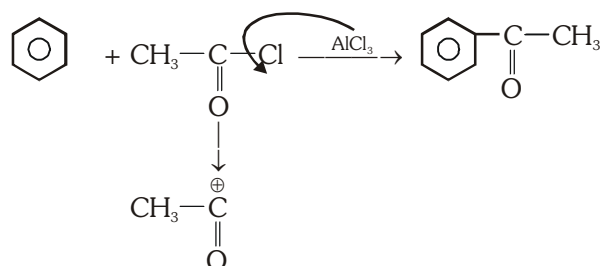
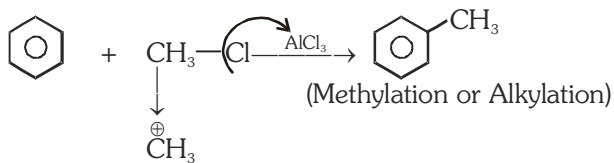
(iii) Sulphonation :



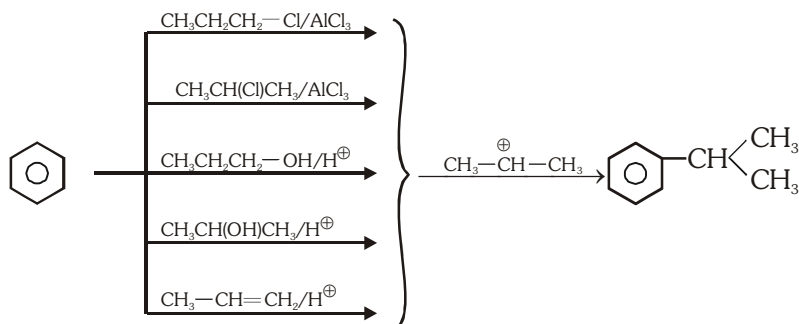
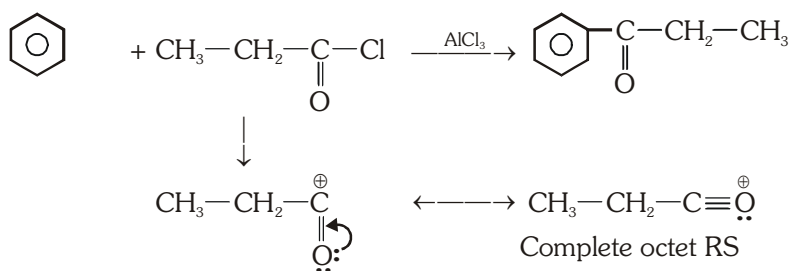
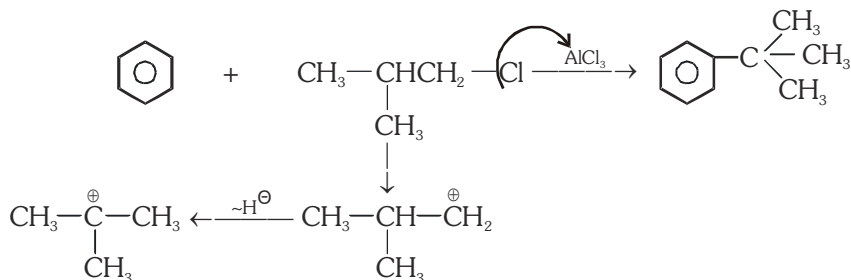
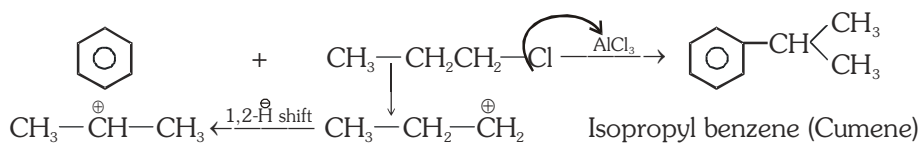
Mechanism :

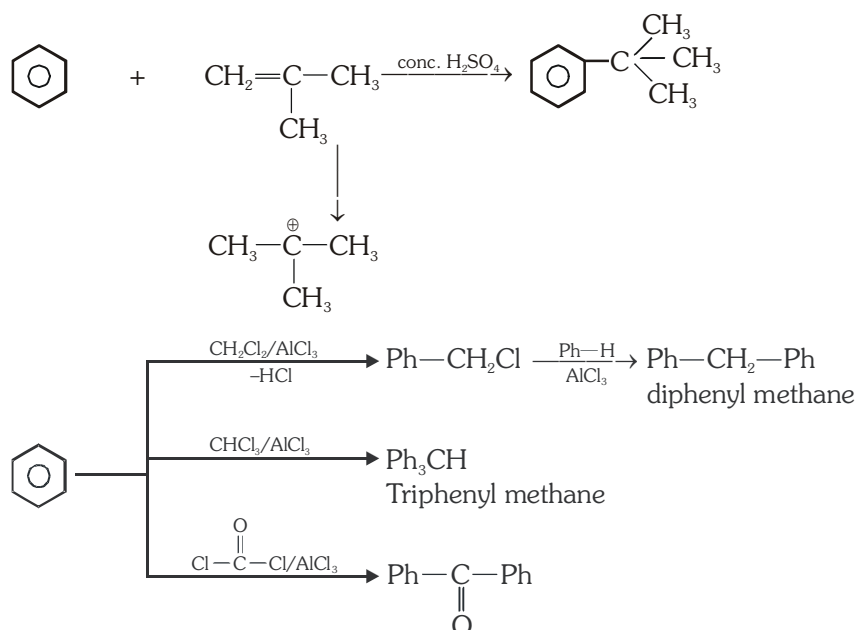


(iv) Friedel crafts reaction [FCR] : Alkylation or acylation of arenes in presence of Lewis acid $[\text{FeCl}_3, \text{AlCl}_3 \text{ or } \text{ZnCl}_2 \dots]$ is called as FCR.

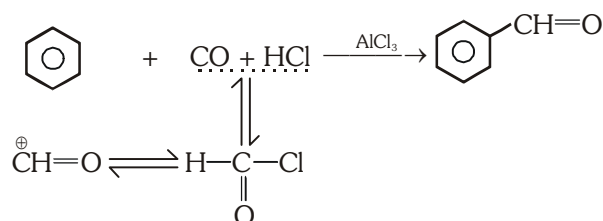


Intermediate carbocation is formed in FCR so rearrangement is possible.

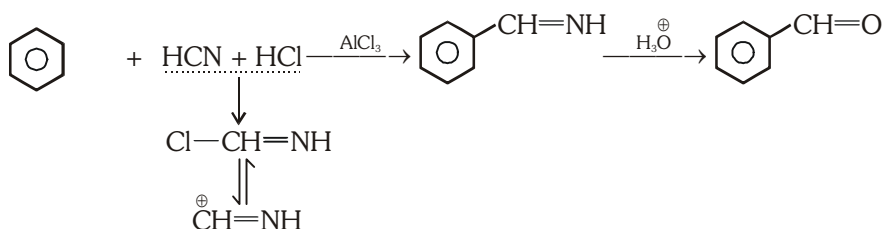




(vi) Gatterman's Koch Reaction :



(vii) Gatterman's Aldehyde synthesis :



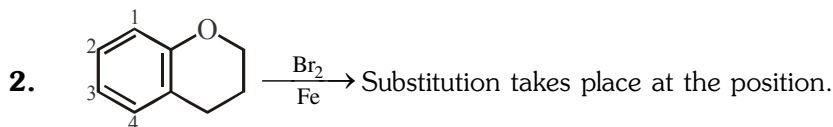
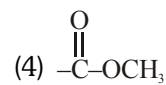
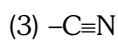
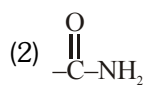
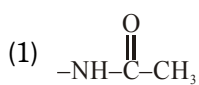
GOLDEN KEY POINTS

The important electrophiles used in the aromatic substitution are the following -

Electrophilic	Source	Name of substitution reaction
Cl^+ (Chloronium)	$\text{Cl}_2 + \text{AlCl}_3$ or FeCl_3	Chlorination
Br^+ (Bromonium)	$\text{Br}_2 + \text{AlBr}_3$ or FeBr_3	Bromination
NO_2^+ (Nitronium)	(conc. $\text{HNO}_3 + \text{H}_2\text{SO}_4$)	Nitration
SO_3 (Sulphurtrioxide)	conc. H_2SO_4 , fuming sulphuric acid	Sulphonation
R^+ (Alkyl carbonium)	$\text{RX} + \text{AlX}_3$ (X= Cl or Br) $\text{ROH} + \text{H}^+$	Friedel crafts (Alkylation)
$\text{R}-\overset{\oplus}{\text{C}}=\text{O}$ (Acyl carbonium)	$\text{RCOCl} + \text{AlCl}_3$	Friedel crafts (Acylation)

BEGINNER'S BOX-5

1. Which of the following group is ortho para director :-



(1) 1

(2) 2

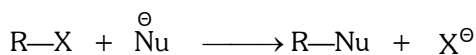
(3) 3

(4) Both (1) and (3)

(C) **Nucleophilic substitution reaction (S_N)** : Due to electronegativity difference the $\begin{array}{c} | \\ -\text{C}-\text{X} \\ | \end{array}$ bond is polarised bond. $\left(\begin{array}{c} \delta^+ \quad \delta^- \\ -\text{C}-\text{X} \\ | \end{array} \right)$

Thus the C-atom of the $\begin{array}{c} \delta^+ \quad \delta^- \\ \text{C}-\text{X} \end{array}$ bond becomes centre to attack by a nucleophile ($\text{Nu}^\ominus$).

$\text{X}^\ominus$ ion from $\text{R}-\text{X}$ molecule is substituted by a $\text{Nu}^\ominus$. i.e. S_N reaction are the most common reactions in $\text{R}-\text{X}$.



Two mechanisms are observed in S_N reaction :

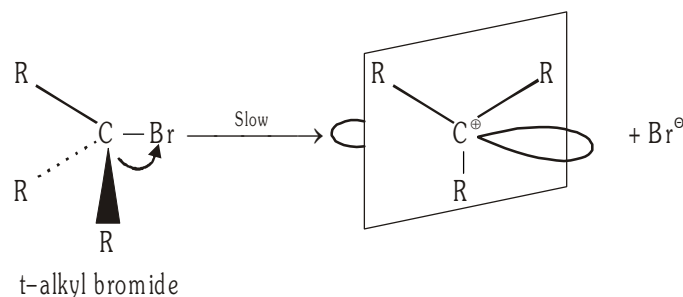
(a) S_{N1} mechanism

(b) S_{N2} mechanism

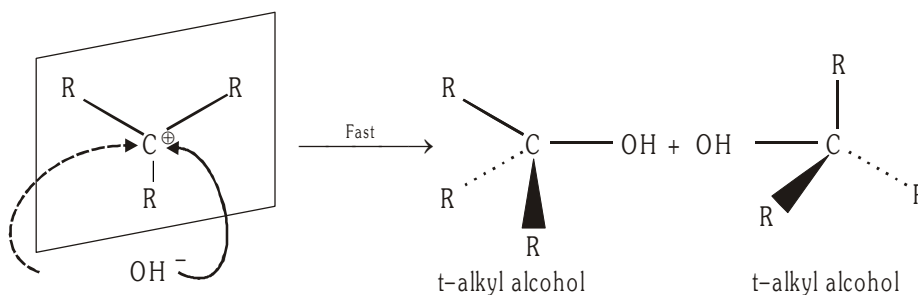
Mechanism of S_{N1} and S_{N2} :

S_{N1} Mechanism : S_{N1} stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionises to give a planar carbonium ion. The carbonium ion is planar because the central positively charged carbon is sp^2 hybridized.



Step-2 : The nucleophile can attack the planar carbonium ion from either side to give the product.



- (i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed depends upon the concentration of tertiary alkyl halide alone.

$$\therefore \text{Rate} = K[R_3C-Br]$$

It is obvious that the reaction follows first order kinetics, therefore reaction is called S_N1 .

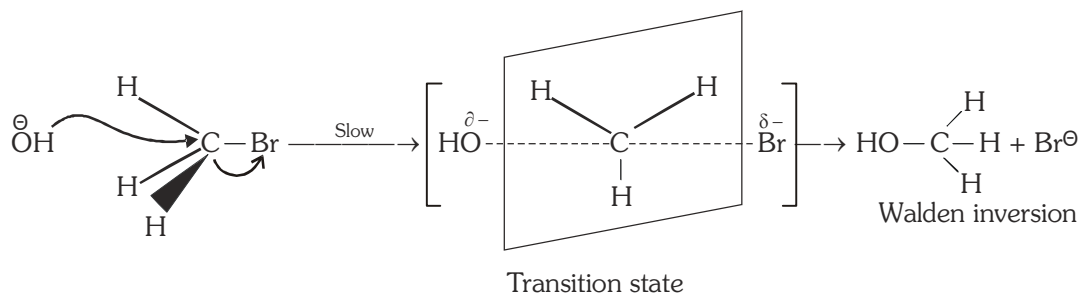
- (ii) The reactivity order for S_N1 reaction $\propto$ stability of carbocations formed by halides.

$\therefore$ reactivity order of halides (S_N1) varies as follows :

Benzyl halide > Allyl 3°halide > Allyl 2° halide > Allyl 1° halide > 3°halide > 2° halide > 1° halide > methyl halide.

- (iii) Remember that in case alkyl halide is optically active, S_N1 reactions lead to racemisation.

S_N2 mechanism : S_N2 stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, bond making and bond breaking process occur simultaneously.



- (i) Reactivity of alkyl halides in S_N2 substitution is governed by steric factors. The bulkier the group, that less reactive it will be.

- (ii) Reactivity order of alkyl halide varies as follows :

allyl halide > CH_3X > 1°halide > 2°halide > 3° halide

- (iii) The order of reactivity among 1° alkyl halides is : **$CH_3X > C_2H_5X > C_3H_7X$** etc.

Remember that in case alkyl halide is optically active, S_N1 reactions lead to Walden inversion.

- (iv) For a given alkyl group the order of reactivity is - (for S_N1 and S_N2 both) : **$RI > RBr > RCl > RF$**

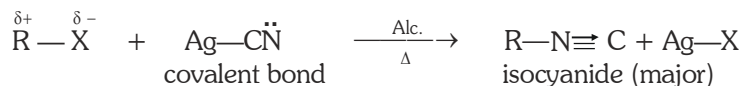
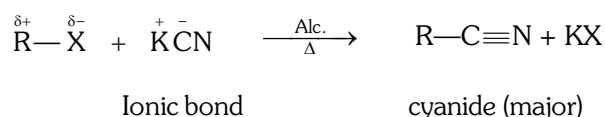
- (v) In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β -elimination it may proceed by E^1 or E^2 mechanism (analogous to S_N1 and S_N2 mechanism).

The order of elimination reaction is : **3° halides > 2° halides > 1° halides**

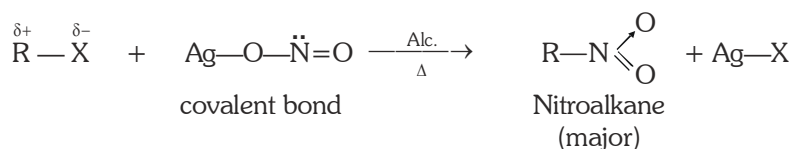
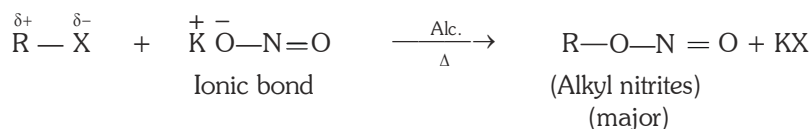
(1) nucleophilic substitution reaction (S_N) in alkyl halide :

	Replacement of	Product
(a)	$HOH(Warm) \rightarrow$	$R-OH$ (alcohol) + HX
(b)	$KOH aq. \Delta \rightarrow$	$R-OH$ (alcohol) + KX
(c)	$moist AgO_2 \rightarrow$	$R-OH$ (alcohol) + AgX
(d)	$R-X \rightarrow$	
	$KSH alc. \Delta \rightarrow$	$R-SH$ + KX Alkane thiol (Mercaptane)
(e)	$NaSR' \rightarrow$	$RSR' + NaX$ Thioether
(f)	$R' COOAg \Delta \rightarrow$	$R' COOR + AgX$ (Alkyl alkanoate) ester

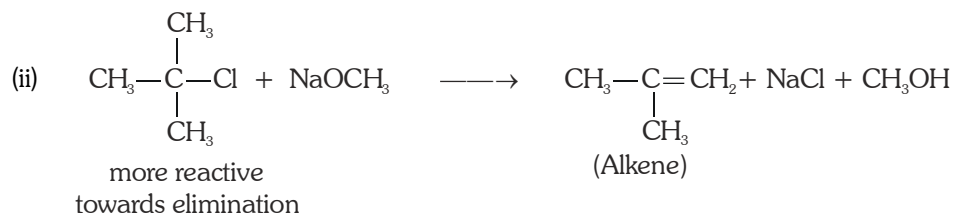
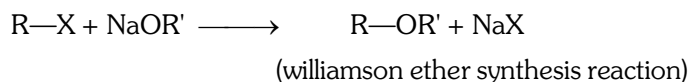
(g) Reaction with KCN and AgCN :



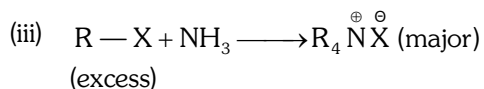
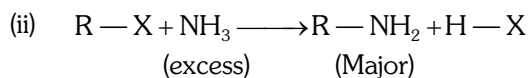
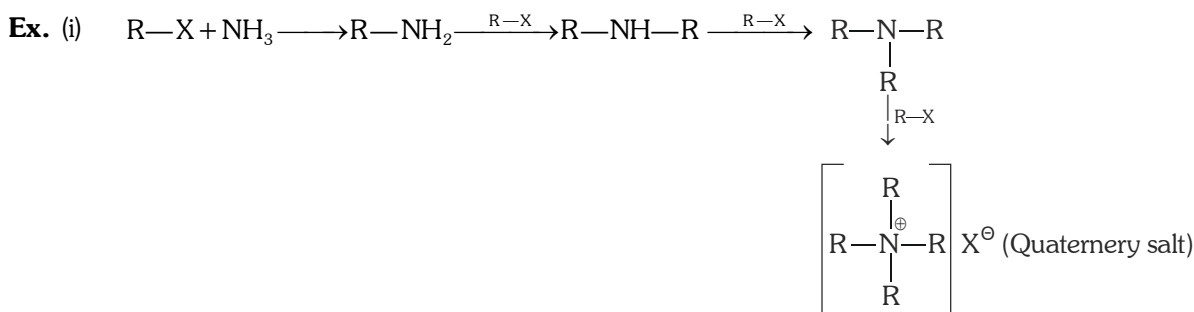
(h) Reaction with KNO₂ and AgNO₂ :



(i) Reaction with NaOR' (Sodium alkoxide) :

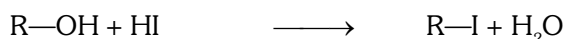


(j) Reaction with NH₃ :



Reactivity order of H—X is : **HI > HBr > HCl**

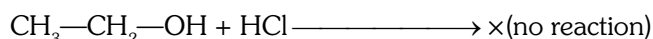
HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.



HCl and also 1° alcohol are less reactive so $ZnCl_2$ or some amount of H_2SO_4 is needed to increase the reactivity.



At normal condition :

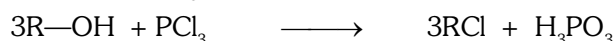
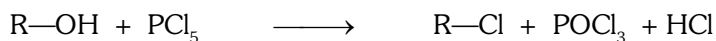


Note : $[HCl_{(conc.)} + ZnCl_{2 (anhydrous)}]$ is called as **lucas reagent**, alcohol gives turbidity with lucas reagent.

Reactivity towards lucas reagent (difference in 1°, 2° and 3° alcohol).

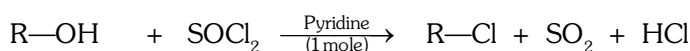
	1° alcohol	2° alcohol	3° alcohol
Time to give turbidity	in 30 min.	in 5 min.	in 2-3 second
	on heating		

(b) Reaction with phosphorus halides :



PBr_3 and PI_3 are less stable, thus for bromides and iodides, $(P + Br_2)$ Or $(P + I_2)$ mixture is used.

(c) Reaction with thionyl chloride - (Darzen's procedure) :



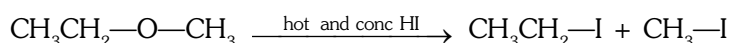
One mole One mole

NSR reaction in ether :-

Reaction with HX : Reactivity of HX **HI > HBr > HCl**

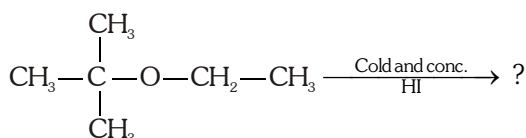
(A) Reaction with cold conc. HX : Ethers forms oxonium salt with cold and conc. HCl (less reactive)
Cold conc. HI and HBr (more reactive) break C—O bond.

(B) Reaction with conc. HI or conc. HBr :



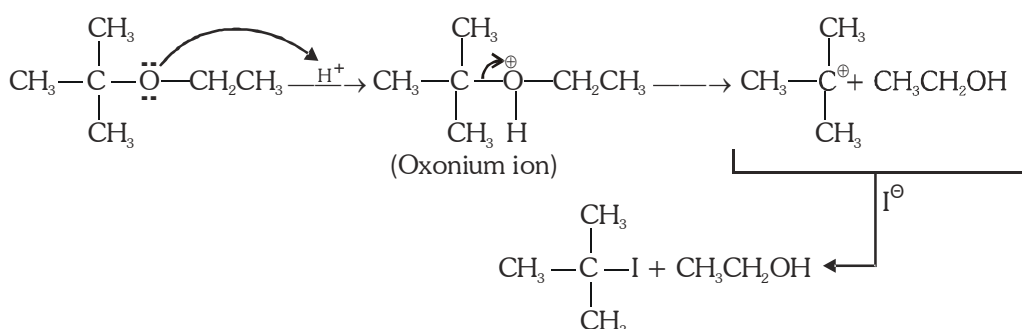
Illustrations

Illustration 3.



Solution.

Mechanism



If oxonium ion gives more stable carbocation [$\text{Ph}\overset{\oplus}{\text{C}}\text{H}_2$, $\text{CH}_2=\text{CH}-\overset{\oplus}{\text{C}}\text{H}_2$, $(\text{CH}_3)_3\overset{\oplus}{\text{C}}$] then $\text{S}_\text{N}1$ reaction occurs.

If oxonium ion gives less stable carbocation [$\text{Ph}^\oplus$, $\text{CH}_2=\overset{\oplus}{\text{C}}\text{H}$, $\text{CH}_3\overset{\oplus}{\text{C}}\text{H}_2$, $(\text{CH}_3)_2\overset{\oplus}{\text{C}}\text{H}$] then $\text{S}_\text{N}2$ reaction occurs, and $\text{X}^\ominus$ attacks at less hindered carbon

Illustration 4. $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{Ph} \xrightarrow[\text{HI}]{\text{Cold conc.}} \text{CH}_3\text{CH}_2-\text{OH} + \text{PhCH}_2-\text{I}$, write mechanism of given reaction.

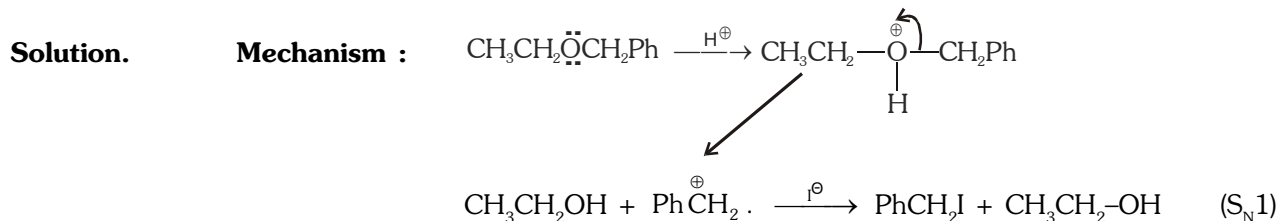
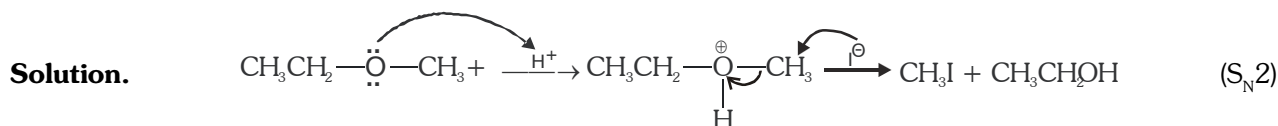
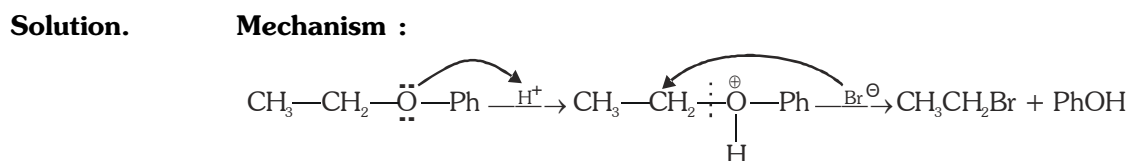


Illustration 5. $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_3 \xrightarrow[\text{conc. and cold HI}]{?}$



Oxonium ion gives less stable carbocation
 $\text{S}_\text{N}2$ reaction $\text{I}^\ominus$ attacks at less hinderd carbon.

Illustration 6. $\text{CH}_3-\text{CH}_2-\text{O}-\text{Ph} \xrightarrow[\text{HBr}]{\text{cold and conc.}} ?$



Note : If excess of HI/Δ is used then two moles of alkyl hallides are formed.

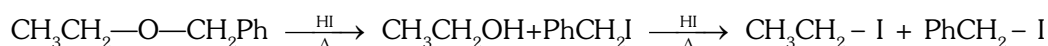
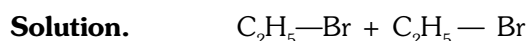
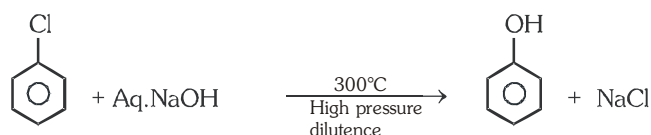


Illustration 7. $\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5 \xrightarrow[\text{hot and conc. HBr}]{?} ? + ?$



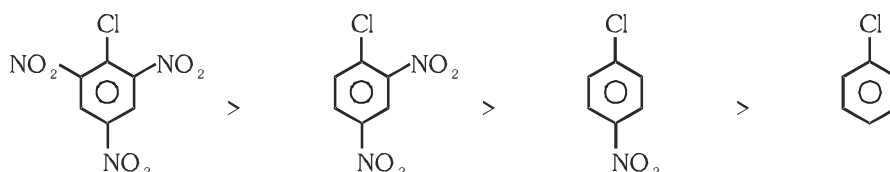
Aromatic nucleophilic substitution :

NSR reaction in halobenzene :-



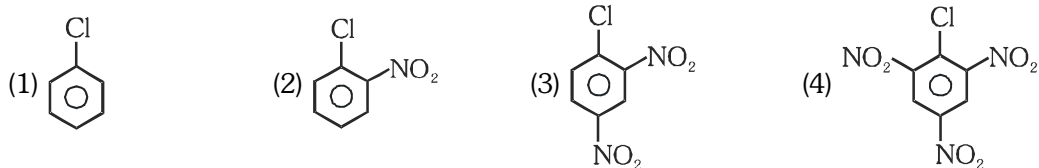
Presence of deactivating group at ortho and para position makes the nucleophilic substitution easier.

Reactivity Order : (Towards nucleophilic substitution)



Illustrations

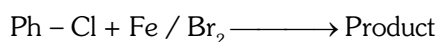
Illustration Which of the following undergoes Hydrolysis most easily :



Solution. If there is more e^- withdrawing groups then there will be more nucleophilic substitution reaction.

Ans. (4)

Illustration The product in the following reaction is :



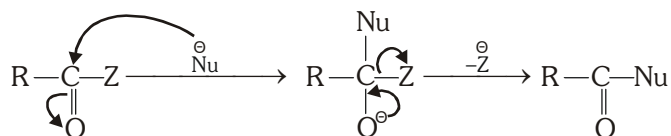
- (1) o-bromo-chloro benzene (2) p-bromo-chloro benzene
(3) (1) and (2) both (4) 2, 4, 6-tribromo chloro benzene

Solution. Since $-\text{Cl}$ group is deactivating and o/p directing group so o- and p- products are formed.

Ans. (3)

NSR in Acid derivatives :

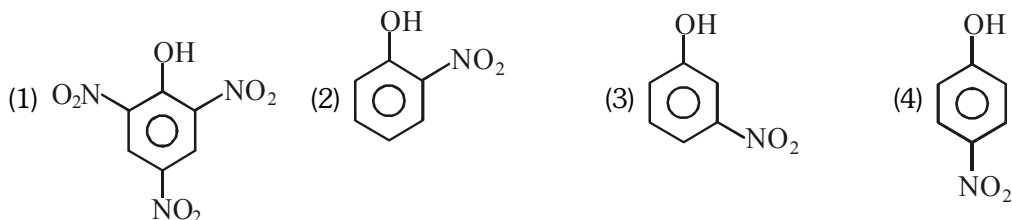
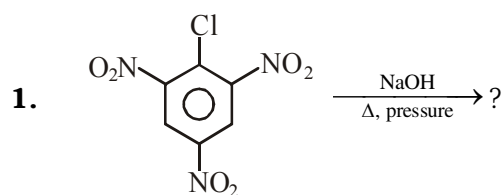
Example : Hydrolysis of acid derivatives :



Where $\text{Z} = -\text{Cl}, -\text{OR}, -\text{NH}_2, -\text{O}-\text{C}(=\text{O})-\text{R}$

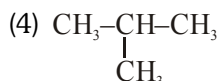
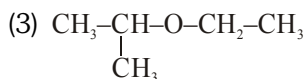
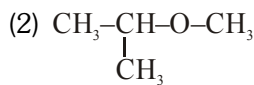
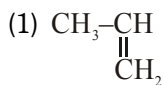
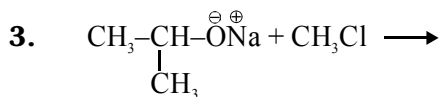
here Z is a good leaving group

BEGINNER'S BOX-7



2. Which one of the following is least reactive with water





4.3 ELIMINATION REACTIONS : These reactions involve elimination of small molecule from the substrate

Elimination

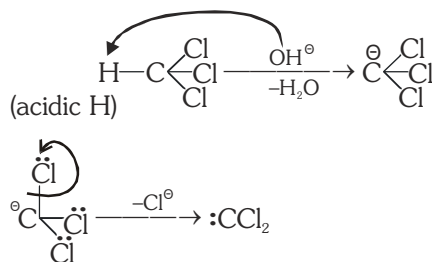
- α -elimination
or 1, 1-elimination

β-elimination
or 1, 2-elimination

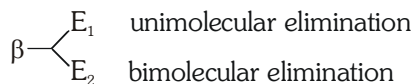
α -Elimination (1, 1-Elimination) : Removal of H and X from one C-atom



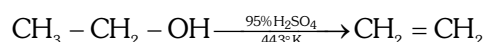
Mechanism :



α , β Elimination (β -elimination) : Removal of H and X from adjacent C-atoms

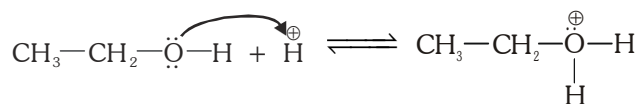


(a) Unimolecular elimination (E_1) :-



Mechanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows :

Step I : Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows:

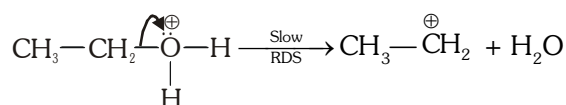


Ethanol

(From acid)

Protonated ethanol

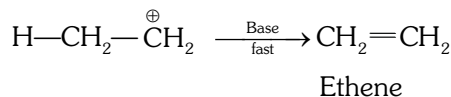
Step II : Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C – O bond becomes weak and cleaves as follows :



Ethyl carbocation

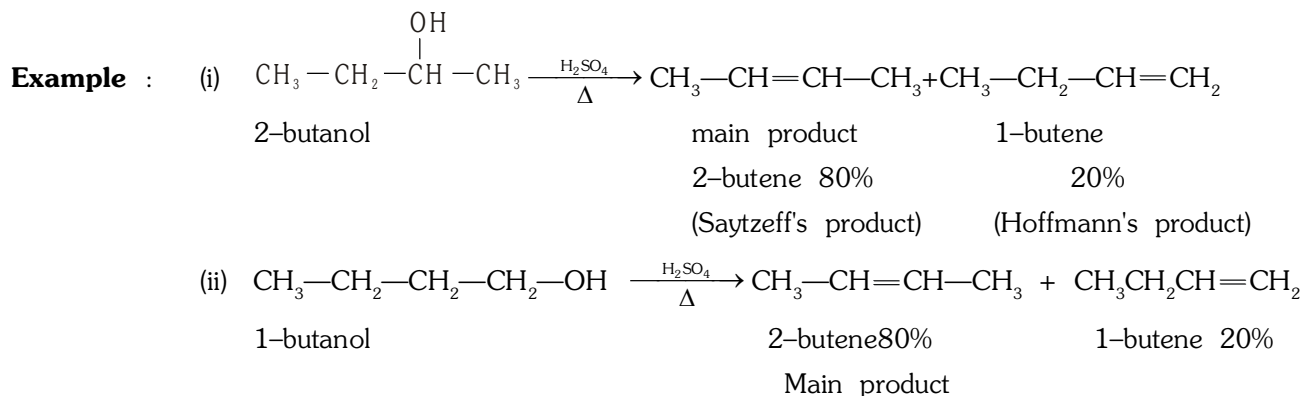
This is a slow and is regarded as **rate determining step** in **E₁** reaction.

Step III : Base removes H α (proton) from carbocation and changes it into ethene in a fast step as follows:

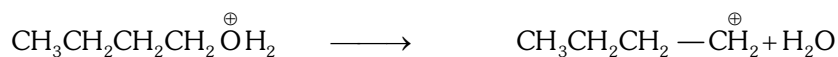
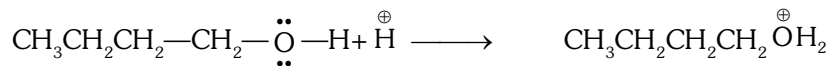


Saytzeff rule : When two possible alkenes are obtained by the elimination reaction then that alkene containing maximum number of alkyl group on double bonded C-atoms is called Saytzeff's product and formed as major product.

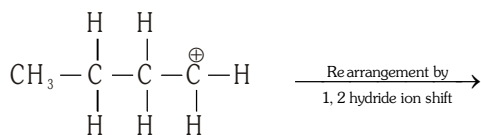
Note : The alkene having less number of alkyl groups on double bonded C-atoms is called Hofmann's product.



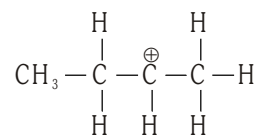
Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.



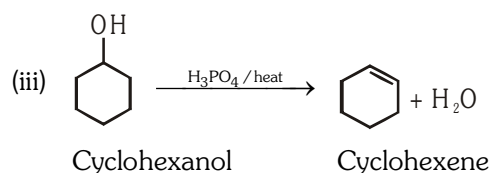
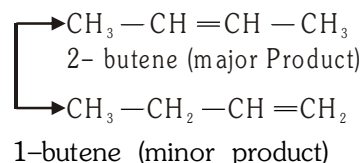
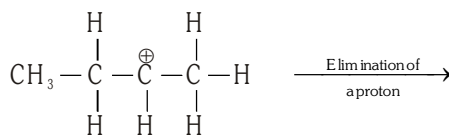
Primary Carbonium ion



1^o Carbonium



2^o Carbonium more stable



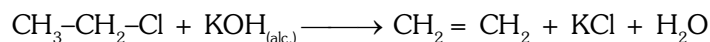
Reactivity order of acidic dehydration of alcohols is : 3^o > 2^o > 1^o R-OH

- ◆ Rate of reaction $\propto$ [substrate]
- ◆ Molecularity of reaction = 1 (So reaction is called as E₁)
- ◆ In reaction intermediate carbocation is formed, so carbocation rearrangement is possible.

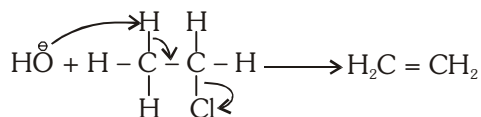
(b) Bimolecular elimination (E₂) :

Example :

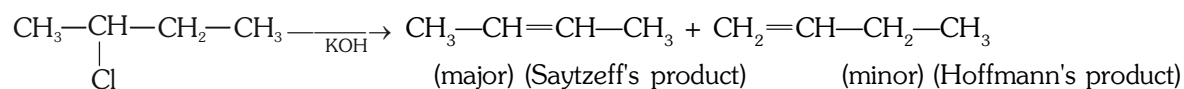
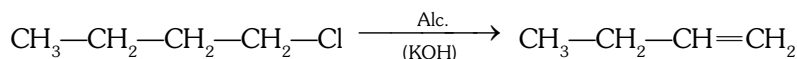
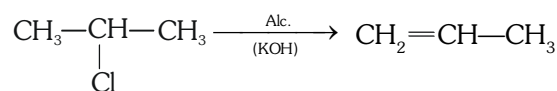
(i) Dehydrohalogenation of halides by alcoholic KOH/NaNH₂ :



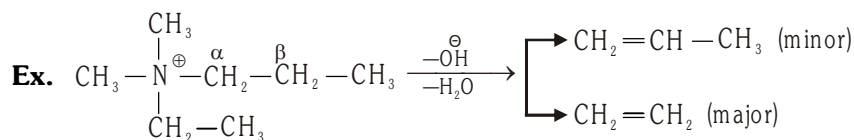
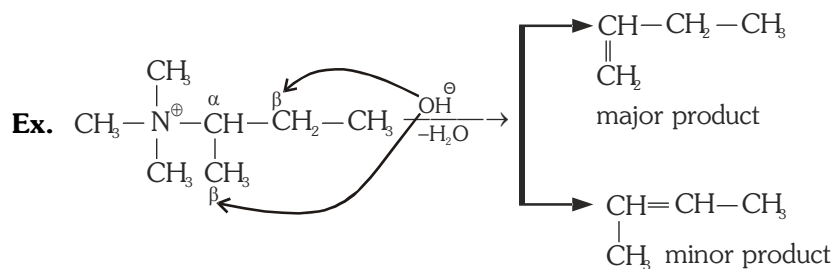
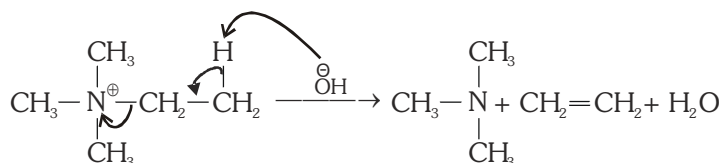
Mechanism :



- ◆ Rate of reaction $\propto$ [substrate] [base]
- ◆ Order of reaction = 2 (So reaction is E₂)
- ◆ In E₂ reaction intermediate (carbocation) is not formed. So there will be no carbocation rearrangement.



