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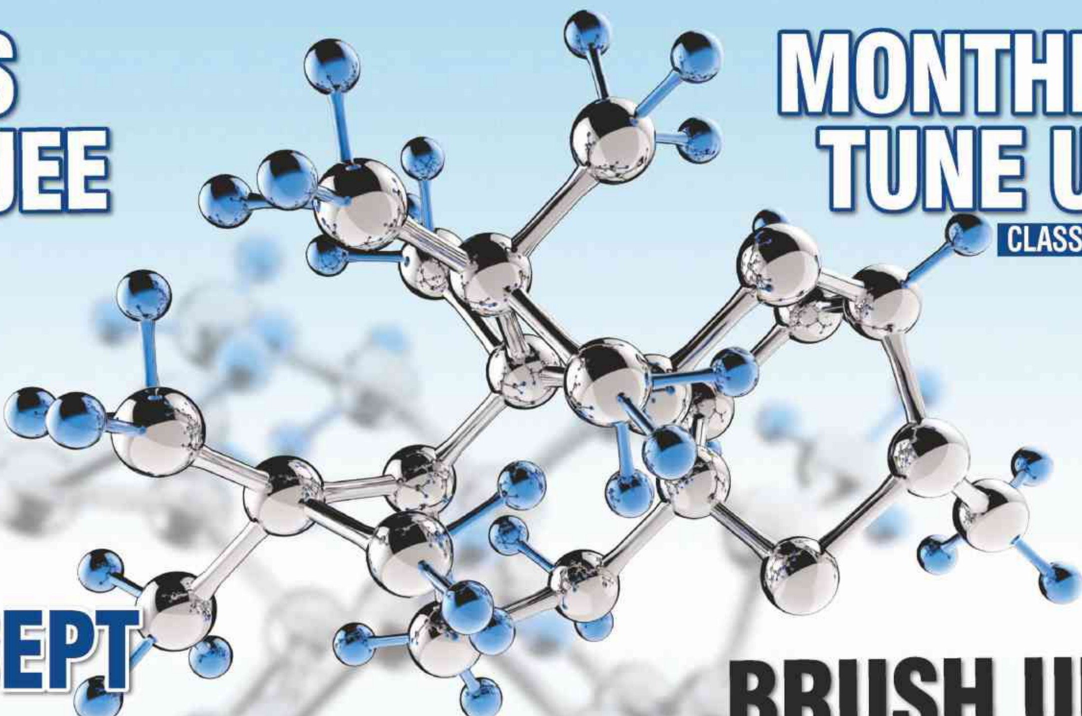

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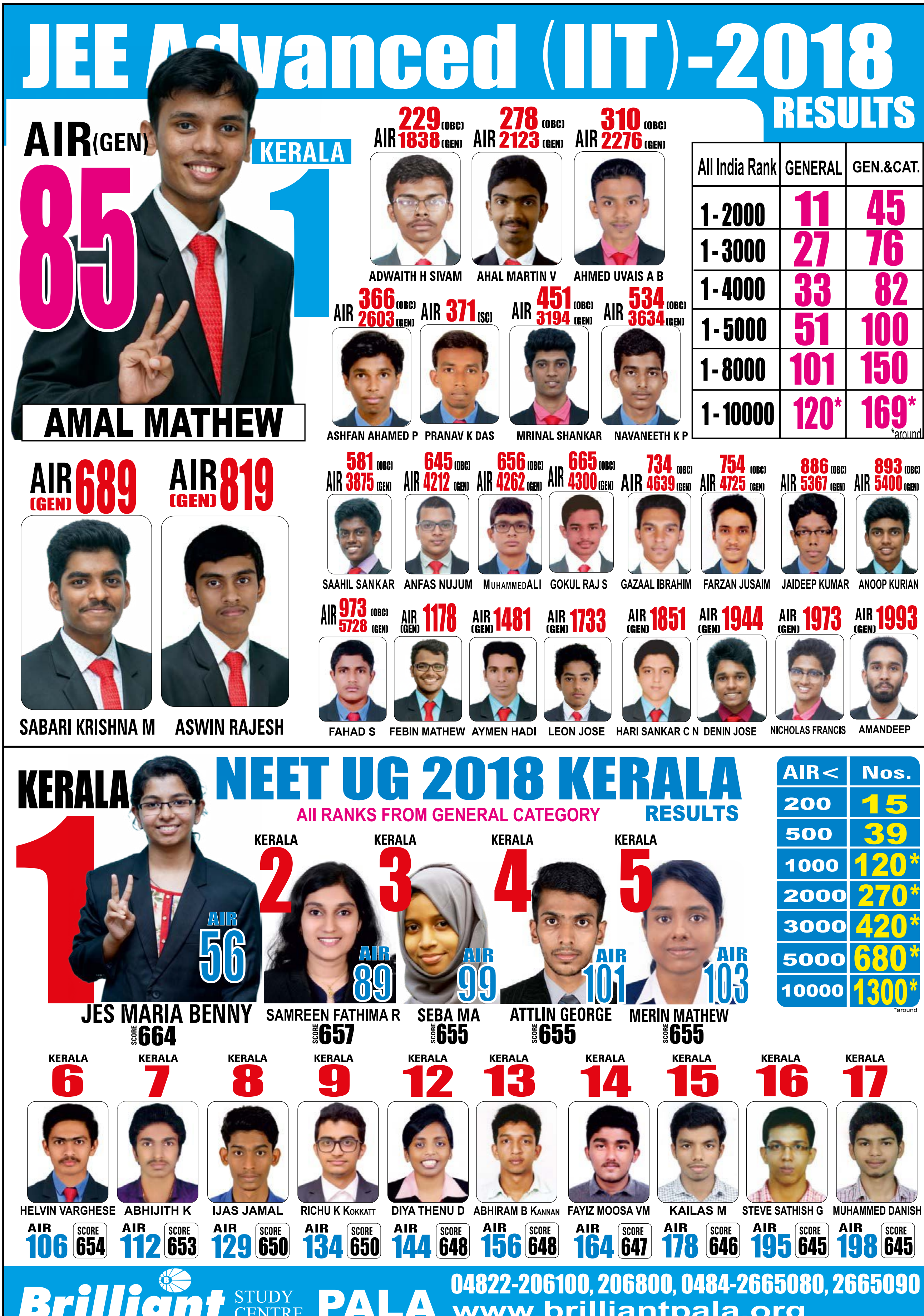

CHEMISTRY today

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Class XI

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UNIT - 3 : States of Matter | Thermodynamics

STATES OF MATTER (GASEOUS & LIQUIDS)

Matter

Matter exists mainly in three states, solid, liquid and gas. The fourth, plasma state, is the ionic state of atoms existing at very high temperatures found only in the interior of stars. The fifth Bose-Einstein condensate (BEC) state, refers to supercooled solid in which atoms lose their separate identity, get condensed and behave like a single super atom.

The Gaseous State

There are few parameters which are important to understand the gaseous state *viz.* mass, volume, pressure and temperature.

Measurable Properties of Gases

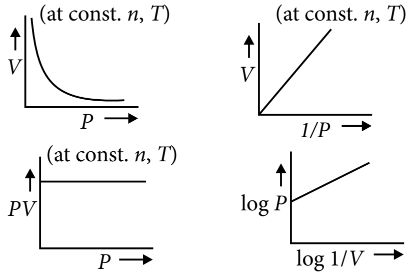
- **Mass** generally expressed in grams (SI unit is kg).
- **Volume** generally expressed in units of L, m^3 or cm^3 or dm^3 (SI unit is m^3).
- **Temperature** generally expressed in °C or K (T(K) = t°C + 273.15).
- **Pressure** generally expressed in units such as atm, mm, cm, torr, bar, etc. (SI units are Pa or kPa).

Gas Laws

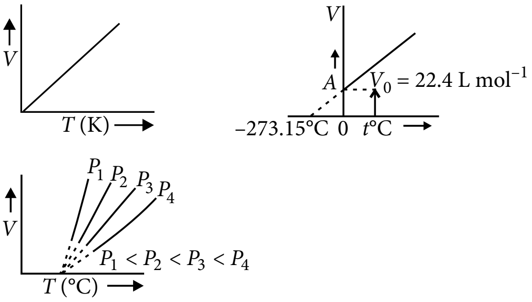
Laws	Mathematical expressions
Boyle's law (*Robert Boyle*)	**At constant T** $V \propto \frac{1}{P}$ or PV = constant or $P_1V_1 = P_2V_2$
Charles' law (*Jacques Charles*)	**At constant P** $V_t = V_0 + \frac{t}{273.15}V_0$ or $V \propto T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay-Lussac's law/ Amonton's law	**At constant V** $P \propto T$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Avogadro's law	**At a given T and P** $V \propto n$
Graham's law of diffusion	$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$
Dalton's law of partial pressures	$P_{total} = p_1 + p_2 + p_3 + ... p_n = (n_1 + n_2 + n_3 + ...)\frac{RT}{V}$

Graphical Representations

- **For Boyle's Law :**



- **For Charles' Law :**



Ideal Gas Equation

The equation which gives the simultaneous effect of pressure and temperature on the volume of a gas is known as ideal gas equation.

$PV = nRT$

(R is the universal gas constant or molar gas constant.)

- Value of R : 0.0821 litre atm K^{-1} mol^{-1}
  8.314×10^7 erg K^{-1} mol^{-1} (C.G.S. unit)
  8.314 J K^{-1} mol^{-1} (M.K.S. unit)
  $1.987 \approx 2$ calorie K^{-1} mol^{-1}

Kinetic Gas Equation

$PV = 1/3\ mnu^2$

where, P = pressure of gas

V = volume of gas

m = mass of one molecule of gas

n = number of molecules of gas

u = root mean square speed of molecules

Relationship between Average Kinetic Energy and Absolute Temperature

$$K.E. = \frac{3}{2}kT \text{ where, } k = \frac{R}{N} = \text{Boltzmann constant}$$

Different Types of Molecular Speeds

- Most probable speed (u_{mp})

$$= \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2RT}{m \times N}}$$

- Average speed (u_{av})

$$= \frac{u_1 + u_2 + u_3 + ...u_n}{n} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi M}}$$

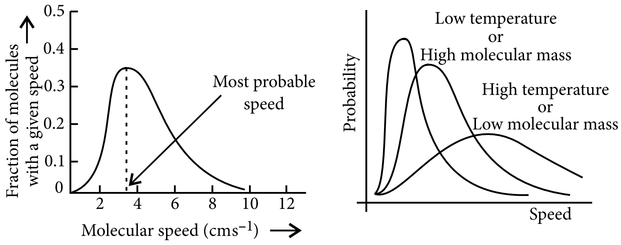
- Root mean square speed (u_{rms})

$$= \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + ...u_n^2}{n}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

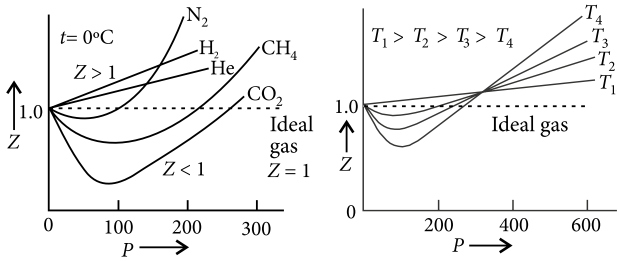
Relation Between Different Types of Speed

$u_{mp} : u_{av} : u_{rms} : 1 : 1.128 : 1.224$

Maxwell - Boltzmann Distribution Curve



Deviation From Ideal Gas Behaviour



- The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z), where

$$Z = \frac{V_m}{V_{m(\text{ideal})}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

  - For an ideal gas : $Z = 1$
  - For a real gas : $Z \neq 1$
  - For negative deviation $Z < 1$ and for positive deviation $Z > 1$.

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- **van der Waals' Equation of State for Real Gases :** To explain the behaviour of real gases, van der Waals modified the ideal gas equation by taking into account :
  (i) the volume of the gas molecules and
  (ii) the forces of attraction between the gas molecules.

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

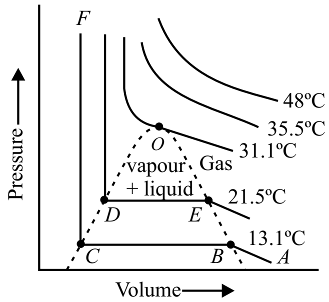
where, a and b are van der Waals' constants and their values depend on the nature of the gas.

van der Waals' constant	Significance	Units
a	Measure of magnitude of attractive forces	atm L^2 mol^{-2} or bar dm^6 mol^{-2}
b	Measure of effective size of the gas molecules	L mol^{-1} or dm^3 mol^{-1}

Liquefaction of Gases and Critical Constants

- A gas can be liquefied by cooling the gas or applying pressure on the gas or the combined effect of both. However, for every gas, there is a particular temperature above which a gas cannot be liquefied howsoever high pressure we may apply on the gas. This temperature is called critical temperature (T_c). The corresponding pressure and volume are called critical pressure (P_c) and critical volume(V_c).

$$T_c=\frac{8a}{27Rb},\ P_c=\frac{a}{27b^2},\ V_c=3b$$



Isotherms for carbon dioxide showing critical region

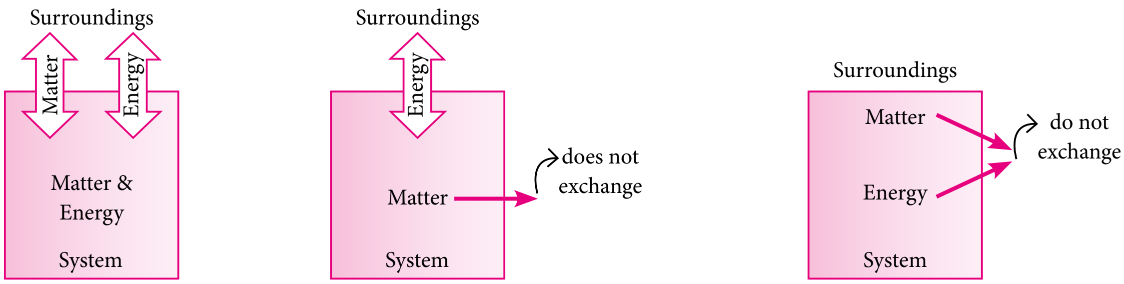
The Liquid State

Property	Mathematical expression	Effect of temperature
Vapour pressure		
The pressure exerted by the vapour of the liquid in equilibrium with its surface at a particular temperature.	$\log\frac{P_2}{P_1}=\frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ (Clausius-Clapeyron equation)	Increases with increase in temperature due to decrease in the magnitude of interparticle forces.
Surface tension		
The force acting on the surface of liquid at right angle to any line of one centimetre length.	$\frac{\gamma_1}{\gamma_2}=\frac{n_1d_2}{n_2d_1}$ (γ_1 and d_1 are the surface tension and density of water and γ_2 and d_2 are the surface tension and density of liquid whose surface tension is to be determined.)	Decreases with increase in temperature.
Viscosity		
The internal resistance, to flow in liquids, which one layer offers to another layer trying to pass over it.	Force of friction between two adjacent layers of liquid having area A cm^2, separated by distance x and having a velocity difference of V cm s^{-1} is given as $f=\eta\frac{AV}{x}$ where, η is coefficient of viscosity.	$\eta = Ae^{-Ea/RT}$, Decreases with increase in temperature (about 2% decrease per degree rise in temperature).

THERMODYNAMICS

Thermodynamics includes the study of all energy correlations and energy transformation, most commonly heat into work and vice-versa.

Types of Systems



Open System (Exchanges matter and energy) | **Closed System** (Exchanges energy) | **Isolated System** (No exchange of matter and energy)

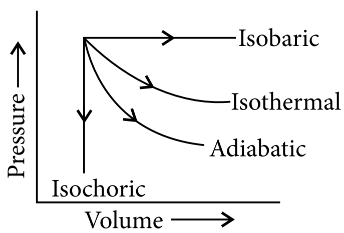
Illustration of exchange of matter and energy with surroundings in open, closed and isolated systems

Macroscopic Properties of A System

- **Intensive Properties**: Independent of the quantity of matter present in the system *e.g.*, temperature, pressure, viscosity, surface tension, refractive index, etc.
- **Extensive Properties**: Depend upon the quantity of matter present in the system *e.g.*, mass, volume, entropy, enthalpy, free energy, internal energy, etc.
- **State Functions**: Variables that depend only on the initial and final states of a system *e.g.*, pressure, volume, etc.
- **Thermodynamic Equilibrium**: Macroscopic properties that do not undergo any change with time. *e.g.*, temperature, pressure, etc.
- **Path Functions**: Variables whose values depend upon the path followed by the system on attaining that state. *e.g.*, work, heat, etc.

Thermodynamic Processes

(i) If $dq = 0$, process is adiabatic.
(ii) If $dT = 0$, the process is isothermal.
(iii) If $dV = 0$, process is isochoric.
(iv) If $dP = 0$, process is isobaric.



First Law of Thermodynamics

- It states that energy can neither be created nor destroyed, although it can be converted from one form to another.

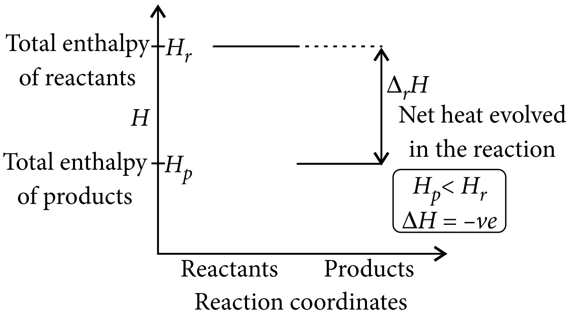
Mathematically : ΔE or $\Delta U = q + W$

- **Sign Convention for *q* and *w* :**
  - Work is done on the system = W (+ve)
  - Work is done by the system = W (–ve)
  - Heat is absorbed by the system = q (+ve)
  - Heat is given out by the system = q (–ve)

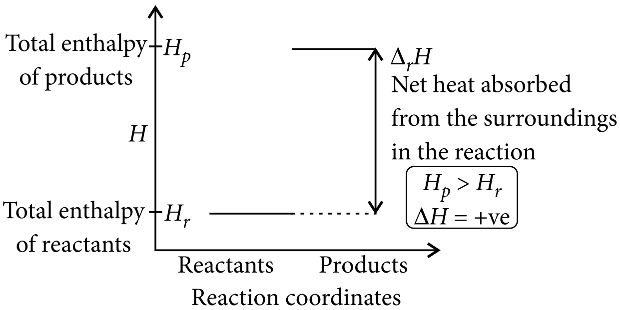
Enthalpy (*H*)

- Total heat content of the system at constant pressure is known as its enthalpy.
  - Its absolute value can not be determined.
  - Mathematically, it is given as $\boxed{\Delta H = \Delta U + P\Delta V}$

Enthalpy Diagram for Exothermic Reactions

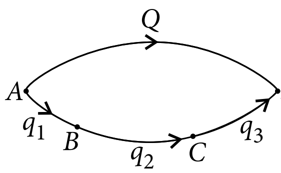


Enthalpy Diagram for Endothermic Reactions



Hess's Law of Constant Heat Summation

- The total amount of heat change in a chemical reaction is same whether the reaction takes place in one step or in number of steps. It depends only upon the nature of the initial reactants and final products and is independent of the path by which this change is brought about.



$Q = q_1 + q_2 + q_3$

Applications of Hess's law

- To calculate the heat changes for those reactions for which experimental determination is not possible.
  - ➢ The thermochemical equations can be treated as algebraic equations which can be added, subtracted, multiplied or divided.
- **Kirchhoff's Equation :** Variation of heat of reaction with temperature.
  - ➢ At constant pressure,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_{p(\text{products})} - C_{p(\text{reactants})}$$

  - ➢ At constant volume,

$$\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = C_{v(\text{products})} - C_{v(\text{reactants})}$$

Second Law of Thermodynamics

- This law states that, 'it is impossible to convert heat into equal amount of work without compensation.'

Entropy (*S*)

- Entropy is defined as a measure of randomness or disorder of the system. The order of randomness or entropy of solid, liquid and gas is, gas > liquid > solid.

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

Free Energy (*G*)

- Free energy of a system is defined as the maximum amount of energy available to the system during a process which can be converted into useful work.

$$\Delta G = -W_{\max}$$

Mathematically, $G = H - TS$

$\Delta G = \Delta H - T\Delta S$ (Gibbs–Helmholtz equation)

For a reaction to be spontaneous ΔG must be negative.

- ➢ $\Delta G° = -nFE°$
- ➢ $\Delta G° = \Sigma G°_{f\,(\text{products})} - \Sigma G°_{f\,(\text{reactants})}$
- ➢ $\Delta G° = -2.303\, RT \log K_{eq}$

- **Effect of Temperature on Spontaneity of Reactions**

$\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$	Description*
–	+	–	spontaneous at all temperatures
–	–	– (at low *T*)	spontaneous at low temperature
–	–	+ (at high *T*)	non-spontaneous at high temperature
+	+	+ (at low *T*)	non-spontaneous at low temperature
+	+	– (at high *T*)	spontaneous at high temperature
+	–	+ (at all *T*)	non-spontaneous at all temperatures

* The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.

Third Law of Thermodynamics

- At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero.
- For solid at temperature, T K

$$\Delta S = S_{T\,\text{K}} - S_{0\,\text{K}} = \int_0^T \frac{C_p dT}{T} = C_p \ln T$$

From third law of thermodynamics, $S_{0\,\text{K}} = 0$

$S_T = C_p \ln T = 2.303\, C_p \log T$

For liquids and gases, the absolute entropy at a given temperature T is given by the expression,

$$S = \int_0^{T_f} \frac{C_{p(s)} dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{p(l)} dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_{p(g)} dT}{T}$$

SPEED PRACTICE

1. Which of the following represents enthalpy of formation of water?
   (a) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$; $\Delta H = -242$ kJ
   (b) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H = -286$ kJ
   (c) $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta H = 286$ kJ
   (d) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$; $\Delta H = -572$ kJ

2. Calculate the temperature of 4.0 mole of a gas occupying 5 dm^3 at 3.32 bar.
   (a) 50 K (b) 60 K (c) 70 K (d) 75 K

3. Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of 100 mL and contains hydrogen. After opening the gas from A to the evacuated bulb B, the pressure falls down by 40%. The volume (mL) of B must be
   (a) 75 (b) 150 (c) 125 (d) 200

4. The standard heat of formation of $CH_{4(g)}$, $CO_{2(g)}$ and $H_2O_{(g)}$ are −76.2, − 398.8 and −241.6 kJ mol^{-1} respectively. The amount of heat evolved (in kJ) by burning 1 m^3 of methane measured under normal conditions is
   (a) 805 (b) 35973 (c) 22.4 (d) 3121

5. From the following data, what is the ΔC_P of reaction?
   $A_2 + B_2 \xrightarrow{273\text{ K}} 2AB$; $\Delta H_1 = -50$ kJ
   $A_2 + B_2 \xrightarrow{373\text{ K}} 2AB$; $\Delta H_2 = -125$ kJ
   (a) − 2.0 kJ K^{-1} (b) − 0.75 kJ K^{-1}
   (c) − 0.31 kJ K^{-1} (d) Unpredictable

6. The average molar heat capacities of ice and water are respectively 37.8 J mol^{-1} and 75.6 J mol^{-1} and the enthalpy of fusion of ice is 6.012 kJ mol^{-1}. The amount of heat required to change 10 g of ice at −10°C to water at 10°C would be
   (a) 2376 J (b) 4752 J (c) 3970 J (d) 1128 J

7. 0.24 g of a volatile gas upon vaporization gives 45 mL vapour at NTP. What will be the vapour density of the substances?
   (a) 95.39 (b) 5.973 (c) 95.93 (d) 59.73

8. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n ?
   (a) 1 (b) 4 (c) 3 (d) 8

9. The lattice enthalpy and hydration enthalpy of four compounds are given below:

Compounds	Lattice enthalpy (in kJ mol^{-1})	Hydration enthalpy (in kJ mol^{-1})
P	+780	−920
Q	+1012	−812
R	+828	−878
S	+632	−600

   The pair of compounds which is soluble in water is
   (a) P and Q (b) Q and R
   (c) R and S (d) P and R

10. Which of the following is the enthalpy of the following reaction?
    $2Fe^{3+} + 3Zn \longrightarrow 2Fe + 3Zn^{2+}$
    (Given that, $\Delta H^\circ_f(Fe^{3+}) = -100$ kJ mol^{-1}, $\Delta H^\circ_f(Zn^{2+}) = -15$ kJ mol^{-1})
    (a) + 85 kJ (b) − 115 kJ
    (c) + 155 kJ (d) − 155 kJ

11. When a gas is heated from 25 °C to 50 °C at constant pressure of 1 bar, its volume
(a) increases from V to $2V$
(b) increases from V to $1.5V$
(c) increases from V to $1.084V$
(d) increases from V to $1.8V$.

12. The root mean square speed (*rms*) of the molecules of diatomic gas is u. When the temperature is doubled, the molecules dissociate into two atoms. The new *rms* speed of the atom is
(a) $\sqrt{2}u$ (b) u (c) $2u$ (d) $4u$

13. The difference between heat of reaction at constant pressure and constant volume for the reaction,
$2C_6H_{6(l)} + 15O_{2(g)} \longrightarrow 12CO_{2(g)} + 6H_2O_{(l)}$
at 25°C in kJ is
(a) −7.43 (b) +3.72 (c) −3.72 (d) +7.43

14. Calculate the enthalpy change when 50 mL of 0.01 M $Ca(OH)_2$ reacts with 25 mL of 0.01 M HCl. Given that $\Delta H°$ neutralisation of a strong acid and a strong base is 140 kcal mol^{-1}.
(a) 14 cal (b) 35 cal (c) 10 cal (d) 7.5 cal

15. Equal volumes of H_2 and CO_2 are filled in a chamber at room temperature. Which of the following is correct *w.r.t.* their partial pressures p_{H_2} and p_{CO_2} ?
(a) $p_{H_2} > p_{CO_2}$ (b) $p_{H_2} < p_{CO_2}$
(c) $p_{H_2} = p_{CO_2}$ (d) Uncertain

16. One litre of gas A at 2 atm pressure at 27 °C and two litres of gas B at 3 atm pressure at 127 °C are mixed in a 4 litre vessel. The temperature of the mixture is maintained at 327 °C. What is the total pressure of the gaseous mixture?
(a) 3.93 atm (b) 3.25 atm
(c) 4.25 atm (d) 6.25 atm

17. Consider the reactions given below. On the basis of these reactions find out which of the following relations is correct ?
(i) $C_{(g)} + 4H_{(g)} \longrightarrow CH_{4(g)}$; $\Delta_r H = x$ kJ mol^{-1}
(ii) $C(\text{graphite}, s) + 2H_{2(g)} \longrightarrow CH_{4(g)}$; $\Delta_r H = y$ kJ mol^{-1}
(a) $x = y$ (b) $x = 2y$ (c) $x > y$ (d) $x < y$

18. Entropy changes for the process, $H_2O_{(l)} \longrightarrow H_2O_{(s)}$, at normal pressure and 274 K are given below
$\Delta S_{system} = -22.13$, $\Delta S_{surr} = +22.05$,
the process is non-spontaneous because
('surr' stands for surrounding and 'u' stands for universe)
(a) ΔS_{system} is – ve (b) ΔS_{surr} is +ve
(c) ΔS_u is – ve (d) $\Delta S_{system} \neq \Delta S_{surr}$

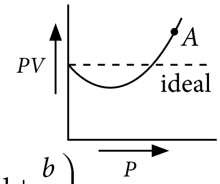
19. Volume of 2.9 g of a gas at 95 °C occupied the same volume as 0.184 g of H_2 gas at 17 °C at the same pressure. What is the molar mass of the gas ?
(a) 40 g mol^{-1} (b) 30 g mol^{-1}
(c) 20 g mol^{-1} (d) 10 g mol^{-1}

20. When latent heat of vaporisation 539 cal is given to 1 g of water at 100°C (d = 1 g cm^{-3}), it gets converted into 1671 cm^3 of steam at 100°C. What will be the change in internal energy of water molecules in changing from water to steam?
($P = 1 \times 10^5$ Nm^{-2} and 1 cal = 4.2 J)
(a) – 579 cal (b) 579 cal
(c) 499 cal (d) – 499 cal

21. Calculate the resonance energy of N_2O from the following data: ΔH_f of N_2O = 82 kJ mol^{-1}. Bond energies of N≡N, N=N, O=O and N=O bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.
(a) – 88 kJ mol^{-1} (b) −170 kJ mol^{-1}
(c) – 82 kJ mol^{-1} (d) −258 kJ mol^{-1}

22. ΔG in $Ag_2O \rightarrow 2Ag + 1/2O_2$ at a certain temperature is – 10 kJ/mole. Pick the correct statement.
(a) Ag_2O decomposes to Ag and O_2.
(b) Ag and O_2 combines to form Ag_2O.
(c) Reaction is in equilibrium.
(d) Reaction does not take place.