(ii) Pyrolysis of tetra alkyl ammonium ion :



Note : Hoffmann's product is formed as major product.

Competition between substitution and elimination reactions

Reactivity order of alkyl halides :

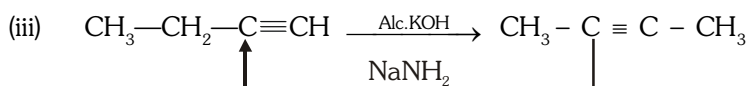
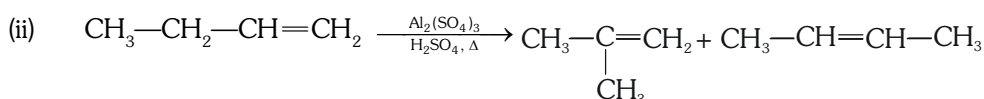
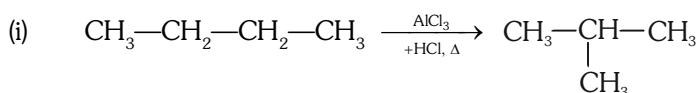
E _T - Reaction :	1° < 2° < 3°
E ₂ - Reaction :	1° < 2° < 3°
S _N 1-Reaction :	1° < 2° < 3°
S _N 2-Reaction :	1° > 2° > 3°

GOLDEN KEY POINTS

- SN^2/E^2 is favoured by high conc. of good nucleophile or strong base. ($\text{CH}_3\text{O}^\ominus$, $\text{HO}^\ominus$)
Rate of Reaction $\propto$ (Substrate) (Reagent)
- SN^1/E^1 is favoured by low conc. of poor nucleophile or weak base (CH_3OH , H_2O)
- If an alkyl halide, undergoes SN^2/SN^1 then SN^2 reaction will be favoured by high conc. of good nucleophile (negatively charged) in presence of polar aprotic solvent whereas SN^1 – reaction is favoured by low conc. of poor nucleophile (neutral) in presence of polar protic solvent.
Polar protic solvent : H_2O , CH_3OH , HCOOH
Polar aprotic solvent : DMSO , CH_3CN , $\text{C}_2\text{H}_5\text{O}-\text{C}_2\text{H}_5$, DMF

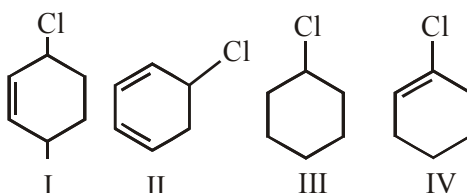
4.4 ISOMERIZATION REACTIONS : These reaction involves the interconversion of one isomer into the another isomer.

For example :



BEGINNER'S BOX-8

- Acidic dehydration of alcohol involves :-
 - E_1 elimination
 - Carbocation rearrangement if possible
 - Saytzeff's product is formed as major product
 - All
- Arrange the following in order of their reactivity toward dehydrohalogenation :-



- (1) $\text{II} > \text{I} > \text{III} > \text{IV}$

(3) $\text{IV} > \text{III} > \text{I} > \text{II}$

(2) $\text{III} > \text{II} > \text{I} > \text{IV}$

(4) $\text{I} > \text{II} > \text{III} > \text{IV}$

REACTION AT A GLANCE :

S.N.	Class of compounds	Types of reactions
(i)	Alkane	Free radical substitution
(ii)	Alkene, alkyne	Electrophilic addition
(iii)	Alkyl halide	Nucleophilic substitution
(iv)	Aldehyde, ketone	Nucleophilic addition
(v)	Acid and their derivatives	Nucleophilic substitution
(vi)	Aromatic compounds	Electrophilic substitution

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	
	Ans.	1	1	3	

BEGINNER'S BOX-2	Que.	1	2	
	Ans.	3	1	

BEGINNER'S BOX-3	Que.	1	2	3	4
	Ans.	1	2	2	2

BEGINNER'S BOX-4	Que.	1	2	3	4
	Ans.	3	3	2	4

BEGINNER'S BOX-5	Que.	1	2	
	Ans.	1	4	

BEGINNER'S BOX-6	Que.	1	2	
	Ans.	2	2	

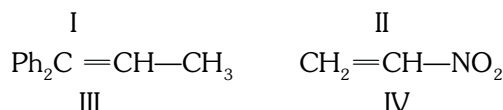
BEGINNER'S BOX-7	Que.	1	2	3	
	Ans.	1	2	2	

BEGINNER'S BOX-8	Que.	1	2	
	Ans.	4	1	

EXERCISE-I (Conceptual Questions)

ELECTROPHILIC ADDITION REACTION

1. Correct reactivity order for EAR of following compounds is



- (1) IV > I > II > III (2) III > II > I > IV
(3) II > III > I > IV (4) II > III > IV > I
2. The intermediate during the addition of HCl to propene in the presence of peroxide is
- (1) $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{Cl}$ (2) $\text{CH}_3\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$
(3) $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{C}}\text{H}_2$ (4) $\text{CH}_3\dot{\text{C}}\text{HCH}_3$
3. Hydroboration of isobutylene followed by oxidative alkaline hydrolysis gives
- (1) 1-butanol (2) 2-butanol
(3) Isobutyl alcohol (4) $(\text{CH}_3)_3\text{C}-\text{OH}$

4. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH} + \text{Br}_2 \longrightarrow \text{A}$
the number of chiral carbons in 'A' are
- (1) 1 (2) 2
(3) 3 (4) 4

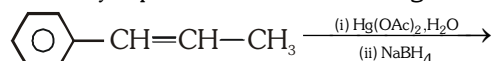
5. $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{dil}/\text{H}_2\text{SO}_4} \text{A}$
 $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{B}_2\text{H}_6} \xrightarrow[\text{-OH}]{\text{H}_2\text{O}_2} \text{B}$

Wrong statement about the product is

- (1) A and B have the same functional group
(2) A and B are position isomers.
(3) A and B show chain isomerism
(4) Mixed ether is the isomer of both A and B
6. Which of the following alkene is most reactive for hydration
- (1) ethene
(2) propene
(3) 1-butene
(4) 2-methyl propene

Build Up Your Understanding

7. The major product of the following reaction is



- (1) $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
(2) $\text{C}_6\text{H}_5-\text{CH}_2-\underset{\text{OH}}{\underset{|}{\text{CH}}}-\text{CH}_3$
(3) $\text{C}_6\text{H}_5-\underset{\text{OH}}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_3$
(4) $\text{HO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{CH}_3$

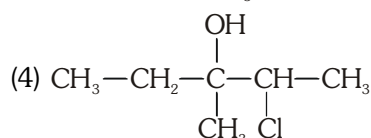
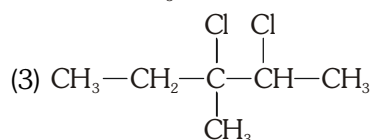
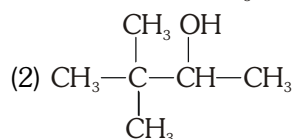
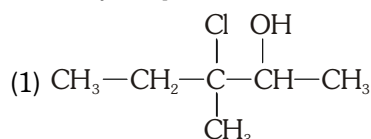
8. $\text{Cyclohexene}-\text{CH}_3 \xrightarrow{\text{A}} \text{Cyclohexane}-\underset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{OH}$; Reagent 'A' is

- (1) $\text{BH}_3/\text{H}_2\text{O}_2/\text{OH}^-$
(2) $\text{H}_2\text{O}/\text{H}^+$
(3) $\text{Hg}(\text{OCOCH}_3)_2/\text{NaBH}_4$
(4) $\text{Cl}_2/\text{aq. NaOH}$

9. Which of the following alkenes on hydration gives a tertiary alcohol

- (1) 2-Butene (2) Isobutylene
(3) Ethene (4) α -Butylene

10. The predominant product formed when 3-methyl-2-pentene reacts with HOCl is



11. Propene on addition with HI, gives

- (1) $\text{CH}_3-\text{CHI}-\text{CH}_3$
(2) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{I}$
(3) $\text{CH}_3-\text{CHI}-\text{CH}_2\text{I}$
(4) None of the above

12. What is the main product of this reaction?



- (1) $\text{CH}_3 - \overset{\text{Cl}}{\underset{|}{\text{C}}} = \text{CH}_2$
 (2) $\text{CH}_3 - \underset{\text{Cl}}{\underset{|}{\text{CH}}} - \underset{\text{Cl}}{\underset{|}{\text{CH}_2}}$
 (3) $\text{CH}_3 - \text{CH}_2 - \text{CH} \begin{matrix} \text{Cl} \\ \diagup \\ \diagdown \\ \text{Cl} \end{matrix}$
 (4) $\text{CH}_3 - \overset{\text{Cl}}{\underset{\text{Cl}}{\underset{|}{\text{C}}}} - \text{CH}_3$

13. Propan-1-ol can be prepared from propene by

- (1) $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$
 (2) $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}_2$ followed by NaBH_4 .
 (3) B_2H_6 followed by H_2O_2 .
 (4) $\text{CH}_3\text{CO}_2\text{H}/\text{H}_2\text{SO}_4$

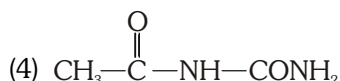
14. 3-Phenyl propene on reaction with HBr gives (as a major product)

- (1) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$
 (2) $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$
 (3) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
 (4) $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}=\text{CH}_2$

NUCLEOPHILIC ADDITION REACTION

15. Acetaldehyde reacts with semicarbazide, product will be :

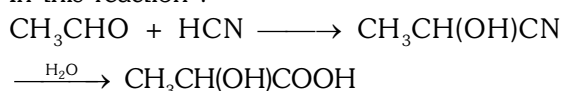
- (1) $\text{CH}_3\text{CH}=\text{NNH}-\text{CO}-\text{NH}_2$
 (2) $\text{CH}_3\text{CH}=\text{NCONHNH}_2$
 (3) $\text{CH}_3\text{CH}=\text{NHNH}_2$



16. Cyanohydrin of the following compound on hydrolysis gives compound that can show optical isomerism :

- (1) HCHO (2) CH_3CHO
 (3) CH_3COCH_3 (4) All the above

17. In this reaction :



an asymmetric centre is generated. The acid obtained would be :-

- (1) D-isomer
 (2) L-isomer
 (3) 50% D + 50% L-isomer
 (4) 20% D + 80% L-isomer

18. When two mole of alcohol reacts with 1 mole of ketone, it gives :-

- (1) Hemiacetal (2) Acetal
 (3) Hemiketal (4) Ketal

19. When acetone reacts with Grignard reagent followed by hydrolysis, it gives :

- (1) 1° -alcohol (2) 2° -alcohol
 (3) 3° -alcohol (4) Methyl alcohol

FREE RADICAL ADDITION REACTION

20. Reaction of HBr with propene in the presence of peroxide gives

- (1) 3-bromo propane (2) Allyl bromide
 (3) n-propyl bromide (4) Isopropyl bromide

21. Isobutene $\xrightarrow[\text{H}_2\text{O}_2]{\text{HBr}}$ "product". The product is

- (1) Isobutyl bromide (2) Tert. butyl bromide
 (3) Tert. butyl alcohol (4) isobutyl alcohol

FREE RADICAL SUBSTITUTION REACTION

22. Alkane reacts with which of the following halogens in dark

- (1) F_2 (2) Cl_2 (3) I_2 (4) Br_2

23. The nitrating agent for the nitration of alkanes is:

- (1) Conc. HNO_3
 (2) Mixture of conc. HNO_3 and conc. H_2SO_4
 (3) Acetyl nitrate
 (4) HNO_3 vapours at high temperature

24. The chain propagating step is fastest in the reaction of an alkane with

- (1) Fluorine free radical (2) Chlorine free radical
 (3) Iodine free radical (4) Bromine free radical

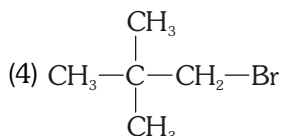
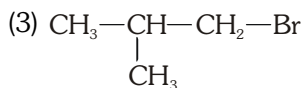
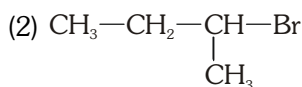
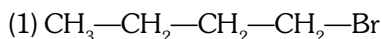
25. In the nitration of propane, the product obtained in maximum yield is

- (1) 1-nitropropane (2) 2-nitropropane
 (3) Nitroethane (4) Nitromethane

26. Only two isomeric monochloro derivatives are possible for (exclude stereo isomers)

- (1) n-butane
 (2) 2, 4-dimethyl pentane
 (3) benzene
 (4) 2-methyl butane

27. What is the chief product obtained when n-butane is treated with bromine in the presence of light at 130°C ?

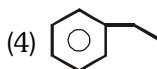
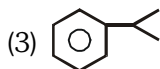
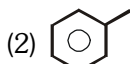
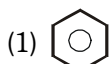


ELECTROPHILIC SUBSTITUTION REACTION

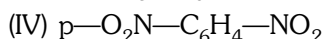
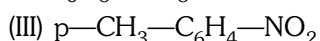
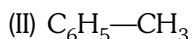
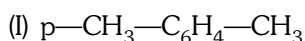
28. The strongest deactivating effect on aromatic ring is

- (1) $\text{—CH}_2\text{Cl}$ (2) —OCH_3
(3) —CH_3 (4) —CCl_3

29. Which of the following is maximum reactive towards E.S.R. :-



30. Correct order of reactivity of following compound with an electrophile :-



- (1) I > II > III > IV (2) II > I > IV > III
(3) III > II > I > IV (4) IV > III > II > I

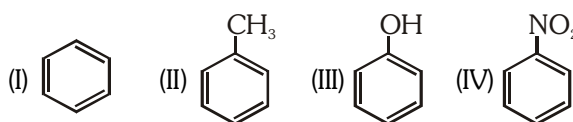
31. Toluene is more reactive than benzene towards electrophilic reagents due to :-

- (1) Inductive effect only
(2) Hyperconjugative effect only
(3) Both inductive as well as hyperconjugative effects
(4) Strong mesomeric effect

32. Nitration of benzene is

- (1) nucleophilic substitution
(2) nucleophilic addition
(3) electrophilic substitution
(4) electrophilic addition

33. Consider the following compounds :



Correct order of their reactivity in electrophilic substitution reactions would be :-

- (1) I > II > III > IV (2) IV > III > II > I
(3) III > II > I > IV (4) III > IV > I > II

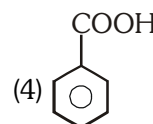
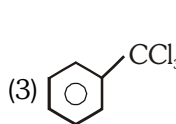
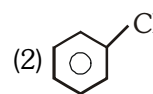
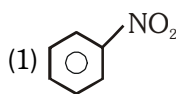
34. The active species in the nitration of benzene is

- (1) NO_2^+ (2) HNO_3
(3) NO_3^- (4) NO_2^-

35. The function of anhydrous AlCl_3 in the Friedel craft's reaction

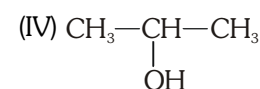
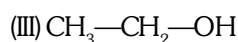
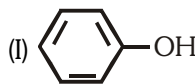
- (1) To absorb water
(2) To absorb HCl
(3) To produce electrophile
(4) To produce Nucleophile

36. In which of the following compound the electrophile attack on o- and p- positions :



NUCLEOPHILIC SUBSTITUTION REACTION

37. The correct reactivity order of alcohols towards H-X will be



- (1) II > I > III > IV (2) IV > III > II > I
(3) II > IV > I > III (4) II > IV > III > I

38. Which of the following product will be obtained when neopentyl alcohol is treated with conc. HCl in presence of ZnCl_2 .

- (1) t-butyl chloride (2) isobutylene
(3) t-pentyl chloride (4) Neo pentyl chloride

- 39.** In S_N1 the first step involves the formation of
 (1) free radical (2) carbanion
 (3) carbocation (4) final product
- 40.** To form alkane isonitrile, alkyl halide is reacted with:
 (1) KCN (2) AgCN
 (3) NaCN (4) NH_4CN
- 41.** The most reactive towards S_N1 is
 (1) $PhCH_2Cl$ (2) $PhCl$
 (3) $PhCHCl(CH_3)$ (4) $p-NO_2C_6H_4CH_2Cl$
- 42.** Alkyl fluorides are synthesised by
 (1) Finkelstein reaction (2) Swart reaction
 (3) Kolbe reaction (4) Wurtz reaction
- 43.** The products of reaction of alcoholic silver nitrite with ethyl bromide are
 (1) Ethane (2) Ethene
 (3) Ethyl alcohol (4) Nitro ethane
- 44.** For the reaction,
 $C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X$, the order of reactivity is
 (1) $HI > HCl > HBr$
 (2) $HI > HBr > HCl$
 (3) $HCl > HBr > HI$
 (4) $HBr > HI > HCl$
- 45.** The reaction, $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ obeys the mechanism
 (1) S_N1 (2) S_N2
 (3) E^1 (4) E^2
- 46.** Butanenitrile may be prepared by heating
 (1) Propyl alcohol with KCN
 (2) Butyl alcohol with KCN
 (3) Butyl chloride with KCN
 (4) Propyl chloride with KCN
- 47.** The given reaction is an example of
 $C_2H_5Br + KCN(aq.) \longrightarrow C_2H_5CN + KBr$
 (1) Elimination
 (2) Nucleophilic substitution
 (3) Electrophilic substitution
 (4) Redox change
- 48.** Most readily hydrolysed halide is
 (1) C_6H_5Cl (2) $(C_6H_5)_2CHCl$
 (3) $C_6H_5CH_2Cl$ (4) $(C_6H_5)_3CCl$
- 49.** An alkyl halide may be converted in to an alcohol by
 (1) Addition (2) Substitution
 (3) Dehydrohalogenation (4) Elimination
- 50.** Compound is most reactive towards NaOH in
 (1) CH_3Cl (2) $CH_2=CHCl$
 (3) C_6H_5Cl (4) $C_6H_5CH_2Cl$
- 51.** Most stable carbocation formed from $(CH_3)_3C-Br$, $(C_6H_5)_3CBr$, $(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be
 (1) $C_6H_5\overset{\oplus}{C}H_2$ (2) $(CH_3)_3\overset{\oplus}{C}$
 (3) $(C_6H_5)_3\overset{\oplus}{C}$ (4) $(C_6H_5)_2\overset{\oplus}{C}H$
- 52.** S_N1 reaction on optically active substrates mainly gives
 (1) Retention in configuration
 (2) Inversion in configuration
 (3) Racemise product
 (4) No product
- 53.** The hydrolysis of alkyl halides by aqueous NaOH is best termed as
 (1) electrophilic substitution reaction
 (2) electrophilic addition reaction
 (3) nucleophilic addition reaction
 (4) nucleophilic substitution reaction
- 54.** Reaction of sodium ethoxide and ethyl iodide will give :-
 (1) Ether (2) Ethyl alcohol
 (3) Acetaldehyde (4) Acetic acid
- 55.** The least reactive chlorine is present in
 (1) Methyl chloride (2) Allyl chloride
 (3) Ethyl chloride (4) Vinyl chloride
- 56.** Arrange the following compounds in the increasing order of their S_N^2 reactivity?
- $\begin{array}{c} CH_3 \\ | \\ CH_3-C-X \\ | \\ CH_3 \end{array}$, $\begin{array}{c} CH_3-CH-X \\ | \\ CH_3 \end{array}$, CH_3-CH_2-X , CH_3-X
 (a) (b) (c) (d)
- (1) (a) < (b) < (c) < (d)
 (2) (a) < (c) < (d) < (b)
 (3) (d) < (c) < (b) < (a)
 (4) (b) < (d) < (c) < (a)

57. Which alcohol produces turbidity with Lucas reagent most slowly

- (1) 2-Butanol (2) t-Butyl alcohol
(3) Isobutyl alcohol (4) Diphenylcarbinol

58. The preparation of ethers from alcohols by using sulphuric acid is called :-

- (1) Williamson's ether Synthesis
(2) Williamson's continuous etherification process
(3) Ziesel's method
(4) Zerewitinoff method

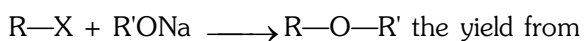
59. The reaction of ethyl iodide with sodium ethoxide is

- (1) An electrophilic substitution reaction
(2) A nucleophilic addition reaction
(3) A nucleophilic substitution reaction
(4) A free radical substitution reaction

60. The Williamson synthesis involves :-

- (1) A nucleophilic addition
(2) An electrophilic substitution
(3) SN^2 displacement
(4) SN^1 displacement

61. In the Williamson synthesis of ethers given by the general equation -



$R-X$ follows the sequence :-

- (1) $CH_3X > 1^\circ > 2^\circ > 3^\circ$
(2) $CH_3X < 1^\circ < 2^\circ < 3^\circ$
(3) $CH_3X < 1^\circ < 2^\circ > 3^\circ$
(4) $CH_3X > 1^\circ < 2^\circ < 3^\circ$

62. With conc. HBr ethyl phenyl ether yields :-

- (1) Phenol and ethyl bromide.
(2) Bromobenzene and ethanol
(3) Phenol and ethane
(4) Bromobenzene and ethane

63. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism :-

- (1) secondary alcohol by $SN1$
(2) tertiary alcohol by $SN1$
(3) secondary alcohol by $SN2$
(4) tertiary alcohol by $SN2$

ELIMINATION REACTION

64. The reactivity of alkyl halides in E^2 elimination reactions follows the order

- (1) $R-I < R-Br < R-Cl < R-F$
(2) $R-F < R-Cl < R-Br < R-I$
(3) $R-I > R-Cl > R-Br < R-F$
(4) $R-I < R-Br < R-F < R-Cl$

65. The unimolecular elimination involves formation of

- (1) A free radical (2) A carbanion
(3) A carbocation (4) A biradical

66. Which of the following alkyl bromides will eliminate HBr fastest

- (1) Ethyl bromide (2) Propyl bromide
(3) Isopropyl bromide (4) t-Butyl bromide

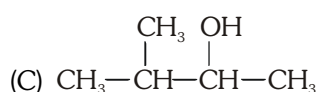
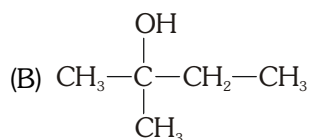
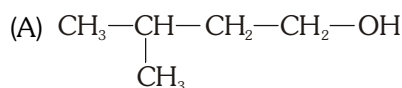
67. 1-phenyl-2-chloropropane on treating with alc. KOH gives mainly :

- (1) 1-phenylpropene
(2) 2-phenylpropene
(3) 1-phenylpropan-2-ol
(4) 1-phenylpropan-1-ol

68. Which of the following alkyl halides gives a mixture of alkenes on dehydrohalogenation

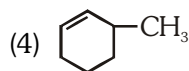
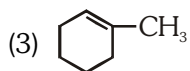
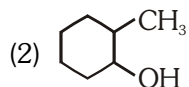
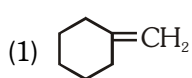
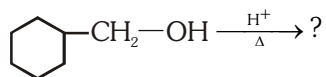
- (1) n-Propyl halide
(2) Isopropyl halide
(3) s-Butyl bromide
(4) t-Butyl bromide

69. Arrange the following alkanols A, B and C in order of their reactivity towards acid catalysed dehydration:-



- (1) $A > B > C$ (2) $B > A > C$
(3) $B > C > A$ (4) $C > B > A$

70. The major product in the following reaction is



71. The major product obtained from the heating of 3,3-dimethyl-1-butanol with H_2SO_4 is

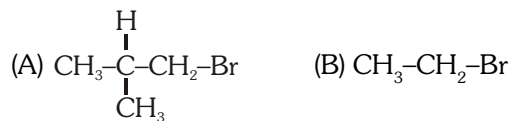
(1) 3,3-dimethyl-1-butene

(2) 2,3-dimethyl-2-butene

(3) 2,3-dimethyl-1-butene

(4) cis and trans isomers of product (2)

72. Arrange the following alkyl halides in decreasing order of the rate of elimination reaction with alcoholic KOH.



(1) $\text{A} > \text{B} > \text{C}$

(2) $\text{C} > \text{B} > \text{A}$

(3) $\text{B} > \text{C} > \text{A}$

(4) $\text{A} > \text{C} > \text{B}$

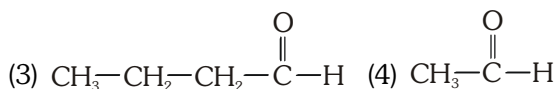
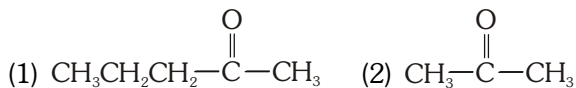
EXERCISE-I (Conceptual Questions)

ANSWER KEY

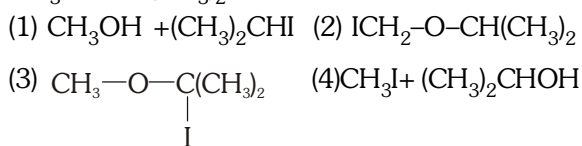
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Ans.	2	2	3	2	3	4	3	1	2	4	1	4	3	2	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	3	4	3	3	1	1	4	1	2	1	2	4	2	1
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	3	3	1	3	2	4	3	3	2	3	2	4	2	2
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	2	4	2	4	3	3	4	1	4	1	3	2	3	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72			
Ans.	1	1	2	2	3	4	1	3	3	3	2	4			

EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2006**

1. Nucleophilic addition reaction will be most favoured in :



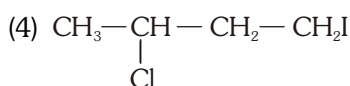
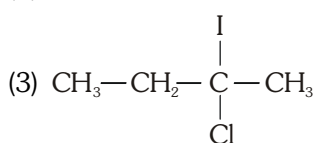
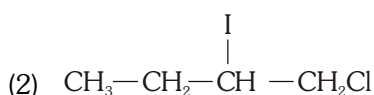
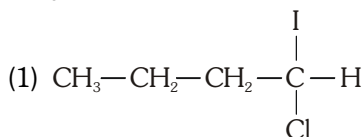
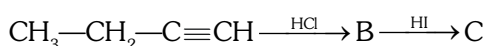
2. The major organic products of reaction are $\text{CH}_3\text{O}-\text{CH}(\text{CH}_3)_2 + \text{HI} \longrightarrow$

**AIIMS 2006**

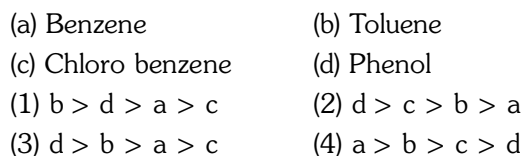
3. The correct increasing order of the reactivity of halides for $\text{S}_{\text{N}}1$ reaction is -
 (1) $\text{CH}_3-\text{CH}_2-\text{X} < (\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_2=\text{CH}-\text{CH}_2-\text{X} < \text{PhCH}_2-\text{X}$
 (2) $(\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_3-\text{CH}_2-\text{X} < \text{CH}_2=\text{CH}-\text{CH}_2\text{X} < \text{PhCH}_2-\text{X}$
 (3) $\text{PhCH}_2-\text{X} < (\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_3-\text{CH}_2-\text{X} < \text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$
 (4) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X} < \text{Ph}-\text{CH}_2-\text{X} < (\text{CH}_3)_2\text{CH}-\text{X} < \text{CH}_3-\text{CH}_2-\text{X}$

AIPMT 2007

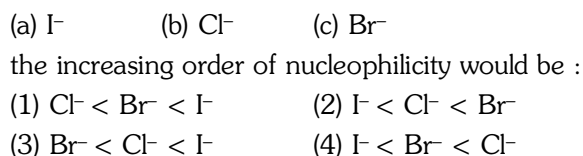
4. Predict the product 'C' obtained in the following reaction of 1-butyne :



5. The order of decreasing reactivity towards electrophilic reagent for the following :

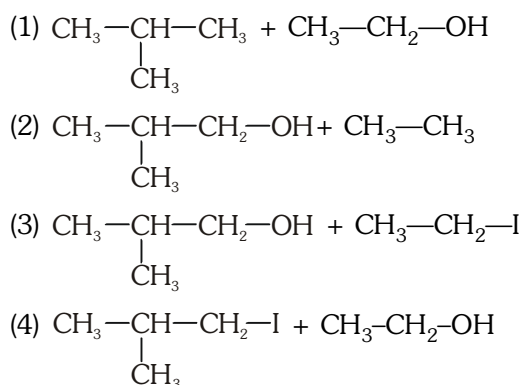


6. For the following :

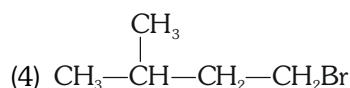
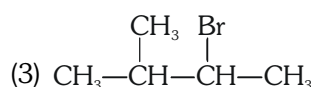
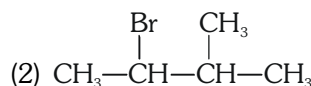
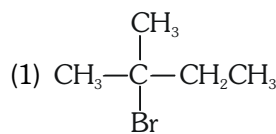


7. In the reaction : $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3 + \text{HI} \longrightarrow \dots\dots\dots$

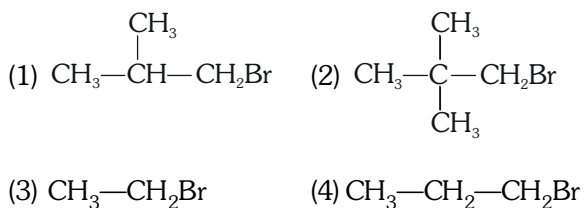
which of following compounds will be formed :

**AIPMT 2008**

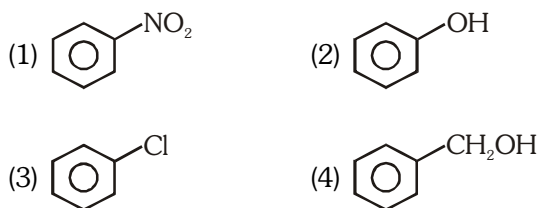
8. $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \text{A}$
 A (Predominantly) is :



9. In a S_N2 substitution reaction of the type $R-Br + Cl^- \xrightarrow{DMF} R-Cl + Br^-$, which one of the following has the highest relative rate ?



10. Which one of the following is most reactive towards electrophilic attack ?



11. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of :-
- (1) Acid anhydride > Amide > Ester > Acyl chloride
 (2) Acyl chloride > Ester > Acid anhydride > Amide
 (3) Acyl chloride > Acid anhydride > Ester > Amide
 (4) Ester > Acyl chloride > Amide > Acid anhydride

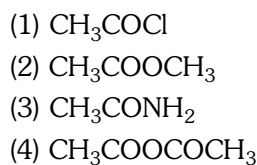
AIPMT 2009

12. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form :-
- (1) Xylene (2) Toluene
 (3) Chlorobenzene (4) Benzylchloride
13. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 . In the mixture, nitric acid acts as a/an :-
- (1) Catalyst (2) Reducing agent
 (3) Acid (4) Base
14. Which of the following reactions is an example of nucleophilic substitution reaction ?
- (1) $RX + Mg \longrightarrow RMgX$
 (2) $RX + KOH \longrightarrow ROH + KX$
 (3) $2RX + 2Na \longrightarrow R-R + 2NaX$
 (4) $RX + H_2 \longrightarrow RH + HX$

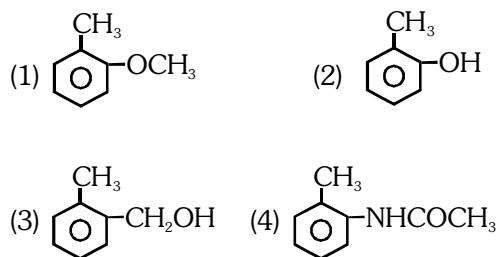
AIPMT 2010

15. Which one is most reactive towards S_N1 reaction?
- (1) $C_6H_5CH_2Br$ (2) $C_6H_5CH(C_6H_5)Br$
 (3) $C_6H_5CH(CH_3)Br$ (4) $C_6H_5C(CH_3)(C_6H_5)Br$

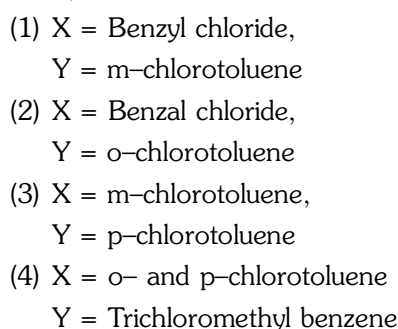
16. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is :-



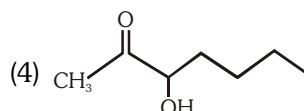
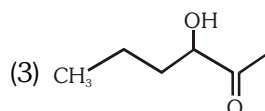
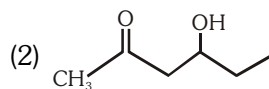
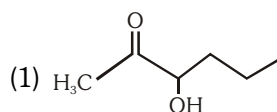
17. Which one is most reactive towards electrophilic reagent ?



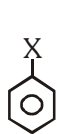
18. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are :-



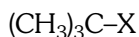
19. Which one of the following compounds will be most readily dehydrated :-



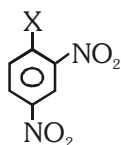
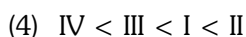
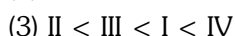
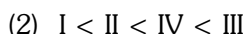
20. The correct order of increasing reactivity of C-X bond towards nucleophile in the following compounds is :-



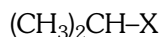
(I)



(III)



(II)



(IV)

AIIMS 2010

21. 2-Butene $\xrightarrow{\text{HBr}}$

Major products of above reaction will be :-

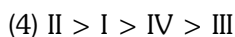
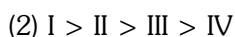
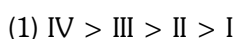
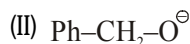
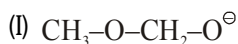
(1) 1

(2) 2

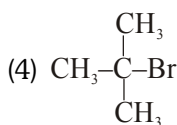
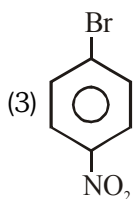
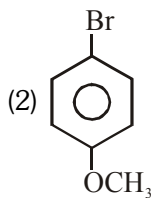
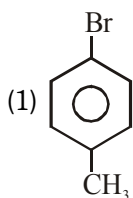
(3) 4

(4) 3

22. Arrange the following in correct order of nucleophilicity :-

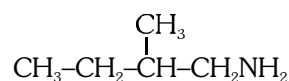
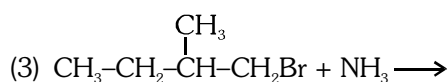
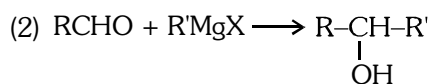
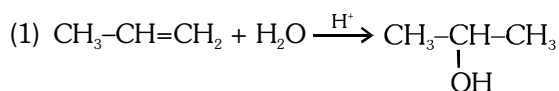


23. Which of the following is maximum reactive towards $\text{S}_\text{N}1$ reaction :-



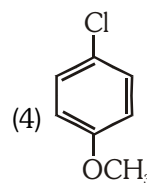
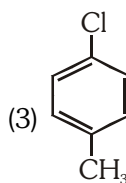
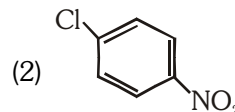
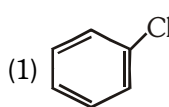
AIPMT Pre-2011

24. Which one is a nucleophilic substitution reaction among the following ?

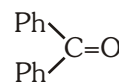
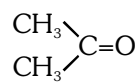
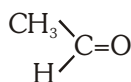


AIPMT Mains-2011

25. Which of the following compounds undergoes nucleophilic substitution reaction most easily ?



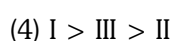
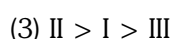
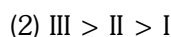
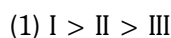
26. The order of reactivity of phenyl magnesium bromide (PhMgBr) with the following compounds :-



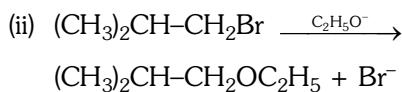
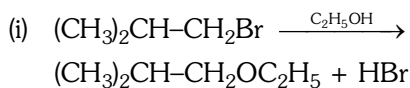
(I)

(II)

(III)



27. Consider the reaction :

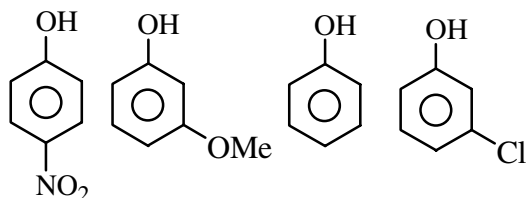


The mechanisms of reaction (i) and (ii) are respectively :-

- (1) S_{N^2} and S_{N^1} (2) S_{N^1} and S_{N^2}
(3) S_{N^1} and S_{N^1} (4) S_{N^2} and S_{N^2}

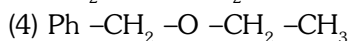
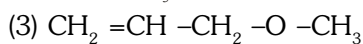
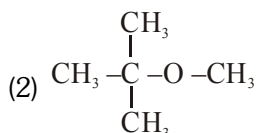
AIIMS 2011

28. The correct increasing order of reactivity for following molecules towards electrophilic aromatic substitution.



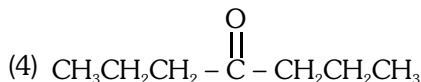
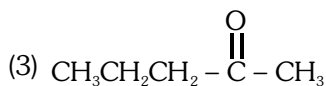
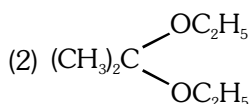
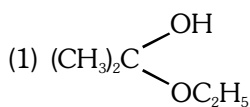
- | | | | |
|-------------------------|------|-------------------------|------|
| (I) | (II) | (III) | (IV) |
| (1) $I < IV < II < III$ | | (2) $I < IV < III < II$ | |
| (3) $I < III < II < IV$ | | (4) $I < III < IV < II$ | |

29. S_N2 reaction readily occurs in:—

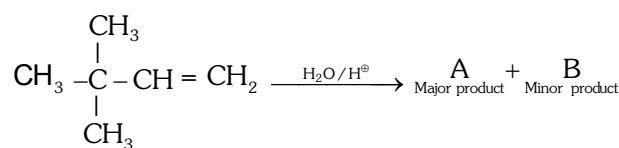


AIPMT Pre.-2012

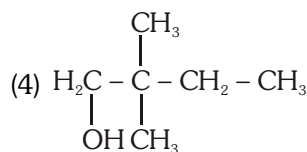
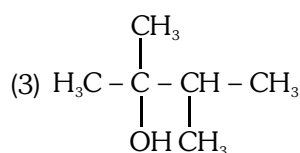
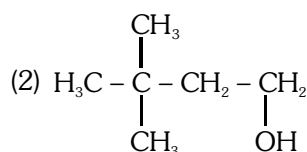
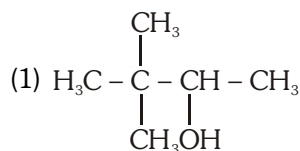
30. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is:



31. In the following reaction:



The major product is :-



32. Among the following compounds the one that is most reactive towards electrophilic nitration is:

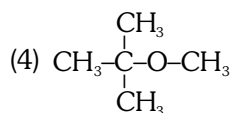
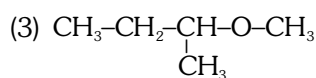
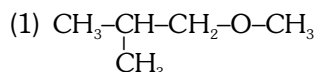
- (1) Toluene (2) Benzene
(3) Benzoic Acid (4) Nitrobenzene

NEET-UG 2013

33. Which of the following compounds will not undergo Friedal-Craft's reaction easily :-

- (1) Toluene (2) Cumene
(3) Xylene (4) Nitrobenzene

34. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI ?



AIIMS 2013

- (I) $\text{C}_6\text{H}_5\text{COCH}_3$ (II) $\text{CH}_3\text{COC}_2\text{H}_5$
 (III) $\text{C}_6\text{H}_5\text{CHO}$ (IV) ClCH_2CHO
 (1) $\text{IV} > \text{III} > \text{II} > \text{I}$ (2) $\text{IV} > \text{II} > \text{III} > \text{I}$
 (3) $\text{I} > \text{II} > \text{III} > \text{IV}$ (4) $\text{III} > \text{IV} > \text{II} > \text{I}$

- (1) Racemic-2, 3-dibromobutane
- (2) Meso-2, 3-dibromobutane
- (3) d-2, 3-dibromobutane
- (4) *l*-2, 3-dibromobutane

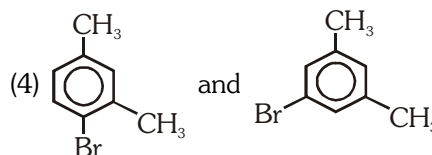


- (4)  + ICH₂OH

AIPMT 2014

- (3) $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2\text{Cl}$ (4) $\text{H}-\overset{\text{CH}_3}{\underset{\text{C}_2\text{H}_5}{\underset{|}{\text{C}}}}-\text{Cl}$

- Cc1ccccc1C



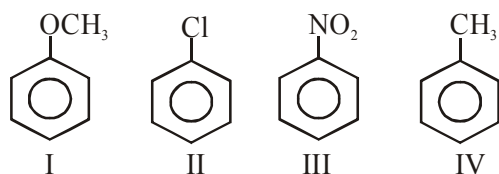
- (1) $\text{CH}_3 - (\text{CH}_2)_3 - \text{O} - \text{CH}_2\text{CH}_3$
- (2) $(\text{CH}_3)_2\text{CH}_2 - \text{O} - \text{CH}_2\text{CH}_3$
- (3) $\text{CH}_3(\text{CH}_2)_4 - \text{O} - \text{CH}_3$
- (4) $\text{CH}_3\text{CH}_2 - \text{CH}(\text{CH}_3) - \text{O} - \text{CH}_2\text{CH}_3$

- (3) 
- (4) 

AIIMS 2014

42. $\text{CH}_3\text{-C}\equiv\text{CH} + 2\text{HBr} \longrightarrow \text{Product ?}$
- (1) $\text{CH}_3\text{-CH(Br)-CH}_2\text{(Br)}$
- (2) $\text{CH}_3\text{-CH}_2\text{-CH} \begin{matrix} \nearrow \text{Br} \\ \searrow \text{Br} \end{matrix}$
- (3) $\text{CH}_2\text{(Br)-CH}_2\text{(Br)-CH}_3$
- (4) $\text{CH}_3\text{-C(Br)(Br)-CH}_3$

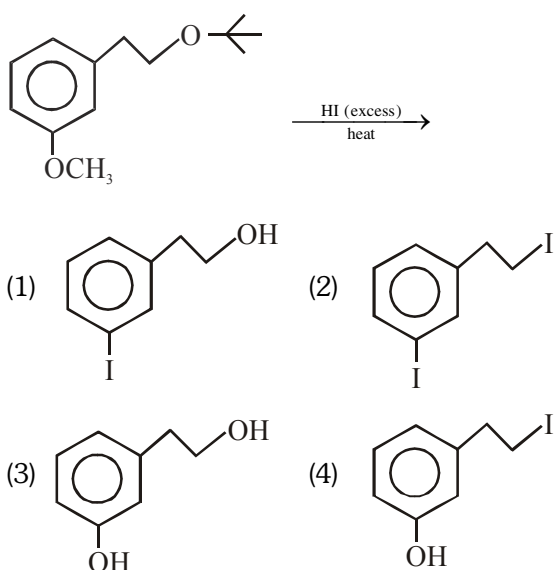
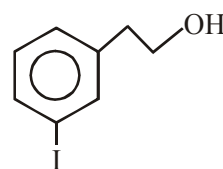
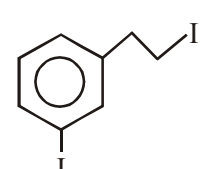
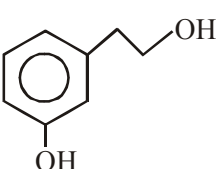
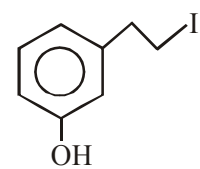
43. Increasing order of reactivity towards E.S.R. for following compounds is ?



- (1) III < II < IV < I (2) II < III < IV < I
- (3) III < II < I < IV (4) III < I < II < IV

44. Correct order of nucleophilicity :-

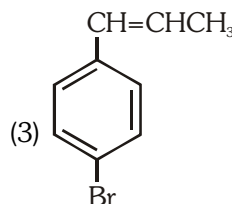
- (1) $\text{CH}_3\text{O}^- > \text{CH}_3^- > \text{NH}_2^- > \text{CH}_3\text{COO}^-$
- (2) $\text{CH}_3^- > \text{NH}_2^- > \text{CH}_3\text{O}^- > \text{CH}_3\text{COO}^-$
- (3) $\text{NH}_2^- > \text{CH}_3^- > \text{CH}_3\text{O}^- > \text{CH}_3\text{COO}^-$
- (4) $\text{CH}_3^- > \text{CH}_3\text{O}^- > \text{NH}_2^- > \text{CH}_3\text{COO}^-$

45. 
- (1)  (2) 
- (3)  (4) 

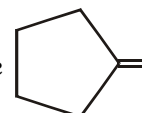
AIPMT 2015

46. The reaction of $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ with HBr produces:-

- (1) $\text{C}_6\text{H}_5\text{CH}_2\text{CH(Br)CH}_3$ (2) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$



- (4) $\text{C}_6\text{H}_5\text{CH(Br)CH}_2\text{CH}_3$

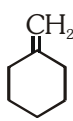
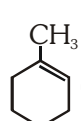
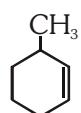
47. Treatment of cyclopentanone  with

methyl lithium gives which of the following species?

- (1) Cyclopentanonyl cation
- (2) Cyclopentanonyl radical
- (3) Cyclopentanonyl biradical
- (4) Cyclopentanonyl anion

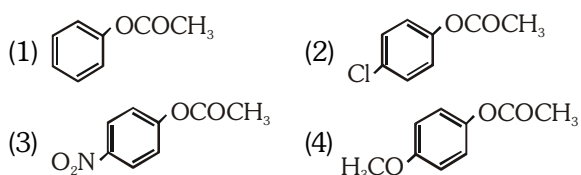
Re-AIPMT 2015

48. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule, to give a product 1-chloro-1-methylcyclohexane. The possible alkene is :-

- (1)  (A) (2)  (B)
- (3) (A) and (B) (4) 

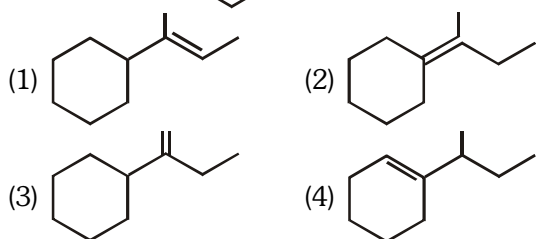
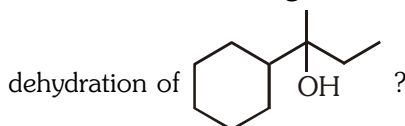
49. Reaction of carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is :
- (1) hydrocyanic acid
- (2) sodium hydrogen sulphite
- (3) a Grignard reagent
- (4) hydrazine in presence of feebly acidic solution

50. Which one of the following esters gets hydrolysed *most easily* under alkaline conditions ?

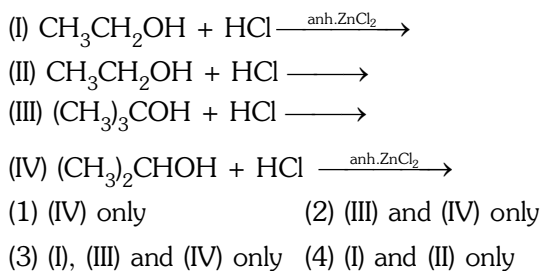


51. In an S_N1 reaction on chiral centres, there is :
 (1) 100% retention
 (2) 100% inversion
 (3) 100% racemization
 (4) inversion more than retention leading to partial racemization

52. Which of the following is not the product of

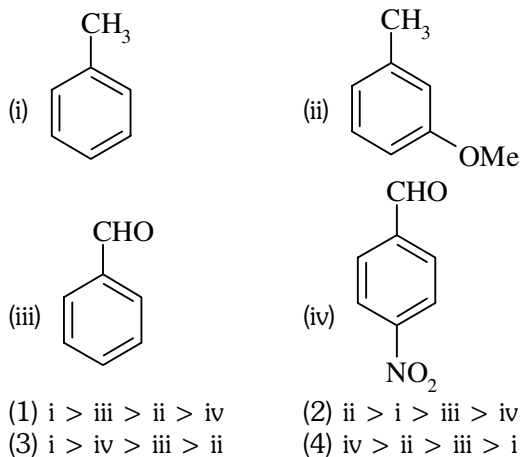


53. Which of the following reaction(s) can be used for the preparation of alkyl halides ?



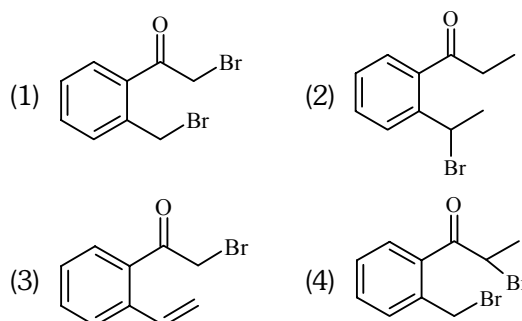
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54. Correct order of reactivity towards ESR is

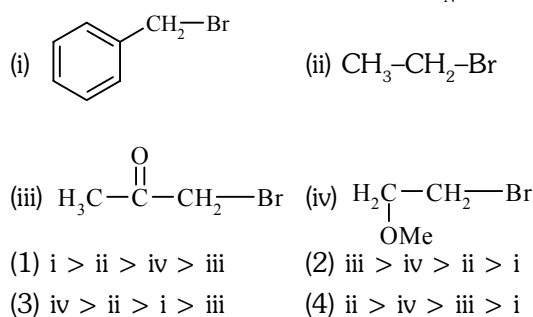


55. product.

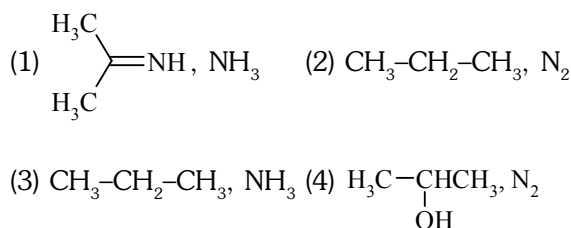
Product of given reaction is



56. Correct order of reactivity towards S_N1 is

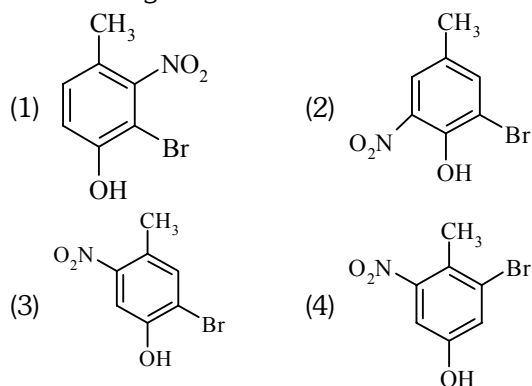


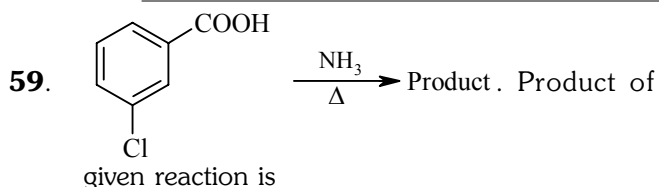
57. product is

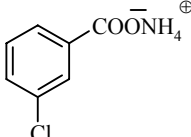
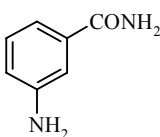
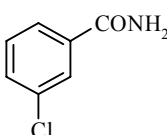
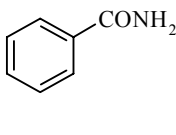


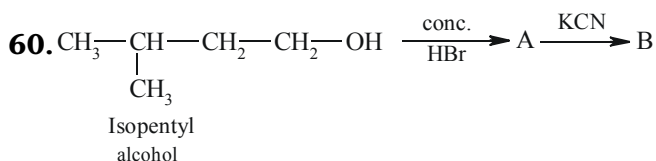
58. product.

Product of given reaction is

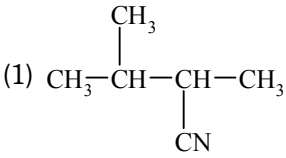
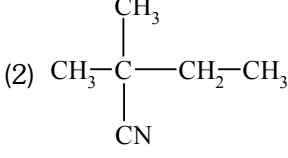
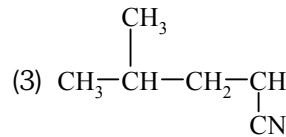
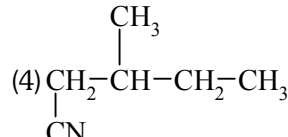




- (1)  (2) 
 (3)  (4) 



What is B ?

- (1)  (2) 
 (3)  (4) 

61. Correct order of reactivity towards elimination reaction

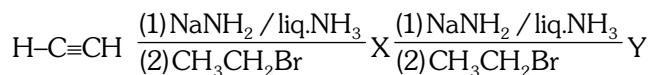
- (i) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2-\text{Br}$
 (ii) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{Br}$
 (iii) $\text{C}_6\text{H}_5\text{CH}_2\underset{\text{Br}}{\text{CH}}-\text{CH}_3$

- (iv) $\text{H}_3\text{C}-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$

- (1) i>ii>iii>iv (2) ii>i>iii>iv
 (3) iii>iv>i>ii (4) iii>i>iv>ii

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62. In the reaction



X and Y are :

- (1) X = 1-Butyne ; Y = 3-Hexyne
 (2) X = 2-Butyne ; Y = 3-Hexyne
 (3) X = 2-Butyne ; Y = 2-Hexyne
 (4) X = 1-Butyne ; Y = 2-Hexyne

63. Which of the following reagents would distinguish cis-cyclopentane-1,2-diol from its trans-isomer?

- (1) Acetone
 (2) Ozone
 (3) MnO_2
 (4) Aluminium isopropoxide

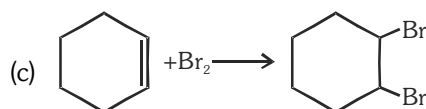
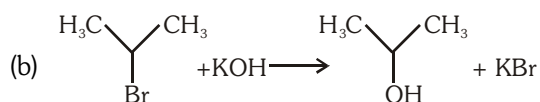
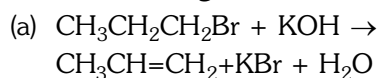
64. The product formed by the reaction of an aldehyde with a primary amine is :-

- (1) Schiff base
 (2) Ketone
 (3) Carboxylic acid
 (4) Aromatic acid

65. Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3 . If a large amount of KHSO_4 is added to the mixture, the rate of nitration will be:-

- (1) faster
 (2) slower
 (3) unchanged
 (4) doubled

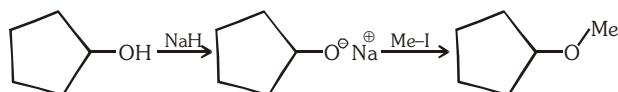
66. For the following reactions :-



Which of the following statement is **correct** ?

- (1) (a) and (b) are elimination reaction and (c) is addition reaction
 (2) (a) is elimination, (b) is substitution and (c) is addition reaction
 (3) (a) is elimination, (b) and (c) are substitution reactions
 (4) (a) is substitution, (b) and (c) are addition reaction

67. The reaction



Can be classified as :-

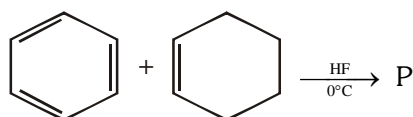
- (1) Williamson ether synthesis reaction
 (2) Alcohol formation reaction
 (3) Dehydration reaction
 (4) Williamson alcohol synthesis reaction

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68. Which of the following compounds shall not produced propene by reaction with HBr followed by elimination or direct only by elimination reaction ?

- (1) $\text{H}_2\text{C}=\text{C}=\text{O}$ (2) $\text{H}_3\text{C}-\overset{\text{H}_2}{\underset{\text{H}_2}{\text{C}}}-\text{CH}_2\text{Br}$
 (3) $\text{H}_2\text{C}-\underset{\text{H}_2}{\underset{\text{C}}{\text{CH}_2}}$ (4) $\text{H}_3\text{C}-\overset{\text{H}_2}{\underset{\text{H}_2}{\text{C}}}-\text{CH}_2\text{OH}$

69. In the given reaction



the product P is :-

- (1) (2)
 (3) (4)

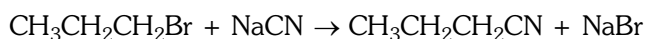
70. The compound that will react most readily with gaseous bromine has the formula

- (1) C_4H_{10} (2) C_2H_4
 (3) C_3H_6 (4) C_2H_2

71. Which of the following can be used as the halide component for Friedel-Crafts reaction ?

- (1) Chloroethene (2) Isopropyl chloride
 (3) Chlorobenzene (4) Bromobenzene

72. Consider the reaction

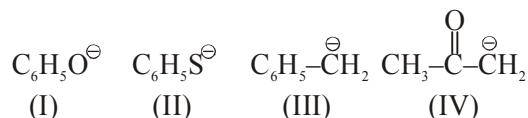


This reaction will be the fastest in

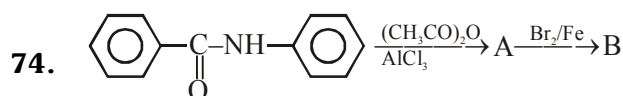
- (1) N,N'-dimethylformamide (DMF)
 (2) water
 (3) ethanol
 (4) methanol

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73. Arrange followings in their nucleophilicity order.



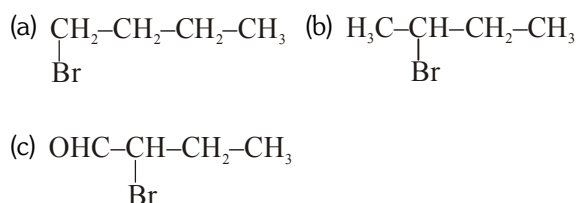
- (1) II > III > IV > I
 (2) I > IV > II > III
 (3) II > IV > III > I
 (4) III > IV > I > II



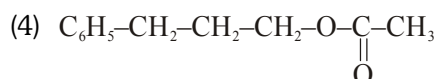
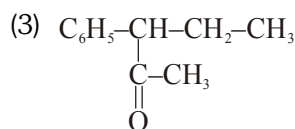
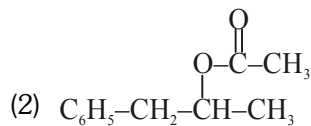
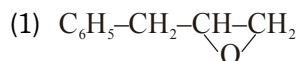
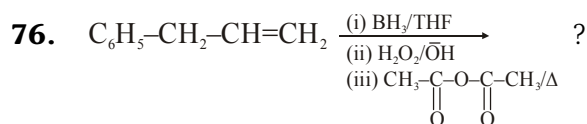
B is :-

- (1) (2)
 (3) (4)

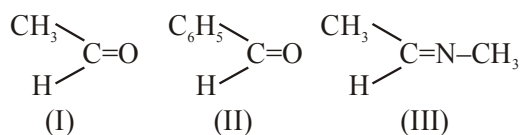
75. Arrange the following compounds in order of reactivity towards $\text{S}_\text{N}1$ reaction.



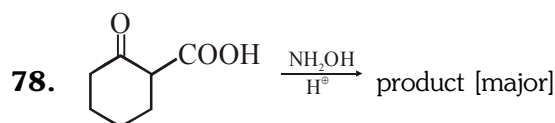
- (1) a > b > c
 (2) b > a > c
 (3) c > b > a
 (4) a > c > b



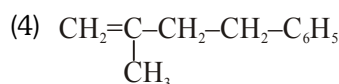
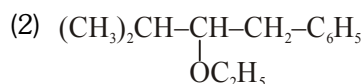
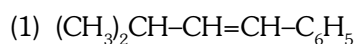
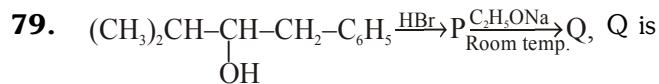
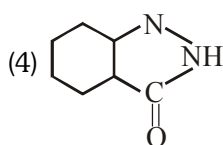
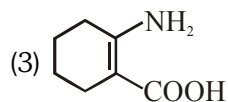
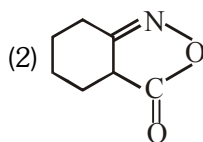
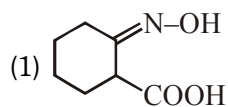
77. Arrange following compounds in reactivity order towards nucleophilic addition reaction



- (1) I > II > III (2) III > II > I
 (3) II > III > I (4) I > III > II

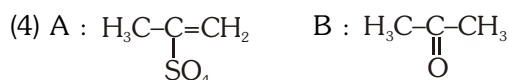
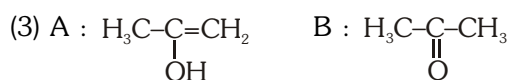
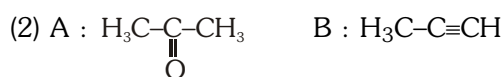
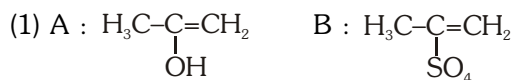
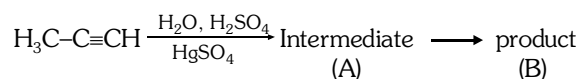


Product will be -

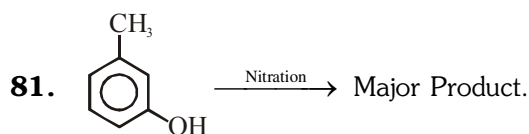


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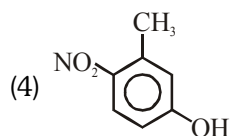
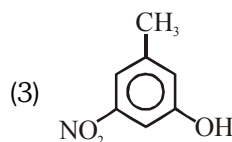
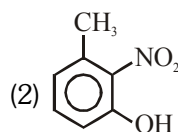
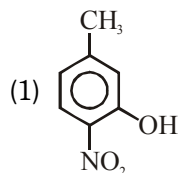
80. Predict the correct intermediate and product in the following reaction :

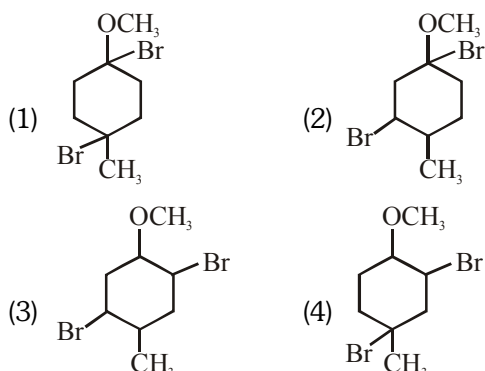
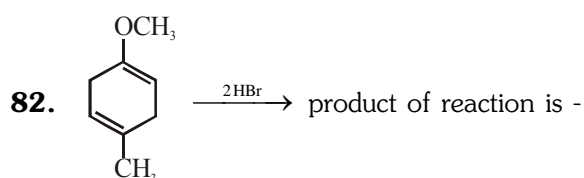


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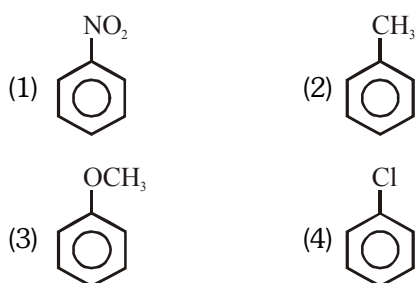


What is major product ?





83. Which of the following shows fastest electrophilic substitution reaction :-

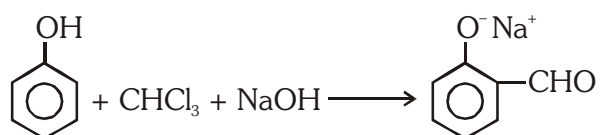


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84. Nitration of aniline in strong acidic medium also gives m-nitroaniline because

- (1) In spite of substituents nitro group always goes to only m-position.
- (2) In electrophilic substitution reactions amino group is meta directive.
- (3) In absence of substituents nitro group always goes to m-position
- (4) In acidic (strong) medium aniline is present as anilinium ion.

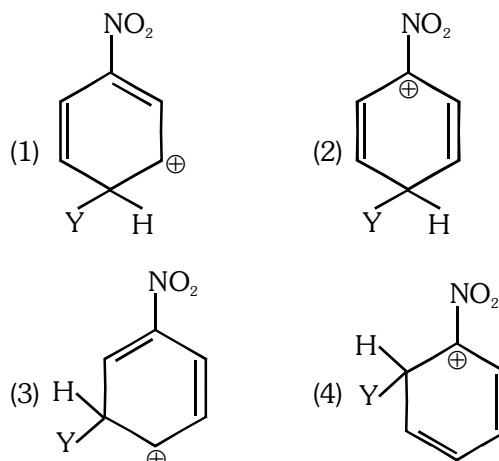
85. In the reaction



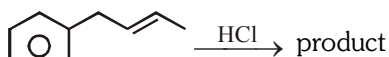
the electrophile involved is

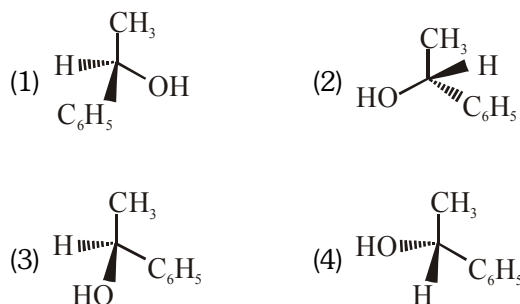
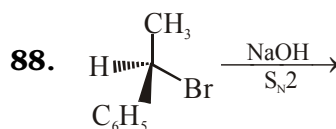
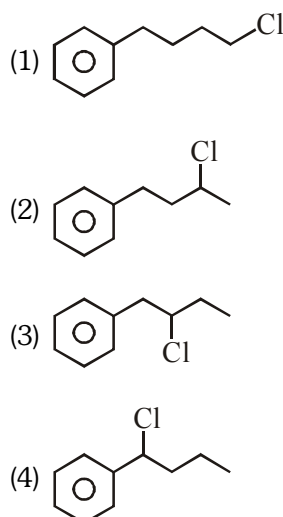
- (1) dichloromethyl cation (CHCl_2^+)
- (2) formyl cation (CHO^+)
- (3) dichloromethyl anion (CHCl_2^-)
- (4) dichlorocarbene ($:\text{CCl}_2$)

86. Which of the following carbocations is expected to be most stable ?

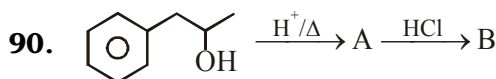
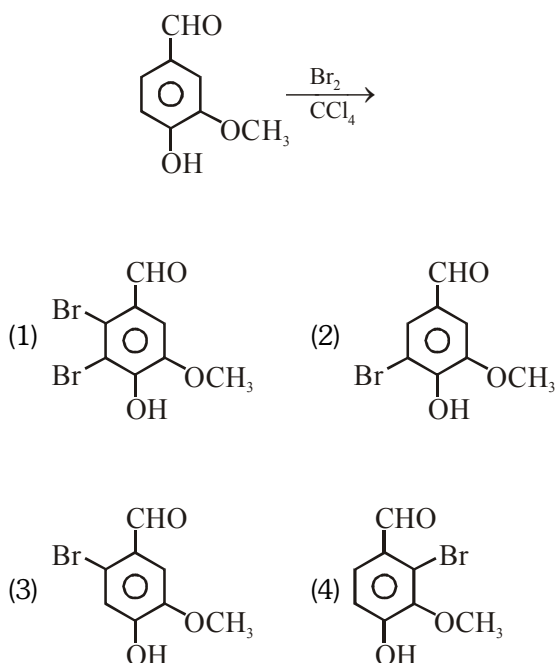


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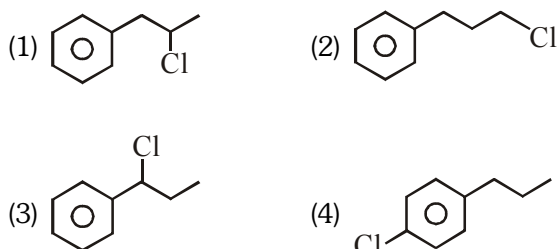
87.  product



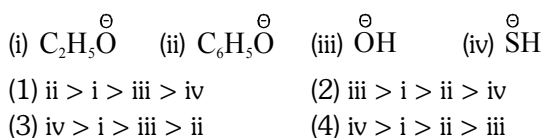
89. The product of the given reaction



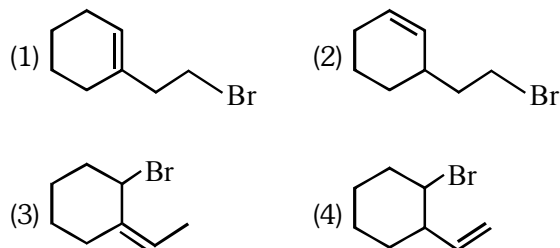
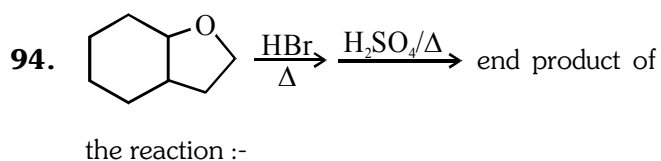
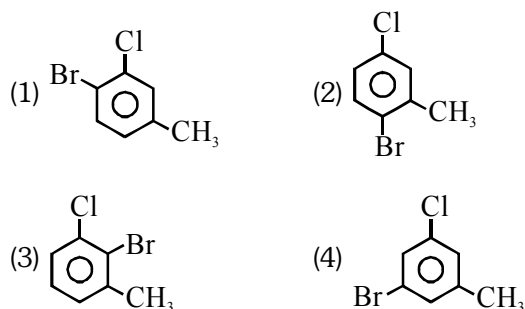
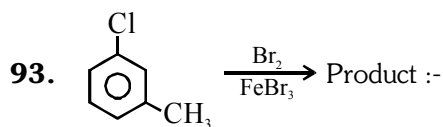
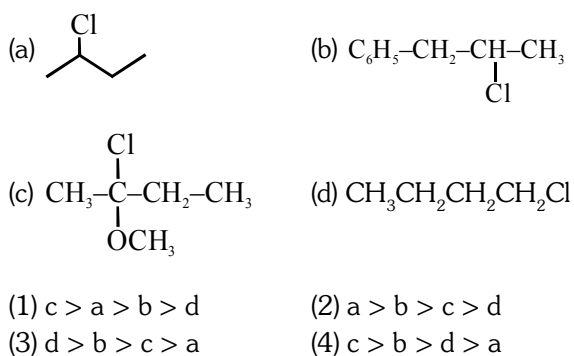
The product 'B' is :



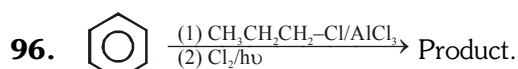
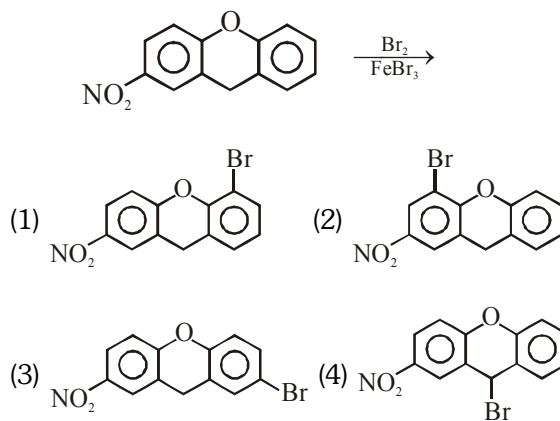
91. The nucleophilicity order of the given nucleophiles :-



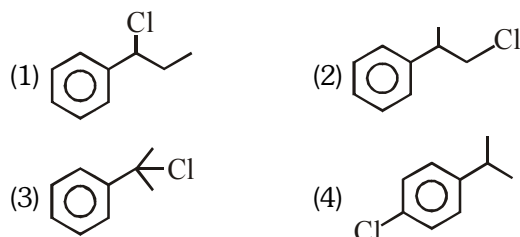
92. Arrange the following in decreasing order of reactivity towards $\text{S}_{\text{N}}1$ reaction :-

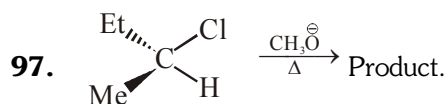


95. Major product of the given reaction :-

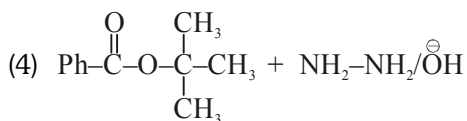
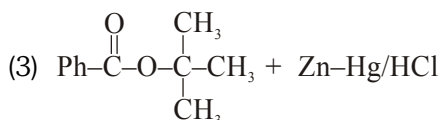
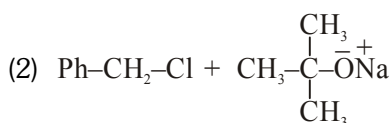
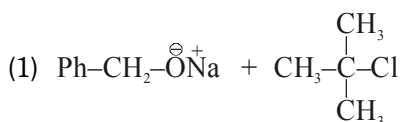
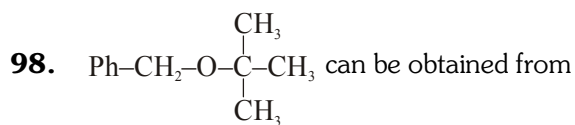
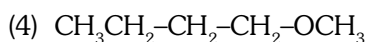
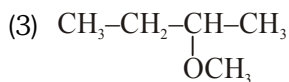
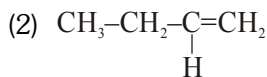
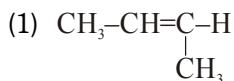


Product of reaction is :-

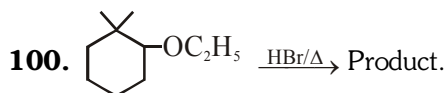
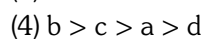
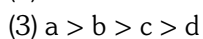
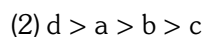
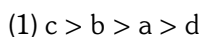
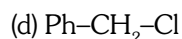
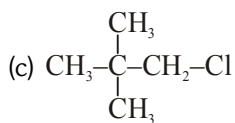
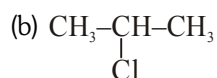




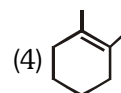
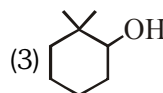
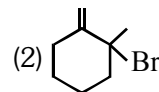
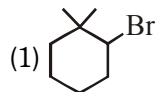
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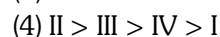
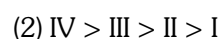
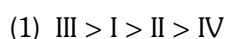
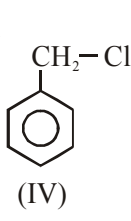
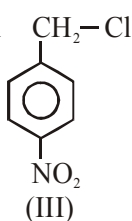
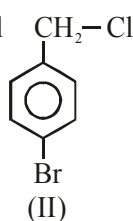
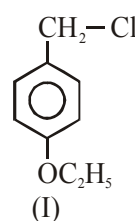
99. Arrange the following in decreasing order of reactivity for $\text{S}_\text{N}2$



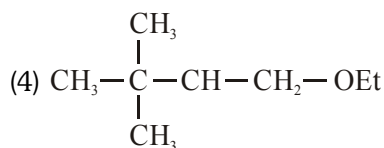
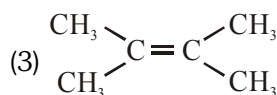
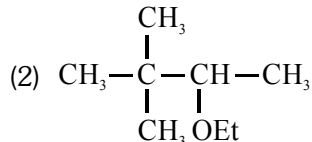
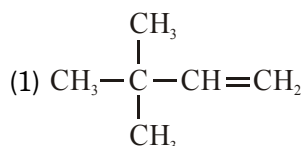
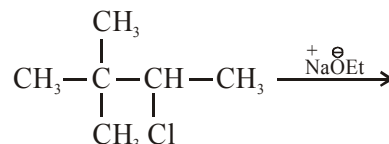
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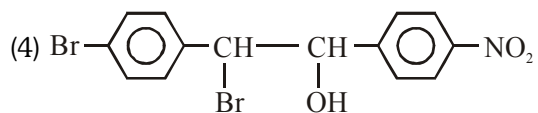
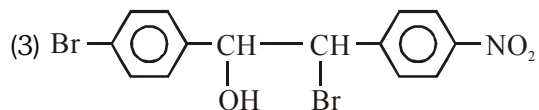
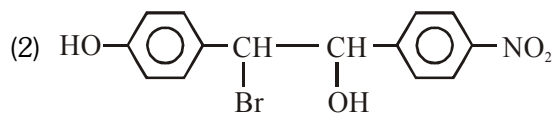
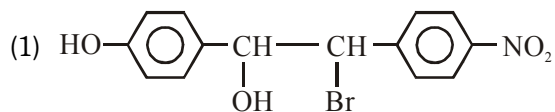
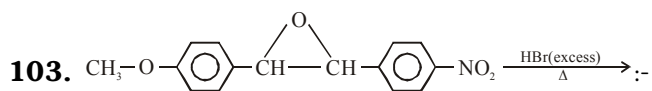


101. Compare the rate of $\text{S}_\text{N}1$ reaction :-



102. Which of the following is major product in the given reaction:-





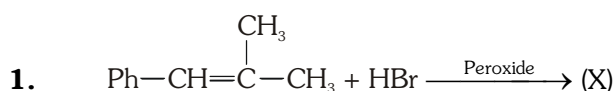
EXERCISE-II (Previous Year Questions)

ANSWER KEY

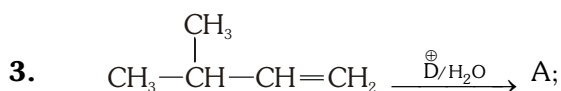
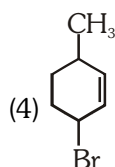
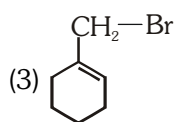
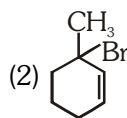
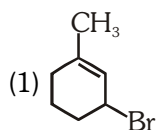
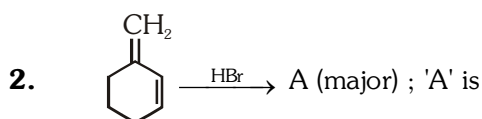
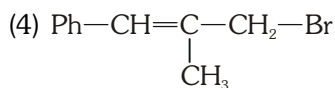
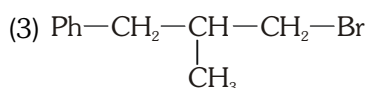
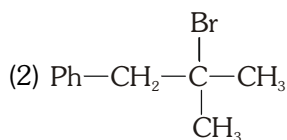
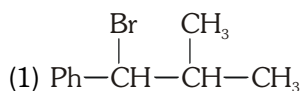
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Ans.	4	4	1	3	3	1	3	1	3	2	3	2	4	2	4
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	1	2	4	2	2	2	1	4	3	2	1	4	2	1	2
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	3	1	4	4	1	2	3	4	3	1	4	4	1	2	4
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	4	4	3	4	3	4	4	3	2	2	1	2	2	3	3
Que.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	4	1	1	1	2	2	1	1	1	3	2	1	1	1	2
Que.	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
Ans.	4	1	2	1	3	1	1	3	4	4	3	2	3	2	3
Que.	91	92	93	94	95	96	97	98	99	100	101	102	103		
Ans.	3	1	2	1	3	3	1	2	2	3	3	1	2		

EXERCISE-III (Analytical Questions)

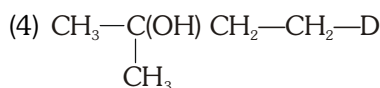
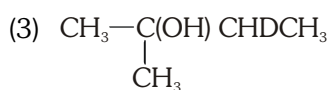
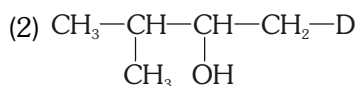
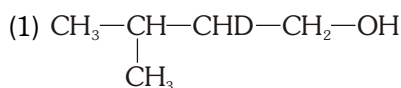
Check Your Understanding



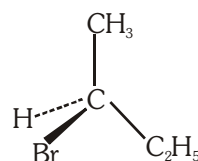
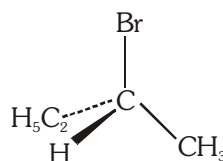
'X' is



A (major product) is



4. The addition of HBr to 1-Butene gives a mixture of products A, B and C.

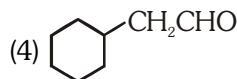
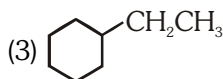
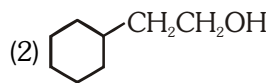
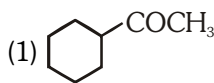


The mixture consists of :-

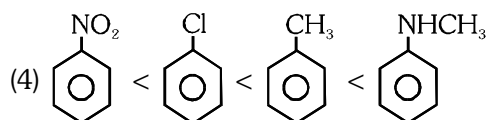
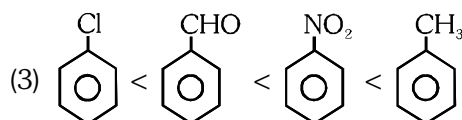
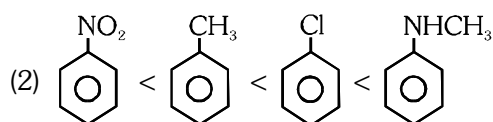
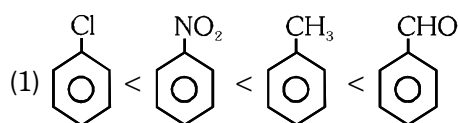
- (1) A and B as major and C as minor products
- (2) B as major, A and C as minor products
- (3) B as minor, A and C as major products
- (4) A and B as minor and C as major products.