23. The isotherm obtained for CO is follows:
The compressibility factor for the gas at point A will be



(a) $\left(1-\frac{b}{V}\right)$ (b) $\left(1+\frac{b}{V}\right)$
(c) $\left(1+\frac{b}{RT}\right)$ (d) $\left(1+\frac{a}{RTV}\right)$

24. The van der Waals' constants for four gases P, Q, R and S are 4.17, 3.59, 6.71 and 3.8 atm L^2 mol^{-2}. Therefore, the ascending order of their liquefaction is
(a) $R < P < S < Q$ (b) $Q < S < R < P$
(c) $Q < S < P < R$ (d) $R < P < Q < S$

25. For a liquid, enthalpy of fusion is 1.435 kcal mol^{-1} and molar entropy change is 5.26 cal mol^{-1} K^{-1}. The melting point of the liquid is
(a) 0 °C (b) −273 °C
(c) 173 K (d) 100 °C

SOLUTIONS

1. **(b):** H_2, O_2 and H_2O all are in their standard states and 1 mol of water is being produced.

2. **(a):** $PV = nRT$

or $3.32 \times 5 = 4 \times 0.083 \times T$

or $T = \dfrac{3.32 \times 5}{4 \times 0.083} = 50$ K

3. **(b):** According to Boyle's law, $P_A \times V_A = P_B \times V_B$

$0.6\ P_A \times 100 = 0.4\ P_A \times V_B \Rightarrow V_B = 150$ mL

4. **(b):** The combustion reaction for methane is

$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}; \Delta H = ?$

$\Delta H° = \Delta H°_{f\,(\text{products})} - \Delta H°_{f\,(\text{reactants})}$

$= \Delta H°_{f(CO_2)} + 2 \times \Delta H°_{f(H_2O)} - \Delta H°_{f(CH_4)} - 2\Delta H°_{f(O_2)}$

$= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0$

$= 805.8$ kJ mol^{-1}

Heat evolved by burning 22.4 litre (1 mole) methane $= -805.8$ kJ.

So, heat evolved by burning 1000 litre (1 m^3) methane

$= -\dfrac{805.8}{22.4} \times 1000 = -35973.2$ kJ

5. **(b):** $\Delta C_P = \dfrac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \dfrac{-125-(-50)}{373-273} = \dfrac{-75}{100}$

$= -0.75$ kJ K^{-1}

6. **(c)**

7. **(d)**

8. **(b):** $\dfrac{r_{H_2}}{r_{HC}} = \sqrt{\dfrac{M_{HC}}{M_{H_2}}}$ (HC = Hydrocarbon)

$3\sqrt{3} = \sqrt{\dfrac{M_{HC}}{2}}$ or $M_{HC} = (3\sqrt{3})^2 \times 2 = 54$

$\therefore$ For C_nH_{2n-2}, $12n + (2n - 2) = 54$ or $n = 4$

9. **(d):** A compound is soluble if hydration enthalpy > lattice enthalpy.

10. **(c)**

11. **(c):** $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2} \Rightarrow \dfrac{V}{298} = \dfrac{V_2}{323}$

$V_2 = V \times \dfrac{323}{298} = 1.084\,V$

12. **(c):** $u = \sqrt{\dfrac{3RT}{M}}$

If $T = 2T$ and $M = M/2$, then $u_1 = \sqrt{\dfrac{3R \times 2T}{M/2}}$

$\therefore \dfrac{u_1}{u} = \sqrt{4} = 2 \Rightarrow u_1 = 2u$

13. **(a):** $\Delta H - \Delta U = \Delta n_g RT$

$= (12 - 15) \times \dfrac{8.314}{1000} \times 298 = -7.433$ kJ mol^{-1}

14. **(b):** Number of moles of HCl

$= \dfrac{MV}{1000} = \dfrac{0.01 \times 25}{1000} = 25 \times 10^{-5}$

$HCl \longrightarrow H^+ + Cl^-$

$n_{H^+} = 25 \times 10^{-5}$

Number of moles of $Ca(OH)_2 = \dfrac{MV}{1000} = \dfrac{0.01 \times 50}{1000}$

$= 50 \times 10^{-5}$

$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$

$n_{OH^-} = 2 \times 50 \times 10^{-5} = 10^{-3}$

In the process of neutralisation, 25×10^{-5} mole H^+ will be completely neutralised.

$\therefore \Delta H = 140 \times 25 \times 10^{-5}$ kcal $= 0.035$ kcal $= 35$ cal

15. **(c)**

16. **(b):** $\dfrac{P_A V_A}{T_A} + \dfrac{P_B V_B}{T_B} = \dfrac{P_{mix} V_{mix}}{T_{mix}}$

$\dfrac{2 \times 1}{300} + \dfrac{3 \times 2}{400} = \dfrac{P_{mix} \times 4}{600} \Rightarrow \dfrac{8+18}{1200} = \dfrac{4P_{mix}}{600}$

$P_{mix} = \dfrac{26 \times 600}{4 \times 1200} = 3.25$ atm

17. **(c):** Same bonds are formed in reactions (i) and (ii) but no bonds are broken in reaction (i) whereas bonds in the reactant molecules are broken in reaction (ii). As energy is absorbed when bonds are broken, energy released in reaction (i) is greater than that in reaction (ii), *i.e.*, $x > y$.

18. **(c):** $\Delta S_u = \Delta S_{system} + \Delta S_{surrounding}$

$= -22.13 + 22.05 = -0.08$

For a spontaneous process, ΔS must be positive *i.e.*, $\Delta S = \Delta S_{system} + \Delta S_{surrounding} \geq 0$

19. **(a):** $n_A = \dfrac{2.9}{M_A}$; $n_{H_2} = \dfrac{0.184}{2} = 0.092$

$\dfrac{(PV)_A}{(PV)_{H_2}} = \dfrac{(nRT)_A}{(nRT)_{H_2}} \Rightarrow 1 = \dfrac{2.9}{M_A} \times \dfrac{(95+273)}{(17+273)} \times \dfrac{1}{0.092}$

$M_A = \dfrac{2.9 \times 368}{290 \times 0.092} = 40$ g mol^{-1}

PUZZLE CORNER

SOLUTION - AUGUST 2018

1	2	3	4	5
3	4	1	5	2
4	1	5	2	3
2	5	4	3	1
5	3	2	1	4

(a) Neon (1 + 2 + 3 + 4) = 10
(b) Magnesium (3 × 4) = 12
(c) Nitrogen (5 + 2) = 7
(d) Manganese (5 × 1 × 5) = 25
(e) Calcium (4 × 1 × 5) = 20
(f) Hydrogen (3 – 2) = 1
(g) Zinc (2 × 5 × 3) = 30
(h) Carbon (4 + 2) = 6
(i) Fluorine (3 + 1 + 1 + 4) = 9

20. (c) : Latent heat $Q = E + p\Delta V$

$$539 = E + \frac{[1\times10^5(1671-1)\times10^{-6}]}{4.2} \Rightarrow E = 499 \text{ cal}$$

21. (a) : $N \equiv N + 1/2\ O = O \longrightarrow N = N = O$

$\Delta H^\circ_f = \Sigma BE$ of reactants – ΣBE of products

$= [BE\ (N \equiv N) + 1/2\ \ BE\ (O = O)]$ – $[BE(N = N) + BE(N = O)]$

$= (946 + 1/2 \times 498) - (418 + 607) = 170$ kJ

Resonance energy

$= \Delta H^\circ_f(\text{observed}) - \Delta H^\circ_f(\text{calculated})$

$= 82 - 170 = -88$ kJ mol^{-1}

22. (a) : ΔG, –ve means the process is spontaneous.

23. (b) : $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

At point A, P is high so that a/V^2 can be neglected.

Hence, $P\ (V - b) = RT$ or $PV - Pb = RT$

or $PV = Pb + RT$ or $\frac{PV}{RT} = 1 + \frac{Pb}{RT}$

i.e. $Z = 1 + \frac{Pb}{RT} \quad \left(\because\ P = \frac{RT}{V}\right)$

$$Z = 1 + \frac{b}{V}$$

24. (c)

25. (a) : $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{m.p.}}}$

$$T_{\text{m.p.}} = \frac{1435}{5.26} = 273 \text{ K, } i.e.\ 0\ ^\circ\text{C}$$

◈◈

How did students with zero or negative marks in Physics, Chemistry qualify in NEET? It's not the fault of NEET

The National Eligibility-cum-Entrance Test (NEET) has brought in much needed transparency in medical college admissions. This has exposed how students with abysmal scores in the entrance examination have got admission for MBBS, mostly in private colleges. This situation has been created by the health ministry and the Medical Council of India (MCI) keeping the qualifying cutoff very low so that private colleges can fill their seats despite their exorbitant fees.

With the Supreme Court ruling that all colleges will have to go by NEET ranking for admissions in 2017, one would have imagined that merit based admissions were finally in place. However, even students with ranks below 6 lakh got admission though there were only about 60,000 MBBS seats in 2017. How did that happen? The exorbitant fees charged by most private colleges forced lakhs of relatively meritorious students to forego seats allotted to them in these colleges, allowing poor performers with more money to get admission.

Many high scoring students cannot afford the exorbitant fees, but the health ministry and MCI, by keeping the cutoff at 50th and 40th percentile for general and reserved categories respectively, have ensured that the private colleges can go further and further down the merit list till they find students rich enough to fill their seats at the price demanded by them. Low cutoffs ensured that over six lakh students qualified for just 60,000 seats.

An analysis of NEET scores indicates that, other than ST, for all other categories even an 88th percentile cutoff would have been enough to comfortably fill the seats available. For the ST category, this would be true at about the 75th percentile. Several students with zero or negative marks in the physics and chemistry papers of NEET qualified for admission as the MCI has not fixed any minimum cutoff in individual subjects.

If zero or negative marks do not make a candidate ineligible for admission, why bother to test in the subject at all? Equally, how can a candidate scoring 15 out of 360, or 4%, in the NEET biology paper be eligible for MBBS? Several such students not only qualified, but also got admission in private colleges, paying average annual tuition fees of Rs 17 lakh. Thus the merit-based admission that NEET promised has been subverted by keeping the qualifying criteria fixed at ridiculously low levels despite the NEET results of 2013, 2016 and 2017 exposing the flaws in them.

If the cutoff was raised and minimum marks for individual subjects made mandatory, there would be fewer students qualifying and the private colleges demanding sky-high fees will not be able to fill their seats. They would be forced to charge more reasonable sums. TOI had analysed the annual tuition fees charged in 210 private colleges to show how 25 colleges averaged Rs 5 lakh or less and about half averaged under Rs 8 lakh. Why does the government allow some to charge up to Rs 25 lakh when they teach the same MCI-stipulated curriculum?

The High fees are the root cause of the dilution of merit. The higher the average fees in a college, the lower the average NEET score of those gaining admission to it

The high fees are the root cause of the dilution of merit. As TOI's analysis of NEET scores and college fees has shown, the higher the average fees in a college, the lower the average NEET score of those gaining admission to it. Seats remain vacant not because there aren't enough meritorious students but because many high scoring students can't afford the fees. Otherwise, why would private colleges not be able to fill their seats despite over 2 lakh students being within the 80th percentile?

The government argues that letting MBBS seats go vacant would be a colossal waste in a country facing a huge shortage of doctors. That's a red herring. Clearly, the shortage of doctors is most acute in rural India. No one, not even the health ministry, can pretend that doctors from these private colleges, where students pay lakhs of rupees as fees every year, will help overcome the rural shortage.

Can we allow such colleges to function in the name of doctor shortage when they not only do not help address the shortage but also actively sabotage and corrupt the medical education system? NEET can only stop the rot if it is not subverted by the Centre fixing low qualifying cutoffs and states refusing to regulate fees.

◈◈

Courtesy : The Times of India

Class XI

Be JEE READY

with exclusive and brain storming MCQs

Practicing these MCQs helps to strengthen your concepts and give you extra edge in your JEE preparation

1. The angular velocity of an electron occupying the second Bohr orbit of He^+ ion is (in sec^{-1})
(a) 2.067×10^{16} (b) 3.067×10^{16}
(c) 1.067×10^{18} (d) 2.067×10^{17}

2. 7 g of nitrogen is present at 127 °C and 16 g of oxygen at 27 °C. Calcualte the ratio of kinetic energy of nitrogen and oxygen.
(a) 4 : 3 (b) 2 : 3 (c) 4 : 5 (d) 5 : 4

3. How many moles of $K_2Cr_2O_7$ can be reduced by 1 mole of Sn^{2+} in acidic medium?
(a) 2/3 (b) 1/6 (c) 1/3 (d) 1

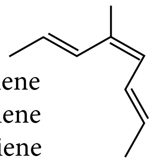
4. In a given energy level, the order of penetration effect of different orbitals is
(a) $f < p < d < s$ (b) $s < p < d < f$
(c) $f < d < p < s$ (d) $s = p = d = f$

5. 10 mL of 0.02 M $KMnO_4$ is required to oxidize 20 mL of oxalic acid of certain strength. 25 mL of the same oxalic acid is required to neutralize 20 mL of NaOH of unknown strength. Find the amount of NaOH in one litre of solution.
(a) 2.5 (b) 1.5 (c) 4.0 (d) 1.25

6. In transforming 0.01 mole of PbS to $PbSO_4$, the volume of '10 volume H_2O_2' required will be
(a) 11.2 mL (b) 22.4 mL
(c) 33.6 mL (d) 44.8 mL

7. During change of O_2 to O_2^- ion, the electron adds on which one of the following orbitals?
(a) σ^*2p_z orbital (b) $\sigma\, 2p_z$ orbital
(c) π^*2p_x/π^*2p_y orbital (d) $\pi 2p_x/\pi 2p_y$ orbital

8. What is the correct IUPAC name of the following compound ?



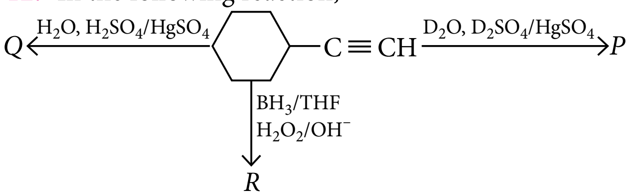
(a) 2*E*, 4*E*, 6*Z* 4-methyloct-2, 4, 6-triene
(b) 2*E*, 4*Z*, 6*Z* 5-methyloct-2, 4, 6-triene
(c) 2*Z*, 4*Z*, 6*Z* 5-methyloct-2, 4, 6-triene
(d) 2*E*, 4*Z*, 6*E* 4-methyloct-2, 4, 6-triene

9. The correct increasing order of *X*—O—*X* bond angle is (*X* = H, F or Cl)
(a) $H_2O > Cl_2O > F_2O$ (b) $Cl_2O > H_2O > F_2O$
(c) $F_2O > Cl_2O > H_2O$ (d) $F_2O > H_2O > Cl_2O$

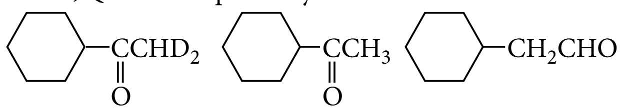
10. Calculate the extent of dissociation if the equilibrium pressure *P* for the system,
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$
is numerically 3 times to its K_p.
(a) 0.5 (b) 0.15 (c) 0.1 (d) 0.05

11. How can the given reaction is made to proceed in forward direction?
$2B(OH)_3 + 2NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + 2H_2O$
(a) Addition of *cis*-1, 2-diol
(b) Addition of borax
(c) Addition of *trans*-1, 2-diol
(d) Addition of Na_2HPO_4

12. In the following reaction,



P, Q and R respectively are :



(X) (Y) (Z)

(a) X, Y and Z (b) Y, X and Z
(c) Y in all cases (d) Z in all cases.

13. In the following sequence of reactions :

$$\underset{\text{Solution}}{Na_2CO_3} \xrightarrow{SO_2} (A) \xrightarrow{Na_2CO_3} (B) \xrightarrow[\text{Heat}]{S} (C) \xrightarrow{AgNO_3} (D)$$

Identify the compounds (A), (B), (C) and (D).
(a) Na_2SO_3, $NaHSO_3$, Na_2S, Ag_2S
(b) $NaHSO_3$, Na_2SO_3, $Na_2S_2O_3$, Ag_2S
(c) $NaHSO_3$, Na_2SO_4, Na_2S, Ag_2O
(d) Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$, Ag

14. For a perfectly crystalline solid $C_{p.m} = aT^3 + bT$, where a and b constant. If $C_{p.m}$ is 0.40 J/K mol at 10 K and 0.92 J/K mol 20 K, then molar entropy at 20 K is :
(a) 0.92 J/K mol (b) 8.66 J/K mol
(c) 0.813 J/K mol (d) 0.427 J/K mol

15. Frequent occurrence of water blooms in a lake indicates
(a) nutrient deficiency (b) oxygen deficiency
(c) excessive nutrient availability
(d) absence of herbivors in the lake.

SOLUTIONS

1. **(a) :** Velocity of an electron in He^+ ion in an orbit (υ)

$$= \frac{2\pi Ze^2}{nh} \quad \text{...(i)}$$

Radius of He^+ ion in an orbit $(r_n) = \dfrac{n^2h^2}{4\pi^2 me^2 Z}$ ...(ii)

By equation (i) and (ii), we get

$$\text{Angular velocity } (\omega) = \frac{\upsilon}{r_n} = \frac{8\pi^3 Z^2 me^4}{n^3h^3}$$

$$= \frac{8\times(22/7)^3\times(2)^2\times(9.108\times10^{-28})\times(4.803\times10^{-10})^4}{(2)^3\times(6.626\times10^{-27})^3}$$

$= 2.067 \times 10^{16}$ sec^{-1}

2. **(b) :** Kinetic energy $= \dfrac{3}{2}nRT$

For two gases, ratio of kinetic energies

$$= \frac{(K.E.)_1}{(K.E.)_2} = \frac{n_1T_1}{n_2T_2} = \frac{7}{28}\times400\times\frac{32}{16}\times\frac{1}{300} = 2:3$$

3. **(c) :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$(Sn^{2+} \rightarrow Sn^{4+} + 2e^-)\times 3$

$CrO_7^{2-} + 14H^+ + 3Sn^{2+} \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$

It is clear from this equation that 3 moles of Sn^{2+} reduce one mole of $Cr_2O_7^{2-}$, hence 1 mole Sn^{2+} will reduce $\dfrac{1}{3}$ mole of $Cr_2O_7^{2-}$.

4. **(c) :** The order of penetration effect of different orbitals depends upon the different energies of the various sub-shells for the same energy level, *e.g.*, electrons in *s*-subshell will have lowest energy and thus will be closest to the nucleus and thus, have highest penetration power, while *p*-subshell electrons will penetrate the electron cloud to lesser extent and so on.

5. **(a) :** In acidic medium
1M $KMnO_4$ = 5 N $KMnO_4$
0.02 M $KMnO_4$ = 0.1 N $KMnO_4$
According to normality equation,
N_1V_1 ($KMnO_4$) = N_2V_2 (Oxalic acid)

$0.1 \times 10 = N_2 \times 20 \quad \Rightarrow \quad N_2 = \dfrac{10\times0.1}{20} = 0.05$ N

Again, N_1V_1 (Oxalic acid) = N_2V_2 (NaOH)
$0.05 \times 25 = N_2 \times 20$

$$N_2 = \frac{0.05\times25}{20} = 0.0625 \text{ N}$$

Strength = Normality × equiv. wt.
= 0.0625 × 40 = 2.5 g L^{-1}

6. **(d) :** $\underset{0.01\text{ mole}}{PbS} + \underset{0.04\text{ mole}}{4H_2O_2} \longrightarrow PbSO_4 + 4H_2O$

$\underset{0.04\text{ mole}}{4H_2O_2} \longrightarrow 4H_2O + \underset{0.02\times22400\text{ mL at N.T.P.}}{2O_2}$

Vol. of O_2 at N.T.P. = 0.02 × 22400 = 448 mL
∴ Volume of 10 volume H_2O_2 solution
= 448/10 = 44.8 mL

7. **(c) :** $O_2 \rightarrow [KK]\sigma2s^2\sigma^*2s^2\sigma2p_z^2\pi2p_x^2\pi2p_y^2\pi^*2p_x^1\pi^*2p_y^1$
$O_2^- \rightarrow [KK]\ \sigma2s^2\sigma^*2s^2\sigma2p_z^2\pi2p_x^2\pi2p_y^2\pi^*2p_x^2\pi^*2p_y^1$
As in O_2 HOMO is π^*2p_x and π^*2p_y and they have one electron each so next electron can be added to any of these orbitals.

8. **(d) :** Higher Priority groups same side $\Rightarrow Z$ – form
Higher Priority groups opposite side $\Rightarrow E$ – form

9. **(b) :** Cl—O—Cl bond angle is more due to large size of Cl and F—O—F bond angle is least due to bent structure.

10. **(a) :** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial	1	0	0
At equil.	$1-x$	x	x

Total moles at equilibrium (if x is extent of dissociation) = $1 - x + x + x = 1 + x$

Partial pressure of $PCl_5 = \frac{1-x}{1+x}P$

Similarly, partial pressures of PCl_3 and Cl_2,

$$\left(p_{PCl_3} = \frac{x}{1+x}P\right) \text{ and } p_{Cl_2} = \frac{x}{1+x}P$$

Equilibrium constant, $K_p = \frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})}$

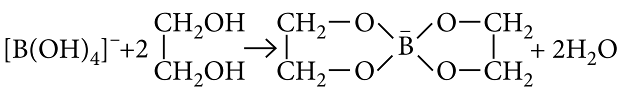
Substituting the values,

$$K_p = \frac{\left(\frac{xP}{1+x}\right)\left(\frac{xP}{1+x}\right)}{\frac{(1-x)P}{1+x}} = \frac{x^2P}{1-x^2}$$

$$\frac{P}{3} = \frac{x^2P}{1-x^2} \text{ or } x^2 = \frac{1}{4} \Rightarrow x = \frac{1}{2}$$

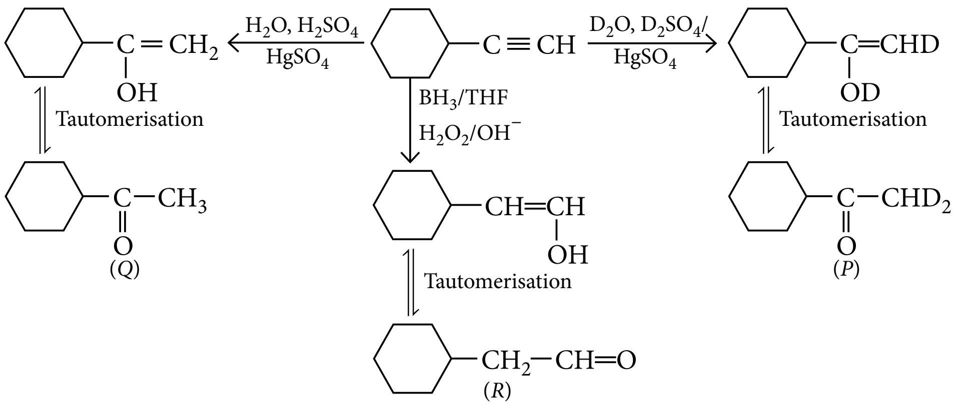
$\therefore$ Extent of dissociation of $PCl_5 = 0.5$

11. **(a) :** Orthoboric acid (H_3BO_3) is a weak monobasic acid due to $p\pi$-$p\pi$ back bonding between B and O. Direct neutralisation with alkali is not complete. In the presence of *cis*-1, 2-diol, a stable complex is formed and reaction goes to completion.



Chelate complex compound

12. **(a) :**



13. **(b) :** $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow \underset{(A)}{2NaHSO_3} + CO_2$

$\underset{(A)}{2NaHSO_3} + Na_2CO_3 \longrightarrow \underset{(B)}{2Na_2SO_3} + H_2O + CO_2$

$\underset{(B)}{Na_2SO_3} + S \xrightarrow{\text{Heat}} \underset{(C)}{Na_2S_2O_3}$

$\underset{(C)}{Na_2S_2O_3} + AgNO_3 \longrightarrow \underset{(D)}{Ag_2S} + H_2SO_4$

14. **(d) :** $0.40 = aT_1^3 + bT_1$

$\Rightarrow \quad 0.40 = a \times (1000) + b \times 10$

$\Rightarrow \quad 0.4 = 1000a + 10b$ ...(i)

$0.92 = aT_2^3 + bT_2$

$\Rightarrow \quad 0.92 = a \times 8000 + 20b$ ...(ii)

from Eqs. (i) and (ii), we get

$a = 2 \times 10^{-5}, b = 0.038$

$$S_m = \int \frac{aT^3 + bT}{T}.dT = \frac{a[T_2^3 - T_1^3]}{3} + b[T_2 - T_1]$$

= 0.427 J/K mol

15. **(b) :** In polluted water, nitrogen and phosphorus (from sewage) are accumulated which results in excessive growth of algae on water surface. Excessive growth of algae called water bloom. Due to death and decomposition of organic matter, O_2 is not available to aquatic animals.

BRUSH UP YOUR CONCEPTS

Class XI

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

STRUCTURE OF ATOM

After the study of subatomic particles, the structure of atom developed to explain the stability, difference of properties of different elements, formation of compounds and origin of electromagnetic radiation and related effects.

Electrons were discovered in the form of particles of cathode rays whose properties do not change by changing the material of glass tube, gas taken in discharge tube and material of electrodes.

In 1897, J.J. Thomson determined the ratio of charge and mass (specific charge) of electron to be -1.75882×10^{11} C kg^{-1} while the charge was determined by Millikan as -1.6022×10^{-19} C. These gave the mass equal to 9.1094×10^{-31} kg.

This mass of electron is called stationary mass. The mass of electron moving with velocity 'v' m s^{-1} is $\dfrac{m_{rest}}{\sqrt{1-\left(\dfrac{v}{c}\right)^2}}$.

Here, c is velocity of light in m s^{-1}.

When H_2 gas was filled in discharge tube, anode rays were found to be composed of protons with same charge as that of electron but positive in nature to explain the neutrality of atom. Mass of proton was determined to be 1.67262×10^{-27} kg.

Neutron was discovered by Chadwick in 1932.

$${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$$

The idea of nucleus present at the centre of atom and having total protons in it, was given by Rutherford using α-rays scattering experiment which was actually expansion of Lenard's (Denmark) experiment on Al.

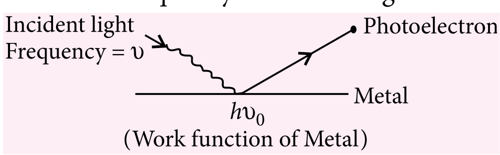
The number of α-particles deflected at angle θ in Rutherford's experiment $\propto \dfrac{Z^2}{\left(\sin\dfrac{\theta}{2}\right)^4}$.

Electrons were supposed to revolve around nucleus in some circular paths which was against the electromagnetic theory of Maxwell which says that when charged particle is accelerated it should emit radiations and as per calculations electron should fall into nucleus in less than 10^{-8} seconds.

Density of nucleus is fixed 1.685×10^{14} g cm^{-3}. Radius of nucleus is $1.33 \times 10^{-13} \times (\text{mass number})^{1/3}$ cm.

In 1900, Max Planck gave the name quantum to the smallest quantity (packet) of energy that can be absorbed or emitted in the form of electromagnetic radiation. This energy E is product of frequency of radiation and Planck's constant h (6.626×10^{-34} J s or 3.99×10^{-10} J s mol^{-1}), *i.e.*, $E = h\nu$. This explains that frequency of emitted radiation, from the black body, goes from a lower frequency to higher by increase in temperature.

In 1887, Hertz performed experiment in which electrons were ejected from certain metals like K, Cs, etc. when they were exposed to light of certain minimum frequency. The phenomenon is called photoelectric effect. The number of electrons ejected is directly proportional to intensity of light and energy of ejected photoelectron is directly proportional to frequency of incident light.



$h\upsilon_0$ is the work function of metal, *i.e.*, the minimum energy required to eject electron.

In 1905, A. Einstein calculated the kinetic energy of photoelectron as $\frac{1}{2}mv^2 = h\upsilon - h\upsilon_0$

If λ and λ_0 are wavelengths of incident light and wavelength that corresponding to υ_0,

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

velocity of ejected electron is

$$v=\left[\frac{2hc}{m}\left(\frac{\lambda_0-\lambda}{\lambda_0\lambda}\right)\right]^{1/2}$$

In 1885, Balmer observed the emission in visible spectrum of hydrogen under excited state. Balmer's formula for this emission was ($\bar{\upsilon}$, wave number $=\frac{1}{\lambda}$, the number of waves in unit length).

Wave number, $\bar{\upsilon}=\left(\frac{1}{2^2}-\frac{1}{n^2}\right)R\ \text{cm}^{-1}$.

Here R, has value 109677 cm^{-1} and $n > 2$

Later, in 1890, Rydberg generalised the equation as $\bar{\upsilon}=\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)R\,Z^2\ \text{cm}^{-1}$, to explain other emissions in one electron species having atomic number Z, like Li^{2+}, He^+, etc.

n_1 = 1, Lyman series – UV region

n_1 = 2, Balmer series – Visible region, H_α – red line, H_β – green line, H_γ – blue line and H_δ – violet line

n_1 = 3, Paschen series – IR region

n_1 = 4, Brackett series – IR region

n_1 = 5, Pfund series – Far IR region

n_1 = 6, Humphrey series – Far IR region

When $n_2 = \infty$, the spectral line is called limiting line.

In 1913, using Planck's theory of quantisation of energy and quantisation of angular momentum of motion of electron, Bohr gave following postulates and calculations (formulae) related to energy, angular momentum, velocity, etc., related to electron in H atom and species having one electron only.

(a) Electrons move around the nucleus in some definite circular paths or shells or orbits or stationary states numbered as 1, 2, 3, ... n (Principal quantum number) or denoted as K, L, M, ... etc. n^{th} shells has n complete electronic waves.

Higher the shell number, higher is the energy $E_1 < E_2 <$ .... but $(E_2 - E_1) > (E_3 - E_2) >$ ....

$$\text{Energy } E_n=-\frac{2\pi^2 me^4Z^2k^2}{n^2\,h^2}\quad [k=9\times10^9\ \text{N m}^2\ \text{C}^{-2}]$$

$$=-\,2.18\times10^{-18}\frac{Z^2}{n^2}\ \text{J atom}^{-1}\ \text{or}\ -13.6\frac{Z^2}{n^2}\ \text{eV atom}^{-1}$$

$$\text{or}\ \ 1.312\times10^6\frac{Z^2}{n^2}\ \text{J mol}^{-1}$$

[1 eV = 1.6×10^{-19} J = 96.48 kJ mol^{-1} = 23.06 kcal mol^{-1}]

–ve sign of energy shell indicates the release of energy of electron as it enters the vicinity of nucleus from infinity where its energy *w.r.t.* force of nucleus is considered zero.

Radius of n^{th} shell,

$$r_n=\frac{n^2h^2}{4\pi^2\,me^2Zk}=0.529\frac{n^2}{Z}\text{Å}=r_0\frac{n^2}{Z}\text{Å}$$

Total energy of an electron = *K.E.* + *P.E.*

$$=\frac{kZe^2}{2r}-\frac{kZe^2}{r}=-\frac{kZe^2}{2r}$$

Velocity of electron in n^{th} shell,

$$V_n = 2.18\times10^8\ Z/n\ \text{cm s}^{-1}$$

Number of revolutions (orbit frequency) per second

$$=6.66\times10^{15}\ Z^2/n^3$$

Time period, time for one revolution

$$=1.5\times10^{-16}\frac{n^3}{Z^2}\ \text{second}$$

(b) Only those shells are possible for which the angular momentum mvr is integral multiple of $\frac{h}{2\pi}$, *i.e.*, $mvr=\frac{nh}{2\pi}$.

(c) So long as an electron is in its normal or ground state, it does not lose energy and the energy of electron is equal to that of the orbit. Jump of electron from higher (excited state) to lower orbit releases the difference of energy between the two orbits as photons and reverse results in absorption of photon.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$=-2.18\times10^{-18}\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)Z^2\ \text{J atom}^{-1}$$

COMIC CAPSULE

(d) Number of spectral lines in H-atom

(i) Jump from n^{th} to 1^{st} shell $= \dfrac{n(n-1)}{2}$ (Total lines)

(ii) Jump from n_2 to n_1 shell $= \dfrac{\Delta n(\Delta n + 1)}{2}$ (Total lines)

(e) Number and types of spectral line in H-atom $= \Sigma\Delta n$
Example : Jump from 6^{th} shell to 2^{nd} shell
$= \Sigma(6 - 2) = \Sigma 4$
$= 4$(Balmer) + 3(Paschen) + 2(Brackett) + 1 (Pfund)
= 10 lines

Limitations of Bohr's Model of Atom

(a) The concept of circular path of electronic motion has now been replaced by a cloud picture with eliptical orbits (Sommerfeld's model).

(b) Explanation of spectra of unielectron species only is possible.

(c) It cannot explain Zeeman and Stark effects which deal with the splitting of spectral line to more finer lines in magnetic and electric field, respectively.

(d) It is not in accordance with the de Broglie's concept of dual nature of matter (1924) and Heisenberg's uncertainty principle.

MULTIPLE CHOICE QUESTIONS

1. The ratio of specific charge of proton to neutron is
(a) 0 (b) 1
(c) infinity (d) uncertain.

2. If an electron is moving with velocity of light, its mass in motion is likely to be
(a) same as mass at rest (b) $m_{rest} \times c$
(c) $m_{rest} \div c$ (d) infinity.

3. In Rutherford's experiment if 2000 alpha particles are scattered at angle 60° when Au is used, how many alpha particles will be scattered at angle 90° when Zr is taken in place of gold?
(At. No: Au = 79, Zr = 40)
(a) 128 (b) 96 (c) 500 (d) 750

4. Chadwick discovered neutron by using the following nuclear reaction :
(a) ${}^{11}_{5}B + {}^{4}_{2}He \longrightarrow {}^{14}_{7}N + {}^{1}_{0}n$
(b) ${}^{13}_{6}C + {}^{4}_{2}He \longrightarrow {}^{16}_{8}O + {}^{1}_{0}n$
(c) ${}^{9}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$
(d) ${}^{7}_{3}Li + {}^{4}_{2}He \longrightarrow {}^{10}_{5}B + {}^{1}_{0}n$

5. Density of nucleus of ${}^{12}_{6}C$ is 1.685×10^{14} g cm^{-3}. The density of nucleus of ${}^{24}_{12}Mg$ will be
(a) 4.21×10^{13} g cm^{-3} (b) 3.37×10^{14} g cm^{-3}
(c) 2.567×10^{14} g cm^{-3} (d) 1.685×10^{14} g cm^{-3}

6. When light with certain frequency υ (or wavelength λ) falls on a specific metal of work function $h\upsilon_0$ (corresponding wavelength λ), the velocity of ejected photoelectron will be
(a) $\left[\dfrac{2hc}{m}\left(\dfrac{\lambda_0 - \lambda}{\lambda_0\lambda}\right)\right]^{1/2}$ (b) $\left[\dfrac{2hc}{m}\left(\dfrac{\lambda_0 - \lambda}{\lambda_0\lambda}\right)\right]^{2}$
(c) $\left[\dfrac{m}{2hc}\left(\dfrac{\lambda_0 - \lambda}{\lambda_0\lambda}\right)\right]^{1/2}$ (d) $\left[\dfrac{2hm}{c}\left(\dfrac{\lambda_0 - \lambda}{\lambda_0\lambda}\right)\right]^{2}$

7. Balmer formula for Balmer series in case of spectrum of H-atom is
(a) $\bar{\upsilon} = \left(\dfrac{1}{2} - \dfrac{1}{n}\right) R$ cm^{-1}
(b) $\bar{\upsilon} = \left(\dfrac{1}{2^2} - \dfrac{1}{n^2}\right) R$ cm^{-1}
(c) $\bar{\upsilon} = \left(\dfrac{1}{n} - \dfrac{1}{2}\right) R$ cm^{-1}
(d) $\bar{\upsilon} = \left(\dfrac{1}{n^2} - \dfrac{1}{2^2}\right) R$ cm^{-1}

8. The ratio of wavelengths of limiting lines of Lyman series to that of Balmer series is
(a) 1 : 1 (b) 2 : 1 (c) 1 : 4 (d) 4 : 1

9. Which of the following is correct for energy related to Bohr's orbits of H-atom?
(a) $E_1 < E_2 < E_3 <$ .....
(b) $(E_2 - E_1) > (E_3 - E_2) >$ ......
(c) $E_1 = -1312$ kJ mol^{-1} (d) All are correct

10. Velocity of electron in shell is $2.18 \times 10^6 \dfrac{Z}{n}$ m s^{-1}. If the velocity of electron can never be more than the velocity of light, the atomic number of the last possible element would be
(a) 137 (b) 140 (c) 147 (d) 150

11. How much energy should be supplied to Li^{2+} ion to make it only electron jump to the 3^{rd} shell?
(a) 1.088 eV atom^{-1} (b) 10.08 eV atom^{-1}
(c) 10.88 eV atom^{-1} (d) 108.8 eV atom^{-1}

12. How many spectral lines, in total and in Brackett series, respectively, will be emitted in H-atom when electron jumps from 6^{th} to 2^{nd} shell?
(a) 10, 2 (b) 8, 3 (c) 6, 3 (d) 8, 2

13. What is the ratio $\lambda_{max} : \lambda_{min}$ in case of Balmer series of H-atom?
(a) 9 : 5 (b) 5 : 9 (c) 4 : 3 (d) 3 : 4

14. Which of the following is correct for black body when temperature is increased?
(a) Emitted frequency goes lower to higher.
(b) Emitted frequency goes higher to lower.
(c) Emitted frequency remains constant.
(d) Emitted frequency depends upon the nature of black body.

15. A metal sheet is irradiated separately with radiations of frequency υ_1 and υ_2. If the ratio of kinetic energies of photoelectrons is 1 : x, the threshold frequency of the metal is
(a) $\frac{x-1}{x\upsilon_1 - \upsilon_2}$ (b) $\frac{\upsilon_1 - x\upsilon_2}{1-x}$
(c) $\frac{x\upsilon_1 - \upsilon_2}{x-1}$ (d) $\frac{x\upsilon_1 + \upsilon_2}{x+1}$

16. An object absorbs a light of wavelength 1200 Å and releases two different radiations of wavelength 3000 Å and 'x' Å. The value of 'x' is
(a) 1500 Å (b) 2000 Å (c) 2500 Å (d) 3000 Å

17. Which of the following is correct for Bohr's model of atom?
(a) It explains Zeeman effect.
(b) It explains Stark effect.
(c) It follows Heisenberg's uncertainty principle.
(d) It uses quantisation of energy and momentum.

18. An electric bulb marked as 60 watt, emits light of 3000 Å. If 25% of the energy is emitted as light, the number of photons emitted in one second is
(a) 2.27×10^{20} (b) 7.22×10^{20}
(c) 2.27×10^{19} (d) 7.22×10^{19}

19. Which of the following is related with the highest velocity of electron?
(a) H, $n = 1$ (b) He^+, $n = 2$
(c) Li^{2+}, $n = 3$ (d) All are equal.

20. If H-atom is supplied with 1230 kJ mol^{-1} energy, its electron will jump to
(a) 2nd shell (b) 3rd shell
(c) 4th shell (d) 6th shell.

SOLUTIONS

1. **(c) :** $\frac{\text{Sp. charge of proton}}{\text{Sp. charge of neutron}}$

$$= \frac{\left(\frac{e}{m}\right)\text{proton}}{\left(\frac{e}{m}\right)\text{neutron}} = \frac{1/1}{0/1} = \text{infinity}$$

[Mass of proton and neutron both is 1 unit each, charge of proton is +1 unit and of neutron is zero]

2. **(d) :** Mass of $\bar{e}$ in motion

$$= \frac{m_{rest}}{\sqrt{1-\left(\frac{v}{c}\right)^2}} = \frac{m_{rest}}{\sqrt{1-1}} = \text{infinity}$$

3. **(a) :** $$\frac{\alpha_{Zr}}{\alpha_{Au}} = \frac{\left[\frac{Z^2}{\left(\sin\frac{\theta}{2}\right)^4}\right]_{Zr}}{\left[\frac{Z^2}{\left(\sin\frac{\theta}{2}\right)^4}\right]_{Au}} = \frac{40\times 40}{(\sin 45°)^4} \times \frac{(\sin 30°)^4}{79\times 79}$$

$$\alpha_{Zr} = \frac{2000\times 40\times 40\times\left(\frac{1}{2}\right)^4}{79\times 79\times\left(\frac{1}{\sqrt{2}}\right)^4}$$

$$= \frac{2000\times 40\times 40\times 4}{79\times 79\times 16} = 128$$

4. **(c)**

5. **(d) :** Density of nucleus is fixed 1.685×10^{14} g cm^{-3}.

6. **(a) :** $$\frac{1}{2}mv^2 = h\upsilon - h\upsilon_0 = h\left(\frac{c}{\lambda} - \frac{c}{\lambda_0}\right) = hc\left(\frac{\lambda_0 - \lambda}{\lambda_0\lambda}\right)$$

$$\Rightarrow \quad v = \left[\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda_0\,\lambda}\right)\right]^{1/2}$$

7. **(b) :** Balmer series is in visible spectrum and is generated by jump of electron to 2nd shell from any higher shell. Wave number is given by

$$\bar{\upsilon} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)\text{cm}^{-1}$$

8. **(c) :** $$\frac{\lambda_{Lyman}}{\lambda_{Balmer}} = \frac{\bar{\upsilon}_{Balmer}}{\bar{\upsilon}_{Lyman}} = \frac{R\left(\frac{1}{2^2}\right)}{R\left(\frac{1}{1^2}\right)} = \frac{1}{4}$$
[n is infinity]

9. **(d)**

10. **(a) :** Maximum value of velocity of electron (highest in 1st shell) = $2.18 \times 10^6 Z = 3 \times 10^8 \Rightarrow Z = 137.6$

11. **(d) :** $E_n = -13.6\frac{Z^2}{n^2}$ eV $atom^{-1}$

For Li^{2+}, $$(E_3 - E_1) = \left(-13.6\times\frac{3^2}{3^2}\right) - \left(-13.6\times\frac{3^2}{1^2}\right)$$
= – 13.6 + 122.4 = 108.8 eV $atom^{-1}$

12. (a) : Number and type of lines = $\Sigma(6-2) = \Sigma 4$
= 4 (Balmer) + 3(Paschen) + 2(Brackett) + 1(Pfund) = 10

13. (a) : $\dfrac{\bar{\upsilon}_{min}\text{ (jump from infinity)}}{\bar{\upsilon}_{max}\text{ (jump from 3}^{rd}\text{ shell)}} = \dfrac{\lambda_{max}}{\lambda_{min}}$

$$= \frac{R\left(\frac{1}{2^2}\right)}{R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)} = \frac{\frac{1}{4}}{\frac{9-4}{36}} = \frac{36}{5} \times \frac{1}{4} = \frac{9}{5}$$

14. (a)

15. (c) : $\dfrac{h(\upsilon_1 - \upsilon_0)}{h(\upsilon_2 - \upsilon_0)} = \dfrac{KE_1}{KE_2} \Rightarrow \dfrac{\upsilon_1 - \upsilon_0}{\upsilon_2 - \upsilon_0} = \dfrac{1}{x}$

$\Rightarrow x\upsilon_1 - x\upsilon_0 = \upsilon_2 - \upsilon_0$

$\Rightarrow x\upsilon_1 - \upsilon_2 = x\upsilon_0 - \upsilon_0 = (x-1)\upsilon_0$

$\Rightarrow \upsilon_0 = \dfrac{x\upsilon_1 - \upsilon_2}{x-1}$

16. (b) : $E_{\text{Absorbed}} = E_{\text{Released I}} + E_{\text{Released II}}$

$$\left(\frac{hc}{\lambda}\right)_{abs.} = \left(\frac{hc}{\lambda}\right)_{I} + \left(\frac{hc}{\lambda}\right)_{II}$$

$$\frac{1}{1200} = \frac{1}{3000} + \frac{1}{x}$$

$$\frac{1}{x} = \frac{1}{1200} - \frac{1}{3000} = \frac{3000 - 1200}{1200 \times 3000}$$

$$= \frac{1800}{1200 \times 3000} = \frac{1}{2000}$$

$x = 2000$ Å

17. (d)

18. (c) : Energy emitted as light (E)
= 25% of (60 W × 1 s) = 15 J

$\lambda = 3000$ Å $= 3000 \times 10^{-10}$ m

Energy ($h\upsilon$) = 1 photon released

$$\text{Energy } (E) = \frac{E}{h\upsilon}\text{ photon released} = \frac{E}{h} \times \frac{\lambda}{c}$$

$$= \frac{15 \times 3000 \times 10^{-10}}{6.6 \times 10^{-34} \times 3 \times 10^{8}}$$

$= 2.27 \times 10^{19}$ photons released

19. (d) : Velocity of electron $= 2.18 \times 10^8 \times \dfrac{Z}{n}$ cm s^{-1}

$\dfrac{Z}{n}$ of all three cases are equal.

20. (c) : $E_n = \dfrac{E_1}{n^2} \Rightarrow n^2 = \dfrac{-1312}{-1312 + 1230} = \dfrac{-1312}{-82} = 16$

$\Rightarrow n = 4$

TOP 10 SKILLS FOR FUTURE

By 2020 over one-third of skills (35%) that are considered important in today's workforce will be changed. The Fourth Industrial Revolution will have brought us advanced robotics and autonomous transport, artificial intelligence and machine learning, advanced materials, biotechnology and genomics.

These developments will transform the way we live, and the way we work. Some jobs will disappear, others will grow and jobs that don't even exist today will become common place. What is certain is that the future work force will need to align its skill set to keep pace.

The 10 skills you need to thrive in the Fourth Industrial Revolution by World Economic Forum are as follows:

1 COMPLEX PROBLEM SOLVING

The skill to craft creative solutions to problems that are yet to appear is a must to keep up with AI (Artificial Intelligence) machines.

2 CRITICAL THINKING

People who can turn data into insightful interpretations will be the most sought-after.

3 CREATIVITY

Randomness and the ability to build something out of ideas is a skill that will pay-off in the future.

4 PEOPLE MANAGEMENT

Robots may acquire analytical and mathematical skill but they can't replace humans in leadership and managerial roles that require people skills.

5 COORDINATION WITH OTHERS

Effective communication and team collaboration skills will be in the top demand in every industry in the post AI era

6 EMOTIONAL INTELLIGENCE

Qualities that relate to emotional intelligence such as empathy and curiosity will be a big consideration factor for hiring managers in AI affected industries.

7 JUDGMENT AND DECISION-MAKING

The ability to condense vast amounts of data, with the help of data analytics, into insightful interpretations and measured decisions is a skill that will be useful in the information age.

8 SERVICE ORIENTATION

Offering value to clients in the form of services and assistance will be in demand as businesses would want to provide solutions to the problems of society.

9 NEGOTIATION

The ability to negotiate with businesses and individuals to come up with a win-win situation would be a survival skill.

10 COGNITIVE FLEXIBILITY

The ability to switch between different personas to accommodate the challenge at hand will be important to be successful in the post AI era.

EXAMiNER'S MiND CLASS XI

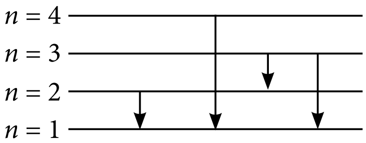
The questions given in this column have been prepared on the basis of pattern of Previous Years' Questions asked in JEE (Main & Advanced)/NEET/AIIMS exams.

STRUCTURE OF ATOM

SECTION - I

Only One Option Correct Type

1. Suppose that a hypothetical atom gives a red, green, blue and violet line spectrum. Which jump according to figure, would give off the red spectral line?



(a) $3 \rightarrow 1$ (b) $2 \rightarrow 1$
(c) $4 \rightarrow 1$ (d) $3 \rightarrow 2$

2. For the electrons of oxygen atom, which of the following statements is correct?
(a) Z_{eff} for an electron in a 2*s* orbital is the same as Z_{eff} for an electron in a 2*p* orbital.
(b) An electron in the 2*s* orbital has the same energy as an electron in the 2*p* orbital.
(c) Z_{eff} for an electron in 1*s* orbital is the same as Z_{eff} for an electron in a 2*s* orbital.
(d) The two electrons present in the 2*s* orbital have same spin quantum number m_s but of opposite sign.

3. If the subsidiary quantum number of a sub-energy level is 4, the maximum and minimum values of the spin multiplicities are
(a) 9, 1 (b) 10, 1 (c) 10, 2 (d) 4, –4

4. Last line of Lyman series for H-atom has wavelength λ_1 Å, 2nd line of Balmer series has wavelength λ_2 Å, then
(a) $\frac{16}{\lambda_1} = \frac{9}{\lambda_2}$ (b) $\frac{16}{\lambda_2} = \frac{3}{\lambda_1}$
(c) $\frac{4}{\lambda_1} = \frac{1}{\lambda_2}$ (d) $\frac{16}{\lambda_1} = \frac{3}{\lambda_2}$

5. The radius of the second Bohr orbit for hydrogen atom is
Given ; Planck's constant $(h) = 6.6262 \times 10^{-34}$ J s;
mass of electron $= 9.1091 \times 10^{-31}$ kg;
charge of electron $= 1.60210 \times 10^{-19}$ C;
permittivity of vacuum (ε_0)
$= 8.854185 \times 10^{-12}$ kg^{-1} m^{-3} A^2
(a) 0.529 Å (b) 2.12 Å
(c) 1.65 Å (d) 4.76 Å
(JEE Main 2017)

SECTION - II

More than One Options Correct Type

6. A hydrogen-like atom has a ground state binding energy of –122.4 eV. Then
(a) its atomic number is 3
(b) a photon of 90 eV can excite it to a higher state
(c) an 80 eV photon cannot excite it to a higher state
(d) none of the above.

7. In which of the following the first orbital has higher energy than the second in H-atom?
(a) $n = 4, l = 3$ and $n = 5, l = 0$
(b) $n = 3, l = 2$ and $n = 3, l = 1$
(c) $n = 3, l = 1$ and $n = 3, l = 2$
(d) $n = 3, l = 2$ and $n = 2, l = 1$

8. According to Bohr's atomic theory, which of the following relations are correct?
(a) Kinetic energy of electron $\propto \frac{Z^2}{n^2}$
(b) The product of velocity of electron and the principal quantum number $\propto Z^2$
(c) Frequency of revolution of the electron in an orbit $\propto \frac{Z^2}{n^3}$

(d) Coulombic force of attraction on the electron $\propto \frac{Z^3}{n^4}$

9. Which of the following statements are correct for an electron of quantum numbers $n = 4$ and $m = 2$?
(a) The value of l may be 2.
(b) The value of l may be 3.
(c) The value of s may be +1/2.
(d) The value of l may be 0, 1, 2, 3.

10. Ground state electronic configuration of nitrogen atom can be represented by
(a) [↑↓] [↑↓] [↑|↑|↑] (b) [↑↓] [↑↓] [↑|↓|↑]
(c) [↑↓] [↑↓] [↑|↓|↓] (d) [↑↓] [↑↓] [↓|↓|↓]

SECTION - III

Paragraph Type

Paragraph for Questions 11 and 12

The position and energy of an electron is specified with the help of four quantum numbers namely, principle quantum number (n), azimuthal quantum number (l), magnetic quantum number (m_l) and spin quantum number (m_s). The permissible values of these are :

$n = 1, 2\ ;\ l = 0, 1, ... (n - 1)\ ;\ m_l = -l\ .....0, ...+l$

$m_s = +\frac{1}{2}$ and $-\frac{1}{2}$ for each value of m_l.

The electrons having the same value of n, l and m_l are said to belong to the same orbital. According to Pauli's exclusion principle, an orbital can have maximum of two electrons and these two must have opposite spin.

11. For an electron having $n = 3$ and $l = 0$, the orbital angular momentum is
(a) $\frac{\sqrt{3}h}{\pi}$ (b) $\sqrt{6}\frac{h}{2\pi}$
(c) zero (d) $2\sqrt{3}\frac{h}{\pi}$

12. Which of the following statements is not correct?
(a) For sodium, the outermost electron has $n = 3$, $l = 0$, $m_l = 0$, $s = +1/2$
(b) The orbitals having $n = 3$, $l = 2$, $m_l = +2$ and $n = 3$, $l = 2$, $m_l = -2$ have same energies.
(c) For 4f electron, $n = 4$, $l = 3$, $m_l = 0$, $s = +1/2$ is not possible.
(d) The orbitals 2d, 3f and 4g are not possible.