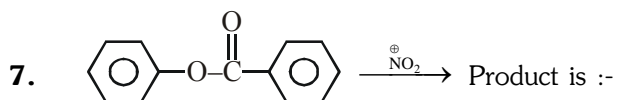
5. Hydration of $\text{Cyclohexyl}-\text{C}\equiv\text{CH}$ in presence of

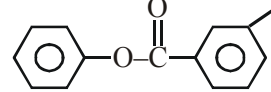
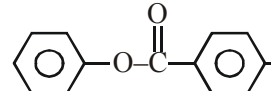
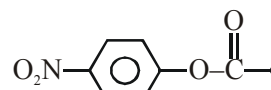
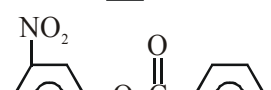
$\text{H}_2\text{SO}_4 / \text{HgSO}_4$ gives



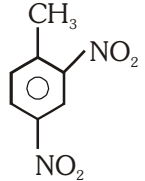
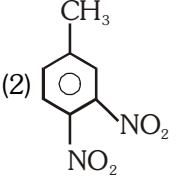
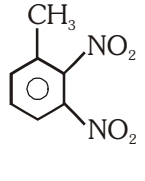
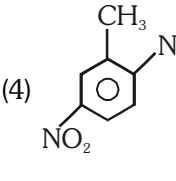
6. Identify correct order of reactivity for electrophilic substitution reaction of the following compounds :-





- (1) 
 (2) 
 (3) 
 (4) 

8. p-nitro toluene on further nitration gives

- (1) 
 (2) 
 (3) 
 (4) 

9. Which of the following reaction gives t-butyl benzene:

- (1) $C_6H_6 + t\text{-butyl chloride} \xrightarrow{AlCl_3}$
 (2) $C_6H_6 + (CH_3)_2C=CH_2 \xrightarrow{HF}$
 (3) $C_6H_6 + t\text{-butyl alcohol} \xrightarrow{H_2SO_4}$
 (4) All of them

10. Halogenation of alkanes gives a mixture of monohalo products. The ease of substitution follows the order

- (1) Tertiary H > primary H > secondary H
 (2) Primary H < secondary H < tertiary H
 (3) Primary H > secondary H > tertiary H
 (4) Secondary H > tertiary H < primary H

11. The number of different substitution products possible when ethane is allowed to react with bromine in sunlight are

- (1) 9
 (2) 6
 (3) 8
 (4) 5

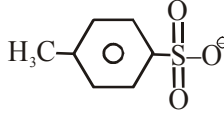
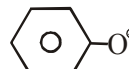
12. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives

- (1) o-cresol
 (2) p-cresol
 (3) 2, 4-dihydroxy toluene
 (4) Benzyl alcohol

13. Which gives maximum yield of C_2H_5Cl

- (1) $C_2H_6 + Cl_2 \xrightarrow[\text{excess}]{h\nu, \text{light}} C_2H_5Cl + HCl$
 (2) $C_2H_6 + Cl_2 \xrightarrow[\text{excess}]{h\nu, \text{light}} C_2H_5Cl + HCl$
 (3) $C_2H_6 + Cl_2 \xrightarrow[\text{light}]{h\nu} C_2H_5Cl$
 (4) $C_2H_6 + Cl_2 \xrightarrow{\text{Dark}} C_2H_5Cl + HCl$

14. Which of the following has maximum nucleophilicity :-

- (1) 
 (2) CH_3-O^-
 (3) $CF_3-C(=O)O^-$
 (4) 

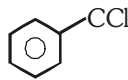
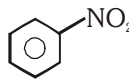
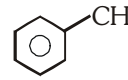
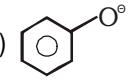
15. Consider thiol anion (RS^-) and alkoxy anion (RO^-). Which of the following statement is correct ?

- (1) RS^- is less basic and less nucleophilic than RO^-
 (2) RS^- is less basic but more nucleophilic than RO^-
 (3) RS^- is more basic and more nucleophilic than RO^-
 (4) RS^- is more basic but less nucleophilic than RO^-

16. Alkaline hydrolysis of 2,2-dichloropropane gives

- (1) Acetone
 (2) 2,2-propanediol
 (3) Propane
 (4) Propan-2-ol

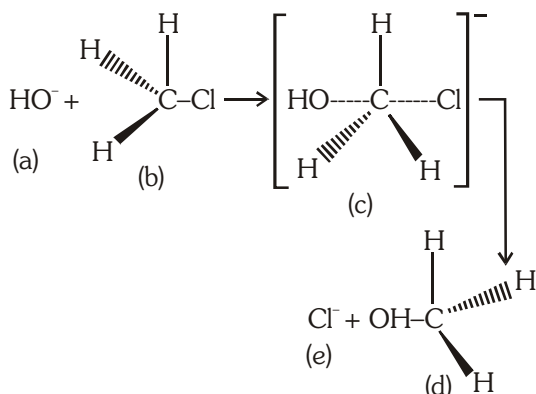
17. Electrophile NO_2^+ attacks the following :

- (1) 
 (II) 
 (III) 
 (IV) 

in which cases NO_2^+ will attack at meta position

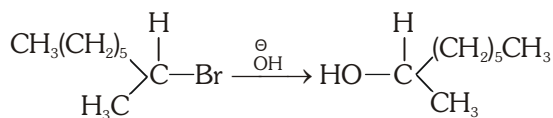
- (1) II and IV
 (2) I, II and III
 (3) III and IV
 (4) I only

18. Which of the following statement is correct for SN^2 mechanism

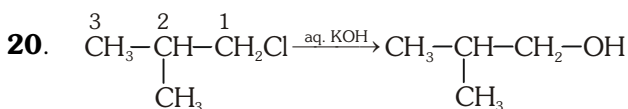


- (1) In (c) carbon atom is sp^3 hybridized
- (2) In (c) carbon atom is sp^2 hybridised
- (3) (a) and (e) are electrophiles
- (4) (c) is more stable than (d)

19. Following reaction is



- (1) E_1
- (2) $\text{S}_{\text{N}}1$
- (3) E_2
- (4) $\text{S}_{\text{N}}2$



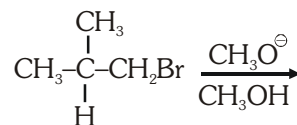
In the above reaction the attack of a nucleophile would be from which side

- (1) On the front side of Cl of C_1 carbon
- (2) On C_2 carbon
- (3) On the rear side of Cl of C_1 carbon
- (4) On C_3 carbon

21. Which of the following ether can not be prepared by Williamson's method :-

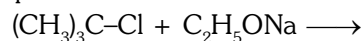
- (1) Di-tert-butyl ether
- (2) Ethyl-tert-butyl ether
- (3) Anisole
- (4) 1 & 2 Both

22. The major product formed in the following reaction is :-



- (1) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_2\text{OCH}_3$
- (2) $\text{CH}_3-\underset{\text{OCH}_3}{\text{CH}}-\text{CH}_2\text{CH}_3$
- (3) $\text{CH}_3-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$
- (4) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{OCH}_3}{\text{C}}}-\text{CH}_3$

23. Major product of the reaction :-



would be :-

- (1) $(\text{CH}_3)_2\text{C}-\text{OC}_2\text{H}_5$
- (2) $(\text{CH}_3)_3\text{C}-\text{C}_2\text{H}_5$
- (3) $(\text{CH}_3)_2\text{C}=\text{CH}_2$
- (4) $\text{CH}_3-\text{CH}=\text{CH}-\text{C}_2\text{H}_5$

24. Among the following the most reactive towards alcoholic KOH is

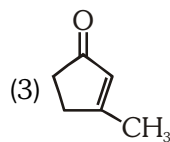
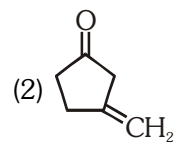
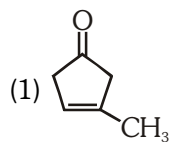
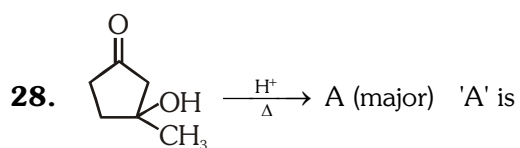
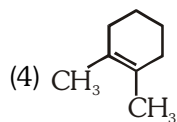
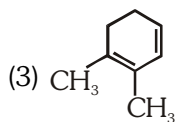
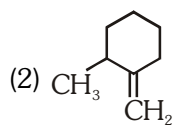
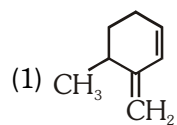
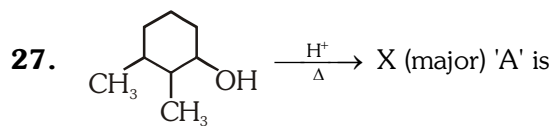
- (1) $\text{CH}_2=\text{CHBr}$
- (2) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{Br}$
- (3) $\text{CH}_3\text{CH}_2\text{Br}$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

25. The major product obtained on treatment of $\text{CH}_3\text{CH}_2\text{CH}(\text{F})\text{CH}_3$ with $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$ is

- (1) $\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_3$
- (2) $\text{CH}_3\text{CH}=\text{CHCH}_3$
- (3) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
- (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$

26. Dehydrohalogenation of neopentyl chloride with alc. KOH mainly gives

- (1) 2-methyl-1-butene
- (2) 2-methyl-2-butene
- (3) 2,2-dimethyl-1-propanol
- (4) 2-pentene



(4) All

EXERCISE-III (Analytical Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	1	4	1	1	4	3	1	4	2	1	4	2	2	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	1	2	2	4	3	1	3	3	2	3	2	4	3		

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

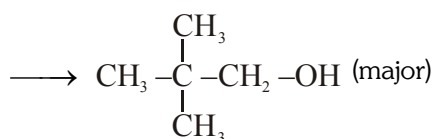
- Assertion :-** trans 2-butene gives racemic mixture when treated with Cl_2 .
Reason :- Addition of Cl_2 is anti.
 (1) A (2) B (3) C (4) D
- Assertion :-** Addition of HBr in presence of peroxide on alkene is free radical addition. This reaction is not shown by HCl.
Reason :- Due to less bond energy of HCl than HBr, homolysis of HCl can not occurs.
 (1) A (2) B (3) C (4) D
- Assertion :-** Addition of CBrCl_3 in presence of peroxides takes place faster to 2-ethyl-1-hexene than to 1-octene.
Reason :- Intermediate free radical in case of 2-ethyl-1-hexene is more stable.
 (1) A (2) B (3) C (4) D
- Assertion :-** Ketone gives 2,4-DNP test easily than aldehyde.
Reason :- Ketone is more reactive than aldehyde.
 (1) A (2) B (3) C (4) D
- Assertion :-** p-nitrophenol gives more electrophilic substituted compound than m-methoxy phenol
Reason :- Methoxy group shows only negative I-effect
 (1) A (2) B (3) C (4) D
- Assertion :** Rates of nitration of benzene and hexadeuterobenzene are different.
Reason : C-H bond is stronger than C-D bond.
 (1) A (2) B (3) C (4) D
- Assertion :-** Major product obtained from FCR of benzene with n-butyl chloride is tert. Butyl benzene.
Reason :- Intermediate 1° carbocation rearrangements in more stable 3° carbocation.
 (1) A (2) B (3) C (4) D
- Assertion :-** When CH_3Cl and AlCl_3 are used in F.C.R. the electrophile is $\text{Cl}^\oplus$.
Reason :- The first attack on benzene is of $\text{Cl}^\oplus$.
 (1) A (2) B (3) C (4) D
- Assertion :-** The correct reactivity order towards sulphonation is –
 meta xylene > Toluene > chlorobenzene > Nitrobenzene
Reason :- m-xylene has the highest electron density & hence most reactive.
 (1) A (2) B (3) C (4) D
- Assertion :-** Iodine monochloride (ICl) reacts with benzene in presence of a lewis acid such as anhyd. AlCl_3 to give iodobenzene and not chlorobenzene.
Reason :- Iodine is less electronegative than chlorine in the reaction.
 (1) A (2) B (3) C (4) D
- Assertion :-** Vinyl halides can not be used in place of alkyl halides in friedel crafts alkylation.
Reason :- Vinyl halides does not give electrophile easily.
 (1) A (2) B (3) C (4) D
- Assertion :-** If the hydrogen atoms of benzene are replaced by deuterium atoms then the reactivity of benzene ring is decreased for ESR.
Reason :- The bond strength of C-D is more than C-H and reaction depends on the bond strength of C-D and C-H.
 (1) A (2) B (3) C (4) D
- Assertion :-** Benzyl chloride is more reactive than p-chloro toluene towards aqueous NaOH.
Reason :- The C-Cl bond in benzyl chloride is more polar than C-Cl bond in p-chloro toluene.
 (1) A (2) B (3) C (4) D

14. **Assertion :-** $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ reacts faster when treated with water than $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Cl}$.
Reason :- Carbonium ion formed by the ionisation of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ is stabilized by resonance.
 (1) A (2) B (3) C (4) D

15. **Assertion :-** p-Chloro aniline and aniliniumchloride can be distinguished by AgNO_3 .
Reason :- p-Chloro aniline is less basic than aniline.
 (1) A (2) B (3) C (4) D

16. **Assertion :-** Phenoxide ion is a poor nucleophile than a methoxide ion.
Reason :- In methoxide ion oxygen is attached to sp^3 carbon.
 (1) A (2) B (3) C (4) D

17. **Assertion :-** $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{Br} + \text{NaOH}$



Reason :- It follows with formation of more stable carbanion
 (1) A (2) B (3) C (4) D

18. **Assertion :-** Aryl sulphonic acid gives phenol on reacting with NaOH at high temperature followed by :
Reason :- This acidification reaction is electrophilic substitution reaction.
 (1) A (2) B (3) C (4) D

19. **Assertion :-** Aryl halides are more reactive than alkyl halide towards NSR .
Reason :- Intermediate carbocation is more stable obtained from Aryl halide.
 (1) A (2) B (3) C (4) D

20. **Assertion :-** In SN^1 reaction if the alkyl halide is optically active then the product is racemic mixture.
Reason :- All tertiary halides gives racemic mixture.
 (1) A (2) B (3) C (4) D

21. **Assertion :-** Chlorobenzene does not react with NaOH where as ethyl chloride reacts.
Reason :- The partial double bond between C and Cl causes less reactivity towards nucleophilic substitution.
 (1) A (2) B (3) C (4) D

22. **Assertion :-** Benzyl bromide when kept in acetone water it produces benzyl alcohol.
Reason :- The reaction follows SN^2 mechanism
 (1) A (2) B (3) C (4) D

23. **Assertion :-** Anisole on reaction with HI gives phenol and CH_3I .
Reason :- Phenyl-oxygen bond is stronger than methyl-oxygen bond in anisole and hence is not cleaved by HI .
 (1) A (2) B (3) C (4) D

24. **Assertion :-** In Lucas test, 3° alcohols react immediately.
Reason :- An equimolar mixture of anhydrous ZnCl_2 and conc. HCl is called Lucas reagent.
 (1) A (2) B (3) C (4) D

25. **Assertion :-** t-butyl methyl ether is prepared by reaction of t-butyl bromide with methoxide ion.
Reason :- Reaction follow SN^2 -mechanism.
 (1) A (2) B (3) C (4) D

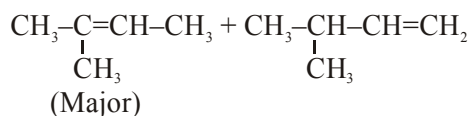
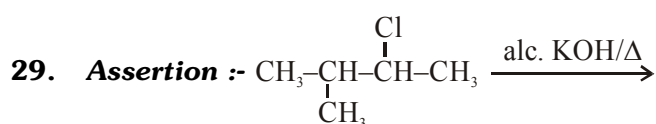
26. **Assertion :-** Treatment of 1,3-dibromopropane with zinc dust produces cyclopropane.
Reason :- The reaction of alkyl halide with Zn dust is nucleophilic substitution.
 (1) A (2) B (3) C (4) D

27. **Assertion :-** 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 2-butene as a major product.
Reason :- 2-Butene is more stable than 1-butene.
 (1) A (2) B (3) C (4) D

28. **Assertion :-** Aldehyde are more reactive than Ketone.
Reason :- Nucleophilic addition reaction in carbonyl compound

$$\propto \frac{1}{\text{Steric hindrance}} \text{ and } \propto \text{positive charge at carbon of carbonyl group.}$$

(1) A (2) B (3) C (4) D



Reason :- In E_2 reaction product formation always takes place by saytzeff rule.

(1) A (2) B (3) C (4) D

30. **Assertion :-** The product of reaction of 2-Methyl cyclo hexanol with HBr at room temperature is 1-Bromo-1-methyl cyclo hexane.

Reason :- Generally dehydration occur and product is 1-methyl cyclo hexene.

(1) A (2) B (3) C (4) D

31. **Assertion :-** Compound $\text{CH}_3-\underset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{OH}$ can

not give ether with conc. H_2SO_4 .

Reason :- It favours the formation of alkene over ether.

(1) A (2) B (3) C (4) D

32. **Assertion :-** In friedel craft's reaction of 1-chloropropane gives isopropyl benzene as product.

Reason :- The primary carbocation rearranges to form secondary carbocation.

(1) A (2) B (3) C (4) D

33. **Assertion :-** Propene reacts with diborane to form tripropyl borane.

Reason :- It follows anti markowni koff's rule.

(1) A (2) B (3) C (4) D

34. **Assertion :-** 2-Bromopentane react with alcoholic KOH to form 2-pentene.

Reason :- Alcoholic KOH follows E_1 , mechanism.

(1) A (2) B (3) C (4) D

35. **Assertion :-** p-Nitrobenzyl ethyl ether on heating with conc. HBr and gives p-Nitrobenzyl bromide.

Reason :- p-Nitrobenzyl carbocation is highly stable.

(1) A (2) B (3) C (4) D

36. **Assertion :-** Phthalic anhydride react with phenol in presence of NaOH gives pink colour.

Reason :- It forms phenolphthalein.

(1) A (2) B (3) C (4) D

37. **Assertion :-** Benzophenone on reaction with NaHSO_3 gives stable addition product.

Reason :- Equilibrium of this reaction lies on the right side.

(1) A (2) B (3) C (4) D

38. **Assertion :-** $\text{C}_6\text{H}_5\text{MgBr}$ on reaction with CO_2 gives benzoic acid

Reason :- CO_2 is a good electrophile

(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	3	1	4	4	4	4	4	1	1	1	4	1	1	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	2	4	3	4	3	1	3	1	2	4	3	1	1	3	3
Que.	31	32	33	34	35	36	37	38							
Ans.	1	1	3	3	3	1	4	3							

HYDROCARBONS

E

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NEET SYLLABUS

Alkanes - Physical properties, chemical reactions, combustion and pyrolysis. Alkenes - Structure of double bond, physical properties, methods of preparation, chemical reactions, ozonolysis, oxidation. Alkynes - Structure of triple bond, physical properties, methods of preparation, chemical reactions, acidic character of alkynes, benzene, resonance, aromaticity, carcinogenicity and toxicity.

OBJECTIVES

After studying this unit, we will be able to :

- learn about various methods of preparation of hydrocarbons;
- distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties;
- appreciate the role of hydrocarbons as sources of energy and for other industrial applications;
- comprehend the structure of benzene, explain aromaticity;
- predict the directive influence of substituents in monosubstituted benzene ring;
- learn about carcinogenicity and toxicity.

"Once your mind stretches to a new level it never goes back to its original dimension"

A.P.J. Abdul Kalam

HYDROCARBONS

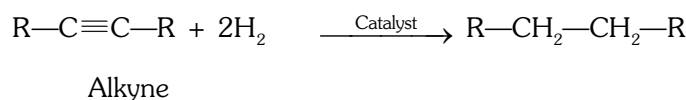
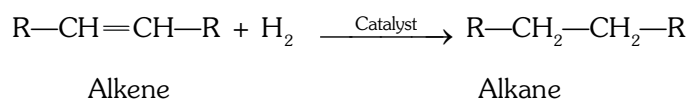
5.0 ALKANES

5.1.1 Introduction of Alkanes

- (a) Branched and unbranched aliphatic saturated open chain hydrocarbons are called member of alkanes.
- (b) CH_4 is also known as Marsh gas (fire damp).
- (c) Calore gas : Mixture of n-butane and isobutane.
- (d) LPG (Liquefied petroleum gas) : liquid propane, isobutane.
- (e) Natural gas : 80% methane + 10% ethane + 10% propane + small amounts of H_2 , N_2 , CO_2 etc.
- (f) Water gas : $\text{CO} + \text{H}_2$ (1:1)
- (g) Synthesis gas : $\text{CO} + 3\text{H}_2$ (1:3)

5.1.2 General Methods of Preparation

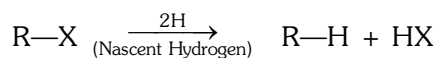
- (1) From alkenes and alkynes (Sabatier and Senderens reaction) or (By hydrogenation of alkenes and alkynes) :** Alkenes and alkynes on catalytic hydrogenation give alkanes.



Catalyst :

- (a) Pd/Pt at ordinary temperature and pressure
- (b) Ni, 200–300° C (sabatier)
- (c) Raney Nickel at room temp.
- (d) Methane can not be prepared by this method

- (2) From alkyl Halides (By reduction) :**



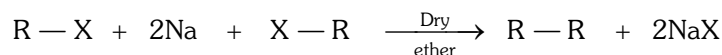
Catalyst :

- (i) $\text{Zn} + \text{HCl}$
- (ii) $\text{Zn} + \text{CH}_3\text{COOH}$
- (iii) $\text{Zn}-\text{Cu}$ couple in $\text{C}_2\text{H}_5\text{OH}$
- (iv) $\text{Red P} + \text{HI}$
- (v) $\text{Al}-\text{Hg} + \text{ethanol}$

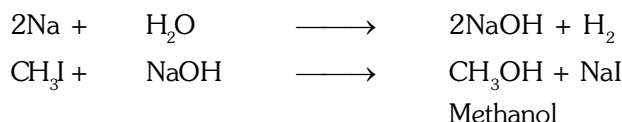
GOLDEN KEY POINTS

- Alkyl halides can also be reduced to alkane by H_2/Pd or LiAlH_4 or H_2/Ni .
- Halogen atom of alkyl halide is replaced by hydrogen atom to obtain an alkane.

(3) From alkyl halide (By Wurtz reaction): A solution of alkyl halide in ether on heating with sodium gives alkane.

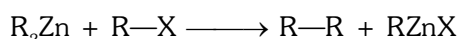
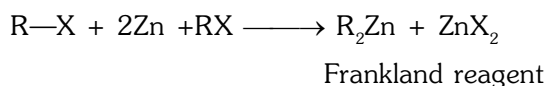


- (a) Two moles of alkyl halide are treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

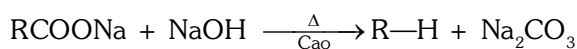


- (b) Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.
- (c) Two different alkyl halides, on wurtz reaction give all possible alkanes.
- (d) The separation of mixture into individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

(4) From Frankland Reagent:



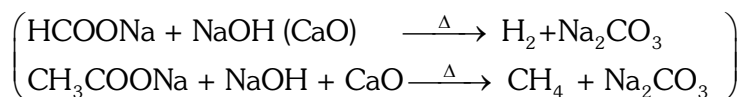
(5) From Carboxylic Acid (By decarboxylation) : Sodium salt of saturated monocarboxylic acid on dry distillation with sodalime give alkane.



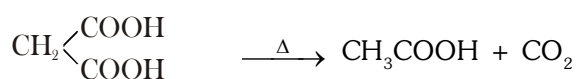
Note :- Sodalime $\Rightarrow$ NaOH + CaO

GOLDEN KEY POINTS

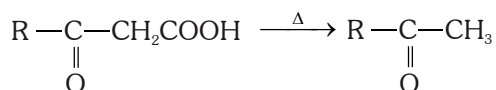
- The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.
- The alkane formed by decarboxylation contains one carbon atom less than the original acid.
- Decarboxylation of sodium formate gives H_2



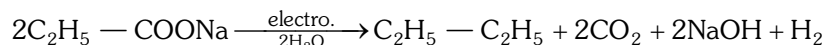
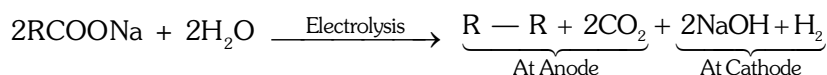
- If in a compound two carboxylic groups are present and they are attached to same carbon atom then decarboxylation of one of the carboxylic groups takes place simply on heating.



- $CH_3-CH_2-CH_3$ can be prepared by Butanoic acid and 2-Methyl propanoic acid.
- β -Keto acids are decarboxylated readily simply on heating (soda lime is not required)

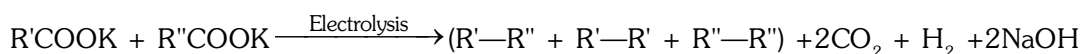


(6) From carboxylic acid (By Kolbe's electrolysis process) : Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.



GOLDEN KEY POINTS

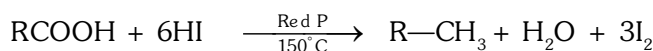
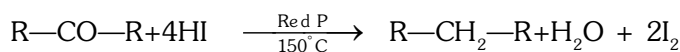
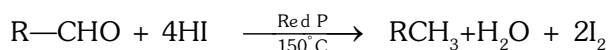
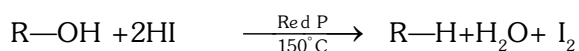
- Electrolysis of an acid salt gives symmetrical alkane, However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.



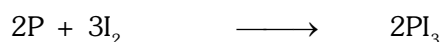
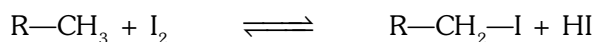
- At anode alkane and CO_2 gas is formed while at cathode NaOH and H_2 gas is formed.
- The concentration of NaOH in solution is increased with time so pH of solution is also increased.

(7) From alkanol, alkanals, Alkanone and alkanic acid (By reduction) :

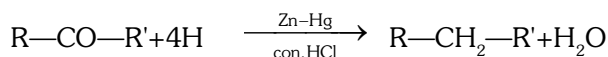
The reduction of either of the above compound in presence of red P and HI gives corresponding alkane.



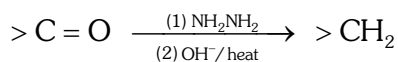
In the above reaction I_2 is formed which may react with alkane to form alkyl halide. So red P is added in the reaction to remove I_2 formed in the reaction.



(8) From alkanones (By Clemmensen's method) : Carbonyl compound may also be reduced with Zinc amalgam and concentrated HCl (Zn-Hg/HCl), this reaction is called Clemmensen reduction.

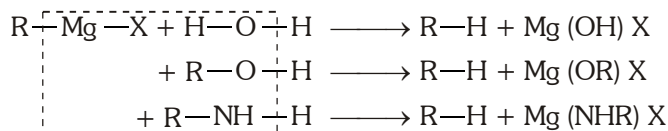


(9) From alkanals and alkanones (By Wolf Kishner reaction) :



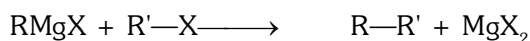
(10) From G.R. :

(a) Formation of alkanes with same number of C atoms : Grignard reagent reacts with the compounds having active hydrogen to form alkane.

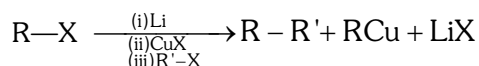


This reaction is used to determine the number of active H-atoms in the compound this is known as Zerewitnoff's method.

(b) G.R. react with alkyl halide to give higher alkanes :



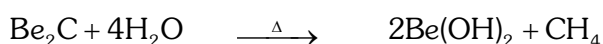
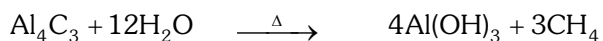
(11) Corey-House Synthesis : This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type $R-R'$



Note: In Corey-house reaction symmetrical and unsymmetrical alkane both can be formed.

(12) From metal carbide (By hydrolysis) :

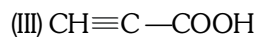
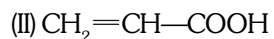
Only CH_4 can be obtained by the hydrolysis of Be or Al carbides



BEGINNER'S BOX-1

- If two moles of Isopropyl chloride reacts with Na in presence of dry ether. Which alkane is obtained.
(1) Hexane (2) 2, 3-Dimethyl butane
(3) Isopentane (4) Neopentane
- If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.
(1) n-Butane (2) 2-Methyl butane
(3) 2, 3-Dimethyl butane (4) All of them
- Which of the following compound can not be obtained from single alkyl halide by wurtz reaction.
(1) ethane (2) butane (3) isobutane (4) hexane
- How many acids can be taken to obtain isobutane by decarboxylation ?
(1) 4 (2) 3 (3) 2 (4) 5

5. Give reactivity order for decarboxylation ?



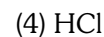
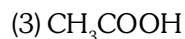
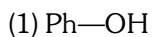
(1) $\text{I} > \text{II} > \text{III}$

(2) $\text{III} > \text{II} > \text{I}$

(3) $\text{III} > \text{I} > \text{II}$

(4) None is correct

6. Which of the following does not give alkane with R—Mg—X .



7. Which of the following reaction can not be used to obtained propane in good yield.

(1) Wurtz reaction

(2) Corey-house reaction

(3) Decarboxylation of acid salt

(4) All of them

5.1.3 Physical & Chemical Properties of alkane

Physical properties

(i) **Solubility** : Alkanes being non polar and thus insoluble in water but soluble in nonpolar solvents

Ex. C_6H_6 , CCl_4 , ether etc.

(ii) **Boiling point** - $\propto$ molecular weight (for n-alkanes)

$\therefore$ $\text{Vander Waals force of attraction} \propto \text{molecular weight} \propto \text{surface area of molecule.}$

i.e. boiling point Pentane < hexane < heptane

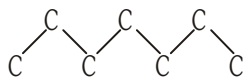
Also boiling point $\propto \frac{1}{\text{number of side chain}}$

because the shape approaches to spherical which results in decrease in van der Waal's forces (as surface area decreases)

Thus boiling point n-Pentane > Isopentane > neopentane

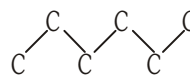
(iii) **Melting Point** : M.P. of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher M.P. than their adjacents alkanes of odd number of carbon atoms.

The abnormal trend in M.P. is due to the fact that alkanes with odd carbon atoms have their end carbon atom on the same side of the molecule and in even carbon atom alkane the end Carbon atom on opposite side. Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.



Odd number of carbon

<

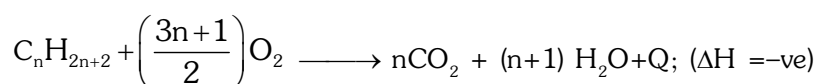


Even number of carbon

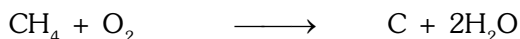
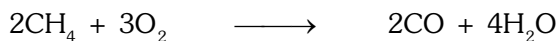
Chemical Properties

(1) Oxidation :

(a) **Complete oxidation or combustion** : Alkanes burn readily with non-luminous flame in presence of air or oxygen to give CO_2 and water with evolution of heat. Therefore, alkanes are used as fuels.



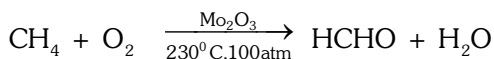
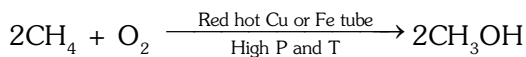
(b) **Incomplete oxidation :** In limited supply of air, alkane gives carbon black and CO.



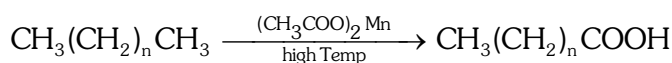
C-black (used in printing ink)

(c) **Catalytic oxidation :**

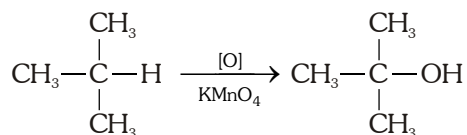
(i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.



(ii) Alkanes on oxidation in presence of manganese acetate give fatty acids.

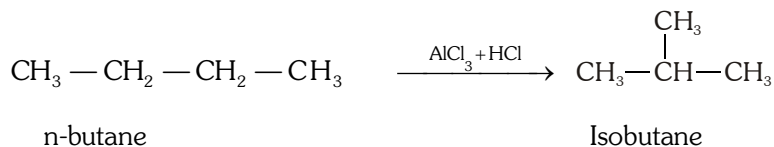


(iii) Tertiary alkanes are oxidized to give tertiary alcohols by KMnO_4 .

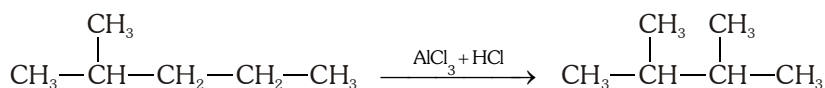


(2) **Substitution Reactions :** Substitution reaction in alkanes shows free radical mechanism.

(3) **Isomerization:** Unbranched chain alkanes on heating with $\text{AlCl}_3 + \text{HCl} / 200^\circ\text{C}$ are converted into branched chain alkanes

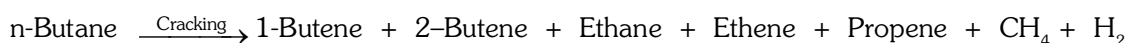
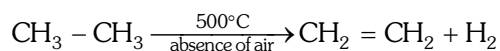
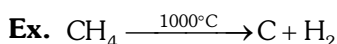


Branched chain alkanes converted to more branched alkane.