SECTION - IV

Matching List Type

13. Match the electronic configurations listed in column II with the descriptions listed in column I :

	Column I		Column II
A.	Violation of Aufbau's rule	p.	[↑↓] [↑↑|↑|]
B.	Violation of Pauli's exclusion principle	q.	[↑↓] [↑↓|↑|]
C.	Violation of Hund's rule	r.	[↑↓] [↑↑|↑|↑]
D.	Violation of both Pauli's and Hund's rules	s.	[↑] [↑↓|↑|↑]

	A	B	C	D
(a)	p	q,s	p,s	r
(b)	s	p,r	p,q	p
(c)	r	r,s	p,q	q
(d)	s	p,q	r,s	q

14. Match the entries in column I with the correct related quantum number(s) in column II.

	Column I		Column II
A.	Orbital angular momentum of the electron in a hydrogen like atomic orbital	p.	Principal quantum number
B.	A hydrogen like one-electron wave function obeying Pauli's principle	q.	Azimuthal quantum number
C.	Shape, size and orientation of hydrogen-like atomic orbitals	r.	Magnetic quantum number
D.	Probability density of electron at the nucleus in hydrogen-like atom	s.	Electron spin quantum number

	A	B	C	D
(a)	q	s	p, q, r	p, q
(b)	p	s	p, q	p
(c)	r	s, p	s	s
(d)	p	q	p, q, s	p, r

(IIT-JEE 2008)

SECTION - V

Numerical Value Type

15. A radiation of wavelength λ illuminates a metal and ejects photoelectrons of maximum kinetic energy of 1 eV. Another radiation of wavelength $\lambda/3$ ejects photoelectrons of maximum kinetic energy of 4 eV. What will be the work function of metal?

16. Ultraviolet light of wavelength 800 Å and 700 Å when allowed to fall on hydrogen atoms in their ground state is found to eject electrons with kinetic energy 1.8 eV and 4.0 eV respectively. Compute the value of Planck's constant (in terms of 10^{-34} J s)?

17. Not considering the electronic spin, the degeneracy of the second excited state (n = 3) of H-atom is 9, while the degeneracy of the second excited state of H^- is (*JEE Advanced 2015*)

SECTION - VI

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

18. Assertion : The transition of electrons $n_3 \rightarrow n_2$ in H-atom will emit radiation of higher frequency than $n_4 \rightarrow n_3$.
Reason : Principal shells n_2 and n_3 have lower energy than n_4.

19. Assertion : Hydrogen has only one electron in its orbit. But it produces several spectral lines.
Reason : There are many excited energy levels available.

20. Assertion : Number of radial and angular nodes for 3p-orbital are 1, 1 respectively.
Reason : Number of radial and angular nodes depends only on principal quantum number.

ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES

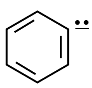
SECTION - I

Only One Option Correct Type

1. Sodium extract of an organic compound is acidified with dil. H_2SO_4 and then treated with excess of chlorine water in presence of carbon disulphide, a colourless solution is obtained. This indicates
(a) absence of chlorine (b) presence of bromine
(c) absence of all halogens
(d) chlorine may or may not be present.

2. Which of the following statements is false about a homologous series of a class of organic compounds?
(a) The adjacent members differ by one — CH_2 group.
(b) The difference between the molecular masses of any two adjacent members is 14.
(c) The homologues can generally be prepared by the same general methods.
(d) The homologues have identical physical and chemical properties.

3. The stability of carbanions in the following compounds,

(i) $RCH{=}\bar{C}H$ (ii) 

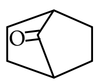
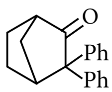
(iii) $R_2C{=}\bar{C}H$ (iv) $R_3C-\bar{C}H_2$

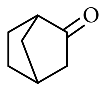
is in the order of
(a) (iv) > (ii) > (iii) > (i)
(b) (i) > (iii) > (ii) > (iv)
(c) (i) > (ii) > (iii) > (iv)
(d) (ii) > (iii) > (iv) > (i)

4. Compound A of the formula $C_5H_8O_2$ liberates carbon dioxide on reaction with sodium bicarbonate. It exists in two diastereomeric forms. On hydrogenation, each diastereomer gives compound B which can be separated into two enantiomorphs. Compounds A and B respectively are

(a) $CH_3-\underset{}{\overset{CH=CH_2}{\overset{|}{C}}}HCOOH$ and $CH_3\overset{CH_2CH_3}{\overset{|}{C}}HCOOH$
(b) $CH_3CH{=}CHCH_3$ and $CH_3CH_2CH_2CH_3$
(c) $CH_3CH{=}C(CH_3)COOH$ and $CH_3CH_2CH(CH_3)COOH$
(d) $(CH_3)_2C{=}CHCOOH$ and $(CH_3)_2CHCH_2COOH$

5. Which among the given molecules can exhibit tautomerism?


I


II


III

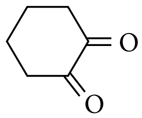
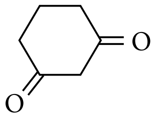
(a) III only (b) Both I and III
(c) Both I and II (d) Both II and III
(*NEET Phase-II 2016*)

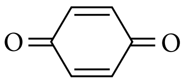
SECTION - II

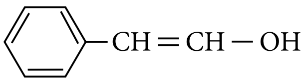
More than One Options Correct Type

6. Number of stereoisomers of lactic acid is
(a) 1 (b) 2 (c) 3 (d) 4

7. Which of the following structures exhibit tautomerism?

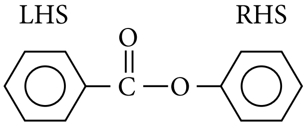
(a)  (b) 

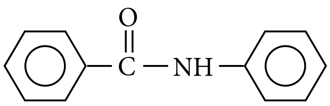
(c) 

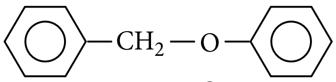
(d) 

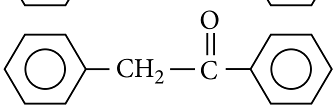
8. In which of the following compounds electrophilic aromatic substitution takes place in phenyl ring present in right hand side (RHS)?

LHS RHS

(a) 

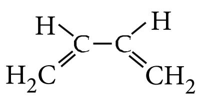
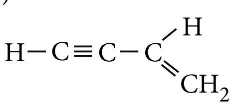
(b) 

(c) 

(d) 

9. In Lassaigne's test, the organic compounds is first fused with sodium metal. The sodium metal is used because
(a) the melting point of sodium is low so it is easily fused with organic substances
(b) sodium is very effective in causing destructive reductions of organic compounds forming the ionic inorganic salts NaCN, Na_2S and NaX
(c) all sodium salts are soluble in water
(d) sodium salts are insoluble in water.

10. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations, is (are)

(a)  (b) 

(c) $H_2C=C=O$ (d) $H_2C=C=CH_2$

(IIT-JEE 2011)

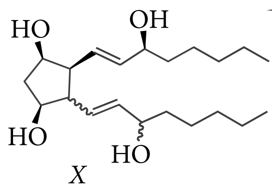
SECTION - III

Numerical Value Type

11. During the estimation of nitrogen by the Dumas method, 0.2033 g of an organic compound gave 31.7 mL of moist N_2, which was collected at 287 K and 758 mmHg. Calculate the percentage of nitrogen in the compound. Aqueous tension at 287 K = 14 mmHg.

12. In the estimation of phosphorus in an organic compound by the Carius method, 2.79 g of the compound gave 1.332 g of magnesium pyrophosphate ($Mg_2P_2O_7$). Calculate the percentage of phosphorus in the compound.

13. For the given compound X, the total number of optically active stereoisomers is _______ .



X

This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed.

This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is **NOT** fixed.

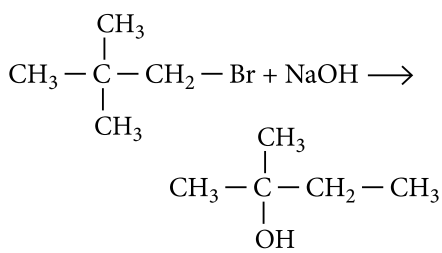
(JEE Advanced 2018)

SECTION - IV

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

14. Assertion : 1-Phenylethanol can be distinguished from 2-phenylethanol by iodoform test.
Reason : 1-Phenylethanol contains CH_3CHOH-group linked to carbon but 2-phenylethanol does not.

15. Assertion : 

Reason : It follows with formation of more stable carbocation.

SOLUTIONS

STRUCTURE OF ATOM

1. (d) : Order of energy, $E_{4\to 1} > E_{3\to 1} > E_{3\to 2}$
According to energy; Violet > Blue > Green > Red
$\therefore$ Red line $\Rightarrow 3 \longrightarrow 2$ transition

2. (d)

3. (c) : $l = 4$; number of degenerate orbitals $= 2l + 1 = 9$

Maximum total spins $= 9 \times \frac{1}{2}$

Minimum total spin $= \frac{1}{2}$

Maximum multiplicity $= 2S + 1 = 2\times\frac{9}{2}+1=10$

Minimum multiplicity $= 2\times\frac{1}{2}+1=2$

4. (b) : $\frac{1}{\lambda_1} = R(1)^2\left[\frac{1}{1^2}-\frac{1}{\infty^2}\right]$ and $\frac{1}{\lambda_2} = R(1)^2\left[\frac{1}{2^2}-\frac{1}{4^2}\right]$

$\therefore\ \lambda_1 = \frac{1}{R}$ and $\lambda_2 = \frac{16}{3R} \Rightarrow \frac{16}{\lambda_2} = \frac{3}{\lambda_1}$

5. (b) : Radius of n^{th} orbit for H-atom is

$$r = \frac{n^2 a_0}{Z}\text{ Å} \Rightarrow r = \frac{(2)^2 \times 0.529}{1}\text{ Å}$$

[$\because$ $n = 2$, for second orbit]

$r = 2.12$ Å

6. (a,c) : Ground state binding energy $= -13.6\, Z^2$
$= -122.4$ eV

$\therefore\ Z = 3$

1st excitation energy $= 10.2\, Z^2 = 91.8$ eV

$\therefore$ An 80 eV photon cannot excite it to a higher state.

7. (a,b,d) **8. (a,c,d)** **9. (a,b,c)**

10. (a,d) **11. (c)**

12. (c) : For $4f$ electron, $n = 4$, $l = 3$, $m_l = 0$ and $s = +\frac{1}{2}$ is possible.

13. (b) **14. (a)**

15. (0.5) : Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$h\frac{c}{\lambda} = w_0 + 1\text{ eV} \quad \text{...(i)}$$

$$3h\frac{c}{\lambda} = w_0 + 4\text{ eV} \quad \text{...(ii)}$$

$3(w_0 + 1\text{ eV}) = w_0 + 4$ eV

$w_0 = 0.5$ eV

16. (6.57) : $(K.E.)_1 = 1.8\text{ eV} = h\upsilon_1 - I.E. = \frac{hc}{\lambda_1} - I.E.$ ...(i)

$(K.E.)_2 = 4.0\text{ eV} = h\upsilon_2 - I.E. = \frac{hc}{\lambda_2} - I.E.$ ...(ii)

From (i) and (ii), we get

$$(K.E.)_2 - (K.E.)_1 = hc\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right)$$

$$(4 - 1.8)\text{ eV} = h \times 3.0 \times 10^8\left(\frac{\lambda_1 - \lambda_2}{\lambda_1\lambda_2}\right)$$

$$= h \times \frac{3.0\times10^8(800-700)\times10^{-10}}{700\times10^{-10}\times800\times10^{-10}}$$

$$h = \frac{(2.2\times1.6\times10^{-19}\text{ J})\times700\times10^{-10}\times800\times10^{-10}\text{ m}^2}{3.0\times10^8(\text{ms}^{-1})\times100\times10^{-10}(\text{m})}$$

$= 6.57 \times 10^{-34}$ J s

17. (3) : In case of H-atom, the energies of the orbitals are in the order :

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \ldots\ldots$

For multielectronic systems, like H^- ion, the order is $1s < 2s < 2p$ ...... [follow $(n + l)$ rule]

For H-atom, $Z = 1$, $1s^1$,

The second excited state ($n = 3$) is $3s = 3p = 3d$

Degenerate orbitals 1 3 5

$\therefore$ Degeneracy $= 1 + 3 + 5 = 9$

For H^- ion, $Z = 1$, $1s^2$, the first excited state would be $1s^1$, $2s^1$ and the second excited state would be $1s^1$, $2s^0$, $2p^1$.

$2p^1$ [↑][ ][ ] $\therefore$ degeneracy = 3

18. (b) **19. (a)**

20. (c) : For $3p$-orbital, number of radial nodes
$= n - l - 1 = 3 - 1 - 1 = 3 - 2 = 1$

Number of angular nodes $= l = 1$

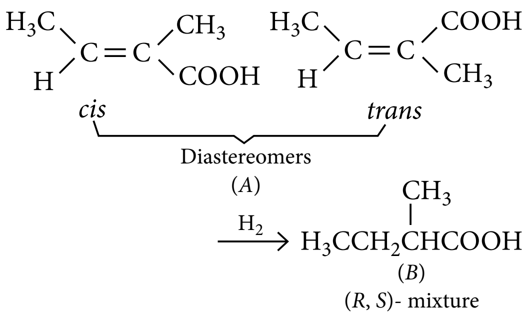
Number of radial and angular nodes depends on both n and l.

MONTHLY TUNE UP XII ANSWER KEY

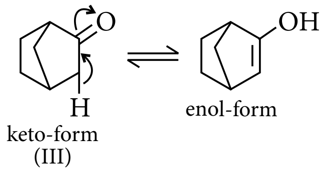
1.	(a)	2.	(c)	3.	(b)	4.	(c)	5.	(c)
6.	(b)	7.	(c)	8.	(c)	9.	(d)	10.	(c)
11.	(b)	12.	(b)	13.	(b)	14.	(c)	15.	(d)
16.	(c)	17.	(c)	18.	(c)	19.	(a)	20.	(b,c)
21.	(a,b)	22.	(a,b,c)	23.	(a,b)	24.	(5×10^{-19})		
25.	(561)	26.	(0.0239)	27.	(c)	28.	(d)	29.	(c)
30.	(d)								

ORGANIC CHEMISTRY : SOME BASIC PRINCIPLES AND TECHNIQUES

1. **(d):** This test is applied only for the detection of I and Br. Violet colour is produced in presence of iodine, while a brown or reddish colour is produced in presence of bromine.
2. **(d)**
3. **(c) :** Higher the no. of electron releasing groups lower will be stability of carbanion, and *vice versa*. So, the order of stability of carbanions is (i) > (ii) > (iii) > (iv).
4. **(c) :**



5. **(a) :** α-Hydrogen at bridge carbon atom never participates in tautomerism. Thus, only (III) exhibits tautomerism.



6. **(b):** Number of stereoisomers, if molecule cannot be divided into two equal halves = 2^n

   $CH_3—CHOH—COOH$
   Lactic acid

   $n = 1$, so stereoisomers = $2^1 = 2$
7. **(a,b,d)**
8. **(a,b,c) :** E^+ attacks on ring which has more e^- density.
9. **(a,b,c)**
10. **(b, c)**
11. **(18.13) :** Mass of substance taken = 0.2033 g

    Volume of nitrogen collected = 31.7 mL

    Atmospheric pressure = 758 mmHg

    Room temperature = 287 K

    Aqueous tension at 287 K = 14 mmHg

    Actual pressure of dry gas (P_1) = 758 – 14 = 744 mmHg

    Now, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{744\times31.7}{287} = \frac{760\times V_2}{273}$ (at STP)

    $V_2 = 29.5$ mL

    22400 mL of nitrogen at STP weigh = 28 g

    ∴ 29.5 mL of Nitrogen at STP will weigh $= \frac{28\times29.5}{22400}$ g

    $$\% \text{ of nitrogen} = \frac{\text{Mass of } N_2 \text{ at STP}}{\text{Mass of the substance taken}}\times100$$

    $$= \frac{28\times29.5\times100}{22400\times0.2033} = 18.13\%$$
12. **(13.33) :** Mass of organic compound = 2.79 g

    Mass of $Mg_2P_2O_7$ = 1.332 g

    222 g of $Mg_2P_2O_7$ contains 62 g of phosphorus.

    ∴ 1.332 g $Mg_2P_2O_7$ contains $\frac{62}{222}\times1.332$ g of phosphorus.

    Since, 2.79 g of the organic compound contains $\frac{62}{222}\times1.332$ g of phosphorus

    ∴ 100 g of the organic compounds contains $\frac{62}{222}\times\frac{1.332}{2.79}\times100 = 13.33\%$ of phosphorus.
13. **(7)**
14. **(a)**
15. **(a)**

Recently researchers have prepared a new high energy compound for use in environmental friendly rocket fuels. Use of this compound could effectively eliminate a hazardous byproduct from the process of jet propulsion.

As safety concerns dictate that rocket fuels be kept away from air, a key component of their formulation is an oxidiser that can serve as an oxygen source to assist the combustion reaction that propels the rocket. Ammonium perchlorate is a widely used oxidiser in rockets and other pyrotechnics. However, a major combustion product of this is hydrochloric acid, HCl, which can have an adverse effect on the ozone layer and cause acid rain. Developing an oxidiser that does not contain chlorine is therefore a worthwhile goal.

Now a study, shows a synthetic route to a bipyrazole molecule that contains no fewer than 10 nitro groups, an important functional group in explosive materials. More importantly, it contains no chlorine, thereby eliminating HCl as a possible byproduct.

CLASS XI

CBSE DRILL

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2018-19.

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 12 are short answer questions and carry 2 marks each.
(iv) Q. no. 13 to 24 are also short answer questions and carry 3 marks each.
(v) Q. no. 25 to 27 are long answer questions and carry 5 marks each.
(vi) Use log tables if necessary, use of calculators is not allowed.

Time Allowed : 3 hours — Maximum Marks : 70

States of Matter (Gaseous, Liquids & Solids)| Thermodynamics

1. Calculate the temperature of 4 moles of a gas occupying 5 dm^3 at 3.32 bar. (R = 0.083 bar dm^3 K^{-1} mol^{-1})

2. Predict the signs for ΔH and ΔS for the following change :
$2Cl_{(g)} \longrightarrow Cl_{2(g)}$

3. Critical temperature of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquefy first when you start cooling from 500 K to their critical temperature?

4. What type of coordination is possible in a crystal if the involved radius ratio is in the range of 0.225 – 0.414 ?

5. Name the state variables which remain constant in
(i) isobaric process
(ii) isothermal process.

6. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298 K. (Given, lattice energy of NaCl = 777.8 kJ mol^{-1}, hydration energy = –774.1 kJ mol^{-1} and ΔS = 0.043 kJ K^{-1} mol^{-1})

7. Answer the following :
(i) Why are falling liquid drops spherical?
(ii) Why do liquids diffuse slowly as compared to gases?

8. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atm. The pressure gauge of the cylinder indicates 12 atm at 27 °C. Due to sudden fire in the building, the temperature starts rising. At what temperature the cylinder would explode?

9. 1 g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation :
$C(graphite) + O_{2(g)} \longrightarrow CO_{2(g)}$
During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ K^{-1}, what is the enthalpy change for the above reaction at 298 K and 1 atm?

OR

Predict in which of the following entropy increases/decreases. Give reason.

(i) Temperature of crystalline solid is raised from 0 K to 115 K.

(ii) $H_{2(g)} \longrightarrow 2H_{(g)}$

10. A compound formed by elements *X* and *Y* crystallizes in a cubic structure in which the *X* atoms are at the corners of a cube and the *Y* atoms are at the face-centers. What will be the formula of the compound?

11. A person inhales 640 g of O_2 per day. If all the O_2 is used for converting sugar into CO_2 and H_2O, how much sucrose ($C_{12}H_{22}O_{11}$) is consumed in the body in one day and what is the heat evolved? [ΔH (combustion of sucrose) = -5645 kJ mol^{-1}]

12. Calculate the standard enthalpy of formation of $C_2H_{4(g)}$ from the following thermochemical equation :

$$C_2H_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(g)}\ ; \quad \Delta_r H = -1323 \text{ kJ}$$

Given that $\Delta_f H$ of $CO_{2(g)}$, $H_2O_{(g)}$ is -393.5 kJ mol^{-1} and -249 kJ mol^{-1} respectively.

13. Calculate **(i)** RMS speed, **(ii)** most probable speed, **(iii)** average *K.E.* of 32 g of oxygen at 27 °C. (R = 8.314 J K^{-1} mol^{-1})

14. (i) Write two wrong assumptions of the kinetic molecular theory of gases which led to the failure of the ideal gas law.

(ii) Out of NH_3 and N_2, which will have

(a) larger value of '*a*'

(b) larger value of '*b*'?

15. Sodium carbonate, Na_2CO_3 can be obtained by heating sodium hydrogen carbonate, $NaHCO_3$ as

$$2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$$

The essential data is

	$NaHCO_{3(s)} \rightarrow$	$Na_2CO_{3(s)}$ +	$CO_{2(g)}$ +	$H_2O_{(g)}$
$\Delta_f H°$ (kJ mol^{-1})	-947.7	-1130.9	-393.51	-241.82
$S°_m$ (J mol^{-1})	102.1	136	188.83	213.74

Calculate the temperature above which $NaHCO_3$ decomposes to give products at 1 bar.

16. (i) Why would water completely fill a fine capillary tube which is open at both ends when one end is immersed in water?

(ii) What is the difference between normal boiling point and standard boiling point?

(iii) Why temperature of a boiling liquid remains constant?

17. When 2.0 g of a gas *A* is introduced into an evacuated flask kept at 25 °C, the pressure is found to be 1 atm. If 3 g of another gas *B* is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molecular weights $M_A : M_B$.

OR

Give reasons for the following :

(i) The size of weather balloon becomes larger and larger as it ascends into higher altitudes.

(ii) Tyres of automobiles are inflated to lesser pressure in summer than in winter.

18. Calculate the value of log K_p for the reaction :

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

at 25 °C. The standard enthalpy of formation of NH_3 is -46 kJ and standard entropies of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ are 191 J K^{-1} mol^{-1}, 130 J K^{-1} mol^{-1} and 192 J K^{-1} mol^{-1} respectively.

19. For the following reaction,

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Calculate

(i) $\Delta G°$ at 1000 °C

(ii) K_p at 1000 °C for this reaction

(iii) partial pressure of CO_2

Use the following data :

	$CaCO_{3(s)}$	$CaO_{(s)}$	$CO_{2(g)}$
$\Delta H_f°$ (kJ)	-1206.9	-635.1	-393.5
$S°$ (J/K)	92.9	38.2	213.7

20. An open bulb containing air at 19 °C was cooled to a certain temperature at which the number of moles of the gaseous molecules increased by 25%. What is the final temperature?

21. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition, then determine

(i) molecular weight

(ii) molar volume

(iii) compression factor (Z) of the vapour.

22. Justify the following statements :

(i) Reactions with $\Delta G° < 0$ always have an equilibrium constant greater than 1.

(ii) Many thermodynamically feasible reactions do not occur under ordinary conditions.

(iii) At low temperature, enthalpy change dominates the ΔG expression and at high temperature, it is the entropy which dominates the value of ΔG.

23. 0.16 g of methane was subjected to combustion at 27 °C in a bomb calorimeter system. The temperature of the calorimeter system (including water) was found to rise by 0.5 °C. Calculate the heat of combustion of methane at **(i)** constant volume and **(ii)** constant pressure. The thermal capacity of the calorimeter system is 17.7 kJ K^{-1}. (R = 8.314 J K^{-1} mol^{-1})

24. KF has NaCl structure. What is the distance between K^+ and F^- in KF, if the density is 2.48 g cm^{-3} ?

25. A gas is enclosed in room. The temperature, pressure, density and number of moles respectively are t °C, P atm, d g cm^{-3} and n moles.

(i) What will be the pressure, temperature, density and number of moles in each compartment if room is partitioned into four equal compartments?

(ii) What will be the values of pressure, temperature, density and number of moles in each compartment if the walls between the two compartments (say 1 and 2) are removed?

(iii) What will be the values of pressure, temperature, density and number of moles, if an equal volume of gas at pressure P and temperature T is let inside the same room?

OR

(i) Define Boyle temperature.

(ii) Calculate the pressure exerted by 110 g of carbon dioxide in a vessel of 2 L capacity at 37 °C. Given that the van der Waals' constants are
a = 3.59 L^2 atm mol^{-2} and b = 0.0427 L mol^{-1}. Compare the value with the calculated value if the gas is considered as ideal.

26. One mole of an ideal gas expands isothermally and reversibly at 25°C from a volume of 10 litres to a volume of 20 litres.

(i) What is the change in entropy of the gas?

(ii) How much work is done by the gas?

(iii) What is q(surroundings)?

(iv) What is the change in the entropy of the surroundings?

(v) What is the change in the entropy of the system plus the surroundings?

OR

(i) Answer the following :

(a) Why does entropy of a solid increases on fusion?

(b) Why a non-spontaneous reaction becomes spontaneous when coupled with a suitable spontaneous reaction?

(ii) A slice of banana weighing 2.502 g was burnt in a bomb calorimeter producing a temperature rise of 3.05 °C. The combustion of 0.316 g of benzoic acid in the same calorimeter produced a temperature rise of 3.24 °C. The heat of combustion of benzoic acid at constant volume is –3227 kJ mol^{-1}. If average weight of banana is 125 g, how many calories can be obtained from one banana?

27. (i) Explain :

(a) Ionic crystals are hard and brittle.

(b) Vacancies are introduced in an ionic solid when a cation of higher valency is added as an impurity in it.

(c) Schottky defects lower the density of solids.

(ii) Calculate the packing efficiency of a metal for a simple cubic lattice.

OR

(i) How will you distinguish between the following pairs of terms?

(a) Hexagonal close packing and cubic close packing.

(b) Crystal lattice and Unit cell.

(c) Tetrahedral void and octahedral void.

(ii) An element with density 2.8 g cm^{-3} forms a fcc unit cell with edge length 4 × 10^{-8} cm. Calculate the molar mass of the element.

SOLUTIONS

1. Apply ideal gas equation, $PV = nRT$

$$T = \frac{PV}{nR} = \frac{3.32 \text{ bar} \times 5 \text{ dm}^3}{4 \text{ mol} \times 0.083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}} = 50 \text{ K}$$

2. $2Cl_{(g)} \longrightarrow Cl_{2(g)}$; ΔH is negative because the reaction involves formation of bond, therefore it is exothermic reaction. Also, two moles of atoms have more randomness than one mole of molecule thus, ΔS = –ve.

3. Higher the critical temperature, more easily the gas liquefies. So, ammonia will liquefy first.

4. For the radius ratio lying between 0.225 – 0.414, coordination number is 4 and tetrahedral structural arrangement.

5. **(i)** In isobaric process, pressure remains constant *i.e.*, $\Delta P = 0$.
(ii) In isothermal process, temperature remains constant *i.e.*, $\Delta T = 0$.

6. ΔH = Hydration energy + Lattice energy
$\Delta H = (-774.1 + 777.8)$ kJ mol^{-1} = 3.7 kJ mol^{-1}
$\Delta G = \Delta H - T\Delta S = 3.7 - 298 \times 0.043 = 3.7 - 12.81$
$\Delta G = -9.11$ kJ mol^{-1}

7. **(i)** To reduce surface tension, liquid drops tries to have minimum surface area and a sphere has minimum surface area for a given volume.
(ii) Intermolecular forces of attraction are stronger in liquids than gases therefore, molecules of liquids have less freedom of movement.

8. For a gas cylinder to explode, the final pressure should be 14.9 atm.
$P_1 = 12$ atm, $P_2 = 14.9$ atm
$T_1 = (273 + 27) = 300$ K and T_2 = ?