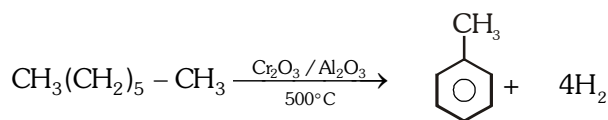


Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

(4) **Pyrolysis or Cracking or thermal decomposition :** When alkanes are heated to $500-700^\circ\text{C}$ they are decomposed into lower hydrocarbon. This decomposition is called pyrolysis.



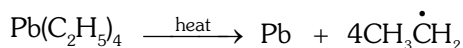
Z:\NODE02\B0A1-B0\TARGET\CHEM\ENG\MODULE-3\0.5 HYDROCARBON\01-THEORY.P65

$$\text{n-hexane} \xrightarrow[500^\circ\text{C}]{\text{Cr}_2\text{O}_3 / \text{Al}_2\text{O}_3} \text{benzene} + 4\text{H}_2$$


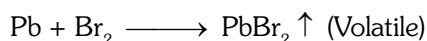
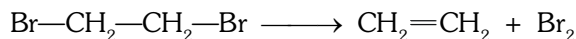
Toluene

Tetra methyl lead – $\text{Pb}(\text{CH}_3)_4$

In cylinder of engine $\text{Pb}(\text{C}_2\text{H}_5)_4$ decomposes in ethyl radicals which combine with the radicals produced due to irregular combustion and this prevents knocking.



but combustion of TEL with petrol gives Litharge (PbO) which deposited in cylinder walls and piston has jammed. So Ethylene dibromide is added with petrol.



BEGINNER'S BOX-2

1. Which of the following reactions of alkanes involve free radical intermediates

- | | |
|------------------|----------------------|
| (1) Halogenation | (2) Pyrolysis |
| (3) Nitration | (4) All of the above |

2. $(\text{CH}_3)_3\text{CMgCl}$ on reaction with D_2O produces

- | | |
|--------------------------------|--------------------------------|
| (1) $(\text{CH}_3)_3\text{CD}$ | (2) $(\text{CH}_3)_3\text{OD}$ |
| (3) $(\text{CD}_3)_3\text{CD}$ | (4) $(\text{CD}_3)_3\text{OD}$ |

3. The compound with the highest boiling point is—

- | | |
|--------------------------|---------------|
| (1) n-hexane | (2) n-pentane |
| (3) 2,2-dimethyl propane | (4) propane |

4. Photochemical chlorination of alkane is initiated by a process of

- | | |
|---------------|------------------|
| (1) pyrolysis | (2) substitution |
| (3) Homolysis | (4) Peroxidation |

5. Isomerization in alkane may be brought about by using :

- (1) Al_2O_3
- (2) Fe_2O_3
- (3) AlCl_3 and HCl
- (4) Concentrated H_2SO_4

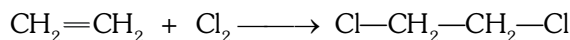
6. Bromination of an alkane as compared to chlorination proceeds

- (1) At a slower rate
- (2) At a faster rate
- (3) With equal rates
- (4) With equal or different rate depends upon the temperature

5.2 ALKENES (OLEFINS)

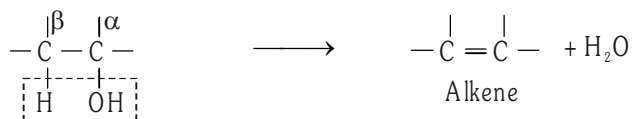
5.2.1 Introduction of Alkenes

Alkene are also called olefins (oil forming) since the first member ethylene (C_2H_4) was found to form an only liquid on reaction with chlorine.



5.2.2 General Methods of Preparation

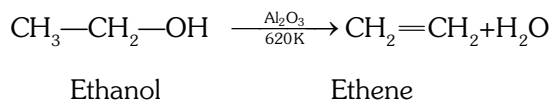
(1) **From Alcohols** : Alkenes can be prepared from monohydric alcohols or alkanols by the loss of H_2O and the reaction is known as **dehydration reaction**.



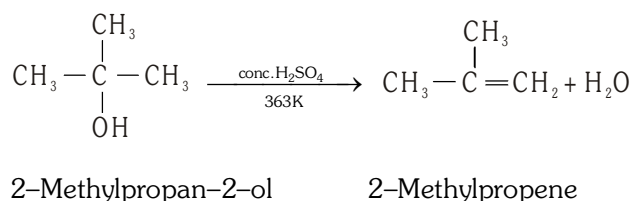
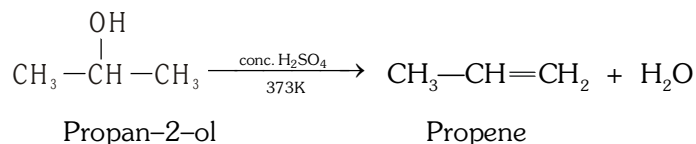
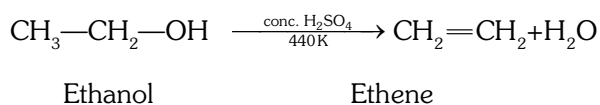
Alcohol

The dehydration can be carried with Al_2O_3 or with **mineral acid** upon heating.

(a) **Dehydration with Al_2O_3** : Ethene is prepared by heating ethanol with Al_2O_3 at 620 K.

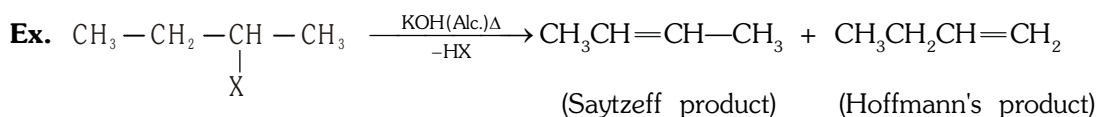
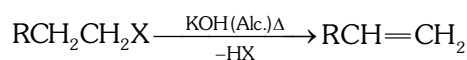


(b) **Dehydration with mineral acid** : Alcohols upon heating with conc. H_2SO_4 form alkenes and the reaction is called **acidic dehydration**.



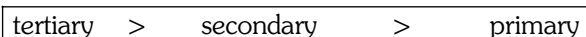
From the above reactions, it is clear that the order of acidic dehydration in different alcohols is Tertiary > Secondary > Primary

(2) **From Alkyl halide (By dehydrohalogenation)**: Removal of HX from a substrate by alcoholic KOH or $NaNH_2$

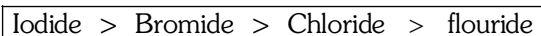


The ease of dehydrohalogenation show the order

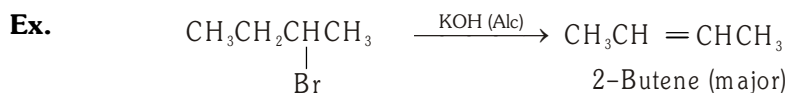
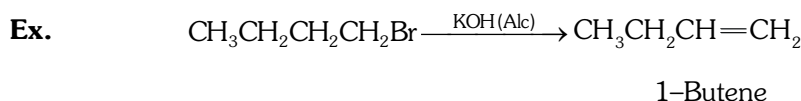
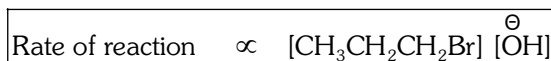
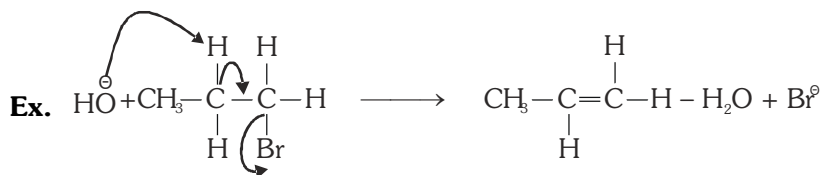
For alkyl group



For halogen in halide

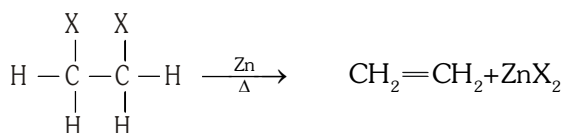


It is single step and synchronous process. Removal of proton, the formation of multiple bond between C α and C β and the release of the leaving group X take place simultaneously. (E₂ mechanism)

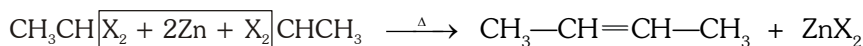


(3) From Alkyl dihalide (By dehalogenation of Vicinal or Gem dihalide) : Removal of X₂ from a substrate by Zn dust or Zn—Cu in alcoholic Solution..

(a) From **Vicinal dihalide** : same number carbon alkene is obtained.



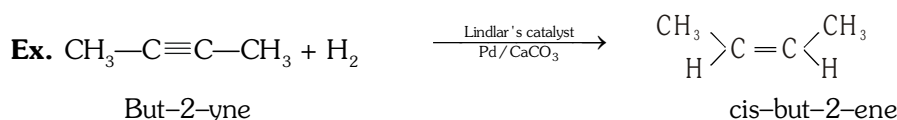
(b) From **gem dihalide** : Higher alkene obtained



(4) By the controlled hydrogenation of alkynes :

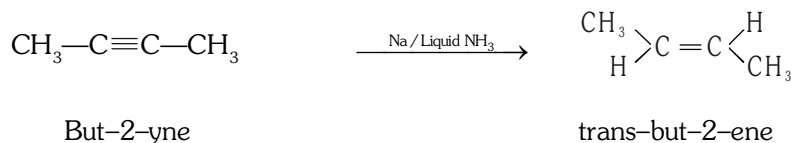
Alkynes can be converted into alkenes as a result of **controlled reduction** in two ways:

(a) **By the use of Lindlar's catalyst** : Lindlar's catalyst is a mixture of palladium catalyst deposited over barium sulphate or calcium carbonate. The catalytic mixture is slightly poisoned by quinoline or sulphur and allows the reduction or hydrogenation of alkyne with hydrogen only upto the alkene stage. The major product is cis-Alkene.

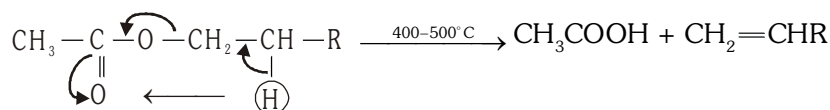


In place of Lindlar's catalyst Nickel-boride (Ni-B also called P-2 catalyst) can also be used.

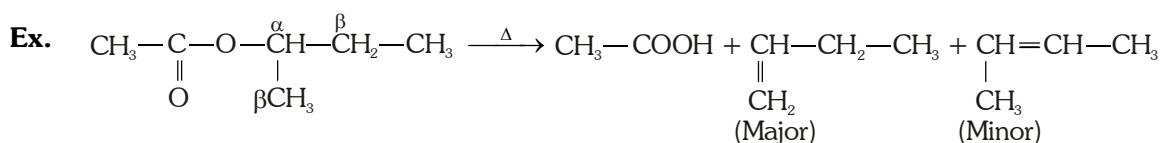
- (b) **By the action of sodium in liquid ammonia :** This is known as **Birch reduction** and the major product is a **trans alkene** i.e., the two hydrogen atoms get attached on the opposite side of the double bond. For example,



(5) By Pyrolysis of ester :



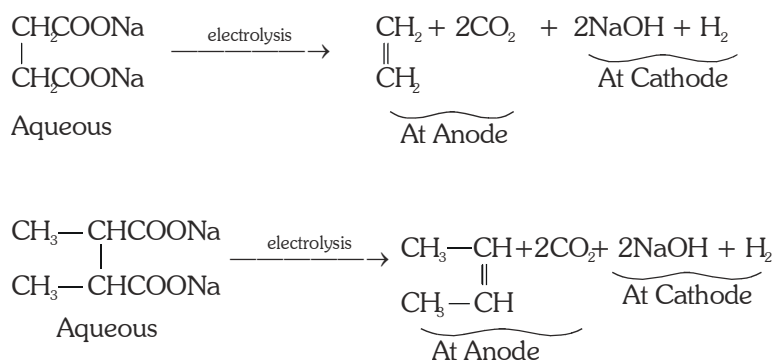
Hoffmann's Rule : Less substituted or less stable alkene is major product.



In the reaction to form an alkene a β -hydrogen from alkyl ester is attracted by oxygen atom of keto group.

(6) By Pyrolysis of tetra alkyl ammonium hydroxide :

- (7) By Kolbe's method:** Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.



5.2.3 PHYSICAL & CHEMICAL PROPERTIES OF ALKENES

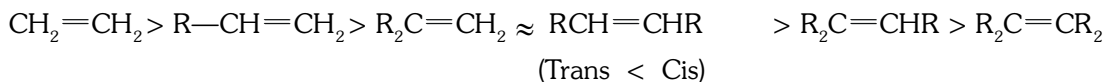
Physical Properties

- (1) All are colourless and have no characteristic odour. Ethene has pleasant smell.
- (2) Lower members (C_2 to C_4) gaseous medium (C_5 to C_{17}) liquid and higher members are solid.
- (3) The B.P., M.P. and specific gravity show a regular increase with increase in molecular weight
- (4) The increase in branching in carbon chain decreases the B.P. among isomeric alkenes.
- (5) The B.P. and M.P. of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable π bond.
- (6) Insoluble in water because they can not form H-bond with water molecule, they dissolve freely in organic solvent like benzene, CHCl_3 , CCl_4 etc.

Chemical Properties : Alkenes are more reactive than alkane this is because -

- (a) The π electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.
- (b) π bond is weaker than σ bond and more easily broken.

The reactivity order for alkenes -



The reactivity order of alkenes has been delt in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation ($\Delta H = -ve$), more is the reactivity, the reactivity of alkene is however also related to

- (i) Steric hinderance
- (ii) Hyperconjugation

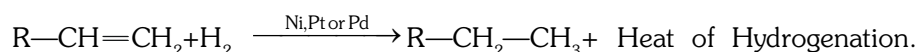
Alkenes give the following type of reactions :

- (A) Addition reaction.
- (B) Oxidation reaction.
- (C) Substitution reaction.
- (D) Polymerization Reaction.
- (E) Isomerisation

(A) Addition Reaction :

[A₁] Free Radical Addition

(1) Addition of H₂ :



- (a) Reaction is exothermic, Heat released in reaction is called heat of hydrogenation.

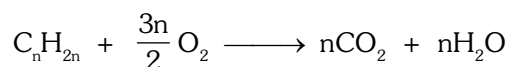
(b)	$\text{Stability of alkene} \propto \frac{1}{\text{heat of hydrogenation}} \propto \frac{1}{\text{reactivity of alkene with H}_2}$
-----	--

- (c) The process is used to obtain vegetable (saturated fats) ghee from hydrogenation of oil.

[A₂] Electrophilic Addition Reactions:

(B) Oxidation Reaction: Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

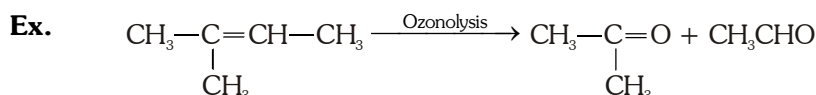
(1) Combustion:



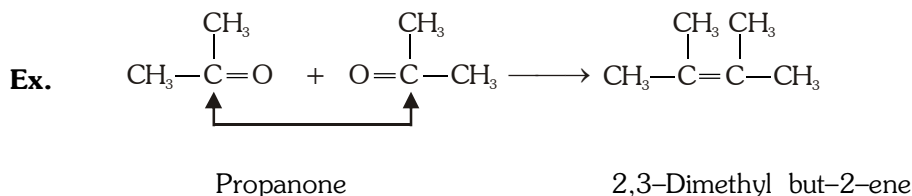
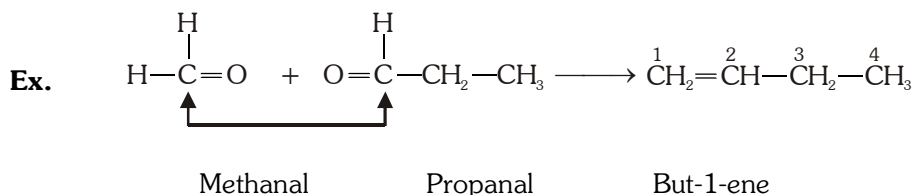
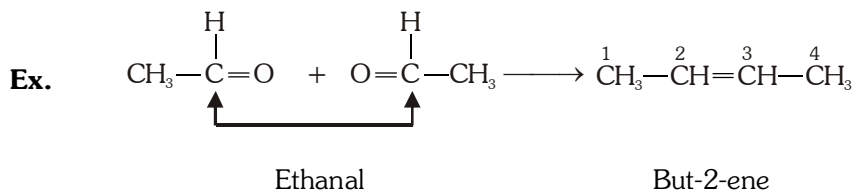
One mole of alkene requires $\frac{3n}{2}$ moles of O₂ for complete combustion.

(2) Ozonolysis : (A test for unsaturation in molecule)

- (i) The addition of ozone on the double bonds and subsequent a reductive hydrolysis of the ozonide formed is termed as ozonolysis.
- (ii) Ozonides are explosive compound.
- (iii) On warming with Zn and H₂O, ozonides cleave at the site of the double bond, the products are carbonyl compound (aldehyde or ketone) depending on the nature of the alkene.



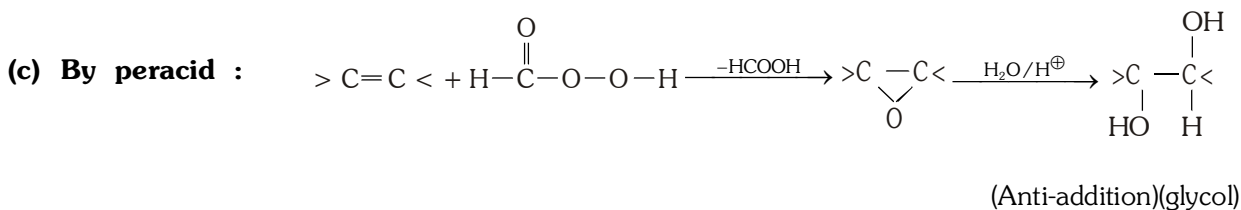
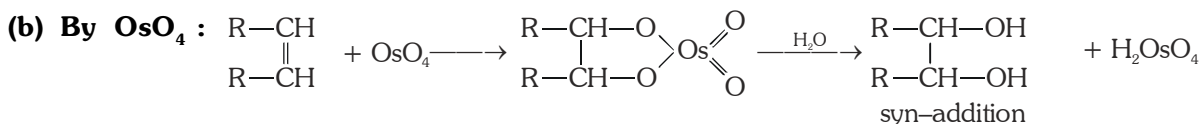
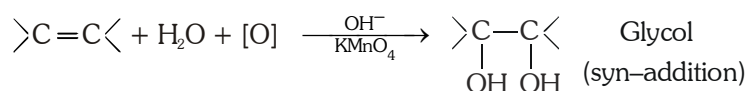
- (iv) Ozonolysis of alkenes helps in locating the position of double bond in an alkene. It can be achieved by joining together the carbon atoms of the two carbonyl compounds formed as the products of ozonolysis with double bond.



It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond.

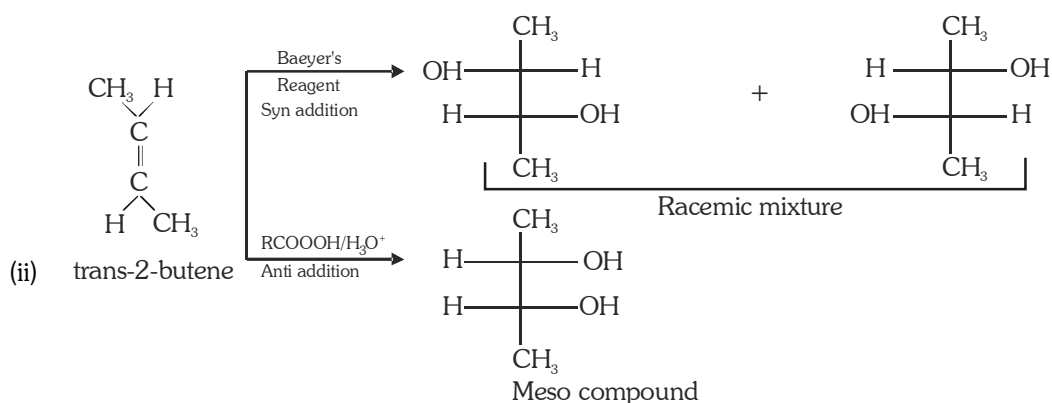
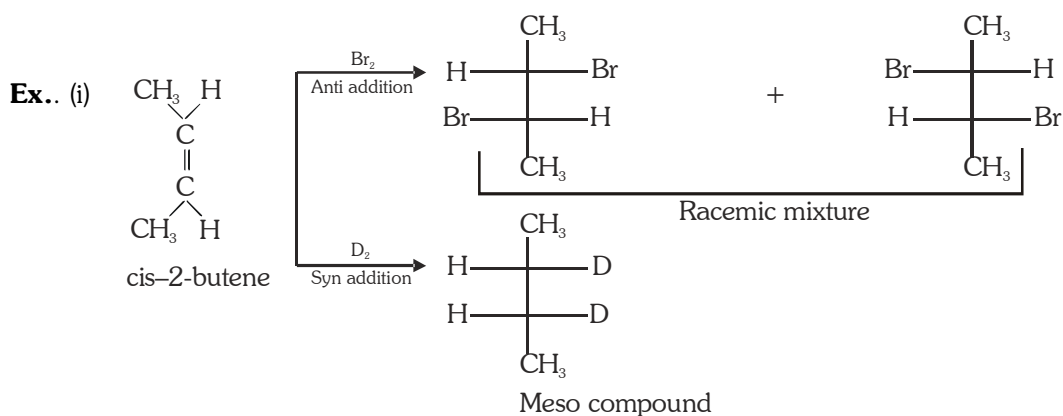
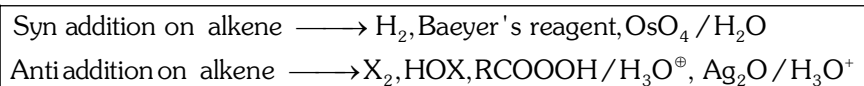
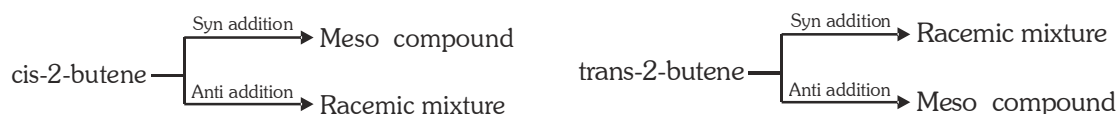
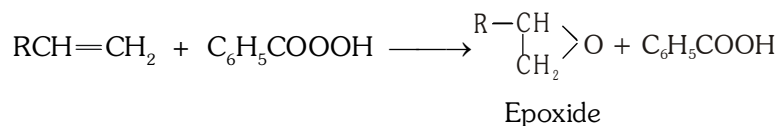
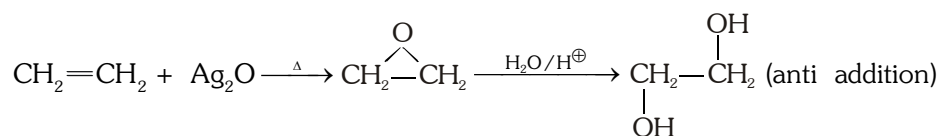
(3) Hydroxylation : Oxidation of carbon-carbon double bond to $\begin{array}{c} | \qquad | \\ -\text{C}-\text{C}- \\ | \qquad | \\ \text{OH} \quad \text{OH} \end{array}$ is known as hydroxylation.

- (a) Oxidation by Baeyer's reagent** (A test for unsaturation) : Alkenes on passing through dilute alkaline 1% cold KMnO_4 (i.e., Baeyer's reagent) decolourise the pink colour of KMnO_4 and gives brown ppt of MnO_2 . The reaction involves syn addition.

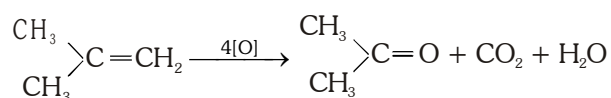
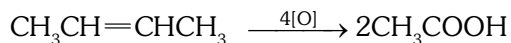
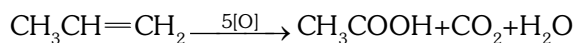


(d) By $\text{Ag}_2\text{O}/\Delta$:

(a) Alkenes reacts with oxygen in the presence of Ag catalyst at $250^\circ\text{--}400^\circ\text{C}$ to form epoxide.

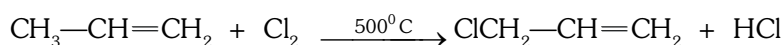


- (4) Oxidation by strong oxidising agent (Oxidative cleavage):** The alkenes themselves are readily oxidised to acid or ketone by means of acid permanganate. If HCOOH is formed, it further oxidized to CO₂ and H₂O. Keep it in mind that no further oxidation of ketones will take place.



(C) Substitution Reaction (Allylic Substitution):

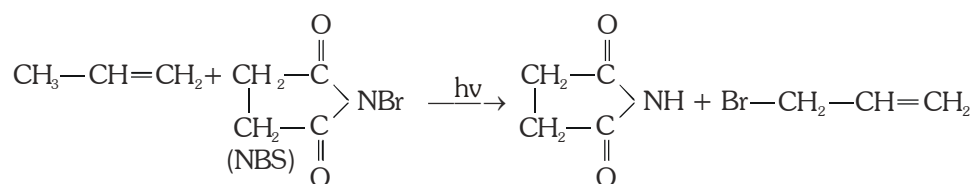
When alkenes are treated with low concentration of Cl₂ or Br₂ at high temperature or with NBS/hν one of their allylic hydrogen is replaced by halogen atom. Allylic position is the carbon adjacent to one of the unsaturated carbon atoms. It is free radical substitution.



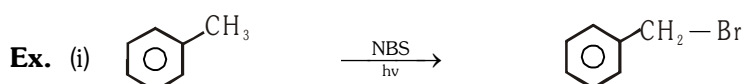
Allyl chloride

(3-Chloro-1-propene)

N-Bromosuccinimide (NBS) is an important reagent used for allylic bromination and benzylic substitution.



Substitution reaction is not given by ethene.



3° (more stable)

(D) Polymerization:

- Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecule having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.
- Molecular weight of polymer is simple multiple of monomer.
- Polymerization can be carried out by free radical or ionic mechanism.

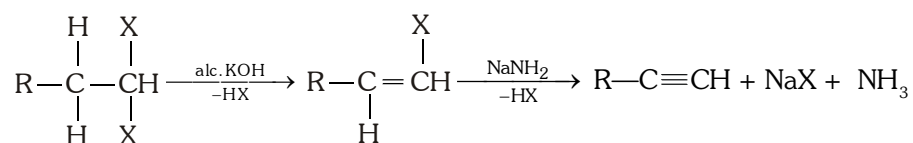
5.3 ALKYNES

5.3.1 Introduction of Alkynes

Alkynes are unsaturated hydrocarbons and characterised by the presence of a triple bond between the two carbon atoms ($C \equiv C$). The carbon-carbon triple bond is also called acetylenic bond. It consists of a strong σ and two weak π bonds. Alkynes are isomers of alkadienes and cycloalkenes.

5.3.2 General Methods of Preparation

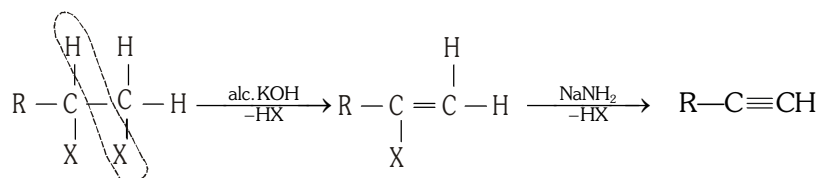
(1) From Gem dihalides (by dehydrohalogenation) : Dehydrohalogenation agents are : $NaNH_2$ (Sodamide) or Alc. KOH or ROH + RNa.



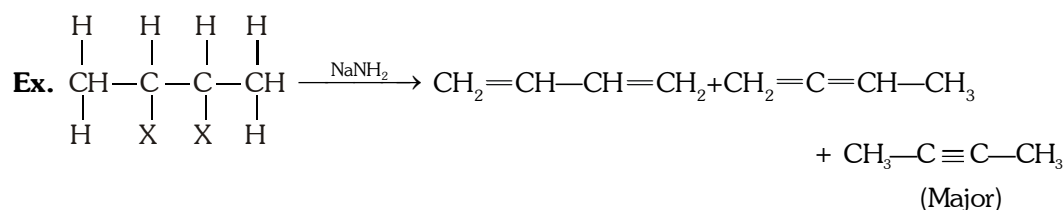
(Stable by resonance)

(Vinyl halide)

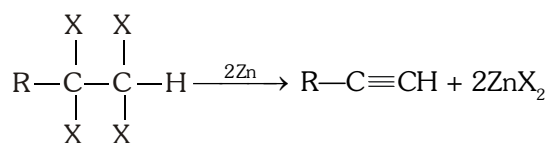
(2) From Vicinal dihalides (by dehydrohalogenation) :



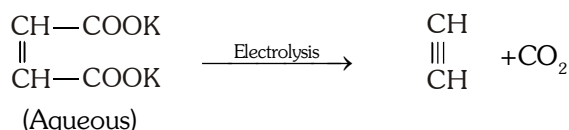
(a) Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.



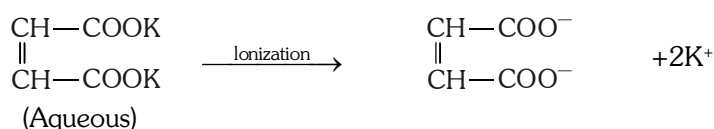
(3) Dehalogenation of tetrahalo alkane : By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



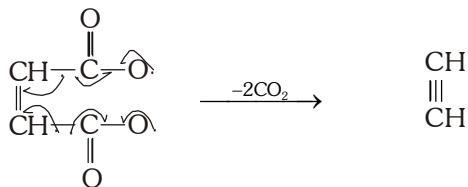
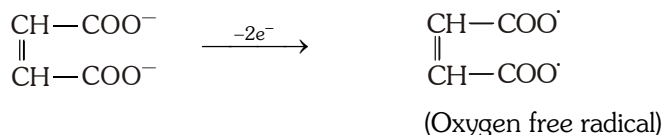
(4) From Kolbe's electrolysis : By the electrolysis of aqueous Solution. of sodium or potassium fumarate or maleate, acetylene is formed at anode.



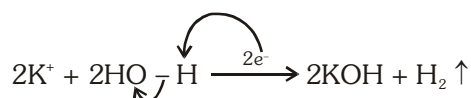
Mechanism :



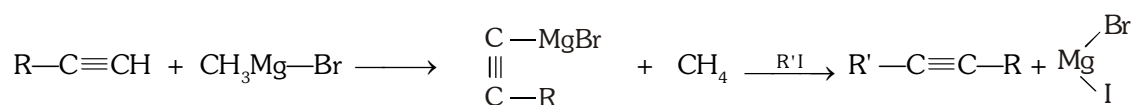
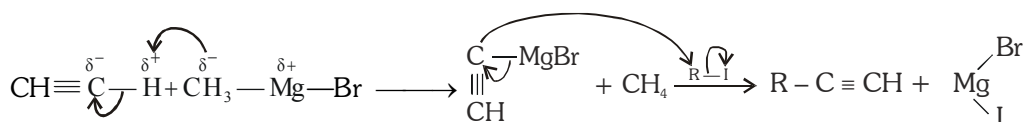
at anode (Alkyne and CO₂ gas is formed)



at cathode (KOH and H₂ gas is formed)

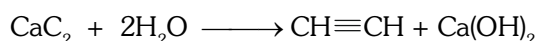


(5) Preparation of higher alkynes by Grignard reagent : By this method lower alkyne is converted in to higher alkyne

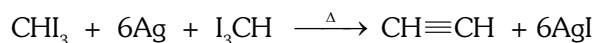


(6) Preparation of Ethyne or Acetylene:

(a) From Metal carbide [Laboratory method] : Acetylene is prepared in the laboratory by the action of water on calcium carbide.



(b) From haloform [CHI₃, CHCl₃] : Pure acetylene is obtained when iodoform or chloroform is heated with Silver powder



5.3.3 Physical & Chemical Properties of Alkynes

Physical Properties

- (i) First three members [C₂ to C₄] are gases, from C₅ to C₁₂ are liquid and after that they are solid.
- (ii) Alkynes are slightly soluble in H₂O but soluble in CCl₄, benzene, acetone and alcohol.
- (iii) B.P., M.P. and densities of alkynes are comparatively more than alkenes and alkanes due to more polarisation.

$\text{B.P.} \propto \text{mol.wt.} \propto \frac{1}{\text{number of side chains}}$

Chemical Properties

The chemical properties of alkynes are due to two factors

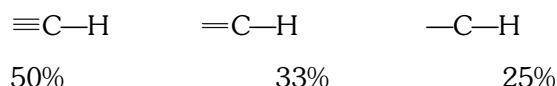
- (a) **Presence of π electrons** : Due to presence of loosely bonded π electrons, alkynes like alkenes, undergo easily electrophilic addition reaction.

Carbon-carbon triple bond is less reactive than the carbon-carbon double bond towards electrophilic addition reactions.

In addition to electrophilic additions, alkynes also undergo nucleophilic addition with nucleophiles

- (b) **Presence of acidic hydrogen atom** : The hydrogen atom attached to the triple bonded carbon can be removed by a strong base and hence acetylene and 1-alkynes are considered as weak acids.

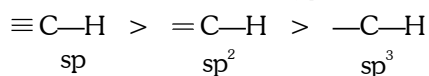
Explanation : The amounts of s-character in various types of C—H bonds is as-



Since s electrons are closer to the nucleus than the p electrons, the electrons present in a bond having more s-character will be closer to nucleus. Due to high s-character of the C—H bond in alkyne (s=50%) the electrons constituting this bond are more strongly held by the carbon nucleus, with the result the H present on $\equiv\text{C}-\text{H}$ can be easily removed as proton.

GOLDEN KEY POINTS

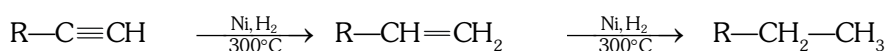
- The acidic nature of the three types of $-\text{C}-\text{H}$ bonds as



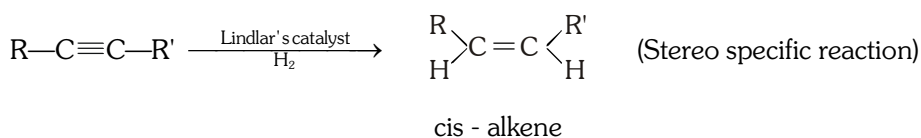
- Relative acidic order $\text{H}_2\text{O} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{HNH}_2 > \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH}_3$

(1) Addition reaction

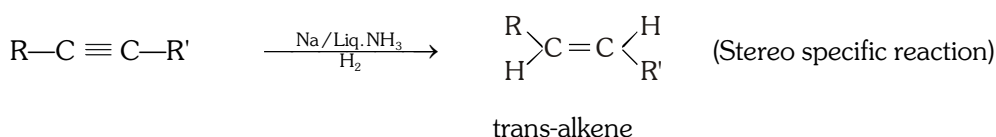
- (a) **Addition of hydrogen** : Alkynes react with hydrogen in presence of a catalyst. In presence of Pt., Pd or Ni alkynes give alkanes with H_2



In presence of Lindlar's catalyst [Pd / CaCO_3 + quinoline or Nickel boride] alkynes give cis - alkene

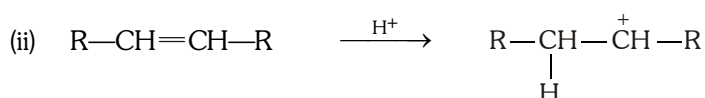
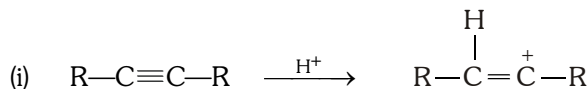


In presence of Na/NH_3 alkynes give trans-alkene. **(Birch Reduction)**



(b) Electrophilic addition : Addition reactions where the addition is initiated by electrophile (positive group). The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in $C\equiv C$, the π electrons are tightly held by carbon nuclei and so they are less easily available for reaction with electrophiles.

Another reasons is : The intermediates when an electrophile attack on alkene and alkynes are :

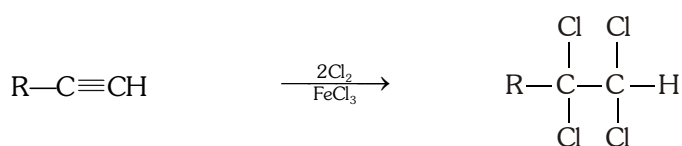


Stability of intermediates :

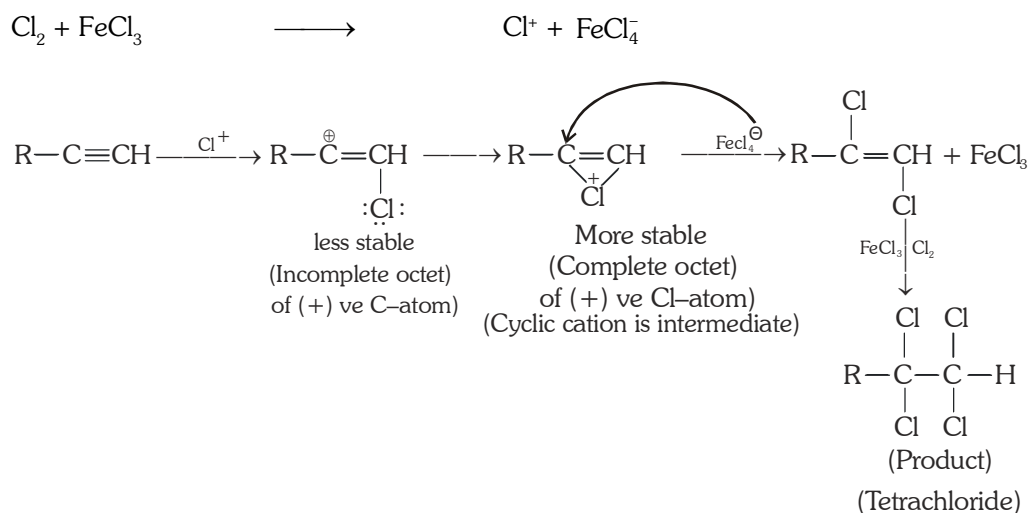


So we can say that alkenes are more reactive towards electrophilic addition reaction.

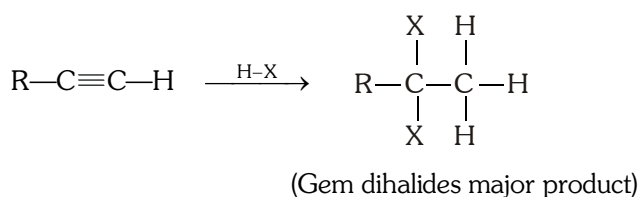
(i) Addition of Halogens : Alkynes react with Cl_2 or Br_2 in dark in presence of metal halide and form di and tetra halo derivatives.

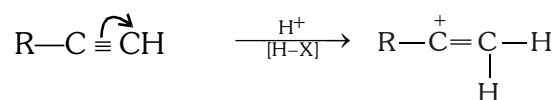


Mechanism :

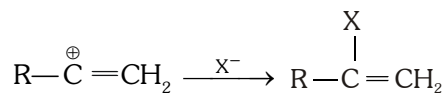


(ii) Addition of halogen acids (H - X) : Addition according to Markovnikov's Rule.

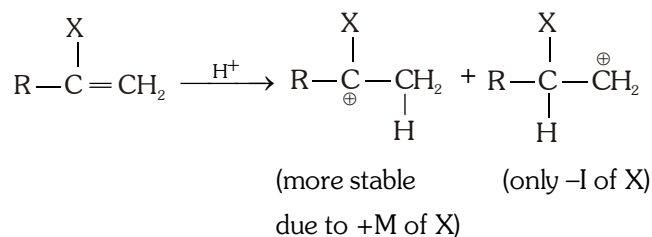


Mechanism :

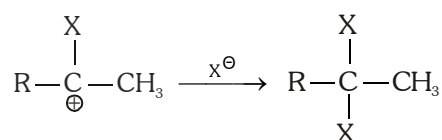
(Intermediate is carbocation)



Further

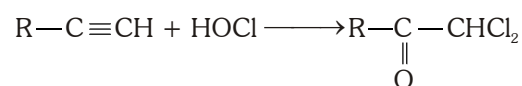
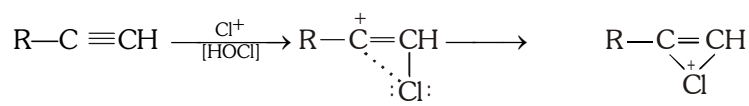


so

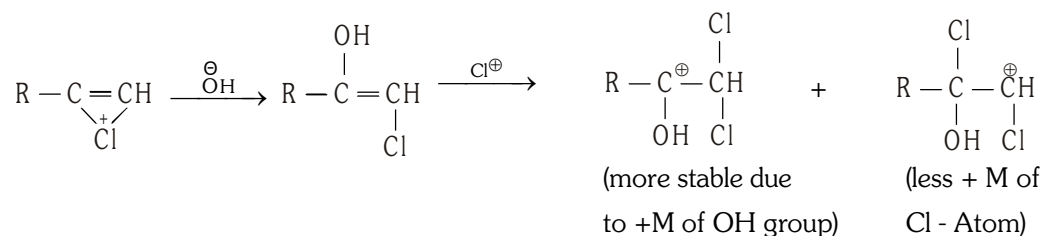


(Major Product)

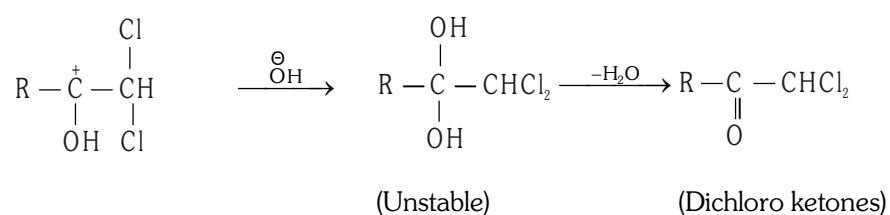
(iii) Addition of HOX : Alkynes react with hypohalous acids according to Markovnikov's rule and form gem diol, which are unstable, lose a molecule of water and form dihalo aldehyde or dihalo ketones.

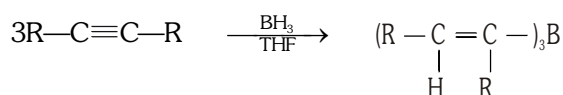
**Mechanism :**

(Cyclic cation)

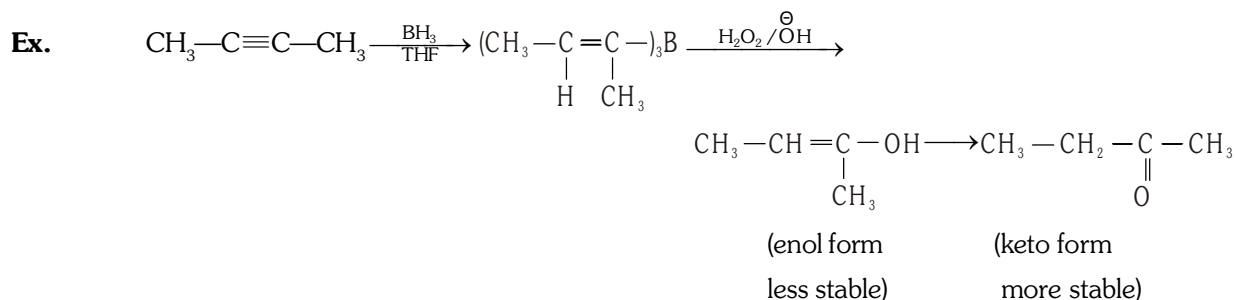
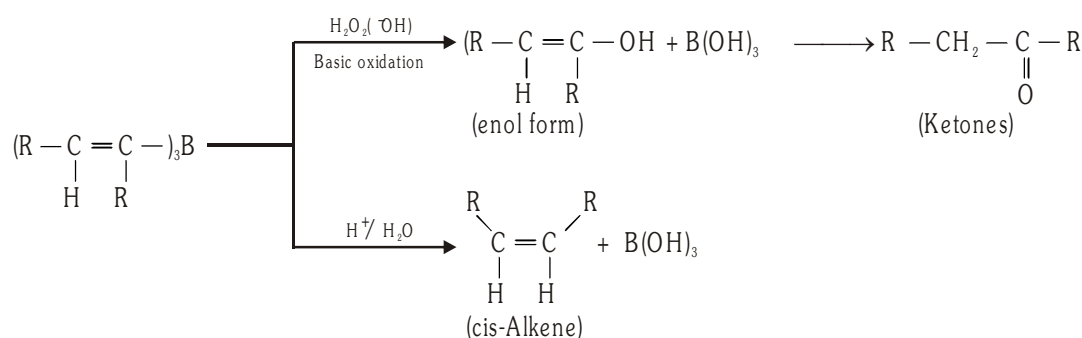
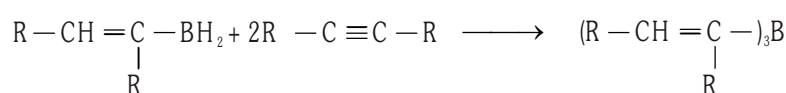
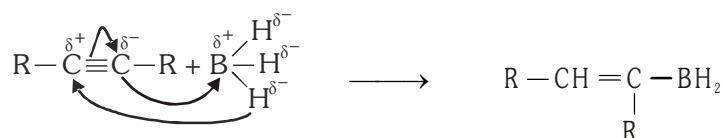


so



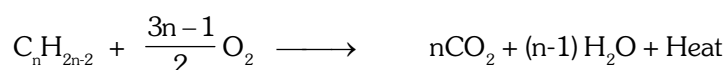


Since BH_3 is not available as monomer so a solvent THF is used for the stability of BH_3 .



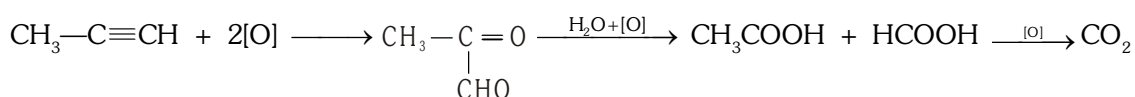
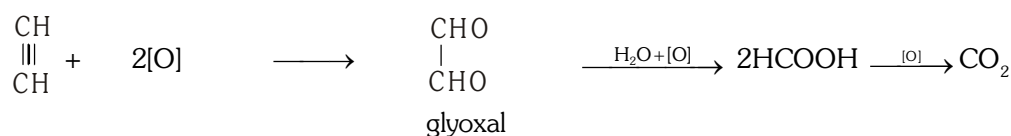
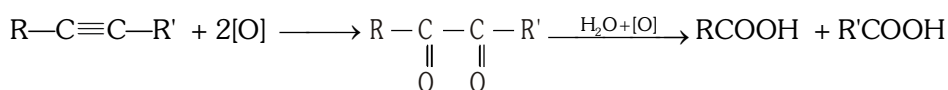
(2) Oxidation Reactions

(a) Combustion :

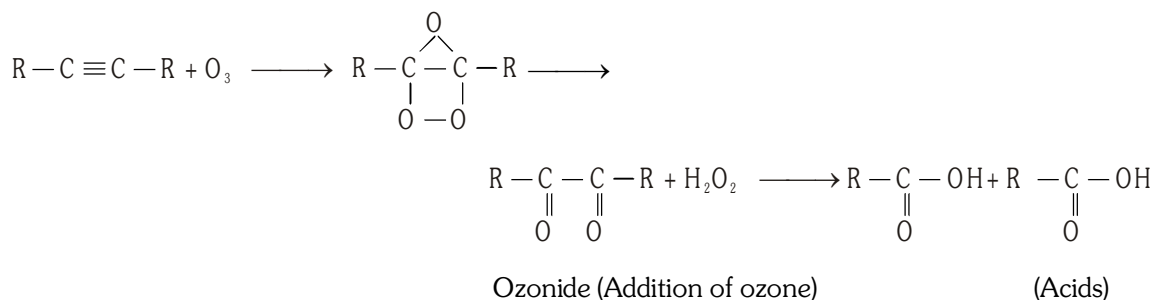


The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000°C) is produced.

(b) Oxidation with acidic $KMnO_4$: In presence of acidic $KMnO_4$, alkynes are oxidised to monocarboxylic acids.

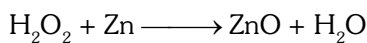


(c) Oxidation with ozone (O₃): In the ozonolysis both sp-C-atoms are converted into $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—C—} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ group.

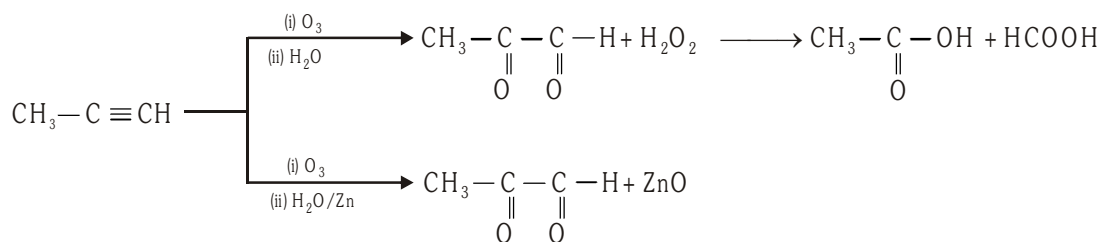


In this reaction H₂O₂ is oxidant which oxidise $\begin{array}{c} \text{R—C—C—R} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ into acids.

But if we use some amount of Zn as reductant with H₂O then it reduce H₂O₂ so oxidation does not take place



Ex.

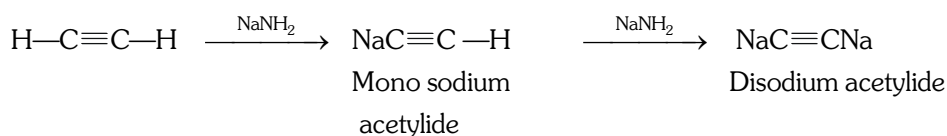


(3) Substitution Reaction : (Formation of metallic derivatives)

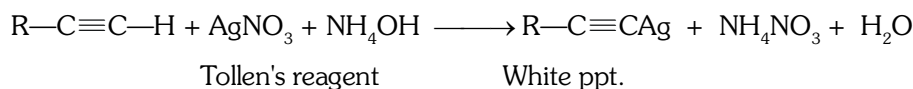
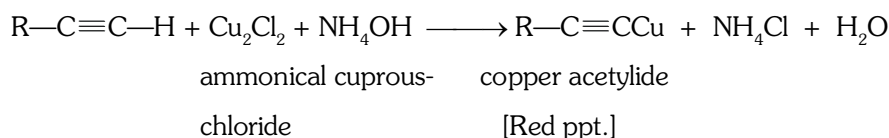
Only 1-alkynes give substitution reaction and show acidic characters $\equiv \overset{\delta^-}{\text{C}}\text{—}\overset{+\delta}{\text{H}}$

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two H⁺ where as propyne can give one H⁺.

(a) Formation of sodium acetylides : Acetylene and 1-alkynes react with sodamide to form acetylides

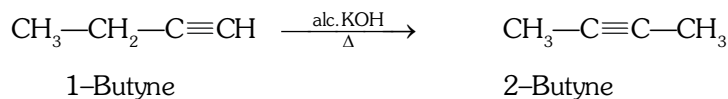


(b) Formation of copper and silver acetylides : Copper and silver acetylides are obtained by passing 1-alkynes in the ammonical Solution. of cuprous chloride and silver nitrate (Tollen's reagent) respectively.

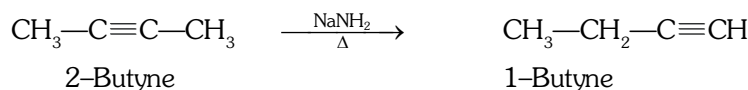


These reactions are used for detecting the presence of acetylenic hydrogen. These are test to distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

(4) Isomerisation: When alkyne-1 is heated with alc. KOH alkyne-2 is obtained.



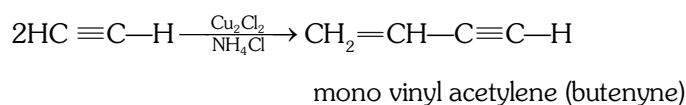
When alkyne -2 is heated with NaNH_2 alkyne -1 is obtained



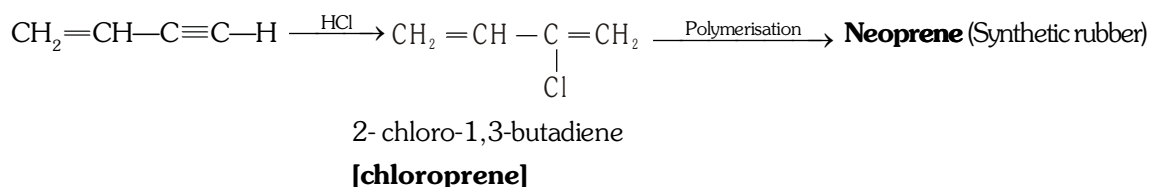
(5) Polymerisation :

(a) Linear polymerisation :

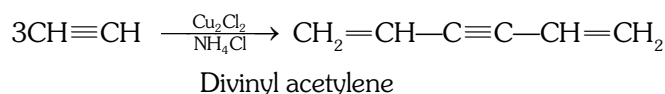
Dimerisation : When two molecules of acetylene passed through a Solution. of Cu_2Cl_2 and NH_4Cl a vinyl acetylene is obtained.



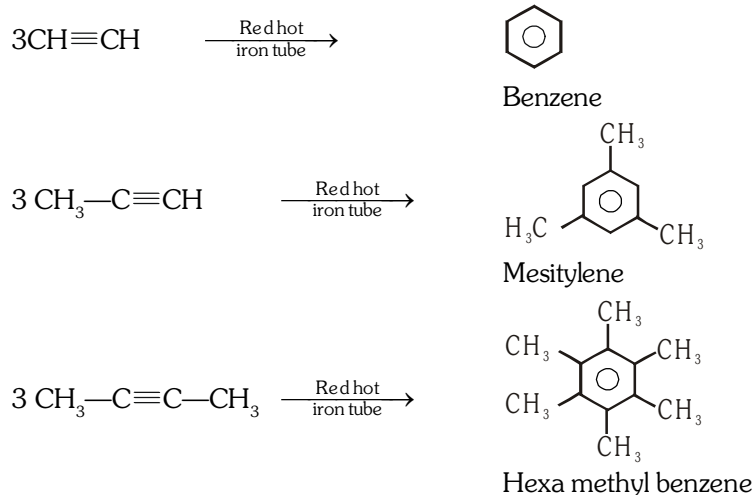
When vinyl acetylene react with HCl then chloroprene is obtained.



Trimerisation : 3 molecules of acetylene.



(b) Cyclic polymerisation : When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound



Uses of Acetylene

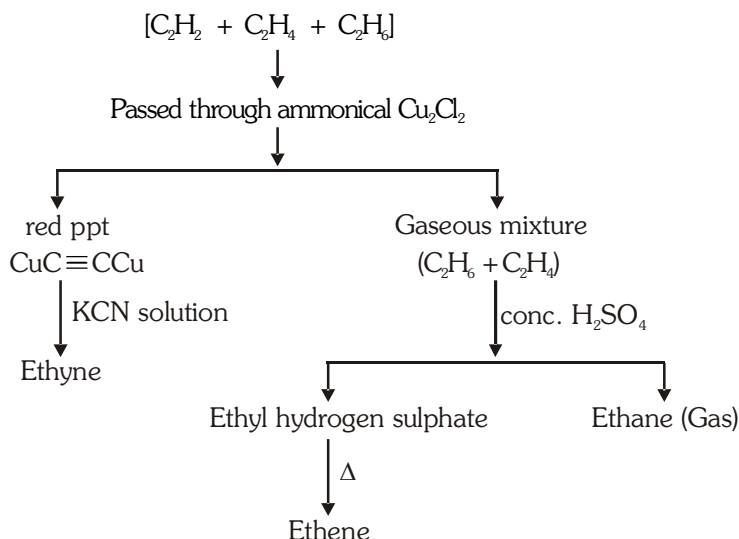
- (i) Oxyacetylene flame used in welding and cutting
- (ii) Acetylene is used as an illuminant
- (iii) Acetylene is used for artificial ripening of fruits
- (iv) Used for manufacture of acetaldehyde, acetic acid, ethyl alcohol, westron, westrosol, PVC, PVA, Chloroprene, butadiene, Lewisite etc.
- (v) It is used as a general anaesthetic.

Test for alkynes :

- (i) Decolourization of Br_2 in CCl_4 Solution..
- (ii) Decolourisation of 1% alkaline KMnO_4 Solution..
- (iii) 1- alkynes give white ppt. with ammonical AgNO_3 and red ppt with ammonical cuprous chloride Solution..

Note : (i) and (ii) tests are used for determination of unsaturation (i.e, presence of double or triple bond in any compound). (iii) Test is used for distinguish between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.

Separation of ethane, ethene and ethyne :



BEGINNER'S BOX-4

1. Propyne and HCl in presence of peroxide gives :
(1) 1,1-dichloro propane (2) 1,2-dichloro propane (3) 1,3-dichloro propane (4) 2,2-dichloro propane
2. $\text{CH}_3-\text{C}\equiv\text{CH} \xrightarrow[\text{(ii) H}_2\text{O}_2/\text{-OH}]{\text{(i) BD}_3} \text{A}$, A is
(1) $\text{CH}_3-\underset{\text{D}}{\text{CH}}-\text{CH}_2-\text{OH}$ (2) $\text{CH}_3-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{D}$ (3) $\text{CH}_3-\underset{\text{D}}{\text{CH}}-\text{CHO}$ (4) $\text{CH}_3-\underset{\text{D}}{\text{CH}}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{D}$
3. Which of the following decolourise 1% alkaline KMnO_4
(1) Propene (2) Propyne (3) 2-butyne (4) All of them
4. 1-Alkyne and 2-Alkyne can not be distinguished by :
(1) Ammonical AgNO_3 (2) Baeyer's reagent (3) Br_2 in CCl_4 (4) 2 and 3 both
5. $\text{CH}\equiv\text{CH} \xrightarrow{\text{CH}_3\text{MgBr}} \text{A (gas)} + \text{B}$, $\text{B} \xrightarrow{\text{CH}_3\text{-I}} \text{C}$. C is :
(1) CH_4 (2) CH_3-CH_3 (3) $\text{CH}\equiv\text{C}-\text{CH}_3$ (4) $\text{CH}_3-\text{C}\equiv\text{C}-\text{I}$

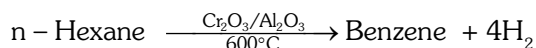
5.4 AROMATIC HYDROCARBONS [ARENES]

5.4.1 Introduction of Arenes

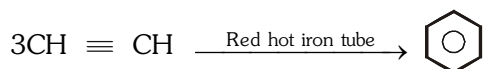
- Arenes are cyclic, planar and follow Huckel's rule.
- There should be cyclic resonance in Arenes.
- General formula of Arenes are $C_n H_{2n-6y}$ where n = Number of carbons
 y = Number of rings
- Characteristic reaction of arenes is Electrophilic substitution reaction (ESR).
- Arenes are cyclic unsaturated compounds but do not give test of unsaturation with Br_2/CCl_4 or alk. $KMnO_4$.
- Main source of Arenes is coaltar.
- They have higher percentage of carbon so burn with smoky flame.

5.4.2 General Methods of Preparation

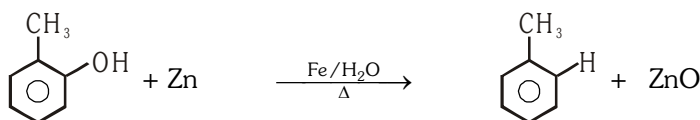
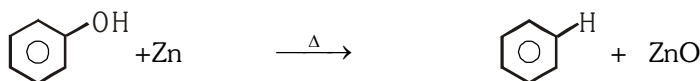
(i) From alkanes (By cyclisation or Aromatisation) Hydroforming or catalytic reforming



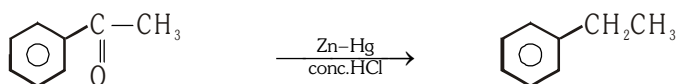
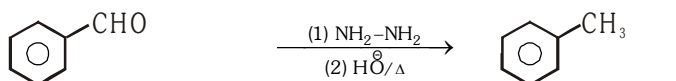
(ii) From alkyne (By cyclic polymerisation) When acetylene is passed through red hot metallic tube cyclic polymerisation takes place and benzene is formed.



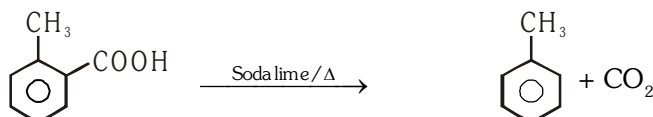
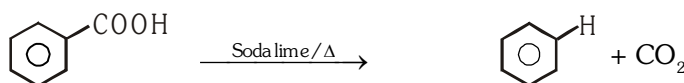
(iii) From Phenolic compounds (By deoxygenation) :



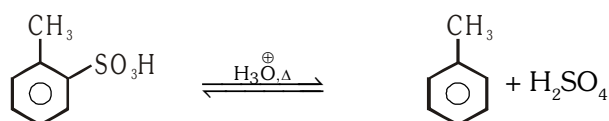
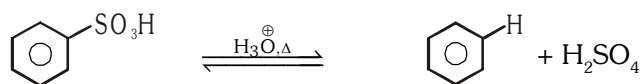
(iv) From carbonyl compounds (By reduction) :



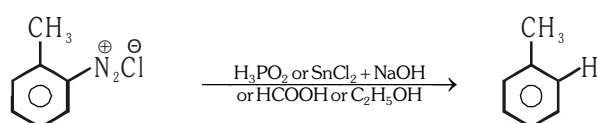
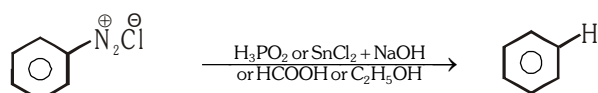
(v) From carboxylic acids (By decarboxylation) :



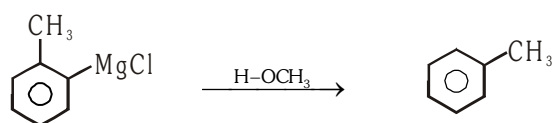
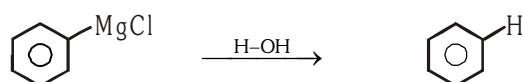
(vi) From sulphonic acids (By hydrolysis) :



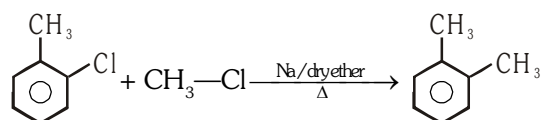
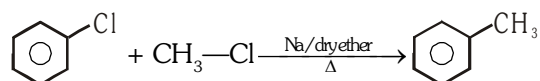
(vii) By diazonium salts :



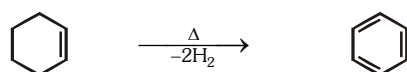
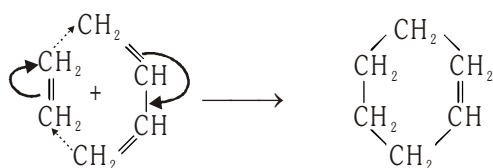
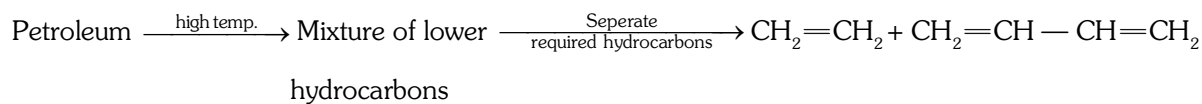
(viii) By Grignard reagent :



(ix) By Wurtz fittig reaction :



(x) From petroleum :



5.4.3 Physical & Chemical Properties of Arenes

Physical properties :

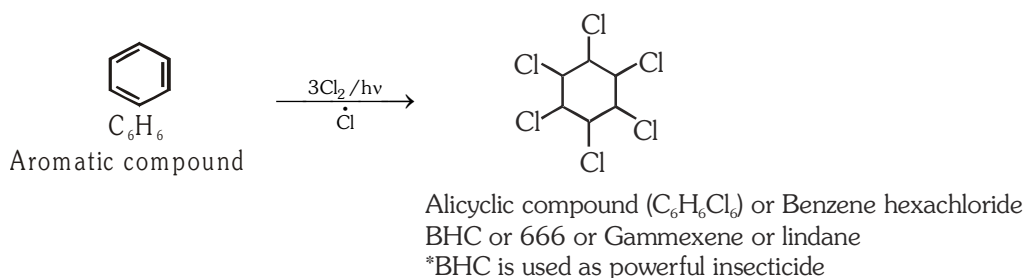
- (i) Benzene is colourless liquid [B.P. is 80°C]
- (ii) Benzene is insoluble in H₂O and density less than H₂O
- (iii) Benzene is used as a solvent and it is soluble in organic solvents.
- (iv) It is highly inflammable and burns with smoky flame.

Chemical properties : Benzene show following types of reaction –

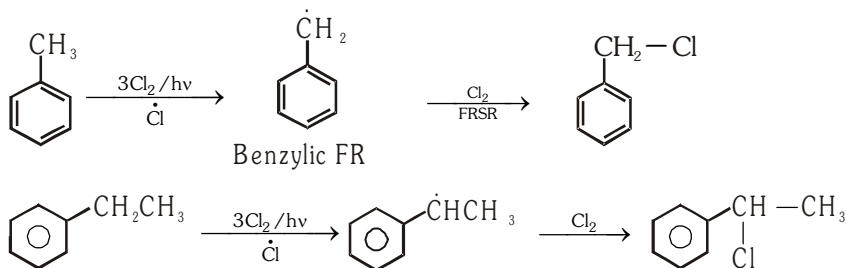
- (A) Addition reactions (B) Electrophilic substitution reactions (C) Oxidation reactions

(A) Addition reaction :

(i) Addition of X₂

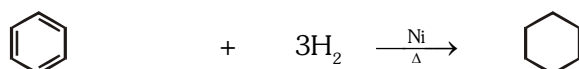


Formation of BHC from C₆H₆ is an example of free radical addition reaction.

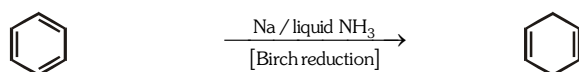


(ii) Addition of H₂ :

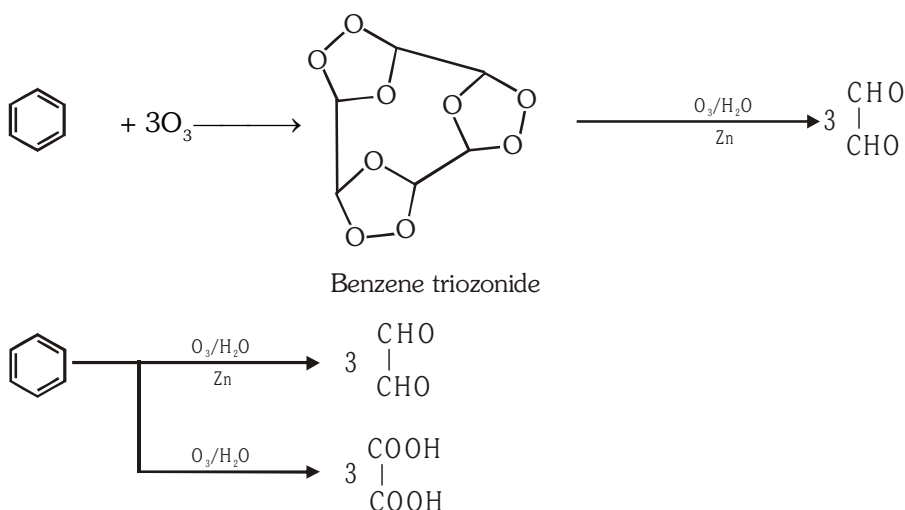
(a) Complete hydrogenation :

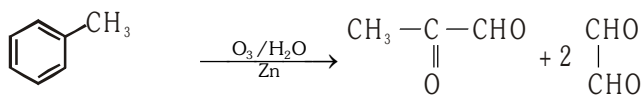


(b) Partial hydrogenation :



(iii) Addition of O₃ :

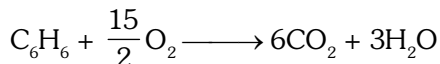




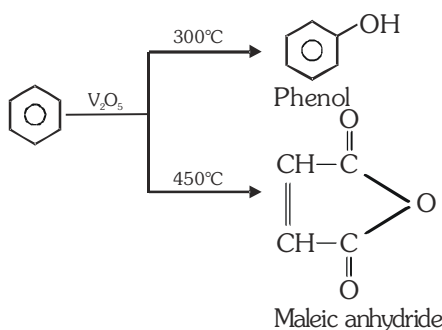
Addition of 3 mole Cl_2 or 3 mole H_2 or 3 mole O_3 on benzene show presence of 3 double bonds in benzene. Benzene does not give addition reaction with Br_2/CCl_4 or alkaline KMnO_4

(C) Oxidation reactions :

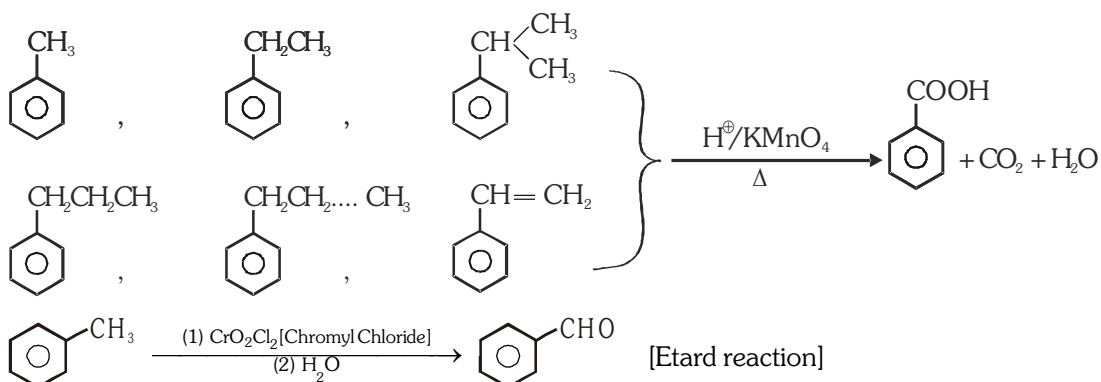
(i) Combustion :



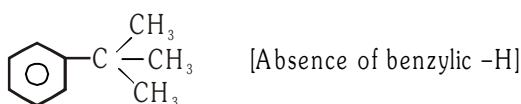
(ii) Catalytic Oxidation :



(iii) Side chain Oxidation : Atleast one benzylic -H containing alkyl benzene gives benzoic acid in presence of strong oxidising agent.



Note : t-butyl benzene does not give benzoic acid in presence of H^+/KMnO_4 , since t-butyl benzene does not contain benzylic-H

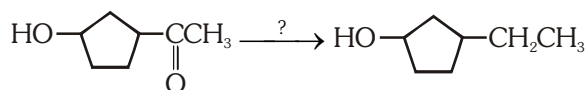


ANSWER KEY

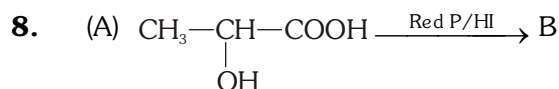
BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7
	Ans.	2	4	3	3	2	2	1
BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	
	Ans.	4	1	1	3	3	1	
BEGINNER'S BOX-3	Que.	1	2	3	4	5		
	Ans.	1	3	3	1	2		
BEGINNER'S BOX-4	Que.	1	2	3	4	5		
	Ans.	4	3	4	4	3		

EXERCISE-I (Conceptual Questions)**ALKANES**

- The order of reactivity of alkyl halides in Wurtz reaction is
 - (1) $R-I > R-Br > R-Cl$
 - (2) $R-I < R-Br < R-Cl$
 - (3) $R-Br > R-I < R-Cl$
 - (4) $R-I > R-Cl > R-Br$
- Kolbe's electrolysis of a mixture of pot. Propanoate and pot. 3-Methylbutanoate gives
 - (1) Butane and isobutane
 - (2) Butane and 2,5-dimethylhexane
 - (3) Butane, 2,5-dimethylhexane and isohexane
 - (4) Butane and isohexane
- The Corey-House alkane synthesis is carried out by treating an alkyl halide with
 - (1) Lithium metal
 - (2) Copper metal
 - (3) Lithium metal followed by reaction with cuprous iodide and then treating the product with an alkyl halide
 - (4) Cuprous iodide followed by reaction with alkyl halide
- Which of the following acids on decarboxylation gives isobutane
 - (1) 2,2-Dimethyl butanoic acid
 - (2) 2,2-dimethyl propanoic acid
 - (3) 3-Methyl pentanoic acid
 - (4) 2-Methyl butanoic acid
- Which of the following compound is not suitable to obtain from wurtz reaction ?
 - (1) ethane
 - (2) butane
 - (3) isobutane
 - (4) hexane
- When ethyl chloride and n-propyl chloride undergoes wurtz reaction which is not obtained
 - (1) n-butane
 - (2) n-pentane
 - (3) n-hexane
 - (4) isobutane
- Which of the following reagent can be used for following conversion

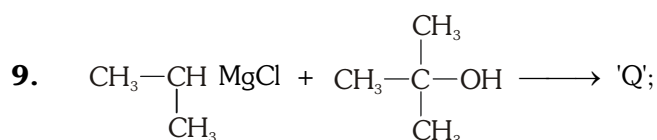


- (1) $\text{Zn} - \text{Hg}/\text{HCl}$
- (2) $\text{Red P} + \text{HI}$
- (3) $\text{NH}_2 - \text{NH}_2/\text{OH}^-$
- (4) All of them

Build Up Your Understanding

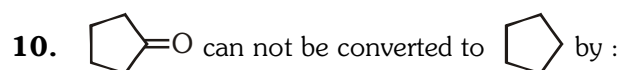
'B' loses its optical activity because of

- (1) Chirality of the molecule destroyed
- (2) Symmetry of molecule is destroyed
- (3) Spatial arrangement is changed
- (4) Racemic mixture is formed

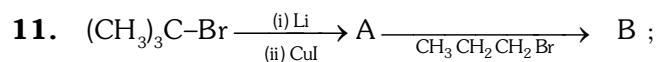


What is 'Q' ?