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ or } T_2 = \frac{P_2}{P_1} \times T_1 = \frac{14.9}{12} \times 300 \text{ K} = 372.5 \text{ K}$$

= 372.5 – 273 = 99.5 °C
Thus, the cylinder would explode above 99.5 °C.

9. Rise in temperature of the calorimeter
= 299 – 298 K = 1 K
Heat capacity of the calorimeter = 20.7 kJ K^{-1}
∴ Heat absorbed by the calorimeter (q) = $C_v \times \Delta T$
= (20·7 kJ K^{-1}) (1 K) = 20.7 kJ
This is the heat evolved in the combustion of 1 g of graphite.
∴ Heat evolved in the combustion of 1 mole of graphite, *i.e.*, 12 g of graphite = 20·7 × 12 = 248.4 kJ mol^{-1}
As this is the heat evolved and the vessel is closed, therefore, enthalpy change of the reaction (ΔU) = –248·4 kJ mol^{-1}

OR

(i) Entropy will increase on increasing the temperature since the particles of solid move with greater speed at higher temperature.
At 0 K, there is perfect order of the constituent particles, entropy is minimum, tends to zero.
(ii) $H_{2(g)} \longrightarrow 2H_{(g)}$
Entropy will increase because the number of particles of product are double than that of reactant.

10. There are eight corners and six faces in a cube. A corner atom is shared by eight cubes, and the face-centered atom by two cubes. Thus,

Effective number of X atoms in a cube = $\frac{1}{8} \times 8 = 1$
and effective number of Y atoms in a cube = $\frac{1}{2} \times 6 = 3$
Therefore, formula of the compound is XY_3.

11. Moles of O_2 inhaled by a person in one day = $\frac{640}{32} = 20$
Given that,
$C_{12}H_{22}O_{11} + 12O_2 \longrightarrow 12CO_2 + 11H_2O\,;\Delta H = -5645$ kJ
Thus, 12 moles of O_2 consume 1 mole of sucrose
or 12 moles of O_2 consume 342 g of sucrose
∴ 20 mole of O_2 consume $\frac{342}{12} \times 20$ = 570 g of sucrose
Further,
342 g (1 mole) of sucrose liberates 5645 kJ
∴ 570 g of sucrose should liberate,

$$\frac{5645}{342} \times 570 = 9408.33 \text{ kJ}$$

12. $\Delta_r H = \sum \Delta_f H$ (Products) – $\sum \Delta_f H$ (Reactants)
$-1323 = [2 \times \Delta_f H(CO_2) + 2 \times \Delta_f H(H_2O)] - [\Delta_f H(C_2H_4) + 3\Delta_f H(O_2)]$
$-1323 = [2 \times (-393.5) + 2 \times (-249)] - [\Delta_f H(C_2H_4) + 3 \times 0]$
∴ $\Delta_f H(C_2H_4) = 1323 - 1285 = +38$ kJ mol^{-1}

13. **(i)** RMS speed, $u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{32 \times 10^{-3}}}$
= 483.56 m s^{-1}
(ii) Most probable speed (u_{mp}) = 0.816 × u_{rms}
= 0.816 × 483.56 = 394.6 m s^{-1}
(iii) Average *K.E.* per mole = $\frac{3}{2}RT$
= $\frac{3}{2}$ × 8.314 J K^{-1} mol^{-1} × 300 K = 3741.3 J mol^{-1}

14. **(i)** Two wrong assumptions of the kinetic molecular theory of gases were :
(a) The molecules were considered as point masses with negligible volume as compared to the space occupied by the gas.
(b) It was assumed that there is no intermolecular forces between the molecules. They move independently.
(ii) **(a)** Out of NH_3 and N_2, NH_3 will have higher magnitude of intermolecular forces of attraction due to hydrogen bonding, hence NH_3 will have larger value of '*a*'.
(b) Since NH_3 molecule is larger in size than N_2, hence NH_3 will have larger value for '*b*' also.

15. $2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$
$\Delta_r H° = \Delta_f H°(Na_2CO_3) + \Delta_f H°(CO_2) + \Delta_f H°(H_2O) - 2\Delta_f H°(NaHCO_3)$

$= -1130.9 + (-393.51) + (-241.82) - 2 \times (-947.7)$
$= -1766.23 + 1895.4 = 129.17 \text{ kJ mol}^{-1}$
$\Delta_r S° = S°_m(Na_2CO_3) + S°_m(CO_2) + S°_m(H_2O) - 2S°_m(NaHCO_3)$
$= 136.0 + 188.83 + 213.74 - 2 \times 102.1$
$= 538.57 - 204.2 = 334.37 \text{ J K}^{-1} \text{ mol}^{-1}$
The temperature at which $\Delta_r G° = 0$ is given by

$$\therefore \quad T = \frac{\Delta_r H°}{\Delta_r S°} = \frac{129.17}{334.37 \times 10^{-3}} = 386 \text{ K}$$

When, $T > 386$ K, $NaHCO_3$ will decompose to form products.

16. (i) The surface tension pulls the water into the capillary. In a fine capillary, the surface tension is large enough to overcome the attraction of gravity on water.
(ii) When vapour pressure of water is equal to the external pressure (*i.e.*, one atmosphere pressure) the boiling point is called normal boiling point and when the external pressure is taken as 1 bar, it is called standard boiling point.
(iii) This is because at the boiling point, the heat supplied is used in breaking off the intermolecular forces of attraction of the liquid to change it into vapours and not for raising the temperature of the liquid.

17. Total pressure = 1.5 atm

Moles of $A = \frac{2}{M_A}$; Moles of $B = \frac{3}{M_B}$

Total moles $= \frac{2}{M_A} + \frac{3}{M_B}$

Partial pressure of $A = \frac{2/M_A}{2/M_A + 3/M_B} \times 1.5$

and partial pressure of $B = \frac{3/M_B}{2/M_A + 3/M_B} \times 1.5$

As given, partial pressure of A = 1 atm
Partial pressure of B = 1.5 – 1 = 0.5 atm

Then, $\frac{\text{Partial pressure of } A}{\text{Partial pressure of } B}$

$$= \frac{\frac{2/M_A}{2/M_A + 3/M_B} \times 1.5}{\frac{3/M_B}{2/M_A + 3/M_B} \times 1.5} = \frac{1}{0.5} = 2$$

or $\frac{2}{3} \times \frac{M_B}{M_A} = 2$ or $\frac{M_A}{M_B} = \frac{1}{3}$

OR

(i) As we go to higher altitudes, the atmospheric pressure decreases. Thus, the pressure outside the balloon decreases. To regain equilibrium with the external pressure, the gas inside expands to decrease its pressure. Hence, the size of the balloon increases.

(ii) In summer, due to higher temperature, the average kinetic energy of the air molecules inside the tyre increases, *i.e.*, molecules start moving faster. Hence, the pressure on the walls of the tube increases. If pressure inside is not kept low at the time of inflation, at higher temperature, the pressure may become so high that the tyre may burst.

18. In reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
$\Delta_r H° = 2\Delta_f H°(NH_3) - [\Delta_f H°(N_2) + 3\Delta_f H°(H_2)]$
$= 2 \times (-46) = -92 \text{ kJ mol}^{-1}$
$\Delta S° = 2S°(NH_3) - [S°(N_2) + 3S°(H_2)]$
$= 2 \times 192 - [191 + 3 \times 130]$
$= -197 \text{ J K}^{-1} \text{ mol}^{-1} = -0.197 \text{ kJ K}^{-1} \text{ mol}^{-1}$
Now, $\Delta G° = \Delta H° - T\Delta S°$
$= -92 - 298 \times (-0.197)$
$= -33.294 \text{ kJ} = -33.294 \times 10^3 \text{ J}$
But, $\Delta G° = -2.303\, RT \log K_p$

$$\therefore \log K_p = -\frac{\Delta G°}{2.303\, RT} = \frac{33.294 \times 10^3}{2.303 \times 8.314 \times 298} = 5.835$$

19. (i) For the given reaction,
$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
$\Delta H° = (-635.1) + (-393.5) - (-1206.9) = 178.3 \text{ kJ}$
$\Delta S° = (38.2) + (213.70) - (92.9) = 159 \text{ J/K}$
$\Delta G° = \Delta H° - T\Delta S°$
$\Delta G° = 178.3 - 1273 \times (159 \times 10^{-3}) = -24.1 \text{ kJ}$

(ii) $\log K = -\frac{\Delta G°}{2.303\, RT}$

$$\log K = -\frac{(-24.1)}{2.303 \times (8.314 \times 10^{-3}) \times 1273} = 0.988$$

$K = K_p = 9.72$
(iii) $K_p = p_{CO_2} = 9.72 \text{ atm}$, as partial pressure of $CaCO_{3(s)}$ and $CaO_{(s)}$ are unity.

20. Suppose the volume of the bulb is V containing n moles at 19 °C *i.e.*, 292 K.
Let the temperature be T K when n moles increases to 1.25 n (*i.e.*, by 25%). Since, 1.25 n moles at T K occupy a volume V.

$\therefore$ n moles at T K should occupy $\frac{V}{1.25}$
Thus, for n moles of the gas,
$T_1 = 292$ K $T_2 = T$ K
$V_1 = V,\ V_2 = \frac{V}{1.25}$ $P_1 = P, P_2 = P$ ($P_1 = P_2$ as the bulb is open)

$$\because \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \frac{PV}{292} = \frac{P \times V/1.25}{T}$$

$$T = \frac{292}{1.25} = 233.6 \text{ K} = -39.4\ °\text{C}$$

21. (i) $\frac{r_g}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_g}}$; $M_g = \frac{32}{(1.33)^2} = 18.09$ g/mole

(ii) Molar volume = $\frac{\text{mol. wt (g / mole)}}{\text{density (g / L)}}$

$= \frac{18.09}{0.36} = 50.25$ L mole^{-1} ($\because$ 1 kg m^{-3} = 1 g L^{-1})

(iii) $Z = \frac{pV}{RT} = \frac{1 \times 50.25}{0.0821 \times 500} = 1.224$

22. (i) $\Delta G° = -2.303\ RT \log K$. Thus, for $\Delta G° < 0$, K should be greater than 1.

(ii) Under ordinary conditions, the average energy of the reactants may be less than threshold energy. They require some activation energy to initiate the reaction.

(iii) $\Delta G = \Delta H - T\Delta S$. At low temperature, $T\Delta S$ is small. Hence, ΔH dominates. At high temperature, $T\Delta S$ is large *i.e.*, ΔS dominates the value of ΔG.

23. (i) Heat gained by the calorimeter system, (at constant volume) is given by,

q_v = 17.7 kJ K^{-1} × 0.5 K = 8.85 kJ

$$\Delta_c U_{(CH_4)} = \frac{q_v}{n_{CH_4}} = \frac{-8.85 \text{ kJ}}{(0.16 \text{ g}/16 \text{ g mol}^{-1})} = -885 \text{ kJ mol}^{-1}$$

Heat of combustion at constant volume, ($\Delta_c U$) = – 885 kJ mol^{-1}

(ii) The combustion of methane at 27 °C is described by the reaction,

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

For this reaction,

$\Delta n_g = (1 + 0) - (1 + 2) = -2$

So, $\Delta_c H = \Delta_c U + \Delta n_g RT$ = – 885 kJ mol^{-1} + (–2) × 8.314 × 300 J mol^{-1}

$$\Delta_c H = \left(-885 + \frac{-2 \times 8.314 \times 300}{1000}\right) \text{kJ mol}^{-1}$$

= (– 885 – 5) kJ mol^{-1} = –890 kJ mol^{-1}

Heat of combustion at constant pressure ($\Delta_c H$) = – 890 kJ mol^{-1}

24. KF has NaCl structure. So, one unit cell should contain 4 K^+F^- units. Therefore, the density of KF is,

$$\text{Density} = \frac{4 \times (\text{Formula mass of } K^+ F^-)}{a^3 \times N_A}$$

Where, a is the edge length of the unit cell,

$$a^3 = \frac{4 \times (39 + 19)}{6.023 \times 10^{23} \times 2.48} \text{ cm}^3$$

$$a = \left(\frac{4 \times 58}{6.023 \times 10^{23} \times 2.48}\right)^{1/3} \text{cm} = 5.37 \times 10^{-8} \text{ cm}$$

From the geometry, we know,

$$d_{K^+-F^-} = \frac{1}{2}a = \frac{5.37 \times 10^{-8}}{2} \text{ cm} = 2.69 \times 10^{-8} \text{ cm} = 269 \text{ pm}$$

25. (i) (a) Pressure in each compartment will remain same (P atm).

(b) Temperature will remain same (t °C).

(c) Density will remain same (d g cm^{-3}).

(d) The number of moles in each compartment will be $n/4$.

(ii) (a) Pressure will remain same (P atm).

(b) Temperature will remain same (t °C).

(c) Density will remain same (d g cm^{-3})

(d) The number of moles in each compartment will be $n/2$.

(iii) (a) Pressure will be doubled ($2P$ atm).

(b) Temperature will remain same.

(c) Density will be doubled ($2d$ g cm^{-3})

(d) Number of moles will be doubled *i.e.*, $2n$.

OR

(i) The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.

(ii) According to van der Waals' equation,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ or } P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Here, $n = \frac{110}{44} = 2.5$ moles

Substituting the given values, we get

$$P = \frac{(2.5 \text{ mol})(0.0821 \text{ L atm K}^{-1}\text{mol}^{-1})(310 \text{ K})}{(2 \text{ L} - 2.5 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.59 \text{ L}^2 \text{ atm mol}^{-2})(2.5 \text{ mol})^2}{(2 \text{ L})^2}$$

= 33.60 atm – 5.61 atm = 27.99 atm

If the gas is considered as ideal gas, applying ideal gas equation,

$PV = nRT$, we get

$$P = \frac{nRT}{V} = \frac{(2.5 \text{ mol})(0.0821 \text{ L atm K}^{-1}\text{mol}^{-1})(310 \text{ K})}{2 \text{ L}}$$

= 31.81 atm

Pressure exerted by real gas is less than the ideal gas due to forces of attraction.

26. (i) $\Delta S = 2.303\ nR\ \log\frac{V_2}{V_1}$

$= 2.303 \times 1 \times 8.314 \times \log\frac{20}{10} = 5.76\ \text{J/K}$

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

$= -2.303 \times 1 \times 8.314 \times 298 \times \log\frac{20}{10} = -1717\ \text{J}$

(iii) For isothermal process, $\Delta U = 0$ and heat is absorbed by the gas,

$q_{rev} = \Delta U - W = 0 - (-1717) = 1717$ J

$\therefore\ q_{surr} = 1717$ J ($\because$ process is reversible)

(iv) $\Delta S_{surr} = -\frac{q_{rev}}{T} = -\frac{1717}{298} = -5.76\ \text{J/K}$

As entropy of the system increases by 5.76 J, entropy of the surroundings decreases by 5.76 J, since the process is carried out reversibly.

(v) $\Delta S_{sys} + \Delta S_{surr} = 0$ for reversible process.

OR

(i) In a solid, the constituent particles are fixed. On melting or fusion, they fall apart and are free to move, *i.e.*, their randomness increases. Hence, the entropy increases.

(ii) The overall free energy change of the coupled reaction is negative (ΔG = –ve), hence overall reaction becomes spontaneous.

(iii) $q = mC_s \cdot \Delta T$

For combustion of benzoic acid

$$\frac{0.316 \times 3227}{122} = mC_s \times 3.24$$

$$mC_s = \frac{0.316 \times 3227}{122 \times 3.24} = 2.58\ \text{kJ/°C}$$

For banana slice; $q = mC_s \times \Delta T$

$q = 2.58 \times 3.05 = 7.87$ kJ per 2.502 g of banana

$\therefore$ Heat produced by 125 g banana $= \frac{7.87 \times 125}{2.502}$

$= 393.18\ \text{kJ} = \frac{393.18}{4.184}\ \text{kcal} = 93.97\ \text{kcal}$

27. (i) (a) Ionic crystals are hard due to the presence of strong interionic electrostatic forces of attraction. However, when an ionic solid is subjected to stress, ions of same charge come close together and the repulsive forces between them cause the crystal to break into pieces. Thus, ionic crystals are hard and brittle.

(b) When a cation of higher valency is added as an impurity in an ionic solid then to maintain electrical neutrality, two or more cations of lower valency are replaced. One position is occupied by added cation and other creates vacancies in the lattice.

(c) Schottky defects occur when equal number of cations and anions are missing from their lattice site. As the mass of unit cell decreases hence, the density of the solid decreases.

(ii) Packing efficiency

$$= \frac{Z \times \text{Volume of one atom}}{\text{Volume of cubic unit cell}} \times 100$$

For a simple cubic lattice, $a = 2r$ and $Z = 1$

$$\therefore \text{Packing efficiency} = \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} \times 100$$

$$= \frac{\pi}{6} \times 100 = 52.4\%$$

OR

(i) (a) In hexagonal close packing, third layer is built by covering tetrahedral voids of second layer and spheres of the third layer are exactly aligned with those of the first layer (*ABAB*, ...pattern).

In cubic close packing third layer is built by covering octahedral voids of second layer and spheres in fourth layer are aligned with those of the first layer (*ABCABC* ... pattern).

(b) Crystal lattice is regular three dimensional arrangement of constituent particles of a crystal.

Unit cell is the smallest portion of a crystal lattice which when repeated in different directions generates the entire lattice.

(c) A simple triangular void surrounded by four spheres is called tetrahedral void. A double triangular void surrounded by six spheres is called octahedral void.

(ii) Density of solid, $d = 2.8$ g cm^{-3}

For *fcc* unit cell, $Z = 4$

Edge length, $a = 4 \times 10^{-8}$ cm,

Molar mass, M = ?

$N_A = 6.022 \times 10^{23}$ mol^{-1}

Using formula, $d = \frac{Z \times M}{N_A \times a^3} \Rightarrow M = \frac{d \times N_A \times a^3}{Z}$

Substituting these values, we get

$$M = \frac{2.8\ \text{g cm}^{-3} \times 6.022 \times 10^{23}\ \text{mol}^{-1} \times (4 \times 10^{-8}\ \text{cm})^3}{4}$$

or $M = \frac{2.8 \times 6.022 \times 6.4}{4} = 26.98\ \text{g mol}^{-1}$

Class XI

MONTHLY TUNE UP!

PRACTICE PROBLEMS

These practice problems enable you to self analyse your extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Performance analysis table given at the end will help you to check your readiness.

- Classification of Elements and Periodicity in Properties
- Chemical Bonding and Molecular Structure

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. The correct order of the ionic character of the following bonds is given by
(a) Be—O < B—O < C—O < N—O
(b) N—O < C—O < B—O < Be—O
(c) Be—O < C—O < N—O < B—O
(d) B—O < Be—O < C—O < N—O

2. Which of the following species is not tetrahedral?
(a) CCl_4 (b) $SiCl_4$ (c) PCl_4^+ (d) XeF_4

3. The formation of the oxide ion, $O^{2-}_{(g)}$, from oxygen atom requires first an exothermic and then an endothermic step as shown below :

$O_{(g)} + e^- \longrightarrow O^-_{(g)}$; $\Delta H° = -141$ kJ mol^{-1}

$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)}$; $\Delta H° = +780$ kJ mol^{-1}

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that,
(a) oxygen is more electronegative
(b) addition of electron in oxygen results in larger size of the ion
(c) electron repulsion outweighs the stability gained by achieving noble gas configuration
(d) O^- ion has comparatively smaller size than oxygen atom.

4. H_2O has a net dipole moment, while BeF_2 has zero dipole moment, because
(a) H_2O molecule is linear while BeF_2 is bent
(b) BeF_2 molecule is linear while H_2O is bent
(c) fluorine is more electronegative than oxygen
(d) Be is more electronegative than oxygen.

5. Which one of the following statements is incorrect related to ionization enthalpy?
(a) Ionization enthalpy increases for each successive electron.
(b) The greatest increase in ionization enthalpy is experienced on removal of electrons from core having noble gas configuration.
(c) End of valence electrons is marked by a large jump in ionization enthalpy.
(d) Removal of electron from orbitals bearing lower *n* value is easier than from orbital having higher *n* value.

6. Which of the following transformations has maximum change in percentage of *s*-character of bonding orbital of underlined central atom?
(a) $BF_3 + F^- \longrightarrow \underline{B}F_4^-$
(b) $NH_3 + H^+ \longrightarrow \underline{N}H_4^+$
(c) $N_2O_5 \longrightarrow NO_2^+.\underline{N}O_3^-$
(d) $BeF_2 \longrightarrow [\underline{Be}F_4]^{2-}$

7. The first, second and third ionization enthalpies of an element are 737, 1450 and 7731 kJ mol^{-1} respectively. What will be the formulae of its oxide and chloride?
(a) M_2O, MCl (b) MO, MCl_2
(c) M_2O_3, MCl_3 (d) MO_2, MCl_4

8. Which molecule/ion out of the following does not contain unpaired electrons?
(a) N_2^+ (b) O_2 (c) O_2^{2-} (d) B_2

9. In the second period of the periodic table, ionization enthalpy follows the order :
(a) Ne > F > O > N > C > B > Se > Li
(b) Ne > F > N > C > O > Be > B > Li
(c) Li > B > Be > C > O > N > F > Ne
(d) Ne > F > N > O > C > Be > B > Li

10. The electronic configurations of two elements, *A* and *B* are given below :

A	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

The molecular formula of the compound formed from *A* and B will be
(a) AB (b) A_2B (c) AB_2 (d) AB_3

11. In any period, the valency of an element with respect to oxygen
(a) increases one by one from IA to VII A
(b) decreases one by one from IA to VII A
(c) increases one by one from IA to IV A and then decreases from V A to VII A one by one
(d) decreases one by one from IA to IV A and then increases from V A to VII A one by one.

12. Which of the following have electrovalent, covalent and coordinate bonds?
(a) NH_4Cl (b) CO_2 (c) H_2O_2 (d) CH_4

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** Atomic radius in general decreases along a period.
Reason : In a period, effective nuclear charge decreases.

14. **Assertion :** XeF_2 is linear but OH_2 is angular though both are AB_2-type molecules.
Reason : F is more electronegative than H.

15. **Assertion :** Decreasing order of van der Waals' radii is Cl > N > O > H.
Reason : van der Waals' radii increases as the number of energy level increases and decreases as nuclear charge increases.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. Which of the following constitutes a group of isoelectronic species?
(a) C_2^{2-}, O_2^-, CO, NO (b) NO^+, C_2^{2-}, CN^-, N_2
(c) CN^-, N_2, O_2^{2-}, CO (d) N_2, O_2^-, NO^+, CO

17. For the processes,
$$K^+_{(g)} \xrightarrow{I} K_{(g)} \xrightarrow{II} K_{(s)}$$
(a) energy is released in (I) and absorbed in (II)
(b) energy is absorbed in (I) and released in (II)
(c) energy is absorbed in both the processes
(d) energy is released in both the processes.

18. $BeCl_2$ and ICl_2^- are linear species. What kinds of hybridisation do Be and I undergo respectively?
(a) sp and sp^3d (b) sp^3d and sp
(c) sp^3d^2 and sp^3 (d) sp^3d and sp^3

19. Be and Mg have zero value of electron affinity, because
(a) Be and Mg have [He]$2s^2$ and [Ne]$3s^2$ configuration respectively
(b) 2*s* and 3*s* orbitals are filled to their capacity
(c) Be and Mg are unable to accept electron
(d) all the above are correct.

More than One Options Correct Type

20. Which of the following statements are true?
(a) The highest oxide of a group-15 element(*E*) is E_2O_5.
(b) The elements of period 2 show anomalous behaviour.
(c) Li/Mg, Be/Al and B/Si are diagonal pairs.
(d) A diagonal relationship exists between two elements because of their similar oxidation states.

21. Ionic radii is
(a) inversely proportional to the effective nuclear charge
(b) inversely proportional to the square of effective nuclear charge
(c) directly proportional to the screening effect
(d) directly proportional to the square of screening effect.

22. Which of the following statements are correct about CO_3^{2-}?
(a) The hybridisation of central atom is sp^3.
(b) Its resonance structure has one C—O single bond and two C=O double bonds.
(c) The average formal charge on each oxygen atom is 0.67 units.
(d) All C—O bond lengths are equal.

23. Ionization energies of atoms *A* and *B* are 350 and 250 kcal mol^{-1} respectively. The electron affinities of these atoms are 70 and 90 kcal mol^{-1} respectively. Then
(a) electron cloud is more attracted by *A*
(b) electron cloud is more attracted by *B*
(c) on Mulliken scale, electronegativity of *A* is more than *B*
(d) on Mulliken scale, electronegativity of *A* is less than *B*.

Numerical Value Type

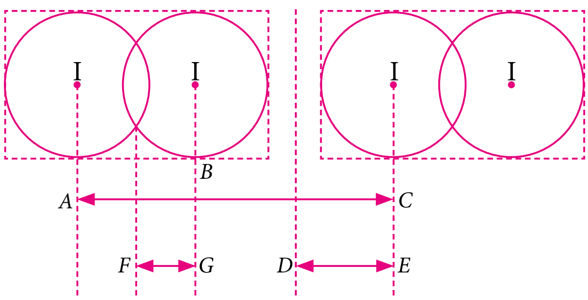
24. Total number of electrons present in πMOs in B_2 molecule is

25. How much energy is given out when 1.0 g of chlorine atoms are converted into $Cl^-_{(g)}$? Electron affinity of Cl = –329 kJ/mol and atomic mass of Cl is 35.5 amu.

26. The dipole moment of LiH is 1.964×10^{-29} cm and the interatomic distance between Li and H in this molecule is 1.596 Å. What is the percent ionic character in LiH?

Comprehension Type

I_2 is a crystalline solid. It is a molecular solid in which I_2 molecules are held together with van der Waals' forces. Given diagram represent two adjacent I_2 molecules in I_2 solid.



If *A* – *C* length = 6.96 Å and covalent radius of iodine is = 1.33 Å.

27. Find van der Waals' radius of I atom.
(a) 4.30 Å (b) 2.15 Å
(c) 2.66 Å (d) 1.33 Å

28. Which of the following data is smaller as compared to 1.33 Å?
(a) Bond length of I – I
(b) Size of I^- ion
(c) Size of Xe atom
(d) Size of I^+ ion

Matrix Match Type

29. Match column I with column II and choose the correct answer using the codes given below :

Column I	Column II
A. Hydrogen bond	p. C
B. Resonance	q. LiF
C. Ionic solid	r. HF
D. Covalent solid	s. O_3

	A	B	C	D
(a)	p	r	q	s
(b)	q	s	r	p
(c)	r	s	q	p
(d)	r	p	q	s

30. Match column I with column II and choose the correct answer using the codes given below :

Column I (Electronic configuration)	Column II (Type of element)
A. $3s^2 3p^6$	p. Metals
B. $6s^1 4f^{14} 5d^{10}$	q. Non-metals
C. $4f^1 5s^2 5p^6 5d^1 6s^2$	r. Noble gases
D. $5s^2 4d^{10} 5p^5$	s. Lanthanides

	A	B	C	D
(a)	q, r	r	q, s	p
(b)	q, r	p	p, s	q
(c)	p, q	r	p, s	q
(d)	p, r	s	p, q	r

Keys are published in this issue. Search now! ☺

CHECK YOUR PERFORMANCE

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

If your score is

> 80%	Your preparation is going good, keep it up to get high score.
60-80%	Need more practice, try hard to score more next time.
<60%	Stress more on concepts and revise thoroughly.

FOCUS NEET/JEE 2019

Class XII

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UNIT - 3 : General Principles and Processes of Isolation of Elements | The *p*-Block Elements (Group 15 to 18)

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Occurrence of Metals

Metals generally occur in combined or native states in the earth's crust. Some of their salts are found in sea water.

- **Minerals:** The combined state in which the metals occur in the earth's crust are known as minerals.
- **Ores:** Minerals from which the metals can be extracted conveniently and profitably. All ores are minerals but all minerals are not ores.
- The unwanted earthy impurities associated with ore is known as gangue or matrix.

Some Important Ores of Metals

Metal	Ore
Magnesium	Carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$
Aluminium	Bauxite, $Al_2O_3 . 2H_2O$
Iron	Haematite, Fe_2O_3 ; Magnetite, Fe_3O_4
Copper	Copper pyrites, $CuFeS_2$ Cuprite, Cu_2O
Tin	Cassiterite, SnO_2
Lead	Galena, PbS
Silver	Argentite, Ag_2S ; Native Silver

Metallurgy

The whole process of extracting metals from their ores is called metallurgy. Metallurgy of a metal involves three main steps :

- Concentration or dressing of the ore
- Extraction and isolation of metal
- Purification or refining.

Concentration or Dressing of the Ore

To remove undesirable impurities, different methods are used for the concentration of ores.

- **Hand picking :** When impurities are of large size.
- **Froth floatation process :** Used for concentration of sulphide ore and based on preferential wetting of ore by oil.
- **Electromagnetic separation :** When either ore or impurities are magnetic in nature.
- **Leaching process :** Ore is treated with suitable reagent that preferentially dissolves the ore particle while impurities remain insoluble.
- **Gravity separation :** Used when ore particles are heavier than impurities.

Extraction and Isolation of Metal

Conversion of ore into metal oxide

- **Roasting :** The concentrated ore (usually sulphide) is heated strongly, in the presence or excess of air below its melting point.

$$\underset{\text{Galena}}{2PbS} + 3O_2 \xrightarrow{\Delta} \underset{\text{Lead oxide}}{2PbO} + 2SO_2$$

- **Calcination :** The process of converting concentrated ore into oxide by, heating it strongly below its melting point in the absence of air.

$$\underset{\text{Bauxite}}{Al_2O_3 \cdot 2H_2O} \xrightarrow{\Delta} \underset{\text{Alumina}}{Al_2O_3} + 2H_2O$$

Reduction of metal oxide to free metal

- **Smelting :** Extraction of metal from its oxide by reduction with carbon (coal or coke). *e.g.*,
  $PbO + C \longrightarrow Pb + CO$
- **Pyrometallurgy :** Extraction of metal by heating the metal oxide with a suitable reducing agent.
- **Goldschmidt aluminothermite process :** It is done by using aluminium. *e.g.*,
  $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$
- **Self-reduction process :** This process is also called auto reduction process. The sulphide ores of less electropositive metals like Hg, Pb, Cu, etc., are heated in air. No external reducing agent is used in this process. *e.g.*, extraction of Hg from cinnabar ore
  $2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$
  $2HgO + HgS \longrightarrow 3Hg + SO_2$
- **Electrolytic reduction :** The highly electropositive metals like Na, K, Mg, Ca, Al, etc. are extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state.

Purification or Refining

Methods	Metals Purified
Liquation	For metals having low melting points (like Sn, Pb, Hg, etc) than impurities.
Distillation	For volatile metals like Zn, Hg, Cd, etc., or metals containing non-volatile impurities.
Poling	For metals which contain impurities of their own oxides *e.g.*, Cu.
Cupellation	For metals containing easily oxidisable impurities *e.g.*, Ag containing Pb impurities.
Electrolytic refining	For metals like Cu, Ag, Au, Al which get deposited at cathode and impurities get deposited under anode as anode mud. Solution of a soluble metal salt acts as electrolyte.
Mond's process	For refining of Ni. $\underset{\text{Impure}}{4CO + Ni} \xrightarrow{60° - 80°C} Ni(CO)_4 \xrightarrow{180°C} 4CO + \underset{\text{Pure}}{Ni}$
Zone refining	To produce extremely pure metals (semiconductors) like Si, Ge, Ga, etc.
van Arkel method	For ultra-pure metals like Ti, Zr which are used in space technology. $\underset{\text{Impure}}{Ti_{(s)}} + 2I_{2(g)} \xrightarrow{523\ K} TiI_{4(g)} \xrightarrow{1673\ K} \underset{\text{Pure}}{Ti_{(s)}} + 2I_{2(g)}$ $\underset{\text{Impure}}{Zr} + 2I_2 \xrightarrow{870\ K} \underset{\text{(Vapour)}}{ZrI_4} \xrightarrow{1800\ K} \underset{\text{Pure}}{Zr_{(s)}} + 2I_{2(g)}$

EXTRACTION OF SOME IMPORTANT ELEMENTS

Extraction of Aluminium

Ore-Bauxite ($Al_2O_3 \cdot 2H_2O$)

↓ NaOH, Δ — Baeyer's Process

Residue (Fe_2O_3, SiO_2 as impurities) | Solution [Sodium meta-aluminate $NaAl(OH)_4$]

Solution ↓ Hydrolysis

Precipitate Aluminium Hydroxide [$Al(OH)_3$]

↓ 1100 °C

Pure Alumina (Al_2O_3)

↓ Electrolytic Reduction (Hall-Heroult's Process)

At cathode : Aluminium (99%) | At anode : Oxygen

Extraction of Zinc

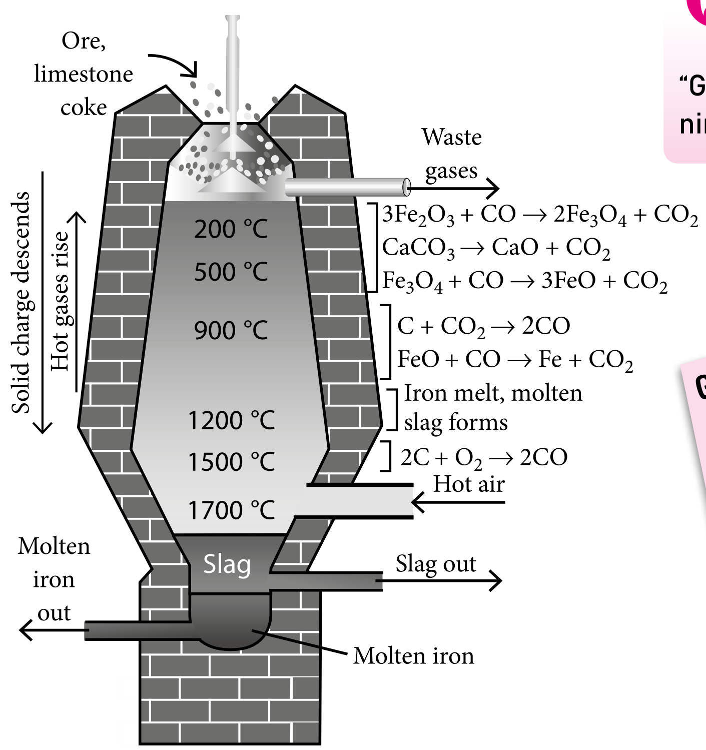
Ore : Zinc blend Concentrated by froth floatation method → **Roasting :** $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$ → **Reduction :** $ZnO + C \rightarrow Zn + CO$ → **Electrolytic refining or distillation :** Refined Zn

Extraction of Copper

Ore : Copper pyrite ($CuFeS_2$) → Concentrated by froth floatation process → **Roasting :**
$2CuFeS_2 + O_2 \rightarrow Cu_2S + FeS + SO_2$
$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ (Partly)
$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ (Partly)
→ $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$
$FeO + SiO_2 \rightarrow FeSiO_3$(Slag)

→ **Smelting :** $2Cu_2O + C \rightarrow 2Cu + O$ → (On cooling) → Blister copper (due to liberation of SO_2, N_2 or O_2) → (Electrolytic refining) → Pure cupper

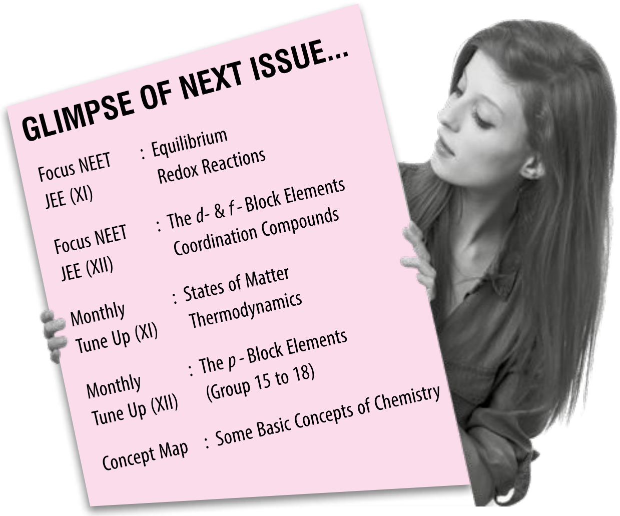
Extraction of Iron (Blast furnace)



Quotable Quote

"Genius is one percent inspiration and ninety-nine percent perspiration."

Thomas Edison



THE p-BLOCK ELEMENTS (GROUP 15 TO 18)

Group 15 Elements (Nitrogen Family)

Group 15 Elements (ns^2np^3)

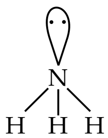
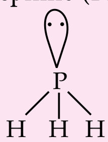
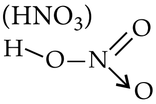
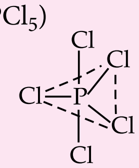
Element	At. No.	Electronic Configuration	Oxidation State
Nitrogen (N)	7	[He] $2s^22p^3$	–3, –2, –1, 0, +1, +2, +3, +4, +5
Phosphorus (P)	15	[Ne] $3s^23p^3$	–3, +3, +5
Arsenic (As)	33	[Ar] $3d^{10}4s^24p^3$	–3, +3, +5
Antimony (Sb)	51	[Kr] $4d^{10}5s^25p^3$	–3, +3, +5
Bismuth (Bi)	83	[Xe] $4f^{14}5d^{10}6s^26p^3$	+3, +5
Moscovium (Mc)	115	[Rn] $5f^{14}6d^{10}7s^27p^3$	–

General Trends

Increasing trends	Decreasing trends
Atomic size	Ionization energy
M.pt. / B.pt. increases from N → As	Electronegativity
Metallic character	M.pt. / B.pt. point decreases, As → Bi
Density	Tendency of covalent bonding
Tendency of lower oxidation state + 3	Thermal stability of hydrides
Reducing character of hydrides (EH_3)	Bond angle in hydrides (EH_3)
Ionic character of compounds	Basic nature of hydrides EH_3

- **Exceptions :**
  - Except N and Bi, All elements exhibit allotropy.
  - B.pt. of EH_3: $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

Important Compounds of Nitrogen Family

Structure	Preparation	Properties	Uses
Ammonia (NH_3) 	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; $\Delta H_f^\circ = -46.1$ kJ/mol (*Haber's process*)	NH_3: $\xrightarrow{O_2} N_2 + H_2O$; $\xrightarrow{Cl_2} NH_4Cl + N_2$ (If NH_3 (excess)); $\xrightarrow{Cl_2} NCl_3 + HCl$ (If Cl_2 (excess)); $\xrightarrow{O_2,\ Pt} NO + H_2O$; $\xrightarrow{AgCl} [Ag(NH_3)_2]Cl$	In refrigerators, manufacturing of rayon, HNO_3 (*Ostwald's process*), $NaHCO_3$ (*Solvay's process*), nitrogenous fertilizers.
Phosphine (PH_3) 	$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3\uparrow$	PH_3: $\xrightarrow{CuSO_4} Cu_3P_2 + H_2SO_4$; $\xrightarrow{HCl} PH_4^+Cl^-$; $\xrightarrow{O_2} H_3PO_4$; $\xrightarrow{N_2O} N_2 + H_3PO_4$	For production of smoke screens. Phosphine in combination with acetylene is used in *Holme's signals*.
Nitric acid (HNO_3) 	$NaNO_3 + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HNO_3$	HNO_3: $\xrightarrow{SO_2} H_2SO_4 + NO_2$; $\xrightarrow{Sn} H_2SnO_3 + NO_2 + H_2O$; $\xrightarrow{HCl} H_2O + NOCl + [Cl]$	As fertilizers, explosives, perfumes, dyes and medicines. As oxidiser in rocket fuels.
Phosphorus pentachloride (PCl_5) 	P_4 (white) $+ 10Cl_2$ (Excess) $\longrightarrow 4PCl_5$	PCl_5: $\xrightarrow{P_4O_{10}} POCl_3$; $\xrightarrow{SO_2} POCl_3 + SOCl_2$; $\xrightarrow{P_4S_{10}} PSCl_3$; $\xrightarrow{H_2O \text{ (in excess)}} H_3PO_4 + HCl$	As chlorinating and dehydrating agent.

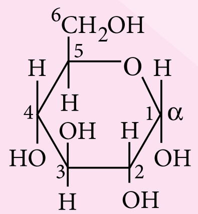
CONCEPT MAP

BIOMOLECULES

Monosaccharides

Simplest carbohydrates which cannot be hydrolysed to smaller molecules.

- **General formula :** $(CH_2O)_n$, $n = 3 - 7$
  e.g., Glucose, fructose, galactose.
- **Source :** Fruits, vegetables, etc.
- These provide energy and converted to glycogen for storage.



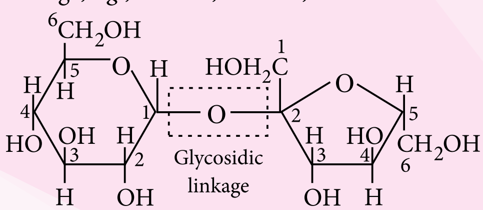
α-*D*-(+)-Glucopyranose

These are polyhydroxyaldehydes or polyhydroxyketones or substances which yield such products on hydrolysis. These are also known as *saccharides*. Their general formula is $C_x(H_2O)_y$ where *x* and *y* can be 3, 4, 5 .... etc.

CARBOHYDRATES

Diasaccharides

- Two monosaccharides units joined by glycosidic linkage, *e.g.*, sucrose, maltose, lactose.



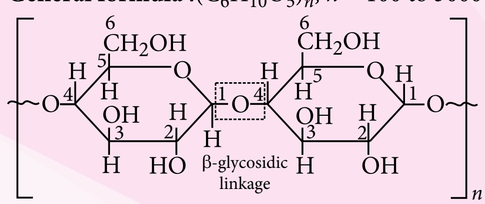
α-*D*-Glucose β-*D*-Fructose

Sucrose

- **Source :** Sugarcane, beet root, milk, etc.
- Excess is stored as fats.

Polysaccharides

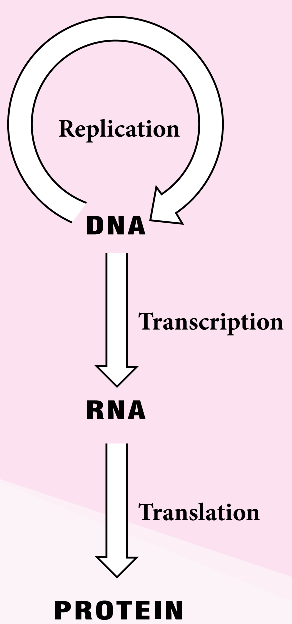
- Large number of monosaccharides units joined by glycosidic linkage. *e.g.*, starch, cellulose, glycogen.
- **General formula :** $(C_6H_{10}O_5)_n$, n = 100 to 3000

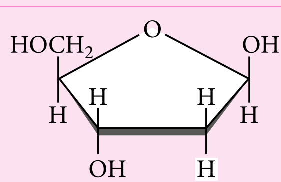
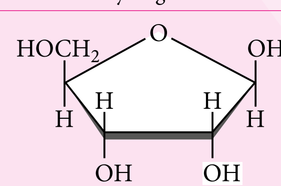
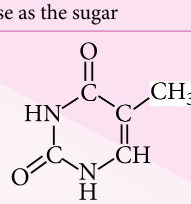
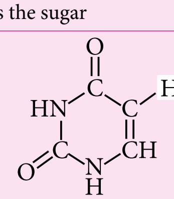


Cellulose

- **Source :** Rice, cereal, bread, etc.
- Used in synthesis of DNA.

NUCLEIC ACIDS



DNA (Deoxyribose Nucleic Acid)	**RNA (Ribose Nucleic Acid)**
 Double-stranded	 Generally single-stranded
 Deoxyribose as the sugar	 Ribose as the sugar
Bases used : Thymine (T), Cytosine (C), Adenine (A), Guanine (G)  Thymine	**Bases used :** Uracil (U), Cytosine (C), Adenine (A), Guanine (G)  Uracil
Storage of genetic information	Expression of genetic information

Nucleic acid are the polymer nucleotides prese nucleus of all living play an important transmission of hereditary charact and biosynthesi proteins.

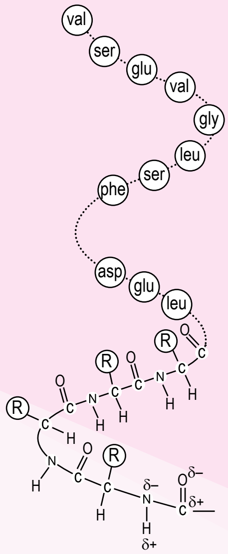
Nucleotide —Hydrolysis→

Hydrolysis Nucleo

Base + Sugar Pho

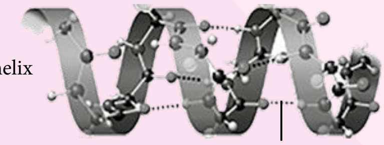
Primary Structure

- Refers to number and linear sequence of α-amino acids held together by peptide bonds.
- Permanent dipoles exist along the length of the chain at very regular intervals.

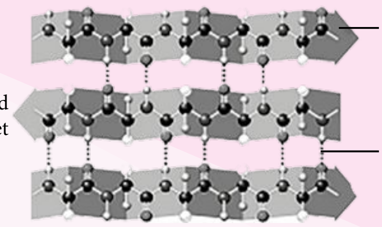


Secondary Structure

- It is due to folding or coiling of the peptide chain.
- **α-helix :** These coils are stabilised by hydrogen bonds between carbonyl oxygen of first amino acid to amide hydrogen of fourth amino acid.



- **β-pleated sheet structure :** β-pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains.



THE FOUR
OLECULES
OF LIFE

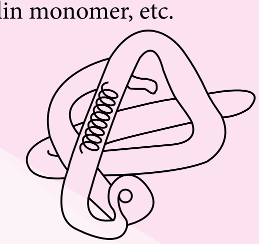
PROTEINS

Proteins are fundamental basic unit of life (structural and functional). They are high molecular mass complex biopolymers of α-amino acids. They occur naturally in milk, cheese, pulses, peanuts, fish, meat, etc.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha\text{-Amino acids}$$

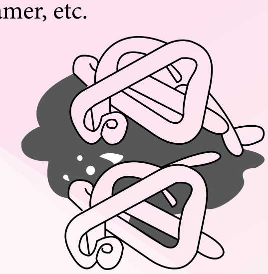
Tertiary Structure

It represents further folding of secondary structure, *e.g.*, myoglobin, insulin monomer, etc.



Quaternary Structure

The globular proteins may further associate to give quaternary structure *i.e.*, haemoglobin, insulin hexamer, etc.



LIPIDS

Lipids are organic compounds found in every type of plant and animal cell. They contain the elements carbon, hydrogen and oxygen (but less oxygen than in carbohydrates). All lipids are insoluble in water.

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oside +
sphoric acid

Types of Lipid

- **Triglycerides :**
  - Most common type of lipid.
  - 3 facty acids and a glycerol molecule are linked by an ester bond formed during dehydration synthesis.
- **Phospholipids :**
  - Same as triglycerides except one of the fatty acid molecule is replaced by a phosphate group (PO_4^{3-}).
  - The phosphate groups is polar and so is attracted to water, therefore the phospholipid has two distinct 'ends'.
  - A hydrophilic end ('water loving') that dissolves in water and a hydrophobic end ('water hating') that is repelled by water.
- **Steroids** having different structure in which four carbon rings are arranged in a specific molecular configuration.

Group 16 Elements (Oxygen Family)

Group 16 Elements (ns^2np^4)

Element	At. No.	Electronic Configuration	Oxidation State
Oxygen (O)	8	[He] $2s^22p^4$	–2, –1, +1, +2
Sulphur (S)	16	[Ne]$3s^23p^4$	–2, +2, +4, +6
Selenium (Se)	34	[Ar]$3d^{10}4s^24p^4$	–2, +2, +4, +6
Tellurium (Te)	52	[Kr] $4d^{10}5s^25p^4$	–2, +2, +4, +6
Polonium (Po)	84	[Xe] $4f^{14}5d^{10}6s^26p^4$	+2, +4, +6
Livermorium (Lv)	116	[Rn] $5f^{14}6d^{10}7s^27p^4$	–

General Trends

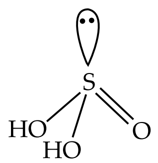
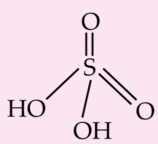
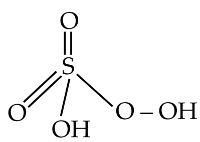
Increasing trends	Decreasing trends
Atomic size	Ionization energy
Density	Electronegativity
Ionic radius	Electron affinity
M.pt./B.pt. increase, O $\rightarrow$ Te	M.pt./B.pt. decreases Te $\rightarrow$ Po
Metallic character	Thermal stability of H_2E
Acidic nature of hydrides (H_2E)	Bond angle in hydrides (H_2E)
Reducing character increases	E—E bond strength

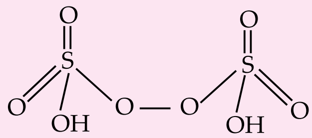
- **Exceptions**
  - O shows tendency of $p\pi$-$p\pi$ bonding others can form $d\pi$-$p\pi$ bonding.
  - EA_1 of O < EA_1 of S
  - S shows some tendency of catenation.

Anomalous Behaviour of Oxygen

- Oxygen differs from the rest of the elements of oxygen family due to
  - small size
  - high electronegativity and
  - non-availability of d-orbitals.
- **Points of difference :**
  - Oxygen is a diatomic gas while others are solids.
  - Oxygen exhibits oxidation states of –2, –1 and +2 only while other members show both negative and positive oxidation states like –2, +2, +4 and +6.
  - Due to high electronegativity of oxygen, hydrogen bonding is present in water.
  - Oxygen is highly non-metallic due to high electronegativity.
  - Oxygen is paramagnetic while others are diamagnetic.

Some Important Oxoacids of Sulphur

Oxoacid	Oxidation state, basicity and salt type	Structure	Properties
Sulphurous acid, H_2SO_3	S = +4, dibasic, and forms two series of salts, sulphites (SO_3^{2-}) and bisulphites (HSO_3^-)		– acts as reducing agent as well as oxidising agent. – exists only in solution.
Sulphuric acid (oil of vitriol), H_2SO_4	S = +6, dibasic and forms two series of salts, sulphates (SO_4^{2-}) and bisulphates (HSO_4^-)		– highly corrosive acts as oxidising agent and dehydrating agent.
Peroxomonosulphuric acid (Caro's acid), H_2SO_5	S = +6, monobasic and forms single type of salt, peroxymonosulphates (HSO_5^-)		– white, crystalline and hygroscopic solid. – powerful oxidising agent.

Peroxodisulphuric acid (Marshall's acid), $H_2S_2O_8$	S = +6 and forms single type of salt, peroxydisulphates ($S_2O_8^{2-}$)		– colourless, crystalline and hygroscopic solid. – strong oxidising agent.

GROUP 17 ELEMENTS (HALOGEN FAMILY)

Group 17 Elements (ns^2np^5)

Element	At. No.	Electronic Configuration	Oxidation State
Fluorine (F)	9	$[He]2s^22p^5$	–1
Chlorine (Cl)	17	$[Ne]3s^23p^5$	–1, +1, +3, +5, +7
Bromine (Br)	35	$[Ar]3d^{10}4s^24p^5$	–1, +1, +3, +5, +7
Iodine (I)	53	$[Kr]4d^{10}5s^2 5p^5$	–1, +1, +3, +5, +7
Astatine (At)	85	$[Xe]4f^{14}5d^{10}6s^26p^5$	–
Tennessine (Ts)	117	$[Rn]5f^{14}6d^{10}7s^27p^5$	–

General Trends

Increasing trends	Decreasing trends
Atomic size	Ionisation energy
Ionic radii	Electronegativity
M.pt./B.pt.	Electron affinity
Intensity of colour	Chemical reactivity
Electropositive character	E^o values
Acidic nature of hydrides (HX)	Oxidising power
Reducing nature of hydrides (HX)	Thermal stability of HX

- **Exceptions**
  - EA_1 of Cl > EA_1 of F
  - F shows oxidation state of – 1 except in HOF where it shows an oxidation state of +1; others show oxidation states – 1, + 1, + 3, + 5, + 7.