- (1) isobutane
- (2) isopropane
- (3) tert. butyl chloride
- (4) propane



- (1) Red P + HI
- (2) Wolf Kishner reduction
- (3) Clemmensen reaction
- (4) LiAlH_4



'B' is

- (1) $\text{CH}_3(\text{CH}_2)_2\text{C}(\text{CH}_3)_3$
- (2) $(\text{CH}_3)_3\text{C-C}(\text{CH}_3)_3$
- (3) $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
- (4) $(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$

12. Which of the following reactions does not involve a C—C bond formation

- (1) Hydrolysis of a Grignard reagent
- (2) Combination of two alkyl free radicals
- (3) Corey-House synthesis of alkanes
- (4) $\text{RNa} + \text{R-Br} \longrightarrow \text{R-R} + \text{NaBr}$

13. The highest boiling point is expected for

- (1) Isooctane
- (2) 2,2,3,3-tetramethylbutane
- (3) n-octane
- (4) n-butane

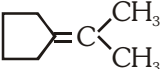
14. Pyrolysis of alkanes is a

- (1) Nucleophilic addition reaction
- (2) Free radical substitution reaction
- (3) Electrophilic addition reaction
- (4) Free radical elimination reaction

15. The antiknocking compound is
 (1) TEL (2) Diethylzinc
 (3) Dimethylcadmium (4) Tetramethyl tin
16. Which of the following reactions of methane is incomplete combustion :-
 (1) $2\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Cu}/523\text{K}/100\text{atm.}} 2\text{CH}_3\text{OH}$
 (2) $\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Mo}_2\text{O}_3} \text{HCHO} + \text{H}_2\text{O}$
 (3) $\text{CH}_4 + \text{O}_2 \longrightarrow \text{C(s)} + 2\text{H}_2\text{O(l)}$
 (4) $\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$

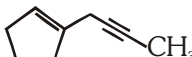
ALKENE

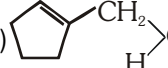
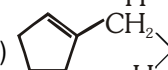
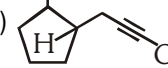
17. Ozonolysis of 3-Methyl-1-butene gives a mixture of
 (1) Propanal and ethanal
 (2) Propanone and ethanal
 (3) 2-Methylpropanal and methanal
 (4) Butanone and methanal
18. Which alkene gives acetone only on ozonolysis
 (1) Isobutylene
 (2) 2,3-Dimethyl-1-butene
 (3) 2,3-Dimethyl-2-butene
 (4) 3,3-Dimethyl-1-butene
19. Oxidation of isobutylene with acid potassium permanganate gives
 (1) Acetone + CO_2
 (2) Acetic acid
 (3) Acetic acid + CO_2
 (4) Acetic acid + acetone
20. Which of the following reactions is used for locating the position of double bond in an alkene
 (1) Hydroboration (2) Hydroxylation
 (3) Chlorohydroxylation (4) Ozonolysis
21. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\Delta]{\text{alc. KOH}} \text{A} \xrightarrow[\text{(ii) Zn, H}_2\text{O}]{\text{(i) O}_3} \text{B} + \text{C}$
 In the above reaction A, B and C are given by the set
 (1) Propylene, acetone, formaldehyde
 (2) Propene, ethanal, methanal
 (3) Propyne, acetaldehyde, formaldehyde
 (4) Propylene, propionaldehyde, formaldehyde
22. Which one of the following has the smallest heat of hydrogenation per mole
 (1) 1-butene (2) Trans-2-butene
 (3) Cis-2-butene (4) Propene

23. An alkene "A" contains three C-C, eight C-H σ -bonds and one C-C π -bond. "A" on ozonolysis gives two moles of an aldehyde of molar mass 44. Which of the following is the IUPAC name of A.
 (1) But-1-ene (2) But-2-ene
 (3) Pent-2-ene (4) But-2-yne
24. The molecules having dipole moment are :-
 (1) 2,2-dimethylpropane
 (2) trans pent-2-ene
 (3) cis-hex-3-ene
 (4) 2 and 3
25. Which of the following alkenes on ozonolysis give a mixture of ketones only?
 (a) $\text{CH}_3\text{-CH=CH-CH}_3$ (b) $\text{CH}_3\text{-CH(CH}_3\text{)-CH=CH}_2$
 (c)  (d) $(\text{CH}_3)_2\text{C=C(CH}_3\text{)CH}_3$
 (1) a and b (2) b and c
 (3) b and d (4) c and d

ALKYNES

26. Kolbe's electrolysis of sodium maleate at anode gives.
 (1) Only acetylene (2) Only CO_2
 (3) Acetylene + CO_2 (4) CO_2 + H_2
27. The pH of solution in Kolbe's electrolysis
 (1) increase with time (2) decrease with time
 (3) remains constant (4) nothing can be said
28. Which of the following compound will not give a precipitate with Tollen's reagent
 (1) ethyne (2) 1-butyne
 (3) 3-methyl-1-butyne (4) 1-pentene
29. $\text{B} \xleftarrow[\text{H}_2\text{O}_2 / ^-\text{OH}]{\text{BH}_3 / \text{THF}} \text{CH}_3\text{-C}\equiv\text{CH} \xrightarrow{\text{HgSO}_4 / \text{H}_2\text{SO}_4} \text{A}$
 A and B are
 (1) $\text{CH}_3\text{CH}_2\text{CHO}$, CH_3COCH_3
 (2) CH_3COCH_3 , $\text{CH}_3\text{CH}_2\text{CHO}$
 (3) CH_3COCH_3 both
 (4) CH_3COCH_3 , $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
30. $\text{MeCH}_2\text{C}\equiv\text{CH} \xrightarrow{\text{NH}_3 / \text{NaNH}_2} \text{A} \xrightarrow{\text{Et Br}} \text{B}$,
 A and B are
 (1) $\text{MeCH}_2\text{C}\equiv\text{CNa}$, $\text{MeCH}_2\text{C}\equiv\text{C-Et}$
 (2) $\text{MeCH}_2\text{CH=CH}_2$, $\text{MeCH}_2\text{-CH=CH-Et}$
 (3) $\text{MeCH}_2\text{CH=CHNH}_2$, $\text{MeCH}_2\text{CH=CH-NHBr}$
 (4) $\text{MeCH}_2\text{C}\equiv\text{C-NH}_2$, $\text{MeC}\equiv\text{C-NH-Br}$

31.  $\xrightarrow[\text{Liq. NH}_3]{\text{Na}}$ product will be :

- (1) 
 (2) 
 (3) 
 (4) 

32. To distinguish between propene and propyne, the reagent would be -

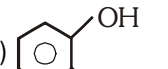
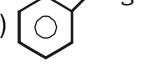
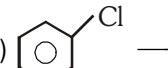
- (1) Bromine (2) Alkaline KMnO_4
 (3) Ammonical silver nitrate (4) Ozone

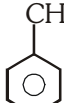
33. When treated with ammonical cuprous chloride, which one among the following forms red precipitate ?

- (1) C_2H_6 (2) C_2H_4 (3) C_2H_2 (4) C_6H_6

AROMATIC HYDROCARBONS

34. In which of the following reactions benzene is obtained

- (1)  $\xrightarrow{\text{NaOH/CaCO}_3}$
 (2)  $\xrightarrow{\text{H}_3\text{O}^+}$
 (3)  $\xrightarrow[360^\circ/300\text{Atm}]{\text{NaOH}}$
 (4)  $\xrightarrow[\Delta]{\text{H}_3\text{O}^+}$

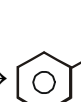
35. A $\xleftarrow{\text{Br}_2}$  $\xrightarrow{\text{KMnO}_4}$ B ; A and B

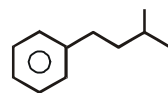
respectively are

- (1) o-bromo styrene, benzoic acid
 (2) p-bromostyrene, benzaldehyde
 (3) m-bromostyrene, benzaldehyde
 (4) Styrene dibromide, benzoic acid.

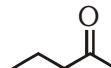
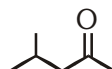
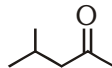
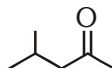
36. The ozonolysis product of 1, 2-dimethyl benzene is/are :-

- (1) Only $\text{CH}_3-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{CH}_3$
 (2) $\text{CH}_3-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{H} + \text{CH}_3-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{CH}_3$
 (3) $\text{H}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{H} + \text{CH}_3-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{CH}_3$
 (4) $\text{CH}_3-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{CH}_3 + \text{H}-\text{C}(=\text{O})-\text{CH}=\text{O} + \text{CH}_3-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{H}$

37. Benzene $\xrightarrow{\text{A}}$  $\xrightarrow{\text{B}}$



; A and B respectively are

- (1) $\text{Zn} - \text{Hg} + \text{HCl}$, 
 (2)  Cl , LiAlH_4
 (3)  Cl , NaBH_4
 (4)  Cl , $\text{Zn} - \text{Hg} + \text{HCl}$

38. Which of the following reaction does not gives benzoic acid

- (1) $\text{C}_6\text{H}_5-\text{CH}_3 \xrightarrow[\text{KMnO}_4]{\text{Acidic}}$
 (2) $\text{C}_6\text{H}_5-\text{CH}_3 \xrightarrow[\text{H}_2\text{O}]{\text{CrO}_2\text{Cl}_2} \xrightarrow{[\text{O}]}$
 (3) $\text{C}_6\text{H}_5-\text{C}\equiv\text{CH} \xrightarrow[\text{KMnO}_4]{\text{Acidic}}$
 (4) $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_2-\text{CH}_3 \xrightarrow[\text{KMnO}_4]{\text{Acidic}}$

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	1	3	3	2	3	4	3	1	4	4	1	1	3	4	1
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	3	3	3	1	4	2	2	2	4	4	3	1	4	2	1
Que.	31	32	33	34	35	36	37	38							
Ans.	2	3	3	2	4	4	4	4							

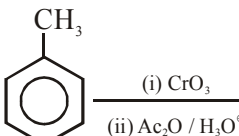
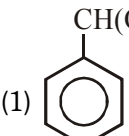
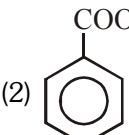
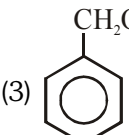
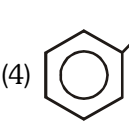
EXERCISE-II (Previous Year Questions)**AIPMT/NEET & AIIMS (2006-2018)****AIPMT 2007**

1. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called
(1) Cope reduction
(2) Dow reduction
(3) Wolf-kishner reduction
(4) Clemmensen reduction
2. Which of the compounds with molecular formula C_5H_{10} yields acetone on ozonolysis
(1) 3-Methyl-1-butene
(2) Cyclopentene
(3) 2-Methyl-1-butene
(4) 2-Methyl-2-butene

AIPMT 2010

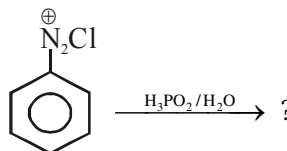
3. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by :-
(1) Hydrolysis
(2) Oxidation
(3) Cracking
(4) Distillation under reduced pressure

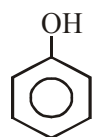
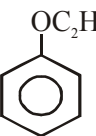
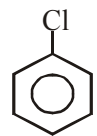
AIIMS 2013

4. ; Product A is :-
(1) 
(2) 
(3) 
(4) 

AIIMS 2014

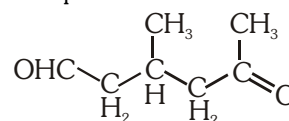
5. The product of the following reaction is :-



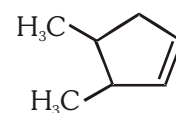
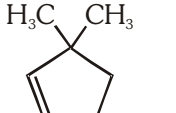
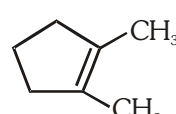
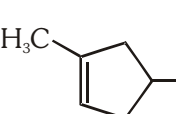
- (1)  (2) 
(3)  (4) 

AIPMT 2015

6. A single compound of the structure :-



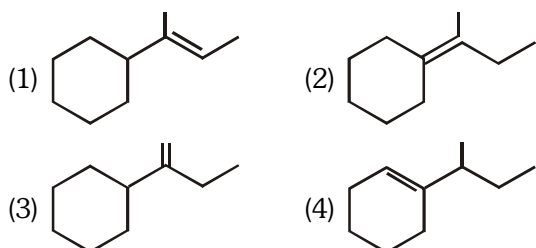
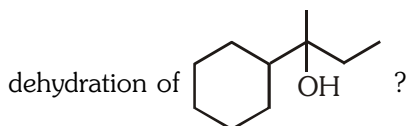
is obtainable from ozonolysis of which of the following cyclic compounds ?

- (1)  (2) 
(3)  (4) 

Re-AIPMT 2015

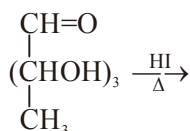
7. 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid ?
(1) $(CH_3)_2C=CH-CH_2-CH_3$
(2) $(CH_3)_2CH-CH_2-CH=CH_2$
(3) $(CH_3)_2CH-CH(CH_3)-CH=CH_2$
(4) $(CH_3)_3C-CH=CH_2$

8. The oxidation of benzene by V_2O_5 in the presence of air produces :
- (1) benzoic acid (2) benzaldehyde
(3) benzoic anhydride (4) maleic anhydride
9. Which of the following is not the product of



AIIMS 2016

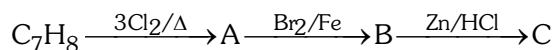
10. Identify product of the reaction



- (1) n-Pentane (2) 2-Pentane
(3) 1,3 Pentadiene (4) 3-Pentene

NEET(UG) 2018

11. Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. (A) is
- (1) $\text{CH}\equiv\text{CH}$ (2) $\text{CH}_2=\text{CH}_2$
(3) CH_3-CH_3 (4) CH_4
12. The compound C_7H_8 undergoes the following reactions :

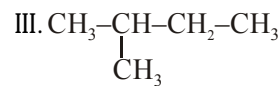
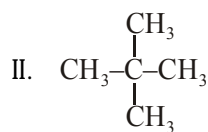


The product 'C' is

- (1) m-bromotoluene
(2) o-bromotoluene
(3) 3-bromo-2,4,6-trichlorotoluene
(4) p-bromotoluene

AIIMS 2018

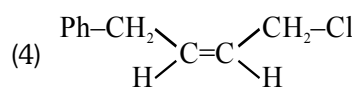
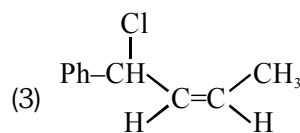
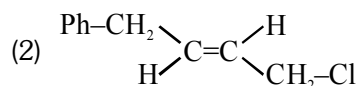
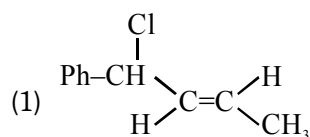
13. Arrange the following alkanes in decreasing order of their boiling point
- I. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



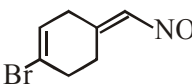
- (1) I > II > III (2) II > I > III
(3) I > III > II (4) III > I > II

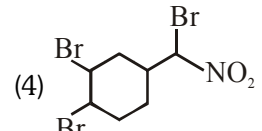
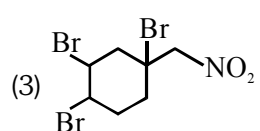
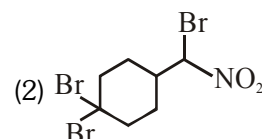
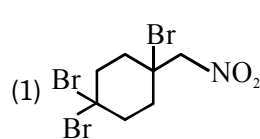
14. $\text{Ph}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow[\text{Liq NH}_3]{\text{Na}} \text{A} \xrightarrow{\text{Cl}_2/h\nu} \text{B}$

The final product 'B' is :-



15. Benzene is :-
- (1) Weakly attracted in the magnetic field
(2) Strongly attracted in the magnetic field
(3) Strongly repelled in magnetic field
(4) Weakly repelled in magnetic field

16.  $\xrightarrow[\Delta]{2\text{HBr}}$ Product.
- Product of reaction is :-



EXERCISE-II (Previous Year Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	4	4	3	4	2	4	4	4	4	1	4	1	3	1	4
Que.	16														
Ans.	1														

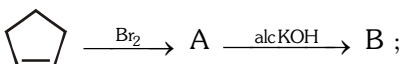
EXERCISE-III (Analytical Questions)**Check Your Understanding**

1. The volume of methane evolved by treatment of 16.6 g of methyl magnesium iodide with water at S.T.P. is

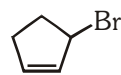
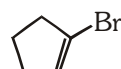
(1) 224 mL (2) 2.24 L
(3) 0.224 L (4) 22.4 L

2. 10 litre of an alkane X require 35 litre of O_2 for complete combustion. X forms only one monochloro derivative Y. The action of alcoholic KOH on Y yields

(1) $CH_3CH_2CH_2OH$
(2) $CH_2=CH_2$
(3) $CH_3CH=CH_2$
(4) $CH_3-\underset{\substack{| \\ OH}}{CH}-CH_3$

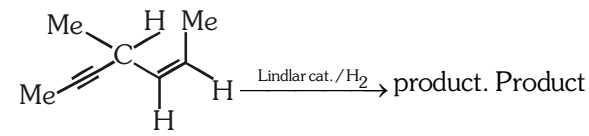
3.  ;

What is the structure of B

(1)  (2) 
(3)  (4) 

4. Which of the following is maximum reactive towards NBS

(1) $PhCH_3$
(2) $Ph-CH_2-CH_3$
(3) $PhCH_2-CH=CH_2$
(4) $Ph-\underset{\substack{| \\ CH_3}}{CH}-CH=CH_2$

5.  product. Product will be

(1) An optically active compound
(2) An optically inactive compound
(3) A racemic mixture
(4) A diastereomeric mixture

6. Which of the following reactions show that there are three C=C bond in benzene

(a) $C_6H_6 + Br_2 \xrightarrow{FeBr_3}$
(b) $C_6H_6 + HNO_3 \xrightarrow{H_2SO_4}$
(c) $C_6H_6 + 3O_3 \longrightarrow$
(d) $C_6H_6 + 3H_2 \xrightarrow{Ni}$

(1) a, c (2) b, d (3) b, c, d (4) c, d

EXERCISE-III (Analytical Questions)**ANSWER KEY**

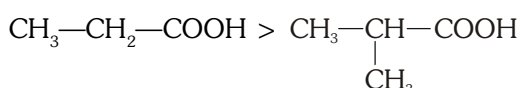
Que.	1	2	3	4	5	6
Ans.	2	2	4	4	2	4

EXERCISE-IV (Assertion & Reason)**Target AIIMS****Directions for Assertion & Reason questions**

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
 (B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
 (C) If Assertion is True but the Reason is False.
 (D) If both Assertion & Reason are false.

1. **Assertion :-** The reactivity order for decarboxylation is



Reason :- Reactivity depends on stability of intermediate carbocation.

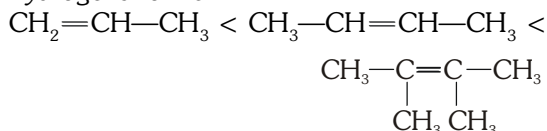
- (1) A (2) B (3) C (4) D

2. **Assertion :-** Baeyer's reagent can be used to distinguish cyclopentane from propene.

Reason :- Baeyer's reagent is decolourised by propene but not by cyclopentane

- (1) A (2) B (3) C (4) D

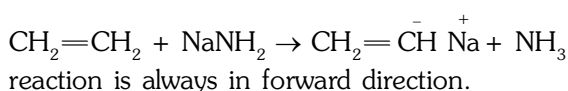
3. **Assertion :-** Increasing order of heat of hydrogenation is



Reason :- Highly substituted alkenes have less stability.

- (1) A (2) B (3) C (4) D

4. **Assertion :-** In the following reaction



reaction is always in forward direction.

Reason :- Ethene is stronger acid than ammonia.

- (1) A (2) B (3) C (4) D

5. **Assertion :-** Ethyne and its derivatives give white precipitate with ammonical silver nitrate solution.

Reason :- Alkynes give white ppt with ammonical silver nitrate solution due to nucleophilic substitution reaction.

- (1) A (2) B (3) C (4) D

6. **Assertion :-** Acetylene gives Red ppt when treated with ammonical Cu_2Cl_2 .

Reason :- Red ppt. is obtained due to formation of Cu.

- (1) A (2) B (3) C (4) D

7. **Assertion :-** 1-alkyne and 2-alkyne can be distinguished by Baeyer's reagent.

Reason :- 1-alkyne decolourise Baeyer's reagent while 2-alkyne does not decolourise.

- (1) A (2) B (3) C (4) D

8. **Assertion :-** Benzene does not decolourise Br_2 -water.

Reason :- Benzene is stabilized by aromaticity and no addition of Br_2 .

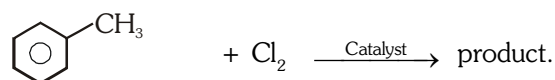
- (1) A (2) B (3) C (4) D

9. **Assertion :-** Benzene reacts with Cl_2 in presence of light to form BHC.

Reason :- Reaction undergoes electrophilic substitution.

- (1) A (2) B (3) C (4) D

10. **Assertion :-**



In product benzene ring is remain unchanged.

Reason :- Hexachloro benzene is an aromatic compound.

- (1) A (2) B (3) C (4) D

11. **Assertion :-** Acetylene gives glyoxal on reductive ozonolysis while benzene does not give glyoxal.

Reason :- Benzene does not show reductive ozonolysis reaction.

- (1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)**ANSWER KEY**

Que.	1	2	3	4	5	6	7	8	9	10	11
Ans.	3	1	4	4	4	3	4	1	3	2	4

E

**ENVIRONMENTAL CHEMISTRY,
PURIFICATION METHODS, QUALITATIVE
AND QUANTITATIVE ANALYSIS**

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NEET SYLLABUS

Environmental pollution : Air; water and soil pollution, chemical reactions in atmosphere, smog, major atmospheric pollutants; acid rain ozone and its reactions, effects of depletion of ozone layer, greenhouse effect and global warming pollution due to industrial wastes; green chemistry as an alternative tool for reducing pollution, strategy for control of environmental pollution.

OBJECTIVES

After studying this unit, we will be able to :

- understand the meaning of environmental chemistry;
- define atmospheric pollution, list reasons for global warming. green house effect and acid rain;
- identify causes for ozone layer depletion and its effects;
- give reasons for water pollution and know about international standards for drinking water;
- describe causes of soil pollution;
- suggest and adopt strategies for control of environmental pollution;
- appreciate the importance of green chemistry in day to day life.

"Failure will never overtake me if my definition to succeed is strong enough"

A.P.J. Abdul Kalam

ENVIRONMENTAL CHEMISTRY, PURIFICATION METHODS, QUALITATIVE & QUANTITATIVE ANALYSIS

ENVIRONMENTAL CHEMISTRY

The branch of science which deals with the chemical phenomena occurring in the environment is called as environmental chemistry.

INTRODUCTION

The environment means surroundings. It has 4 following component.

Atmosphere

Function of the atmosphere :

- It **contain all the gases** which are essential for the life on the earth.
- It is a **carrier of water vapour** which are needed for all life.
- Ozone (O_3) is present in stratosphere which is responsible for absorption of 99.5% of harmful U.V. radiations.
- It maintain heat balance of the earth by absorbing infrared radiation, coming from the sun and re-emit from the earth.

ENVIRONMENTAL POLLUTION & ENVIRONMENTAL POLLUTANT

The **addition of any undesirable material** to air, water and soil by a natural source (or due to human activity) which affects the **quality of environment** is called as environmental pollution.

The undesirable material which is added to the environment is called as pollutant.

Causes of pollution :

- Fast growth.
- Excessive trialisation.
- Rapid urbanisation.
- Use of pesticides in agriculture.

Types of Pollutants

Bio Degradable and Non Bio Degradable Pollutants

(A) Bio degradable pollutants : The materials (such as cow dungs) which are easily decomposed by the micro-organism. These are not harmful, but in the excess in environment, they do not undergo degradation completely and thus become pollutant. Eg. Discarded vegetables

(B) Non bio degradable pollutants :- The material (such as Hg, Al, DDT) which do not undergo degradation (or degrade very slowly) but their presence even in very small amount in the environment is very harmful. They may react with other compounds present in the environment and produce more toxic compound. Eg. Plastic materials, DDT, heavy metal, many chemicals, nuclear wastes etc.

TYPES OF POLLUTION

Depending on the Part of the Environment Polluted

(A) Air pollution **(B)** Water pollution **(C)** Soil pollution (or land pollution)

(A) Air pollution : It is defined as the undesirable materials into the atmosphere either due to natural phenomena (or due to human activity on the earth). Which affect the quality of the air and also affect the life on the Earth.

Major source of air pollution :

(i) Natural sources :

Ex. due to CO , H_2S , SO_2 , Forest fire

(ii) Man made air pollution or source due to human activity :

Natural sources :

Ex. Burning of fossil fuels which produce some poisonous gases as CO, CO₂, CH₄, oxide of nitrogen .

Combustion of gasoline in the automobiles : The automobiles emit the CO, oxide of nitrogen (NO, NO₂)

Deforestation : Due to this % of CO₂ is increased and % of O₂ is decreased.

Fast industrialisation : The smoke of carbon and CO, CO₂, SO₂, H₂S, NO, NO₂ are coming out from the industries. The industries are responsible for 20% of total air pollution.

Agriculture activities : The pesticides are added in the soil. They give a foul smell and affect the health of animals and human being.

Wars : The nuclear weapons are used in war which emit the radiation.

Air pollutants :

(A) CO as pollutant : It is mainly realised by automobile exhaust due to incomplete combustion of carbon. It binds to haemoglobin to form carboxyhaemoglobin, which is about **300 times** more stable than the oxygen-haemoglobin complex. In blood, if the concentration of carboxyhaemoglobin reaches 3-4 percent then oxygen carrying capacity is greatly reduced.

Sink of CO : A large amount of CO are added in the atm. But the level of CO does not rise too much as CO is converted in CO₂ by the micro organism which is present in the soil.

The micro organism (bacteria) act as sink for CO.

Harmful effect of CO :

(i) The CO is poisonous because it combine with haemoglobin of R.B.C. about 300 times easily than O₂, to form carboxy haemoglobin.

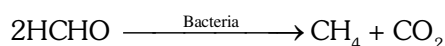
(ii) Oxygen deficient results into headache, weak eyesight, nervouness and cardiovascular disorder.

(iii) In pregnant women who have the habit of smoking the increased CO level in blood may induce premature birth, spontaneous abortions and deformed babies.

(B) Hydro carbon : Hydrocarbons are carcinogenic, i.e., they cause cancer. They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

(a) Natural sources :

(i) Due to decomposition of organic matter in soil.



(b) Man made sources :

(i) Due to burning of stationary fuel. (ii) Evaporation of organic solvent.

(C) Sulphur compounds : Produced by burning of fossil fuel. The most common species, sulphur dioxide, is a gas that is poisonous to both animals and plants.

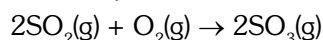
Harmful effect of Sulphur compounds :

(i) Even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma, bronchitis, emphysema in human beings.

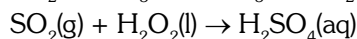
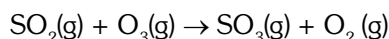
(ii) Causes irritation to the eyes, resulting in tears and redness.

(iii) High concentration of SO₂ leads to stiffness of flower buds which eventually fall off from plants.

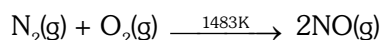
Sulphur dioxide Uncatalysed oxidation of sulphur dioxide is slow. However, the presence of particulate matter in polluted air catalyses the oxidation of sulphur dioxide to sulphur trioxide.



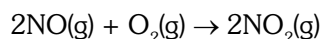
The reaction can also be promoted by ozone and hydrogen peroxide.



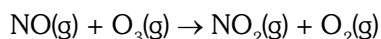
(D) Nitrogen compound : At high altitudes when lightning strikes, O_2 and N_2 combine to form oxides of nitrogen. NO_2 is oxidised to nitrate ion, NO_3^- which is washed into soil, where it serves as a fertilizer. In an automobile engine, (at high temperature) when fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2) as given below:



NO reacts instantly with oxygen to give NO_2



Rate of production of NO_2 is faster when nitric oxide reacts with ozone in the stratosphere.



Harmful effects of nitrogen compounds

- (i) The irritant red haze in the traffic and congested places is due to oxides of nitrogen.
- (ii) Higher concentrations of NO_2 damage the leaves of plants and retard the rate of photosynthesis.
- (iii) Nitrogen dioxide is a lung irritant that can lead to an acute respiratory disease in children.
- (iv) It is toxic to living tissues also. It is also harmful to various textile fibres and metals.

(E) Carbon dioxide : Normally it forms about 0.03 per cent by volume of the atmosphere. If the amount of carbon dioxide crosses the delicate proportion of 0.03 percent, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming.

BEGINNER'S BOX-1

- Domestic waste will lead to -

(1) Biodegradable pollution	(2) Nondegradable pollution
(3) Thermal pollution of soil	(4) Air pollution
- The major source of BOD in the river Ganga is

(1) Leaf litter	(2) Fishes	(3) Human waste	(4) Aquatic plants
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- If a lake is contaminated with DDT, its highest concentration would be found in

(1) Primary consumer	(2) Secondary consumer	(3) Tertiary consumer	(4) None of these
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- The most harmful air pollutant produced by automobiles is

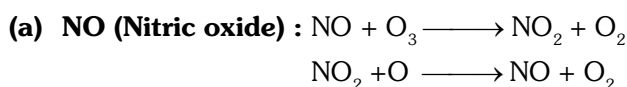
(1) HNO_2	(2) NO	(3) SO_2	(4) CO
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- Sewage water can be purified by

(1) Aquatic plant	(2) Micro organism	(3) Penicillin	(4) Fishes
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STRATOSPHERIC POLLUTION

Depletion of Ozone Layer

Due to human activity 2 compounds **NO** and **CFC** are responsible for depletion of O_3 layer.

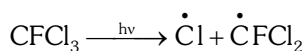
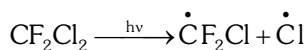


The NO react with O_3 so decrease the amount of O_3 and forms NO_2 which react with oxygen atoms available in the stratosphere and producing back NO.

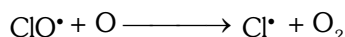
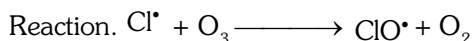
Thus no NO is consumed but O_3 gets depleted.

(b) Chlorofluoro carbons (CFC) or freons :

The freons decomposes in the presence of U.V. radiation coming from the Sun.



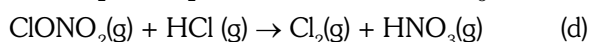
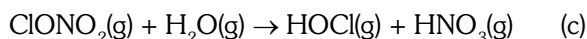
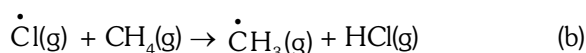
The reactive chlorine atoms then destroy the ozone layer through the following sequence of reaction. Which are repeated because chlorine atom are regenerated in the second reaction :



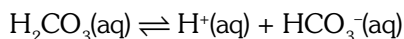
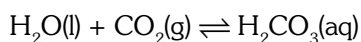
The one molecule CFC can destroy more than one thousand O_3 molecules in the stratosphere.

(c) Effect of depletion of O_3 layer : Due to depletion of O_3 layer, U.V. radiation fall on the Earth.

- The U.V. radiation, damage the cornea and lens of the eyes.
- The U.V. radiation affect the plant proteins so reduce the chlorophyll.
- The U.V. radiation, up set the heat balance of the Earth.
- **Ozone hole :** It was found that a unique set of conditions was responsible for the ozone hole. In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction a) and chlorine atoms (reaction b) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction a) gets hydrolysed to form hypochlorous acid (reaction c). It also reacts with hydrogen chloride produced as per (reaction b) to give molecular chlorine.

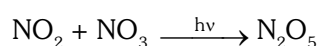
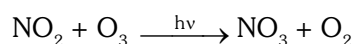
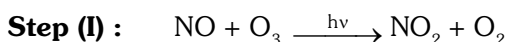


Acid Rain : The rain containig H_2SO_4 , HNO_3 (and small amount of HCl) which are formed from the **oxide of S** and **N_2** present in the air is called as acid rain. Normally rain water has a pH of 5.6 due to the presence of H^+ ions formed by the reaction of rain water with carbon dioxide present in the atmosphere.



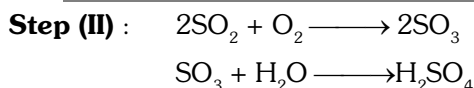
When the pH of the rain water drops below 5.6, it is called acid rain.

Formation of acid rain : The oxide of nitrogen undergo oxidation reaction. The reaction with the water vapour present in the atm to form HNO_3 .



HNO_3 come down with rain to Earth.

The SO_3 react with water vapour and form H_2SO_4 .



Ammonium salts are also formed and can be seen as an atmospheric haze (aerosol of fine particles). Aerosol particles of oxides or ammonium salts in rain drops result in wet-deposition. SO_2 is also absorbed directly on both solid and liquid ground surfaces and is thus deposited as dry-deposition.

Harmful effect of acid-rain

- It causes respiratory ailments in human beings and animals.
- It **corrodes water pipe**. So heavy metal (like Fe, Pb, Cu) are mixed with water which have toxic effect.
- The acid rain **increase the acidity of the lake**. Which is harmful to aquatic ecosystem.
- It is harmful for **agriculture, trees, plants** as it dissolves and washes away nutrients needed for their growth and also damages buildings.

Taj Mahal and Acid Rain : Taj Mahal is reported to be affected by SO_2 and other air pollutants released by oil refinery of Mathura. Acid rain reacts with marble, CaCO_3 of Taj Mahal ($\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$) causing damage to this wonderful monument that has attracted people from around the world.

Green House Effect : The warming of earth due to remission of sun's energy absorbed by the earth. The remission of earth's energy is absorbed by CO_2 molecules and H_2O vapour present near the earth's surface and then its radiation back to the earth, is called as green house effect. So the temp. of the earth is increased is called as global warming.

Important Green House Gases : Methane, water vapour, nitrous oxide, CFCs, ozone and CO_2 .

Particulates in Atmospheric Pollution

Smoke is composed of particulate matter. Particulates are the tiny solid or liquid particles suspended in air. These particles are usually individually invisible to the naked eye. Collectively, however, small particles often form a haze that restricts visibility.

Particulates in the atmosphere may be **viable** or **non-viable** :-

(i) Viable particulates - These are the minute living organisms that are dispersed in atmosphere.

Eg. bacteria, fungi, moulds, algae etc.

(ii) Non-viable - These are formed either by the breakdown of larger materials or by the condensation of minute particles and droplets. There are four types of non-viable particulates in the atmosphere : **mists, smoke, fumes and dust**.

- Mists** are produced by particles of spray liquids and the condensation of vapours in air. Examples are portions of herbicides and insecticides that miss their targets and travel through the air to form mists.
- Smoke** denotes very small soot particles produced by burning and combustion of organic matter. Oil smoke, tobacco smoke and carbon smoke are typical examples of this type of particulate emission.
- Fumes** are condenses vapours : fumes of metals are the well-known particulates of this type. Examples of this category also include metallurgical fumes and alkali fumes.
- Dust** consists of the particles produced during crushing, grinding and attribution of solid materials. Non-viable dust particulates in the atmosphere consist of ground limestone, sand tailings from floatation, pulverised coal, cement, fly ash and silica dust.

The effect of particulate pollutants are largely dependent on the particle size. Airborne particles such as dust, fumes, mist etc., are dangerous for human health. Particulate pollutants bigger than **5 microns are likely to lodge in the nasal passage**, whereas particles of about **10 micron enter into lungs easily**. Lead used to be a major air pollutant emitted by vehicles. Leaded petrol used to be the primary source of air-borne lead emission in Indian cities. Lead interferes with the development and maturation of red blood cells.

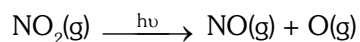
Smogs

Smogs which describe the "smoke-fog" like condition, are the best-known examples of air pollution that occurs in many cities throughout the world.

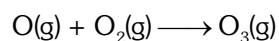
There are two types of smogs :

- (i) **Classical smogs** - Which occur in cool humid climate and are the result of buildup of **sulphur oxides** and **particulate matter** from fuel combustion. Chemically it is a reducing mixture so also called **reducing smog**.
- (ii) **Photochemical smogs** - Which occur in warm, dry and sunny climate and result from the action of sunlight on the nitrogen oxides and hydrocarbons produced by automobiles and factories. Photochemical smog is an **oxidising smog** having a high concentration of oxidising agents whereas classical smog is chemically reducing smog with high concentrations of SO_2 . Mostly in those cities which have very large populations and high vehicular density.

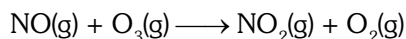
Formation of photochemical smog : The chemistry of formation of photochemical smog centres around nitric oxide (NO). At the high temperatures, in the petrol and diesel engines of cars and trucks, N_2 and O_2 react to form a small quantity of NO, which is emitted into troposphere with the exhaust gases. This NO oxidised in air to NO_2 which in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom. (Photochemical decomposition)



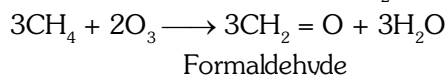
Oxygen atoms are very reactive and can combine with O_2 to form ozone;



The O_3 formed in the above reaction reacts rapidly with the $\text{NO}(\text{g})$ formed in reaction to regenerate NO_2 . NO_2 is brown gas at high levels can contribute to haze.



Both NO and O_3 are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN) that cause the eyes to water and burn and are harmful to the respiratory system. The brownish haze of photochemical smog is largely attributed to the brown colour of NO_2 .



Acrolein and peroxyacetyl nitrate (PAN) are particularly noxious.



Effects of Photochemical Smog

The common components of photochemical smog are ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Photochemical smog causes serious health problems. Both ozone and PAN act as powerful eye irritants. Ozone and nitric oxide irritate the nose and throat and their high concentration causes headache, chest pain, dryness of the throat, cough and difficulty in breathing. Photochemical smog leads to cracking of rubber and extensive damage to plant life. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

Control of Photochemical Smog

If we control the primary precursors of photochemical smog, such as NO_2 and hydrocarbons, the secondary precursors such as ozone and PAN, the photochemical smog will automatically be reduced. Usually catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants **e.g., Pinus, Juniparus, Quercus, Pyrus** and **Vitis** can metabolise nitrogen oxide and therefore, their plantation could help in this matter.

(B) WATER POLLUTION

The quality of drinking water is very important for human welfare. The pollution of water by sewage has been linked to the spread of diseases such as cholera and typhoid fever. Potassium permanganate or bleaching powder are used in water tanks.

Point Source : Easily identified source or place of pollution is called as point source. e.g., municipal and industrial discharge pipes

Non-point Sources : Those where a source of pollution cannot be easily identified, e.g., agricultural run off (from farm, animals and crop-lands), acid rain, storm-water drainage (from streets, parking lots and lawns) etc. Table lists the major water pollutants and their sources.

Pollutant	Source
Microorganisms	Domestic sewage
Organic wastes	Domestic sewage, animal waste, decaying animals and plants and discharge from food processing factories
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Cooling water used by industrial plants (which is discharged as hot water)

In addition, industrial wastes also contaminate water.

- (i) **Heavy Metals :** Metals such as Cd, Pb and Hg may be present in industrial or mining waste. These metals can prove poisonous to humans – Cadmium and mercury can damage kidneys, liver brain and central nervous system. All of these metals are cumulative poisons the body does not excrete them and their concentration builds up.
- (ii) **Detergents and Fertilizers :** These may contain phosphates as additives. The addition of phosphates to water, in the form of the phosphate anion PO_4^{3-} , encourages the formation of algae, which reduces the dissolved oxygen concentration of water. The process, known as eutrophication, impedes the development of higher life forms, such as fish.
- (iii) **Acid-polluted water (pH < 3) :** This is deadly to most forms of aquatic life. Water downstream from a mine may be contaminated by acid mine drainage, the result of microbial oxidation of discarded waste material at the mine site. Acid mine water principally contains sulphuric acid produced by the oxidation of iron pyrites (FeS_2). Industrial wastes and acid rain may also contribute to the acidity of natural waters.
- (iv) **Polychlorinated biphenyls (PCBs) :** These chemicals are relatively recent additions to the list of contaminants of water. Having high stabilities, PCBs find many applications, for example they are used as fluids in transformer capacitors. PCBs are resistant to oxidation and their release into the environment causes skin disorders in humans. They are reported to be carcinogenic.

Chemical Pollutant

Acids (like sulphuric acid) from mine drainage and salts from many different sources including raw salt used to melt snow and ice in the colder climates (sodium and calcium chloride) are water soluble chemical pollutants. The organic chemicals are another group of substances that are found in polluted water. Petroleum products pollute many sources of water e.g., major oil spills in oceans.

The quality of water is of vital concern for mankind since it is directly linked with human welfare. There are some international standards for drinking water, which must always be obeyed if water is to be used for drinking purposes. These are :

Fluoride : Soluble fluoride is often added to drinking water to bring it up to a concentration of 1 ppm or 1 mg dm^{-3} . The F^- ions make the enamel on teeth much harder by converting hydroxyapatite, $[\text{3}(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2)]$, the enamel on the surface of the teeth, into much harder fluorapatite, $[\text{3}(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2)]$. However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth.