Oxoacids

Name	O.N. of *X*	F	Cl	Br	I
Hypohalous acid, HXO	+1	HOF	HOCl	HOBr	HOI
Halous acid, HXO_2	+3	–	$HClO_2$	–	–
Halic acid, HXO_3	+5	–	$HClO_3$	$HBrO_3$	HIO_3
Perhalic acid, HXO_4	+7	–	$HClO_4$	$HBrO_4$	HIO_4

Thermal stability, acidic strength decreases →

HXO_4, HXO_3, HXO_2, HXO

Oxidising nature increases →

Interhalogen Compounds

Type	Hybridisation	Shape	Geometry
XX'	sp^3	Linear	Tetrahedral
XX'_3	sp^3d	T-shaped	Trigonal bipyramidal
XX'_5	sp^3d^2	Square pyramidal	Octahedral
XX'_7	sp^3d^3	Pentagonal bipyramidal	Pentagonal bipyramidal

GROUP 18 ELEMENTS (NOBLE GASES)

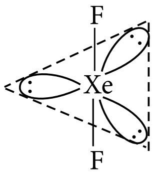
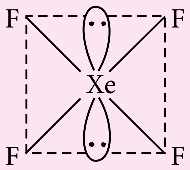
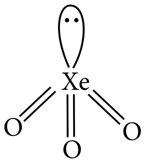
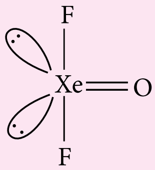
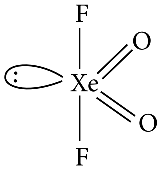
Group 18 Elements (ns^2np^6)

Element	Atomic no.	Electronic configuration
Helium (He)	2	$1s^2$
Neon (Ne)	10	$[He]\ 2s^2\ 2p^6$
Argon (Ar)	18	$[Ne]\ 3s^2\ 3p^6$
Krypton (Kr)	36	$[Ar]\ 3d^{10}\ 4s^2\ 4p^6$
Xenon (Xe)	54	$[Kr]\ 4d^{10}\ 5s^2\ 5p^6$
Radon (Rn)	86	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$
Oganesson (Og)	118	$[Rn]\ 5f^{14}\ 6d^{10}\ 7s^2\ 7p^6$

MONTHLY TUNE UP CLASS XI ANSWER KEY

1. (b)	2. (d)	3. (c)	4. (b)	5. (d)
6. (d)	7. (b)	8. (c)	9. (d)	10. (d)
11. (a)	12. (a)	13. (c)	14. (b)	15. (a)
16. (b)	17. (d)	18. (a)	19. (d)	20. (a,b,c)
21. (a,c)	22. (c,d)	23. (a,c)	24. (2)	25. (9.26)
26. (76.8)	27. (b)	28. (d)	29. (c)	30. (b)

Compounds of Xenon

Compound	Structure	Preparation	Properties
XeF_2 (Xenon difluoride)	 (+2) Linear, sp^3d	$Xe + F_2 \xrightarrow[400°C]{\text{Ni tube}} XeF_2$ (2 : 1) $Xe + O_2F_2 \xrightarrow{-178°C} XeF_2 + O_2$	$XeF_2 \xrightarrow{H_2} Xe + 2HF$ $XeF_2 \xrightarrow{H_2O} Xe + 2HF + \frac{1}{2}O_2$ $XeF_2 \xrightarrow[BF_3]{I_2} 2IF + Xe$ $XeF_2 \xrightarrow{2HCl} Xe + 2HF + Cl_2$ – Acts as fluorinating agent.
XeF_4, (Xenon tetrafluoride)	 (+4) Square planar, sp^3d^2	$Xe + F_2 \xrightarrow[600°C]{\text{Ni tube}} XeF_4$ (1 : 5)	– Colourless, crystalline solid with melting point, 117.1°C. – $XeF_4 + 2H_2 \longrightarrow Xe + 4HF$ – Undergoes disproportionation in water. $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$ – $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$ – Acts as fluorinating agent.
XeO_3, (Xenon trioxide)	 (+6) Pyramidal, sp^3	Complete hydrolysis of XeF_4 and XeF_6: $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 3O_2 + 24HF$ $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$	– Colourless, highly explosive and powerful oxidising agent. – Undergoes disproportionation when dissolved in alkali. $2XeO_3 + 4OH^- \longrightarrow Xe + O_2 + XeO_6^{4-} + 2H_2O$
$XeOF_2$, (Xenon oxydifluoride)	 (+4) T-shaped, sp^3d	Partial hydrolysis of XeF_4: $XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$	– Unstable
XeO_2F_2 (Xenon dioxy-difluoride)	 Distorted trigonal bipyramidal, sp^3d	Partial hydrolysis of $XeOF_4$ or XeF_6: $XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$ $XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$ Action of SiO_2 on $XeOF_4$: $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$	– Colourless solid. – Undergoes hydrolysis readily. $XeO_2F_2 + H_2O \longrightarrow XeO_3 + 2HF$

- XeF_6 cannot be stored in glass vessels because with glass, it form explosive XeO_3
  $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$
  $2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$
  $2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$
  (From glass) (Explosive)

Uses of Noble Gases

- Helium is used as breathing mixture (or oxygen dilutant) for divers.
- Mixture of O_2 and He is used in the treatment of asthma.
- Neon lighting is used for advertising.
- Argon is primarily used to create an inert atmosphere in light bulbs, welding and fluorescent bulbs.
- The light emitted by krypton in an electric discharge tube is used for runway and approach lights in airports.
- Xenon is used in electrical flash bulbs for high speed photography.
- Radon is used in radiotherapy of cancer.

SPEED PRACTICE

1. A certain compound on burning in air forms three oxides. One of the oxides turned lime water milky, the other turned anhydrous $CuSO_4$ blue and third formed a solution of pH = 9. Compound is formed of
   (a) S, N and H (b) S, N and C
   (c) S, C and H (d) S, H and Na

2. A colourless gas with rotten fish smell, burns spontaneously with a bright flash, giving beautiful vortex rings of white smoke, is
   (a) PH_3 (b) P_2O_3 (c) P_2O_5 (d) P_2S_5

3. Carbon cannot be used in the reduction of Al_2O_3 because
   (a) the enthalpy of formation of CO_2 is more than that of Al_2O_3
   (b) pure carbon is not easily available
   (c) the enthalpy of formation of Al_2O_3 is very high
   (d) it is an expensive proposition.

4. In the cyanide process for extraction of gold and silver from ores, the cyanide solution acts as a
   (a) reducing agent to reduce the gold and silver compounds present in the ores into the metallic states
   (b) leaching agent to bring the gold and silver into solution as cyanide complexes and thus separate these metals from the ores
   (c) leaching agent to dissolve all the other constituents of the ores leaving the gold and silver as metals
   (d) leaching agent to bring the ores into solution.

5. Thomas slag is prepared by reaction between
   (a) MnO and SiO_2 (b) CaO and SiO_2
   (c) CaO and P_4O_{10} (d) FeO and SiO_2

6. Which of the following statements is incorrect regarding the structure of the ClO_2 molecule?
   (a) The ClO_2 molecule is angular with O—Cl—O bond angle being 118°.
   (b) The two Cl—O bonds lengths are equal.
   (c) Both Cl—O bond lengths are greater than expected for a single Cl—O bond.
   (d) Both Cl—O bond lengths are shorter than expected for a single Cl—O bond.

7. Consider the following compounds :
   (i) Sulphur dioxide (ii) Hydrogen peroxide
   (iii) Ozone
   Among these compounds, those which can act as bleaching agents would include
   (a) (i) and (iii) (b) (ii) and (iii)
   (c) (i) and (ii) (d) (i), (ii) and (iii)

8. Consider the following metallurgical process :
   Metal sulphide $\xrightarrow{x}$ Metal oxide $\xrightarrow{y}$ Impure metal $\xrightarrow{z}$ Pure metal
   x, y and z are respectively
   (a) roasting, smelting, electrolysis
   (b) roasting, calcination, smelting
   (c) calcination, auto-reduction, bassemerisation
   (d) none of the above.

9. Chemical reduction is not suitable for
   (a) conversion of bauxite to aluminium
   (b) conversion of cuprite to copper
   (c) conversion of haematite to iron
   (d) conversion of zinc oxide to zinc.

10. Goldschmidt thermite process is used for
    (a) welding of broken iron pieces
    (b) converting iron into steel
    (c) extraction of sulphur
    (d) reduction of metallic oxide by magnesium.

11. In cyclotrimetaphosphoric acid, number of P—O—P bonds, P=O bonds and P—OH bonds are respectively
    (a) 6, 3, 3 (b) 5, 0, 3 (c) 4, 3, 0 (d) 3, 3, 3

12. The correct order of solubility in water for He, Ne, Ar, Kr, Xe is
    (a) He > Ne > Ar > Kr > Xe
    (b) Xe > Kr > Ar > Ne > He
    (c) Ne > Ar > Kr > He > Xe
    (d) Ar > Ne > He > Kr > Xe

13. Pick up the incorrect statement.
    (a) Asbestos and willemite are silicate minerals.
    (b) Anglesite and barytes are sulphate minerals.
    (c) Sylvine and fluorspar are halide minerals.
    (d) Calamine and zincite are the minerals of calcium.

14. Hard steel can be further hardened by heating it to red hot and then cooling it by plunging it into cold water, this process is called

(a) annealing (b) quenching
(c) smelting (d) tempering.

15. Brown colour of HNO_3 can be removed by
(a) adding Mg powder (b) boiling the acid
(c) passing NH_3 through acid
(d) passing air through warm acid.

16. Select the false statement.
(a) Bleaching powder loses its bleaching property when it is kept in an open bottle for a long time.
(b) Sulphur melts to a clear mobile liquid at 119 °C but on further heating above 160 °C it again becomes viscous.
(c) Graphite is used as a solid lubricant.
(d) Rhombic sulphur is prepared by melting monoclinic sulphur in a dish and cooling till crust is formed.

17. $$\boxed{\text{Bauxite}} \xrightarrow[N_2]{+C} \boxed{\text{AlN}} \xrightarrow{H_2O} Al(OH)_3 \xrightarrow{\Delta} Al_2O_3$$ (with CO ↑ evolved at the AlN step)
This flow-sheet is for
(a) Bayer's process (b) Serpeck's process
(c) Hall's process (d) Kroll's process.

18. The strongest reducing agent amongst the following is
(a) $P_2O_7^{-4}$ (b) $P_2O_6^{-4}$
(c) H_3PO_4 (d) $H_2PO_2^-$

19. For the extraction of sodium from NaCl, the electrolytic mixture NaCl + KCl + $CaCl_2$ is used. During extraction process, only sodium is deposited on cathode but K and Ca do not, because
(a) Na is more reactive than K and Ca
(b) Na is less reactive than K and Ca
(c) NaCl is less stable than KCl and $CaCl_2$
(d) the discharge potential of Na^+ is less than that of K^+ and Ca^{2+} ions.

20. Formation of metallic copper from the sulphide ore in the normal thermo-metallurgical process essentially involves which of the following reactions?
(a) $Cu_2S + 2O_2 \longrightarrow 2CuO + SO_2$;
(b) $Cu_2S + 3/2\ O_2 \longrightarrow Cu_2O + SO_2$;
$Cu_2O + C \longrightarrow 2Cu + CO$
$2\ Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$
(c) $Cu_2S + 2O_2 \longrightarrow 2CuSO_4$;
(d) $Cu_2S + 3/2\ O_2 \longrightarrow Cu_2O + SO_2$;
$CuSO_4 + Cu_2S \longrightarrow 3Cu + 2SO_2$
$Cu_2O + CO \longrightarrow 2Cu + CO_2$

21. An aqueous solution of a gas shows following reactions :
(i) It turns red litmus blue.
(ii) When added in excess to a copper sulphate solution a deep blue colour is obtained.
(iii) On addition to ferric chloride solution a brownish precipitate soluble in HNO_3 is obtained.
Identify the gas.
(a) SO_2 (b) SO_3 (c) NH_3 (d) CO_2

22. The true statement for the acids of phosphorus, H_3PO_2, H_3PO_3 and H_3PO_4 is
(a) the order of their acidity is $H_3PO_4 > H_3PO_3 > H_3PO_2$
(b) all of them are reducing in nature
(c) all of them are tribasic acids
(d) the geometry of phosphorus is tetrahedral in all the three.

23. Consider the following statements :
(i) Copper is extracted by hydrometallurgy from high grade ore.
(ii) $2Cl^-_{(aq)} + 2H_2O_{(l)} \longrightarrow 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$
The $\Delta G°$ for this reaction is –422 kJ.
(iii) Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum.
(iv) Nickel steel alloy is used for making cables, automobile and aeroplane parts, armour plates and gears.
Which of the above statements are correct?
(a) (i), (ii), (iii), (iv) (b) (ii) and (i)
(c) (iii) and (iv) (d) (i) and (iii)

24. A collector
(a) collects impurities from surface of ore *e.g.*, pine oil
(b) collects impurities from the bottom of the sulphide ore, *e.g.*, alkyl xanthate
(c) enhances the non-wettability of the ore particles, *e.g.*, fatty acids
(d) collect ore particles, form precipitate, *e.g.*, lime.

25. Oxygen is more electronegative than sulphur. Yet H_2S is acidic while H_2O is neutral. This is because
(a) water is a highly associated compound
(b) molecular mass of H_2S is more than that of H_2O
(c) H_2S is gaseous under ordinary conditions while H_2O is a liquid
(d) H — S bond is weaker than H — O bond.

SOLUTIONS

1. **(d):** One oxide turns lime water milky thus it can be CO_2 or SO_2. Oxide turns $CuSO_4$ (anhydrous) blue thus oxide is H_2O. Oxide is basic (pH = 9) thus it is of alkaline metal.

2. **(a)**

3. **(c) :** The enthalpy of formation of Al_2O_3 is very high and therefore, it cannot be reduced by carbon. It is reduced by electrolytic method.

4. **(b)**

5. **(c) :** $6CaO + P_4O_{10} \longrightarrow \underset{\text{Thomas slag}}{2Ca_3(PO_4)_2}$

6. **(c) :** Due to delocalization of electrons on three atoms, the Cl—O bond length decreases.

7. **(d)**

8. **(a) :** The conversion of metal sulphide to metal oxide involves the process of roasting (*i.e.*, *x* is roasting). The metal oxides can then be converted to impure metal by reduction. *i.e.*, '*y*' is smelting.
The conversion of impure metal to pure metal involves a process of purification. Thus, it is electrolysis.

9. **(a) :** Bauxite is not chemically reduced to Al, as aluminium is fairly electropositive and reactive metal, hence it may react with the reducing agent.

10. **(a) :** $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$
The molten iron produced by Goldschmidt thermite process can be used to weld broken parts of heavy machinery such as rail, girders, etc.

11. **(d)**

12. **(b):** As the size of the noble gas atoms increases down the group, the polarisation of the electron cloud becomes easier. So, heavier noble gas atoms are easily polarised in polar water. Thus, solubility increases down the group.

13. **(d):** Calamine is $ZnCO_3$ and zincite is ZnO. Both are minerals of zinc.

14. **(b)**

15. **(d):** Brown colour of HNO_3 can be removed by passing air through warm acid.

16. **(d):** Monoclinic sulphur is proposed by melting the rhombic sulphur in a dish and cooling it till a crust is formed.

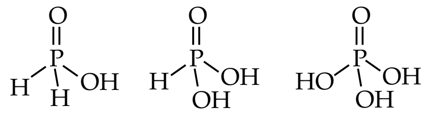
17. **(b)**

18. **(a) :** The oxidation state of P is least (+1) in $H_2PO_2^-$ and thus it is the strongest reducing agent.

19. **(d)** 20. **(b)**

21. **(c) :** The gas (*X*) is NH_3.
(i) Its aqueous solution is NH_4OH which turns red litum to blue.
(ii) $CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2 + (NH_4)_2SO_4$
$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \longrightarrow$
$[Cu(NH_3)_4]SO_4 + 4H_2O$
Tetrammine copper (II) sulphate (blue copper)
(iii) $FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{Brownish ppt.}}{Fe(OH)_3} + 3NH_4Cl$
$Fe(OH)_3 + 3HNO_3 \longrightarrow \underset{\text{Soluble}}{Fe(NO_3)_3} + 3H_2O$

22. **(d):** The order of acidity is $H_3PO_2 > H_3PO_3 > H_3PO_4$



H_3PO_2 H_3PO_3 H_3PO_4

Reducing nature depends on no. of P—H bonds. More the no. of P—H bonds, more will be the reducing nature. Thus, H_3PO_2 is stronger reducing agent than H_3PO_3 while H_3PO_4 does not act as reducing agent at all.
H_3PO_2, H_3PO_3 and H_3PO_4 contain one, two and three ionisable hydrogen atoms (P—OH bonds) respectively. As P is sp^3 hybridised, therefore all are tetrahedral.

23. **(c)** 24. **(c)**

25. **(d):** H—S bond is weaker than H—O bond thus, H_2S has higher tendency to release proton.

TOP 5 SECTORS IN 2020

Technology and computational thinking
Lifelong learning
Social Intelligence and new media literacy
Adaptability and Business Acumen
Care giving

THE 10 MOST IN-DEMAND JOBS

Data Analysts
Customer service representative
Medical technicians, physical therapists and workplace ergonomics experts
Management analysts
Sales and Marketing Specialists
Software developers and computer programmers
Veterinarians
Product Designers
Teachers and trainers
Accountants and auditors

(Source: World Economic Forum)

BRUSH UP YOUR CONCEPTS

Class XII

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

SOLUTIONS

- A binary solution is a homogeneous dispersion in which the size of dispersed phase particles (solute), is less than one nanometer, in dispersion medium (solvent) which determines the physical state of solution.
- Based on the states of solute and solvent, solutions are classified into nine types, *e.g.*, solid in solid (Cu in Au), liquid in solid (amalgam of Hg in Na), etc.
- It is important to note that all intravenous injections are always solutions of medicines in 0.91% or 0.155 M aqueous NaCl which are isotonic with the fluid inside the blood cell.
- Henry found that the dissolution of a gas in a liquid at a given temperature is directly proportional to the pressure on the gas.
  (a) Mole fraction of gas in solution $\left(x_{\text{gas}}\right)=\dfrac{P}{K_H}$.
  Here, K_H is Henry's law constant and has units of pressure.
  (b) Molarity of a gas in solution, $(M) = PK_H$. Here, K_H is Henry's law constant and has units mol L^{-1} atm^{-1} (or bar^{-1} or N m^{-2}).
  It is very important to note that at higher temperatures x_{gas} decreases and therefore K_H increases.
- Raoult studied liquid in liquid and solid in liquid solutions.
  (a) Partial pressure of each component in solutions of volatile liquids is directly proportional to its mole fraction.
  $p_A \propto x_A \Rightarrow p_A = p_A^\circ x_A$
  p_A° is vapour pressure of liquid in pure state at experimental condition of temperature.
  (b) Total pressure of binary solution,
  $P_T = p_1 + p_2 = p_1^\circ x_1 + p_2^\circ x_2$
  Also, $P_T = p_1^\circ + (p_2^\circ - p_1^\circ)x_2$
  (*A* or 1 stands for solvent. *B* or 2 stands for solute)
  (c) Partial pressure of each component in vapour phase is directly proportional to its mole fraction in vapour phase *y*.
  $p_A \propto y_A \Rightarrow p_A = P_T\, y_A$
  (According to Dalton's law of partial pressure)
  (d) Raoult's law and Henry's law become the same if $p_A^\circ = K_H$
  Raoult's law : $p_A = p_A^\circ x_A$;
  Henry's law ; $p_A = K_H\, x_A$
- When two liquids having very close strengths of intermolecular forces are mixed, the strength of new intermolecular forces is also similar. *e.g.*, liquids *A* and *B* are mixed : *A* ····· *B* forces = *A* ····· *A* forces = *B* ····· *B* forces. There is no heat change on mixing, *i.e.*, $\Delta_{\text{mix}} H = 0$ and no change in volume, *i.e.*, $\Delta_{\text{mix}} V = 0$. Such solutions are called Ideal solutions.
- If new forces *A*····· *B* are stronger than both *A* ····· *A* and *B* ····· *B* forces than, $\Delta_{\text{mix}}H < 0$ and $\Delta_{\text{mix}}V < 0$. The solution is said to show negative deviation from Raoult's law. The solution at a specific composition has minimum total vapour pressure and distills unchanged in composition. This solution is called maximum boiling (point) azeotrope.
  Similarly, the reverse is observed when the new forces *A* ····· *B* are weaker than either *A* ····· *A* or *B* ····· *B* forces, $\Delta_{\text{mix}}H > 0$, $\Delta_{\text{mix}}V > 0$. The solution is said to show positive deviation from Raoult's law. At a certain composition, the total vapour pressure is maximum and the solution distills unchanged in composition. This solution is called minimum boiling (point) azeotrope.

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

- **Examples**

(a) Positive deviation :

(i) C_2H_5OH and acetone
(ii) H_2O and C_2H_5OH
(iii) $CHCl_3$ and CCl_4, etc.

(b) Negative deviation :

(i) $CHCl_3$ and CH_3COCH_3
(ii) HCl and H_2O
(iii) $C_2H_5NH_2$ and CH_3COCH_3, etc.

- These solutions showing negative or positive deviation from Raoult's law are called Non-ideal solutions.
  Properties of solution like relative lowering of vapour pressure, depression in freezing point, elevation in boiling point and osmotic pressure, depend upon the total number of particles related to the solute present in solution, are called colligative properties.
- Relative lowering of vapour pressure (RLVP)
  i.e., $\frac{\Delta P}{P_A^\circ} = x_B \simeq \frac{W_B}{M_B} \times \frac{M_A}{W_A}$
  Elevation in b.pt., $\Delta T_b = K_b m = \frac{1000 \times K_b \times W_B}{W_A \times M_B}$
  Depression in f.pt., $\Delta T_f = K_f m = \frac{1000 \times K_f \times W_B}{W_A \times M_B}$
  K_f is called freezing point depression constant or molal depression constant or cryoscopic constant of solvent.
  $$K_f = \frac{RMT_f^2}{1000\ \Delta_{\text{fus}}H}$$
  [T_f is freezing point and $\Delta_{\text{fus}}H$ is latent molar heat of fusion.]
  K_b is called boiling point elevation constant or molal elevation constant or ebullioscopic constant of solvent.
  $$K_b = \frac{RMT_b^2}{1000\ \Delta_{\text{vap}}H}$$
  [T_b is boiling point and $\Delta_{\text{vap}}H$ is latent molar heat of vaporisation].
- Osmosis is the phenomenon of passage of solvent through semipermiable membrane when two solutions of different concentrations are separated by it, to decreases the concentration of solution of higher concentration.
  When a solution is separated from pure solvent by a semipermiable membrane, the pressure applied on the solution to check osmosis, is the measure of the osmotic pressure (π) of the solution.
  $\pi \propto$ molarity ; $\pi = CRT$
  (a) If two solutions have equal osmotic pressures at same temperature, they have equal molarities, are called isotonic solutions.
  (b) On comparing osmotic pressure of two solutions, the one which has higher osmotic pressure, is called hypertonic while the other hypotonic.
- Osmotic pressure is specially used for finding out the molar mass of a polymer because other colligative properties $\left(\propto \frac{1}{\text{Molar mass}}\right)$ have negligible value but osmosis will occur.
- When solute molecules associate or dissociate in solution we get abnormal molecular mass by using colligative properties. *e.g.*, molar mass of ethanoic acid in benzene solvent comes to 120 instead of 60.
- In 1880, van't Hoff suggested a factor '*i*' known as van't Hoff factor. It is the total number of moles of species obtained from one mole of solute in solution.
  i = Total number of moles of all types obtained from 1 mole of solute is solution.

$$i = \frac{\text{Total moles of particles obtained from solute}}{\text{Number of moles of solute dissolved in solution}}$$

$$i = \frac{\text{Actual or normal molecular weight}}{\text{Experimental or abnormal molecular weight}}$$

$$i = \frac{\text{Experimental or observed colligative property}}{\text{Theoretical (calculated) colligative property}}$$

- Corresponding, all formulae of colligative properties are to be modified as :
  (a) $\pi = iCRT$ (b) $\Delta T_f = iK_f m$
  (c) $\Delta T_b = iK_b m$ (d) $\frac{\Delta P}{P_A^\circ} \simeq i\frac{n_B}{n_A}$
  Degree of dissociation $(\alpha) = \frac{i-1}{n-1}$
  (n moles produced from 1 mole of solute on 100% dissociation)
  Degree of association $(\alpha) = \frac{1-i}{1-\frac{1}{n}}$
  (n moles of solute produce 1 mole)

MULTIPLE CHOICE QUESTIONS

1. If mole fraction of nitrogen in air at 25 °C and one atm is 0.78 and K_H for N_2 is 8.5×10^{-7} mol L^{-1} $(mmHg)^{-1}$, the concentration of nitrogen gas in 100 mL of water is
(a) 4.1×10^{-3} mol L^{-1} (b) 5.04×10^{-4} mol L^{-1}
(c) 6.2×10^{-5} mol L^{-1} (d) 7.05×10^{-6} mol L^{-1}

2. Taking K_H of H_2S equal to 285.7 atm what will be the solubility in mole per kg of water at STP?
(a) 0.0159 (b) 0.0195 (c) 0.195 (d) 0.591

3. Two liquids A and B have pressures p_A° and p_B° in pure state. If total pressure of a specific mixture of these two liquids is $[200 + 215\, x_B]$ mmHg. What are the value of p_A° and p_B° respectively?
(a) 200 and 415 mmHg (b) 415 and 200 mmHg
(c) 200 mmHg each (d) 415 mmHg each

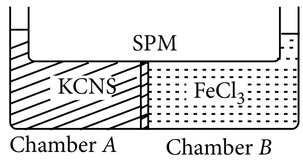
4. 0.5 g of non-volatile and non electrolyte A_x (Atomic mass of A = 32 u) is dissolved in 26 g of benzene (molar mass = 78 g mol^{-1}). The depression in vapour pressure of benzene is 0.005 bar. If the pure benzene has vapour pressure 0.85 bar, what is the value of x?
(a) 2 (b) 4 (c) 6 (d) 8

5. A solution containing 10 gram glucose in 1 kg of water, boils at 373.44 K at 1.013 bar. What is the f.pt. of the same solution? (K_b and K_f for water are 0.52 and 1.86 K kg mol^{-1} respectively)
(a) 373.047 K (b) 373.253 K
(c) 273.047 K (d) 273.253 K

6. If $\Delta_{vap}H$ of water is 540 cal g^{-1}, the value of K_b will be (R = 2 cal K^{-1} mol^{-1})
(a) 0.515 (b) 0.53 (c) 0.50 (d) 0.498

7. The osmotic pressure of a solution is 30 Pa when one gram of a polymer is dissolved in 500 mL of aqueous solution at 37 °C. The molar mass of the polymer is ($R = 8.314 \times 10^3$ Pa L $K^{-1}mol^{-1}$)
(a) 16800 g (b) 161723 g
(c) 170538 g (d) 171823 g

8. $KCNS_{(aq)}$ reacts with $FeCl_3$ to produce blood red coloured $Fe(CNS)_3$ according to the reaction,
$3KCNS + FeCl_3 \rightarrow 3KCl + Fe(CNS)_3$
When a 10 mol L^{-1} solution of KCNS is separated from 1 mol L^{-1} solution of $FeCl_3$ by SPM as shown in figure. Which chamber will have blood red colour?



(a) Chamber A
(b) Chamber B
(c) Both the chambers A and B
(d) None of A or B

9. 10 g L^{-1} solution of an unknown compound is isotonic with 3.42% of sucrose solution. The molar mass of unknown compound is (molar mass of sucrose = 342 g L^{-1})
(a) 80 (b) 90 (c) 100 (d) 110

10. What mass of water be added to 115 g of ethanol to have a solution of mole fraction of ethanol 0.7?
(a) 12.8 g (b) 15.7 g (c) 19.3 g (d) 22.7 g

11. If a solution of a non-volatile solute has vapour pressure 4% below the vapour pressure of pure water under experimental conditions, the molality of solution is
(a) 1.125 (b) 1.876 (c) 2.315
(d) data is insufficient to decide.

12. We have two solutions, one is 12 g L^{-1} urea solution and other 68.4 g L^{-1} sucrose solution. The lowering of vapour pressure of 1st solution at the same temperature is
(a) $\left(\frac{1}{5}\right)^{th}$ of 2nd solution
(b) double of 2nd solution
(c) 5 times of 2nd solution
(d) same as 2nd solution.

13. At 300 K, the total vapour pressure of an ideal solution containing one mole of A and 3 moles of B is 550 mmHg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of solution increases by 10 mmHg. What is the V.P. of B in pure state?
(a) 200 mmHg (b) 250 mmHg
(c) 500 mmHg (d) 600 mmHg

14. 3 g of ethanoic acid is added to half litre of water. If the acid is 23% dissociated, the depression of freezing point will be
($K_{f\,(H_2O)}$ = 1.86 K kg mol^{-1}, d_{H_2O} = 0.997 g cm^{-3})
(a) 0.109 K (b) 0.149 K
(c) 0.229 K (d) 0.389 K

15. A solution containing 1.248 g $BaCl_2$ (Molar mass = 208.34) in 100 g of water boils at 100.0832 °C. The degree of dissociation of $BaCl_2$ is
(K_b = 0.52 K kg mol^{-1})
(a) 35.8% (b) 53.8% (c) 38.5% (d) 83.5%

16. A 2% (w/v) KCl solution shows 90% ionisation of KCl. The osmotic pressure at 27 °C is
(a) 9.12 atm (b) 10.23 atm
(c) 12.56 atm (d) 15.26 atm.