Lead : The upper limit for the concentration of lead ions in drinking water is 50 ppb. If water is relatively acidic and lead pipes are used for water transport, then the water is liable to get contaminated with lead.

pH : The pH of drinking water should be between 5.5 and 9.5. A decrease in the pH of the water increases the solubility of metal ions.

Other Metals : The maximum recommended levels of common metals in drinking water are as follows.

Metal	Max. concentration (ppm or mg dm ⁻³)
Zn	5
Fe	0.2
Mn	0.05
Cu	3
Cd	0.005
Al	0.2

Sulphate : Sulphate is harmless at moderate levels, but excessive sulphate (> 500 ppm) is thought to have a laxative effect.

Nitrate : Excess nitrate in drinking water can lead to methemoglobinemia (blue-baby syndrome). A maximum limit of 50 ppm for the nitrate ion in drinking water has been set.

Causes of Water Pollution

(i) Pathogens: The most serious water pollutants are the disease causing agents called pathogens. Pathogens include bacteria and other organisms that enter water from domestic sewage and animal excreta. Human excreta contain bacteria such as *Escherichia coli* and *Streptococcus faecalis* which cause gastrointestinal diseases.

(ii) Organic wastes: The other major water pollutant is organic matter such as leaves, grass, trash etc. They pollute water as a consequence of run off. Excessive phytoplankton growth within water is also a cause of water pollution. These wastes are biodegradable.

Importance of Dissolved Oxygen in Water

The large population of bacteria decomposes organic matter present in water. They consume oxygen dissolved in water. The amount of oxygen that water can hold in the solution is limited. In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm (parts per million), whereas oxygen in air is about 200,000 ppm. That is why even a moderate amount of organic matter when decomposes in water can deplete the water of its dissolved oxygen. The concentration of dissolved oxygen in water is very important for aquatic life. If the concentration of dissolved oxygen of water is below 6 ppm, the growth of fish gets inhibited. Oxygen reaches water either through atmosphere or from the process of photosynthesis carried out by many aquatic green plants during day light. However, during night, photosynthesis stops but the plants continue to respire, resulting in reduction of dissolved oxygen. The dissolved oxygen is also used by microorganisms to oxidise organic matter.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

If too much of organic matter is added to water, all the available oxygen is used up. This causes oxygen dependent aquatic life to die. Thus, anaerobic bacteria (which do not require oxygen) begin to break down the organic waste and produce chemicals that have a foul smell and are harmful to human health. Aerobic (oxygen requiring) bacteria degrade these organic wastes and keep the water depleted in dissolved oxygen. Thus, the amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called **Biochemical Oxygen Demand (BOD)**. The amount of BOD in the water is a measure of the amount of organic material in the water, in terms of how much oxygen will be required to break it down biologically. Clean water, in terms of how much oxygen will be required to break it down biologically. Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

Chemical Oxygen Demand (COD) :

COD is the oxygen requirement by chemical $K_2Cr_2O_7$ for oxidation of total organic matter (biodegradable + non biodegradable) in water.

Note : COD value is always higher than BOD value.

BEGINNER'S BOX-2

- Major pollutant in Jet plane emission is -
(1) SO_2 (2) CFC (3) CO (4) CCl_4
- What is B.O.D.
(1) The amount of O_2 utilised by organisms in water
(2) The amount of O_2 utilized by micro organisms for decomposition
(3) The total amount of O_2 present in water
(4) All of the above
- What is the intensity of sound in normal conversation
(1) 10 – 20 decibal (2) 30 – 60 decibal (3) 70 – 90 decibal (4) 120 – 150 decibal
- Which of the following is absent in polluted water
(1) Hydrilla (2) Water hyacinth (3) Larva of stone fly (4) Blue green algae
- Maximum green house gas released by which country
(1) India (2) France (3) U.S.A (4) Britain

(C) LAND OR SOIL POLLUTION

Most of the land pollution is caused by pesticides and other chemicals which are added to the soil grow better crops. Often, a pesticide poisons many more organisms than those intended. Some of these poison pass through food chains and eventually reach harmful proportions. Solid wastes are another cause of land pollution.

Pesticides

Pesticides are substances that are used to kill or block the reproductive processes of unwanted organisms. Pesticides are basically synthetic toxic chemicals with ecological repercussions. **Eg. DDT, Malathion**

The repeated use of the same or similar pesticides give rise to pests that are resistant to that group of pesticides thus making the pesticides ineffective. Therefore, as insect resistance of DDT increased, other organic toxins such as **Aldrin** and **Dieldrin** were introduced in the market by pesticide industry. Most of the organic toxins are water insoluble and nonbiodegradable. These high persistent toxins are, therefore, transferred from lower trophic level to higher trophic level through food chain. Over the time, the concentration of toxins in higher animals reach a level which causes serious metabolic and physiological disorders.

In respon chlorinated org; to high persistence of ; toxins, a new series of less persistent or more bio-degradable products called **organo-phosphates** and **carbamates** have been introduced in the market. But these chemicals are severe nerve toxins and hence more harmful to humans. As a result, there are reports of some pesticides related deaths of agricultural field workers. Insects have become resistant to these insecticides also. The insecticide industry is engaged in developing new groups of insecticides.

These days, the pesticide industry has shifted its attention to **herbicides** such as **sodium chlorate ($NaClO_3$)**, **sodium arsinite (Na_3AsO_3)** and many others. During the first half of the last century, the shift from mechanical to chemical weed control had provided the industry with flourishing economic market. But one must remember that these are also not environment friendly.

Most herbicides are toxic to mammals but are not as persistent as organo-chlorides. These chemicals decompose in a few months. Like organo-chlorides, these too become concentrated in the food web. Some herbicides cause birth defects. Studies show that cornfields sprayed with herbicides are more prone to insect attack and plant disease than fields that are weeded manually.

INDUSTRIAL WASTE

Industrial solid wastes : (i) Biodegradable - Biodegradable wastes are generated by cotton mills, food processing units, paper mills and textile factories.

(ii) Non-biodegradable - These wastes are generated by thermal power plants which produce fly ash; integrated iron and steel plants which produce blast furnace slag and steel melting slag.

Industries manufacturing aluminium, zinc and copper produce mud and tailings. Fertilizer industries produce gypsum. Hazardous wastes such as inflammables, composite explosives or highly reactive substances are produced by industries dealing in metals, chemicals, drugs, pharmaceuticals, dyes, pesticides, rubber goods etc.

STRATEGY FOR CONTROL OF ENVIRONMENTAL POLLUTION

The management of waste : The production and improper disposal of waste are causes for a great deal of environmental pollution. In addition to the household waste which included sewage and municipal garbage, many toxic industrial wastes from manufacturing processes require treatment and/or safe disposal.

Recycling : When materials are recycled, there are several benefits, apart from saving on the cost of raw materials, waste disposal costs are reduced. Examples of recycling by industry are :

1. the collection and recycling of glass (in bottle banks);
2. the use of scrap metal in the manufacture of steel;
3. the recovery of energy from burning combustible waste.

Thus recycling converts waste into wealth.

Green Fuel : Fuel obtained from plastic waste has high octane rating. It contains no lead and is known as “green fuel”.

Biogas : A pilot plant has been set up, where after removing ferrous metals, plastic, glass, paper etc. from garbage, it is mixed with water. It is then cultured with bacterial species for producing methane, commonly known as biogas. The remaining product is used as manure and biogas is used to produce electricity.

Digestion : Anaerobic digestion occurs when microorganisms degrade wastes in the absence of oxygen. It may be used to treat sewage sludge, but the process can also be used to degrade a variety of toxic organic wastes. Carbon dioxide and methane, which may be used as a fuel, are the products. The overall process is the conversion of the organic material into carbon dioxide and methane i.e.

Dumping : Ocean dumping of sewage sludge has been widely practiced in the seas around the world. However, the practice of application to sludge the land is increasing. The sludge contains nitrogen and phosphorus which make it useful as a fertilizer. Urban areas produce sludge with high toxic metal content, so the amount of such sludge dumped in this way must be carefully controlled.

Incineration : Incineration converts organic materials to CO_2 and H_2O . It may serve to destroy household waste, chemical waste and biological waste (e.g. from hospitals). A high temperature is required usually in excess of 1000°C , and a plentiful supply of oxygen. Exhaust gases must be filtered. The process greatly reduced the volume of waste-an inorganic ash is left behind, which is disposed of as landfill.

GREEN CHEMISTRY (A NEW ROUTE TO PROTECTION OF ENVIRONMENT)

Green chemistry is a way of thinking and is about utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Green chemistry is a production process that would bring about minimum pollution or deterioration to the environment. The byproducts generated during a process, if not used gainfully, add to the environmental pollution. Such processes are not only environmentally unfriendly but also cost-ineffective. The waste generation and its disposal both are economically unsound. Utilisation of existing knowledge base for reducing the chemical hazards along with the developmental activities is the foundation of green chemistry.

Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.

It is well known that organic solvents such as benzene, toluene, carbon tetrachloride etc., are highly toxic. It may be worthwhile to carry out synthetic reactions in aqueous medium since water has high specific heat and low volatility. Water is cost effective, noninflammable and devoid of any carcinogenic effects.

Green Chemistry in day-to-day Life

(i) Dry Cleaning of Clothes

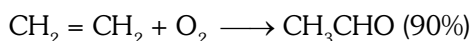
Tetra chloroethene ($\text{Cl}_2\text{C}=\text{CCl}_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. The process using this compound is now being replaced by a process, where liquefied carbondioxide, with a suitable detergent is used. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water. These days hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundry, which gives better results and makes use of lesser amount of water.

(ii) Bleaching of Paper

Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst, which promotes the bleaching action of hydrogen peroxide, is used.

(iii) Synthesis of Chemicals

Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with a yield of 90%.



Some important points :

- Stratosphere - In this ozone is present and it extends from 10 - 50 km from sea level.
- The lowest region of atmosphere in which human beings along with other organisms live is called troposphere. which extends upto 10 km from sea level
- Bhopal gas tragedy - A major gas tragedy took place on the night of december 2, 1984, when a dense cloud of deadly methyl isocyanate (MIC) gas leaked from a storage tank of the Union Carbide Ltd. plant in Bhopal.

PURIFICATION METHODS

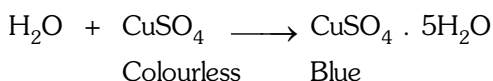
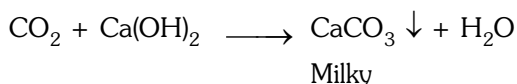
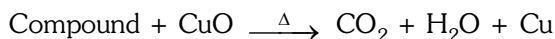
Distillation Techniques :

Type	Conditions	Examples
(A) Simple distillation	(i) When liquid sample has non volatile impurities (ii) When boiling point difference is 80°K or more.	(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K) (ii) Mixture of Ether (BP = 308K) & Toluene (BP = 384K) (iii) Hexane(342K) and Toulene(384K)
(B) Fractional distillation	When BP difference is 10°	(i) Crude oil in petroleum industry (ii) Acetone (329) and Methyl alcohol(338K)
(C) Distillation under reduced pressure (Vacuum distillation)	When liquid boils at higher temperature and it may decompose before BP is attained.	(i) Concentration of sugar juice (ii) Recovery of glycerol from spent lye. (iii) Glycerol
(D) Steam distillation	When the substance is immiscible with water and steam volatile. $P = P_1 + P_2$ Vapour pressure of Organic liquid Vapour pressure of water	(i) Aniline is separated from water (ii) Turpentine oil (iii) Nitro Benzene (iv) Bromo Benzene (v) Naphthalene (vi) o-Nitrophenol

QUALITATIVE AND QUANTITATIVE ANALYSIS OF ORGANIC COMPOUND

Qualitative analysis : Detection of element present in compound :-

(i) Detection of C and H : Compound heated with cupric oxide and produced vapour is passes through lime water or anhydrous CuSO_4 . If lime water turn milky, it shows presence of CO_2 or carbon. If anhydrous CuSO_4 turn blue than it shows presence of H_2O or hydrogen.

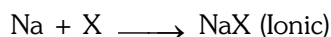
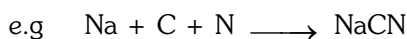


(ii) Detection of Nitrogen, Sulphur and halogen :- [Lassaigne's Test]

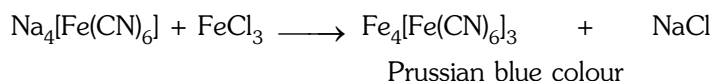
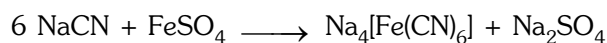
Preparation of lassaigne's solution or sodium extract.

Compound is heated with sodium in combustion tube and poured in cold water and heated for some time it gives lassaigne's solution or sodium extract.

In lassaigne solution elements present in compound get converted from covalent to ionic.

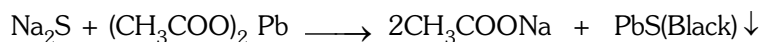


(i) Test of Nitrogen : Sodium extract is boiled with FeSO_4 which gives sodium hexacyano ferrate (II). Now few amount of FeCl_3 is added which gives prussian blue coloured ferro ferri cyanide that shows presence of Nitrogen.



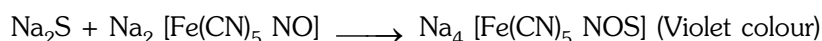
(ii) Test of sulphur : Sulphur is present in form of Na_2S

(a) Sodium Extract is acidified with acetic acid and lead acetate is added to it which gives black ppt of PbS and shows the presence of Sulphur

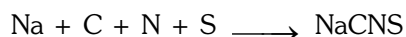


(b) Nitroprusside test

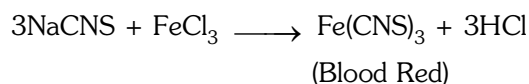
Sodium extract + Sodium Nitroprusside $\longrightarrow$ Violet colour.



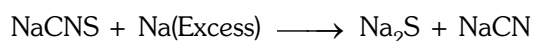
Note : If Nitrogen and sulphur both are present in compound then they form sodium thiocyanate in sodium extract.



during test of Nitrogen in place of prussian blue, we get blood red colour of Fe(CNS)_3



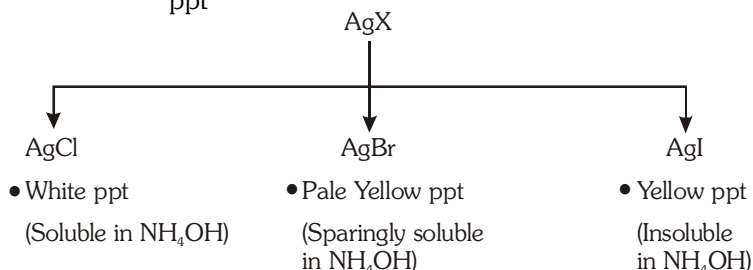
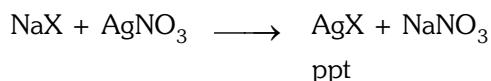
Therefore sodium extract is prepared in presence of excess of sodium which decomposes sodium thiocyanate.



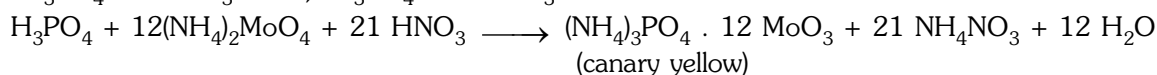
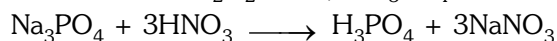
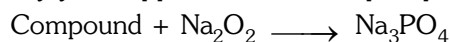
- (iii) **Test of halogen** : Before the test of halogen sodium extract is boiled with conc. HNO_3 to decompose the Na_2S and NaCN in form of H_2S and HCN



Now sodium extract is treated with silver nitrate which gives precipitate of AgX .



- (iv) **Test of phosphorous** : Compound is heated with an oxidising agent [Na_2O_2] so the phosphorus in compound is converted in to phosphate which on further reaction with ammonium molybdate in presence of HNO_3 gives canary yellow ppt of ammonium phospho molybdate and shows the presence of phosphorus.



Quantitative analysis : Calculation of percentage of element in compound.

- (i) **Estimation of carbon and hydrogen** : [Leibigs method]

A known mass of organic compound is burnt in presence of excess of CuO so carbon and hydrogen oxidise to CO_2 and H_2O respectively.

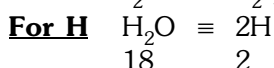
Now above vapour is passed through weighed u-tube having anhyd. CaCl_2 followed by KOH solution. anhyd. CaCl_2 absorbs H_2O while KOH absorbs CO_2 .

Now we can calculate the amount of H_2O and CO_2 produced in combustion.

Calculation of % of C and H :-

If mass of organic compound is W gm.

mass of H_2O or CO_2 produced is m gm



$\therefore$ 18 gm of H_2O contains 2 gm of hydrogen

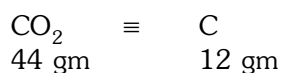
$\therefore$ 1 gm of H_2O contains $\frac{2}{18}$ gm of hydrogen

$\therefore$ m gm of H_2O contains $\frac{2}{18} \times m$ gm of hydrogen

Percentage of hydrogen in W gm organic substance =

$$\% \text{ of H} = \frac{2}{18} \times \frac{m}{W} \times 100$$

For C



$\therefore$ 44 gm CO_2 contain 12 gm carbon

1 gm CO_2 contain $\frac{12}{44}$ gm carbon

m gm CO_2 contain $\frac{12}{44} \times m$ gm carbon

$$\% \text{ of C in W gm organic substance} = \boxed{\% \text{ of C} = \frac{12}{44} \times \frac{m}{W} \times 100}$$

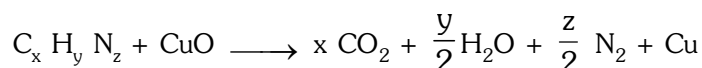
Estimation of Nitrogen :

These are two method for the estimation of nitrogen

- (i) Duma's method [in form of N_2]
- (ii) Kjeldhal's method [in form of NH_3]

(1) Duma's method :

Organic compound is heated with CuO to give free Nitrogen, CO_2 and H_2O .



Now the above mixture is collected over Aq. KOH in nitrometer tube which absorb all the gases except N_2 .
Now volume of nitrogen is calculated at STP.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad V_1 = \text{Volume of } N_2 \text{ gas.}$$

P_1 = Pressure of N_2 - Aqueous tension

T_1 = Room temperature

$$\boxed{V_2 = \frac{P_1 V_1 \times 273}{T_1 \times 760}}$$

Calculation of % of Nitrogen

$\therefore$ 22400 ml of N_2 at STP weight = 28 gm

$\therefore$ V ml of N_2 at STP weight = $\frac{28}{22400} \times V$ gm

$$\% \text{ of Nitrogen in W gm organic substance} = \boxed{\% \text{ of N} = \frac{28}{22400} \times \frac{V}{W} \times 100}$$

(2) Kjeldhal's method : Compound containing nitrogen is heated with H_2SO_4 so compound gets converted into ammonium sulphate.

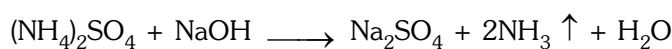
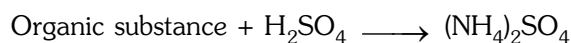
Now above mixture is heated with excess of NaOH which liberates Ammonia gas.

Ammonia gas is absorbed in excess of standard solution of H_2SO_4 .

The amount of ammonia produced is determined by estimating the amount of H_2SO_4 consumed.

Estimation of H_2SO_4 is done by titrating the H_2SO_4 left after absorption of ammonia with standard alkali solution.

The difference between the initial amount of acid taken and that left after absorption of ammonia is the amount of H_2SO_4 used.



If Normality of H_2SO_4 taken = N_1

Volume of H_2SO_4 taken = V_1

If Normality of NaOH used = N_2

Volume of NaOH used = V_2

$\therefore$ Milli equivalent of H_2SO_4 used for neutralisation of produced NH_3 = $(N_1 V_1 - N_2 V_2)$

Which is equal to the milli equivalent of NH_3

$\therefore$ 1000 ml of 1N NH_3 contain 14 gm Nitrogen.

$\therefore (N_1V_1 - N_2V_2)$ ml of 1N NH_3 contain $\frac{14}{1000} \times (N_1V_1 - N_2V_2)$ gm Nitrogen.

If mass of organic substance is W g.

$$\text{Then \% of N} = \frac{14}{1000} \times \frac{(N_1V_1 - N_2V_2)}{W} \times 100$$

$$\boxed{\% \text{ of N} = \frac{1.4}{W} \times (N_1V_1 - N_2V_2)} \quad \text{or} \quad \boxed{\% \text{ of N} = \frac{1.4}{W} \times NV}$$

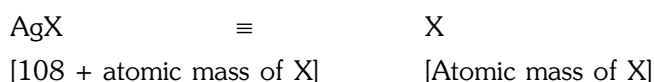
N = Normality of H_2SO_4 V = Volume of H_2SO_4 used in neutralisation.

(3) Estimation of halogen : (by carius method)

A known mass of organic compound is heated with fuming HNO_3 in presence of AgNO_3 . The halogen gets ppt in the form of AgX which can be filtered, washed and dried and weighed.

If mass of organic substance = W gm

mass of ppt = m gm



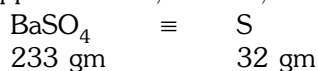
$$\text{mass of halogen in m gm AgX is} = \frac{\text{Atomic mass of X}}{\text{Molar mass of AgX}} \times m \text{ gm}$$

$$\boxed{\% \text{ of halogen} = \frac{\text{Atomic mass of X}}{\text{Molar mass of AgX}} \times \frac{m}{W} \times 100}$$

(4) Estimation of sulphur : (by Carius method)

Sulphur is estimated in the form of BaSO_4 .

Now ppt is filtered, washed, dried and weighed.



$$\text{mass of sulphur in m gm ppt of BaSO}_4 = \frac{32}{233} \times m \text{ gm}$$

% of sulphur in W gm organic sub.

$$\boxed{\% \text{ of S} = \frac{32}{233} \times \frac{m}{W} \times 100}$$

(5) Estimation of phosphorus : (by Carius method)

Phosphorus is estimated in the form of magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$)



mass of sulphur in m gm $\text{Mg}_2\text{P}_2\text{O}_7$ is

$$\frac{62}{222} \times m \text{ gm}$$

% of P in W gm organic sub.

$$\boxed{\% \text{ of P} = \frac{62}{222} \times \frac{m}{W} \times 100}$$

SOME SOLVED EXAMPLES

Q.1 0.3960 gm of an organic compound on combustion gives 0.792 gm CO₂ and 0.324 gm of H₂O. Calculate the % of C and H

Ans. % of C = $\frac{12}{44} \times \frac{\text{Wt. of CO}_2}{\text{Wt. of compound}} \times 100$

$$= \frac{12}{44} \times \frac{0.792}{0.396} \times 100 = 54.55\%$$

% of H = $\frac{2}{18} \times \frac{\text{Wt. of H}_2\text{O}}{\text{Wt. of compound}} \times 100$

$$= \frac{2}{18} \times \frac{0.324}{0.396} \times 100 = 9.09\%$$

Q.2 0.25 gm of an organic compound at NTP gives 31 ml of N₂ gas by Duma's method. Find out of % of N

Ans. % of N = $\frac{28}{22400} \times \frac{V}{W} \times 100$

$$= \frac{28}{22400} \times \frac{31}{0.25} \times 100 = 15.5\%$$

Q.3 31.7 ml of moist N₂ was obtained from 0.2033 gm of an organic compound in Duma's method at 14°C and 758 mm pressure. If aq. tension at 14°C = 14 mm then calculate % of N

Ans. P₁ = Pressure of N₂ – Aq. tension = 758 – 14 = 744 mm

P₂ = 760 mm T₂ = 273

V₁ = 31.7

T₁ = 273 + 14

T₂ = 287

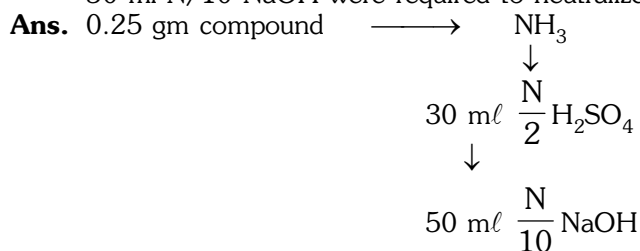
$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{744 \times 31.7 \times 273}{287 \times 760} = 29.51$$

$$\% \text{ N} = \frac{28}{22400} \times \frac{V}{W} \times 100 = \frac{28}{22400} \times \frac{29.51}{0.2033} \times 100 = 18.15\%$$

Q.4 30 ml 0.25 N H₂SO₄ are used in neutralizing NH₃ obtained from 0.75 gm of an organic compound in Kjeldhal's method find out % of N in the compound

Ans. N% = $\frac{1.4}{W} \times NV = \frac{14}{0.75} \times 30 \times 0.25 = 14\%$

Q.5 In Kjeldhal's method, NH₃ evolved from 0.25 gm of an organic compound was passed into 30 ml N/2 H₂SO₄. 50 ml N/10 NaOH were required to neutralize the unreact acid, calculate % of N.



$$50 \text{ ml} \times \frac{N}{10} = 5 \text{ ml N NaOH} \equiv 5 \text{ ml N H}_2\text{SO}_4$$

Remaining acid = 5 ml N H₂SO₄

Consumed acid

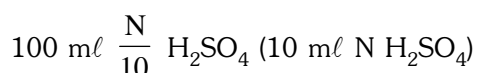
$$= \left(30 \text{ ml} \times \frac{N}{2} - 5 \text{ ml N} \right) = 10 \text{ ml N H}_2\text{SO}_4$$

$$\% \text{ N} = \frac{1.4}{W} \times NV = \frac{1.4}{0.25} \times 10 = 56 \%$$

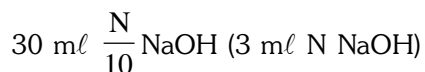
Q.6 0.35 gm of an organic compound was analysed by Kjeldhal's method. Ammonia evolved was absorbed in

100 ml $\frac{N}{10}$ H₂SO₄. Unused acid required 30 ml $\frac{N}{10}$ NaOH for neutralisation calculate % of N

Ans. W=0.35 gm $\rightarrow$ NH₃
 $\downarrow$



$\downarrow$



Remaining acid 3 ml N H₂SO₄

Consumed acid (10 ml N - 3 ml N) = 7 ml N H₂SO₄

$$\% \text{ of N} = \frac{1.4}{W} \times NV = \frac{1.4}{0.35} \times 1 \times 7 = 28 \%$$

Q.7 In Duma's method estimation of nitrogen, 0.3g of an organic compound gave 50 ml of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K = 15 mm)

Ans. Volume of nitrogen collected at 300K and 715 mm pressure is 50 ml

Actual pressure = 715 - 15 = 700 mm

$$\text{Volume of nitrogen at STP} = \frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ ml}$$

22,400 ml of N₂ at STP weighs = 28 g

$$41.9 \text{ ml of nitrogen weighs} = \frac{28 \times 41.9}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$$

Q.8 During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 ml of 1 M H₂SO₄. Find out the percentage of nitrogen in the compound.

Ans. 1 M of 10 ml H₂SO₄ = 1M of 20 ml NH₃ 1000 ml of 1M ammonia contains 14 g nitrogen.

20 ml of 1 M ammonia contains $\frac{14 \times 20}{1000}$ g nitrogen.

$$\text{Percentage of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0\%$$

Q.9 In carius method of estimation of halogen, 0.15g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Ans. Molar mass of AgBr = 108 + 80 = 188 g mol⁻¹

188g AgBr contains 80 g bromine.

0.12 g AgBr contains $\frac{80 \times 0.12}{188}$ g bromine.

Percentage of bromine = $\frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04\%$

Q.10 In sulphur estimation, 0.157g of an organic compoud gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound ?

Ans. Molecular mass of BaSO₄ = 137 + 32 + 64 = 233g

233g BaSO₄ contains 32 g sulphur

0.4813g BaSO₄ contains $\frac{32 \times 0.4813}{233}$ g sulphur

Percentage of sulphur = $\frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10\%$

ANSWER KEY

BEGINNER'S BOX-1

Que.	1	2	3	4	5
Ans.	1	3	3	4	2

BEGINNER'S BOX-2

Que.	1	2	3	4	5
Ans.	2	2	2	3	3

EXERCISE-I (Conceptual Questions)

1. Which is not a renewable source
(1) Forest (2) Coal
(3) Water (4) Forest organism
2. Noosphere is synonyms of
(1) Environment (2) Atmosphere
(3) Hydrosphere (4) Stratosphere
3. When biosphere turns into human dominated environment it is called
(1) Noosphere (2) Troposphere
(3) Mesosphere (4) Man sphere
4. The living organisms on or around the earth constitute
(1) Biome
(2) Biosphere
(3) Community
(4) Biocoenosis
5. What is the correct sequence of atmospheric layers starting from earth
(1) Stratosphere troposphere, mesosphere, thermosphere
(2) Troposphere, stratosphere, mesosphere, thermosphere
(3) Mesosphere, troposphere, stratosphere, thermosphere
(4) Thermosphere, mesosphere, stratosphere, troposphere
6. On earth all living organisms constitute
(1) Community (2) Biome
(3) Association (4) Biosphere
7. Which of the following is the non conventional source of energy
(1) Coal
(2) Petroleum
(3) Electricity from nuclear power plants
(4) Solar radiations
8. Petroleum resource is
(1) Renewable
(2) Non renewable
(3) Synthetic & biodegradable
(4) Infinite & unconventional

Build Up Your Understanding

9. The main aim of plant conservation is -
(1) To conserve the necessary ecological activities and life supporting systems
(2) To conserve species diversity and range of genetic material
(3) Both the above
(4) None of the above
10. Which will not cause any atmospheric pollution
(1) Hydrogen (2) Sulphur dioxide
(3) Carbon dioxide (4) Carbon monoxide
11. Which of the following is the main factor of water pollution
(1) Smoke (2) Industrial waste
(3) Detergent (4) Ammonia
12. Main air pollutant among the following is
(1) CO (2) CO₂
(3) N₂ (4) Sulphur
13. Which is more important for water pollution
(1) Sound (2) SO₂
(3) Salts of arsenic (4) Sewage
14. Pollution can be controlled by
(1) Sewage treatment
(2) Checking atomic blasts
(3) Manufacturing electrically operated vehicles
(4) All the above
15. In cities like Bombay and Calcutta the major air pollutants are
(1) Ozone
(2) Carbon monoxide and oxides of Sulphur
(3) Hydrocarbons and not air
(4) Algal spores and marsh gas
16. Which is the greatest air pollutant these days
(1) Factories (2) Motor vehicles
(3) Domestic appliances (4) animals
17. Removal of the soil by the action of wind and water is known as
(1) Erosion (2) Fossilization
(3) Leaching (4) Calcification
18. Acid rain occurs due to atmospheric pollution of
(1) SO₂ (2) NH₃
(3) CO₂ (4) N₂O

- 19.** Photochemical smog was first observed in -
 (1) London (2) Los Angeles
 (3) Paris (4) Tokyo
- 20.** Ozone layer of upper atmosphere is being destroyed by
 (1) Sulphur dioxide (2) Carbon dioxide
 (3) Chlorofluorocarbon (4) Smog
- 21.** Most hazardous metal pollutant of automobile exhaust is
 (1) Hg (2) Cd (3) Pb (4) Cu
- 22.** SO₂ pollution is indicated by
 (1) Grasses (2) Mosses (3) Lichens (4) Fossils
- 23.** B.O.D. is connected with
 (1) Organic matter (2) Microbes
 (3) Both (4) None
- 24.** Acid rain is due to increase in atmospheric concentration of
 (1) Ozone and dust (2) CO₂ and CO
 (3) SO₃ and CO (4) SO₂ and NO₂

- 25.** Soil erosion is greater when
 (1) No rain occurs
 (2) Winds do not blow
 (3) The rainfall is evenly distributed
 (4) The Rainfall is received in heavy down pour
- 26.** Soil erosion can be prevented by
 (1) Over grazing
 (2) Removal of vegetation
 (3) Afforestation (Plantation)
 (4) Increasing bird population
- 27.** Soil conservation is the process where
 (1) Soil is aerated
 (2) Soil erosion is allowed
 (3) Soil is protected against loss
 (4) Sterile soil is converted into fertile soil
- 28.** Ether and benzene can be separated by :-
 (1) Filtration (2) Distillation
 (3) Crystallization (4) Sublimation

EXERCISE-I (Conceptual Questions)

ANSWER KEY

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	2	1	1	2	2	4	4	2	1	1	2	1	3	4	2
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28		
Ans.	2	1	1	2	3	3	3	3	4	4	3	3	2		

EXERCISE-II (Previous Year Questions)**AIPMT 2008**

1. An organic compound contains carbon, hydrogen and oxygen. Its elemental analysis gave C, 38.71% and H, 9.67%. The empirical formula of the compound would be :-
 (1) CHO (2) CH₄O (3) CH₃O (4) CH₂O

AIPMT Pre.-2011

2. Which one of the following statement is not true ?
 (1) pH of drinking water should be between 5.5–9.5
 (2) Concentration of DO below 6 ppm is good for the growth of fish
 (3) Clean water would have BOD value of less than 5 ppm
 (4) Oxides of sulphur, nitrogen and carbon are the most widespread air pollutant
3. In Dumas' method of estimation of nitrogen 0.35g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be :
 (Aqueous tension at 300 K = 15 mm)
 (1) 15.45 (2) 16.45 (3) 17.45 (4) 14.45
4. The Lassaigne's extract is boiled with conc HNO₃ while testing for the halogens. By doing so it :-
 (1) decomposes Na₂S and NaCN, if formed
 (2) helps in the precipitation of AgCl
 (3) increases the solubility product of AgCl
 (4) increases the concentration of NO₃⁻ ions

AIPMT Pre.-2012

5. Which one of the following statements regarding photochemical smog is not correct?
 (1) Photochemical smog is formed through photochemical reaction involving solar energy
 (2) Photochemical smog does not cause irritation in eyes and throat.
 (3) Carbon monoxide does not play any role in photochemical smog formation
 (4) Photochemical smog is an oxidising agent in character

AIIMS 2013

6. Which of the following is not a green house gas:-
 (1) Hydrogen (2) Carbon dioxide
 (3) Methane (4) Nitrous oxide or N₂O

AIPMT 2014

7. Which one of the following is **not** a common component of Photochemical Smog?
 (1) Ozone (2) Acrolein
 (3) Peroxyacetyl nitrate (4) Chlorofluorocarbons

AIPMT/NEET & AIIMS (2006-2018)

8. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H₂SO₄. The percentage of nitrogen in the soil is :
 (1) 37.33 (2) 45.33
 (3) 35.33 (4) 43.33

AIIMS 2014

9. Concentration of Peroxy Acetyl Nitrate (PAN) is maximum in :-
 (1) Fog (2) Smoke
 (3) Smog (4) Photochemical smog

AIPMT 2015

10. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is :-
 (1) 18.20 (2) 16.76
 (3) 15.76 (4) 17.36

AIIMS 2015

11. If BOD of a water body has a 20 ppm then what can you conclude?
 (1) polluted (2) light polluted
 (3) clean water (4) highly polluted

NEET(UG) 2017

12. The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is :
 (1) Chromatography (2) Crystallisation
 (3) Steam distillation (4) Sublimation
13. Which of the following is a sink for CO ?
 (1) Micro organism present in the soil
 (2) Oceans
 (3) Plants
 (4) Haemoglobin

AIIMS 2017

14. Which of the following is Herbicide
 (1) Sodium chlorate
 (2) Organo carbonates
 (3) Potassium dihydrogen phosphate
 (4) Ammonium nitrate

NEET(UG) 2018

15. Which oxide of nitrogen is **not** a common pollutant introduced into the atmosphere both due to natural and human activity ?
 (1) N₂O₅ (2) NO₂
 (3) N₂O (4) NO

EXERCISE-II (Previous Year Questions)**ANSWER KEY**

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	3	2	2	1	2	1	4	1	4	2	4	3	1	1	1

EXERCISE-III (Analytical Questions)

- The term biosphere is used for the zone of the earth where life exists
(1) On the lithosphere
(2) In the hydrosphere
(3) In the lithosphere and hydrosphere
(4) In the lithosphere, hydrosphere and atmosphere
- The population of India is 15% of the world but its annual energy consumption is only
(1) 0.2% (2) 2.0% (3) 10% (4) 25%
- Environmental laning organisation is
(1) CSIR (2) CEPHERI
(3) ICAR (4) NEERI
- Which of the following atmospheric pollutants is not produced by the exhaust of motor vehicle in Delhi
(1) SO_2 (2) Hydrocarbon gases
(3) Fly ash (4) CO
- If water pollution continues at its present rate, it will eventually
(1) Stop water cycle
(2) Prevent precipitation
(3) Make oxygen molecules unavailable to water plants.
(4) Make nitrate molecules unavailable to water plants.

Check Your Understanding

- Recent reports of acid rains industrial cities are due to the effect of atmospheric pollution by
(1) Excessive release of NO_2 and SO_2 by burning of fossil fuels.
(2) Excessive release of CO_2 by burning of fuel like wood and charcoal, cutting of forests and increased animal population.
(3) Excessive release of NH_3 by industrial plants and coal gas.
(4) Excessive release of CO in atmosphere by incomplete combustion of cock, charcoal and other carbonaceous fuels in pancity of oxygen,
- Pollution is a change in physical, chemical or biological characters of our land and water that may be
(1) Desirable and harmful to human
(2) Desirable and useful to human
(3) Undesirable and harmful to human
(4) undesirable and useful to human
- An increase in CO_2 concentration in the atmosphere will result in
(1) Adverse effects of natural vegetation
(2) Global warming
(3) Temperature decrease in global atmosphere
(4) Genetic disorders in plants and animals
- Identify the incorrect statement from the following :-
(1) Oxides of nitrogen in the atmosphere can cause the depletion of ozone layer
(2) Ozone absorbs the intense ultraviolet radiation of the sun
(3) Depletion of ozone layer is because of its chemical reactions with chlorofluoro alkanes
(4) Ozone absorbs infrared radiation

EXERCISE-III (Analytical Questions)**ANSWER KEY**

Que.	1	2	3	4	5	6	7	8	9
Ans.	4	2	4	3	3	1	3	2	4

EXERCISE-IV (Assertion & Reason)**Target AIIMS****Directions for Assertion & Reason questions**

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
(C) If Assertion is True but the Reason is False.
(D) If both Assertion & Reason are false.

1. **Assertion :-** Classical smog is different from photo chemical smog.
Reason :- Because classical smog is oxidising and photo chemical smog is reducing.
(1) A (2) B (3) C (4) D

EXERCISE-IV (Assertion & Reason)**ANSWER KEY**

Que.	1
Ans.	3

IMPORTANT NOTES