17. Density of one molar KBr solution is 1.1 g mL^{-1}. The boiling point of solution is
(K_b = 0.52 K kg mol^{-1}, molar mass of KBr = 119 g)
(a) 373.106 K (b) 373.506 K
(c) 374.01 K (d) 374.21 K

18. 0.2 g of acetic acid dimerises when dissolved in 20 g of benzene, decreasing the freezing point by 0.45 °C. The degree of association of acetic acid in benzene is [K_f (benzene) = 5.12 K kg mol^{-1}]
(a) 45.9% (b) 94.6% (c) 69.4% (d) 54.9%

19. Which solution will show the highest value of any colligative property?
(a) 1 M glucose solution
(b) 1 M urea solution
(c) 1 M alum solution
(d) 1 M NaCl solution

20. The value of Henry's constant K_H
(a) increases with increase in temperature
(b) decreases with increase in temperature
(c) first increases then decreases
(d) remains constant.

SOLUTIONS

1. (b) : $\frac{p_{N_2}}{P_T} = x_{N_2}$ (Dalton's law of partial pressures)
$p_{N_2} = 0.78 \times 760$ mmHg
According to Henry's law, $M = p_{N_2} \times K_H$
$= 0.78 \times 760 \times 8.5 \times 10^{-7}$ mol L^{-1}
$= 5.04 \times 10^{-4}$ mol L^{-1}

2. (c) : $K_H \times x_{H_2S}$ = Partial pressure of H_2S

$$x_{H_2S} = \frac{1 \text{ atm}}{285.7 \text{ atm}} \Rightarrow \frac{n_{H_2S}}{n_{H_2S} + n_{H_2O}} = \frac{1}{285.7}$$

$$\frac{n_{H_2S} + n_{H_2O}}{n_{H_2S}} = 285.7 \Rightarrow 1 + \frac{n_{H_2O}}{n_{H_2S}} = 285.7$$

$$\frac{55.56}{n_{H_2S}} = 284.7 \quad [\because n_{H_2O} \text{ (in 1 kg)} = 55.56]$$

$$n_{H_2S} = \frac{55.56}{284.7} = 0.195 \text{ moles}$$

Molality = 0.195 mole per kg of water.

3. (a) : According to Raoult's law, $P_T = p_A^\circ + (p_B^\circ - p_A^\circ)x_B$
On comparing, $P_T = 200 + 215\, x_B$
p_A° = 200 mmHg; $p_B^\circ - p_A^\circ$ = 215 mmHg
p_B° = 215 + 200 = 415 mmHg

4. (d) : $\frac{\Delta P}{P_A^\circ} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$

$$M_B = \frac{W_B \times M_A \times P_A^\circ}{W_A \times \Delta P} = \frac{0.5 \times 78 \times 0.85}{26 \times 0.005} = 255$$

Hence, $A_x = 32x = 255$
$\Rightarrow x = 8$

5. (c) : There is no need to use the data of elevation of boiling point.

$$\Delta T_f = \frac{K_f \times 1000 \times W_B}{W_A \times M_B} = \frac{1.86 \times 1000 \times 10}{1000 \times 180} = 0.103$$

f.pt. = 273.15 – 0.103 = 273.047 K

6. (a) : K_b (K kg mol^{-1}) $= \frac{R \times T_b^2}{1000 \times \Delta_{vap}H \text{ (per g)}}$

$$= \frac{2 \times (373.15)^2}{1000 \times 540} = 0.515$$

7. (d) : $\pi = \frac{W_B \times RT}{M_B \times V_L}$

$$M_B = \frac{(1 \text{ g}) \times (8.314 \times 10^3 \text{ Pa L K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K})}{(30 \text{ Pa}) \times (0.5 \text{ L})}$$

= 171823 g mol^{-1}

8. (d) : Semipermeable membrane allows only solvent to pass through it.
Decreasing the concentration of solution of higher concentration and not the solute particles. Hence, blood red colour will not be observed in any chamber.

9. (c) : Let the molar mass of unknown compound be X g mol^{-1}.
Molality of unknown solution = molarity of sucrose solution

$$\Rightarrow \frac{10}{X} = \frac{3.42 \times 10}{342} \quad \text{[for 1 L solution of each]}$$

$$\Rightarrow X = \frac{342 \times 10}{3.42 \times 10} = 100 \text{ g mol}^{-1}$$

10. (c) : $x_{Ethanol} = (0.7) = \frac{N_{Ethanol}}{N_{Ethanol} + n_{H_2O}}$

$$\frac{\frac{115}{46}}{\frac{115}{46} + \frac{x}{18}} = 0.7$$

$$\frac{2.5}{2.5+\left(\frac{x}{18}\right)}=\frac{7}{10} \Rightarrow \frac{2.5+\left(\frac{x}{18}\right)}{2.5}=\frac{10}{7}$$

$$1+\frac{x}{18\times 2.5}=\frac{10}{7} \Rightarrow x=\left(\frac{10}{7}-1\right)\times 18\times 2.5$$

$$=\frac{3}{7}\times 18\times 2.5=19.3 \text{ g}$$

11. (c) : If $P^\circ = 100$, $\Delta P = 4$

$$x_{\text{solute}}=\frac{\Delta P}{P_A^\circ}=\frac{4}{100}=0.04 \Rightarrow \frac{n_B}{n_B+n_{H_2O}}=\frac{0.04}{1}$$

$\Rightarrow \quad n_B = 0.04,\ n_B + n_{H_2O} = 1$

or $\quad n_{H_2O} = 1 - 0.04 = 0.96$

$$\Rightarrow \quad 0.96=\frac{W_{H_2O}}{18}$$

$$\Rightarrow W_{H_2O}=\frac{0.96\times 18}{1000}\text{ kg}=0.01728\text{ kg}$$

$$\text{Molality}=\frac{n_{\text{solute}}}{W_{H_2O}(\text{kg})}=\frac{0.04}{0.01728}=2.315$$

12. (d) : $RLVP \propto$ number of moles of solute

$$\frac{(RLVP)_{\text{urea}}}{(RLVP)_{\text{sucrose}}}=\frac{n_{\text{urea}}}{n_{\text{sucrose}}}$$

$$\frac{\frac{(\Delta P)_{\text{urea}}}{p^\circ_{H_2O}}}{\frac{(\Delta P)_{\text{sucrose}}}{p^\circ_{H_2O}}}=\frac{\left(\frac{12}{60}\right)}{\left(\frac{68.4}{342}\right)} \Rightarrow \frac{(\Delta P)_{\text{urea}}}{(\Delta P)_{\text{sucrose}}}=1$$

13. (d) : Initially, $P_T = p_A^\circ x_A + p_B^\circ x_B$

$$550=P_A^\circ\left(\frac{1}{1+3}\right)+p_B^\circ\left(\frac{3}{1+3}\right)$$

$p_A^\circ + 3p_B^\circ = 2200$ ...(i)

On adding 1 mol of B,

$$560=p_A^\circ\left(\frac{1}{1+4}\right)+p_B^\circ\left(\frac{4}{1+4}\right)$$

$P_A^\circ + 4P_B^\circ = 2800$ ...(ii)

Subtracting (i) from (ii), $P_B^\circ = 600$ mmHg

14. (c) : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	CH_3COOH	CH_3COO^-	H^+
At $t = 0$	1 mol	—	—
At $t_{\text{equ.}}$	$1 - \alpha$	α	α

$i = (1 - \alpha) + \alpha + \alpha = 1 + \alpha$

$$=1+\frac{23}{100}=1.23$$

$$m=\frac{W_B}{M_B}\times\frac{1000}{W_A}=\frac{3}{60}\times\frac{1000}{(500\times 0.997)}=0.1$$

$\Delta T_f = i \times K_f \times m = 1.23 \times 1.86 \times 0.1 = 0.229$ K

15. (d) : $\Delta T_b=\dfrac{1000\ K_b\ W_B i}{W_A\quad M_B}$

$$i=\frac{(100.0832-100)\times 100\times 208.34}{1000\times 0.52\times 1.248}=2.67$$

$$\alpha=\frac{i-1}{n-1}=\frac{2.67-1}{3-1}=0.835 \Rightarrow 83.5\%$$

16. (c) : $\alpha=\dfrac{i-1}{n-1} \Rightarrow 0.9=\dfrac{i-1}{2-1} \Rightarrow i=1.9$

$$\pi=\frac{w_{\text{KCl}}}{M_{\text{KCl}}}\times\frac{R\times T\times i}{V_L}=\frac{2}{74.5}\times\frac{0.0821\times 300\times 1.9}{0.1}$$

$$=\frac{93.59}{7.45}=12.56\text{ atm}$$

17. (d) : 1 M KBr solution $\Rightarrow$ $n = 1$, $V_{\text{soln.}} = 1000$ mL

Mass of 1 mole KBr = 39 + 80 = 119 g

$W_{\text{soln.}} = 1000 \times 1.1 = 1100$ g

$$W_{H_2O}=1100-119=981\text{ g}=\frac{981}{1000}\text{ kg}$$

$$\Delta T_b=i\,K_b\times\frac{n_B}{W_A(\text{kg})}$$

$$=2\times 0.52\times\frac{1}{981/1000}\quad[\text{for KBr, } i=2]$$

$$=\frac{2\times 0.52\times 1000}{981}=1.06\text{ K}$$

B.pt. 373.15 + 1.06 = 374.21 K

18. (b) : $i=\dfrac{M_B\Delta T W_A}{1000\ K_f\ W_B}=\dfrac{60\times 0.45\times 20}{1000\times 5.12\times 0.2}=0.527$

$$\alpha=\frac{1-i}{1-\left(\frac{1}{n}\right)}=\frac{1-0.527}{1-\left(\frac{1}{2}\right)}=0.473\times 2=0.946$$

$= 94.6\%$

19. (c) : Colligative properties $\propto$ number of particles related to solute

Here, alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$ produces $2K^+$, $5SO_4^{-2}$ and $2Al^{3+}$, *i.e.*, total 9 ions from one molecules on 100% dissociation.

20. (a) : $K_H x = P$

At constant pressure, increase in temperature will decrease the solubility of gas, *i.e.*, x and hence K_H should increase (as pressure is constant).

◈◈

Class XII

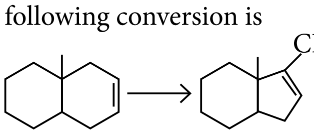
Be NEET READY

with exclusive and brain storming MCQs

Practicing these MCQs helps to strengthen your concepts and give you extra edge in your NEET preparation

1. Which property of white phosphorus is common to red P ?
(a) It gives vapours on heating.
(b) It reacts with hot caustic soda solution to gives phosphine.
(c) It shows chemiluminescence.
(d) It is soluble in carbon disulphide.

2. Correct sequence of reagents required for the following conversion is



(a) $\xrightarrow{O_3/Zn, H_2O} \xrightarrow{OH^-} \xrightarrow{\Delta}$
(b) $\xrightarrow{CrO_3} \xrightarrow{H^+}$ (c) $\xrightarrow{N_2H_4} \xrightarrow{OH^-} \xrightarrow{\Delta}$
(d) $\xrightarrow{KMnO_4/H^+} \xrightarrow{OH^-}$

3. Given that (in S cm^2 eq^{-1}) at T = 298 K, Λ°_{eq} for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 228.8, 120.3 and 129.8 respectively. Specific conductance for 0.2 N NH_4OH solution is 4.766×10^{-4} S cm^{-1}, then the pH of given NH_4OH solution will be
(a) 9.2 (b) 11.3 (c) 12.1 (d) 7.9

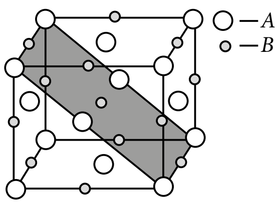
4. *D*-glucose, on treating with methanol in presence of dry HCl gives methyl glucoside according to the following reaction :

$$D\text{-glucose} \xrightarrow[\text{dry HCl}]{CH_3OH} \begin{matrix} \text{Methy } \alpha\text{-}D\text{-glucoside} \\ + \\ \text{Methy } \beta\text{-}D\text{-glucoside} \end{matrix}$$

Mention true (T) and false (F) from the following statements :
S_1 : The glucosides do not reduce Fehling's solution.
S_2 : The glucosides do not react with hydrogen cyanide or hydroxylamine.
S_3 : Behaviour of glucosides as stated in S_1 and S_2 indicates the absence of free —CHO group.
S_4 : The two forms of glucosides are enantiomers.
(a) TTFF (b) FTTT
(c) TTTF (d) TFTF

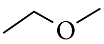
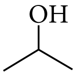
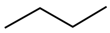
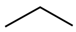
5. The temperature of blast furnace to produce iron from its ore, Fe_2O_3 varies from 500 °C at the top of the furnace to about 1900 °C at the bottom of the furnace. The reaction between the ore Fe_2O_3 and CO at the lowest temperature (~500°C) is
(a) $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
(b) $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$
(c) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
(d) $Fe_2O_3 + CO + CaCO_3 \rightarrow 2FeO + 2CO_2 + CaO$

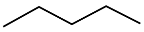
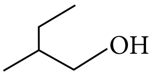
6. A crystal is made of particles *A* and *B*. *A* forms *fcc* packing and *B* occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then the formula of the crystal would be

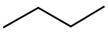
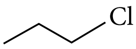


(a) AB (b) A_5B_7
(c) A_7B_5 (d) none of these.

7. In which of the following pairs first has higher melting point than second?

(a)  and  (b)  and 

(c)  and 

(d)  and 

8. The Rubin number which was proposed by Ostwald as an alternative to the gold number in order to measure the protective efficiency of a lyophillic colloid may be defined as the
(a) mass in milligrams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo - Rubin from red to violet when 0.16 g eq. KCl is added to it.
(b) mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo - Rubin from red to violet when 0.1 M KCl is added to it
(c) mass in grams of a colloid per 100 c.c. of solution which just prevents the colour change of standard sol of dye Congo - Rubin from red to violet when 0.2 M KCl is added to it.
(d) mass in grams of a colloid per 100 c.c. of solution which just prevents the colour - change of standard sol of dye Congo - Rubin from red to violet when 1 M KCl is added to it.

9. Match column-I with column-II and select the correct answer using the codes given below :

Column I	Column II
(A) $Hg^{2+}_{(aq)} + I^{-}_{(aq)} \rightarrow$	(p) Yellow precipitate
(B) $Cu^{2+}_{(aq)} + [Fe(CN)_6]^{4-}_{(aq)} \rightarrow$	(q) Brown precipitate
(C) $Mg^{2+}_{(aq)} + NH_{3(aq)} + HPO^{2-}_{4(aq)} \rightarrow$	(r) White precipitate
(D) $Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)} \rightarrow$	(s) Red precipitate

	A	B	C	D
(a)	s	q	r	p
(b)	p	r	s	q
(c)	r	s	q	p
(d)	q	p	r	s

10. For the reaction, $2NO_2 \rightarrow N_2O_2 + O_2$, rate expression is as follows : $\frac{d[NO_2]}{dt} = k[NO_2]^n$, where, $k = 3 \times 10^{-3}$ mol^{-1} L sec^{-1}. If the rate of formation of oxygen is 1.5×10^{-4} mol L^{-1} sec^{-1}, then the molar concentration of NO_2 in mol L^{-1} is
(a) 1.5×10^{-4} (b) 0.0151
(c) 0.214 (d) 0.316

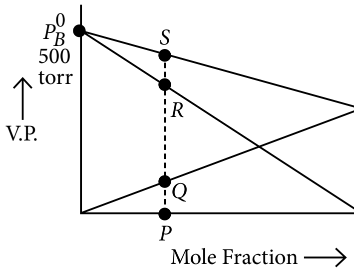
11. In the following reaction,
$$C_2H_5Cl + KNO_2 \xrightarrow{DMF} A_{(Major)}$$
The bond absent in 'A' is
(a) C—N (b) C—O
(c) C—H (d) C—C

12. Match column-I with column-II and select the correct answer using the codes given below :

Column I (Equiv. conductance at infinite dilution)	Column II (Formula)
(A) 229	(p) $[Pt(NH_3)_5Cl]Cl_3$
(B) 97	(q) $[Pt(NH_3)_3Cl_3]Cl$
(C) 404	(r) $[Pt(NH_3)_4Cl_2]Cl_2$
(D) 523	(s) $[Pt(NH_3)_6]Cl_4$

	A	B	C	D
(a)	r	p	q	s
(b)	p	r	s	q
(c)	p	s	r	q
(d)	r	q	p	s

13. If SR = 100 torr and PR = 350 torr then the mole fraction of A in vapour phase and mole fraction of A in liquid phase respectively are



(a) $\frac{3}{10}, \frac{2}{9}$ (b) $\frac{7}{9}, \frac{3}{10}$ (c) $\frac{2}{9}, \frac{7}{10}$ (d) $\frac{2}{9}, \frac{3}{10}$

14. Match column-I with column-II and select the correct answer using the codes given below :

Column I	Column II
(A) penicillin F	(p) *N*–(4–ethoxyphenyl) acetamide
(B) penicillin G	(q) benzyl penicillin
(C) penicillin X	(r) 2–pentenyl penicillin
(D) phenacetin	(s) *p*–hydroxybenzyl penicillin

	A	B	C	D
(a)	r	q	p	s
(b)	r	q	s	p
(c)	q	p	s	r
(d)	r	s	q	p

15. Which of the following amide does not undergo Hoffmann's degradation ?

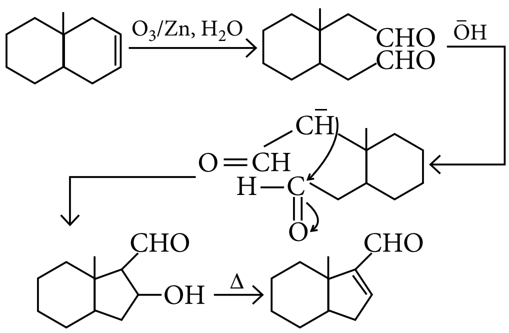
1. Propionamide 2. *N*-methyl butanamide
3. Butanamide 4. *N*, *N*-dimethyl butanamide

(a) 4 only (b) 3 only (c) 3 and 4 (d) 2 and 4

SOLUTIONS

1. **(a)**

2. **(a) :**



3. **(b) :** $\Lambda^\circ_{eq}(Ba(OH)_2) = \lambda^\circ_{Ba^{2+}} + \lambda^\circ_{OH^-}$ ...(i)

$\Lambda^\circ_{eq}(BaCl_2) = \lambda^\circ_{Ba^{2+}} + \lambda^\circ_{Cl^-}$ ...(ii)

$\Lambda^\circ_{eq}(NH_4Cl) = \lambda^\circ_{NH_4^+} + \lambda^\circ_{Cl^-}$ ...(iii)

$\Lambda^\circ_{eq}(NH_4OH) = \lambda^\circ_{NH_4^+} + \lambda^\circ_{OH^-}$

eq. (i) + eq. (iii) – eq. (ii), we get

$= 228.8 + 129.8 - 120.3 = 238.3$ S cm^2 eq^{-1}

Now, major conductivity of NH_4OH,

$$\Lambda_{eq} = K \times \frac{1000}{\text{Normality}} = \frac{4.766 \times 10^{-4} \times 1000}{0.2} = 2.383$$

$$\alpha = \frac{\Lambda_{eq}(NH_4OH)}{\Lambda^\circ_{eq}(NH_4OH)} = \frac{2.383}{238.3} = 0.01$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$C(1-\alpha)$ $C\alpha$ $C\alpha$

$[OH^-] = 0.2 \times 0.01 = 2.0 \times 10^{-3}$

pOH = 3 – log2 = 3 – 0.3010 = 2.7

pH = 14 – 2.7 = 11.3

4. **(c) :** S_1, S_2 and S_3 are true but S_4 is false because the glycosides are not mirror images of each other hence they are diastereomers.

5. **(c) :** The reaction at 500 °C is

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

6. **(a) :** In new arrangement, A particles

$$= \left(\frac{1}{8}\times 8 + \frac{1}{2}\times 6\right) - \left(\frac{1}{8}\times 4 + \frac{1}{2}\times 2\right) = \frac{5}{2}$$

and B particles $= \left(\frac{1}{4}\times 12 + 1\right) - \left(1 + \frac{1}{4}\times 2\right) = \frac{5}{2}$

So, formula is AB.

7. **(b) :** In (b), compound first has high molecular mass than second. So, first has higher melting point.

8. **(a)** **9.** **(a)**

10. **(d) :** From the unit of k, it is evident that it is a second order reaction.

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} \quad \therefore -\frac{d[NO_2]}{dt} = 2 \times \frac{d[O_2]}{dt}$$

$= 2 \times 1.5 \times 10^{-4} = 3 \times 10^{-4}$

$3 \times 10^{-4} = k[NO_2]^2 = 3 \times 10^{-3}[NO_2]^2$

$\therefore$ $[NO_2] = 0.316$

11. **(b)** **12.** **(d)**

13. **(d) :** $PQ = SR = P_A = 100$ torr

and $PR = P_B = 350$ torr

$P_T = P_A + P_B = 100 + 350 = 450$ torr

and $P_B = P_B^\circ X_B$

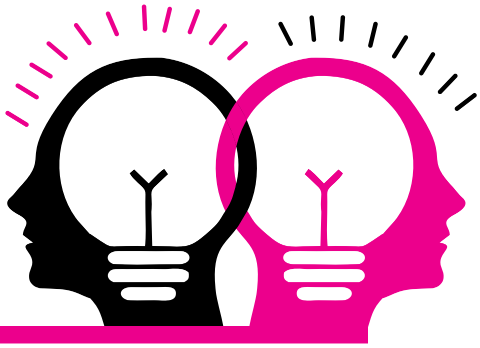
$$X'_B \text{ (vapour phase)} = \frac{P_B}{P_T} = \frac{350}{450} = \frac{7}{9}$$

$350 = 500\, X_B \Rightarrow X_B = 7/10$

$X'_A = 1 - X'_B = 2/9$; $X_A = 1 - X_B = 3/10$

14. **(b)** **15.** **(d)**

EXAMINER'S MIND CLASS XII



The questions given in this column have been prepared on the basis of pattern of Previous Years' Questions asked in JEE (Main & Advanced)/NEET/AIIMS exams.

SOLUTIONS

SECTION - I

Only One Option Correct Type

1. A solution has an osmotic pressure of 0.821 atm at 300 K. Its concentration would be
   (a) 0.066 M (b) 0.66 M
   (c) 0.033 M (d) 0.33 M

2. Which of the following are actual practical uses of colligative properties?
   I. Melting of snow by salt
   II. Desalination of sea water
   III. Determination of molar mass
   IV. Determination of melting point and boiling point of solvent
   (a) I, II (b) III, IV
   (c) I, II, III (d) II, III, IV

3. At 40 °C, the total vapour pressure (in torr) of methyl alcohol (A) and ethyl alcohol (B) solution is represented by , $P = 120X_A + 138$, where X_A is mole fraction of methyl alcohol. The value of p_B° at $\lim_{X_A \to 0}$ and p_A° at $\lim_{X_B \to 0}$ are
   (a) 138, 258 (b) 258, 138
   (c) 120, 138 (d) 138, 125

4. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.01 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
   (a) 25% (b) 50% (c) 75% (d) 85%

5. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20 °C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is
   (a) 128 (b) 488 (c) 32 (d) 64
   (JEE Main 2015)

SECTION - II

More than One Options Correct Type

6. Consider following solutions :
   I. 1 M aqueous glucose solution
   II. 1 M aqueous sodium chloride solution
   III. 1 M aqueous ammonium phosphate solution
   IV. 1 M benzoic acid in benzene
   Select correct statements for the above solutions.
   (a) All are isotonic solutions.
   (b) III is hypertonic of I, II and IV.
   (c) IV is hypotonic of I, II and III.
   (d) II is hypotonic of III but hypertonic of I and IV.

7. Which of the following are correct statements?
   (a) When mixture is more volatile, there is positive deviation from Raoult's law.
   (b) When mixture is less volatile, there is negative deviation from Raoult's law.
   (c) Ethanol and water form ideal solution.
   (d) $CHCl_3$ and water form ideal solution.

8. 5.3% (w/v) Na_2CO_3 solution and 6.3% (w/v) $H_2C_2O_4 . 2H_2O$ solution have same
   (a) molality (b) molarity
   (c) normality (d) mole fraction.

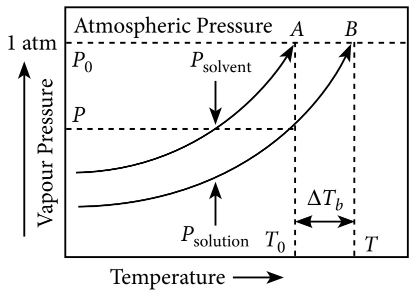
9. Which of the following statements are false for a solution of chloroform and acetone?
   (a) The solution formed is an ideal solution.
   (b) The solution formed is a non-ideal solution with positive deviation from Raoult's law.
   (c) The solution formed is a non-ideal solution with negative deviation from Raoult's law.
   (d) The solution behaves ideally or non-ideally depending upon its composition.

10. Mixtures showing positive deviation from Raoult's law at 35°C is(are)
(a) carbon tetrachloride + methanol
(b) carbon disulphide + acetone
(c) benzene + toluene
(d) phenol + aniline. *(JEE Advanced 2016)*

SECTION - III
Paragraph Type

Paragraph for Questions 11 and 12

Figure explains elevation in boiling point when a non-volatile solute is added to a solvent.



11. Given that ΔT_b is the elevation in boiling point of the solvent in a solution of molality '*m*', then $\lim_{m\to 0}\left(\frac{\Delta T_b}{m}\right)$ is equal to
(a) K_b (molal elevation constant)
(b) L_v (latent heat of vaporisation)
(c) ΔS (entropy change)
(d) X (mole fraction of solute).

12. Elevation in b.pt. of an aqueous urea solution is 0.52° (K_b = 0.52° mol^{-1} kg). Hence, mole fraction of urea in this solution is
(a) 0.982 (b) 0.0567 (c) 0.947 (d) 0.018

Paragraph for Questions 13 and 14

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution *M* is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water ($K_{f\ water}$) = 1.86 K kg mol^{-1}

Freezing point depression constant of ethanol ($K_{f\ ethanol}$) = 2.0 K kg mol^{-1}

Boiling point elevation constant of water ($K_{b\ water}$) = 0.52 K kg mol^{-1}

Boiling point elevation constant of ethanol ($K_{b\ ethanol}$) = 1.2 K kg mol^{-1}

Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K
Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40 mm Hg
Molecular weight of water = 18 g mol^{-1}
Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

13. The freezing point of the solution *M* is
(a) 268.7 K (b) 268.5 K
(c) 234.2 K (d) 150.9 K.

14. The vapour pressure of the solution *M* is
(a) 39.3 mmHg (b) 36.0 mmHg
(c) 29.5 mmHg (d) 28.8 mmHg.
(IIT JEE 2008)

SECTION - IV
Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

15. Assertion : The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.
Reason : Elevation of boiling point is directly proportional to the number of species present in the solution.

16. Assertion : An ideal solution obeys Raoult's law.
Reason : In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interactions.

17. Assertion : The solubility of a gas in a liquid increases with increase of pressure.
Reason : The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

SECTION - V

Numerical Value Type

18. Chloroacetic acid, a monoprotic acid, has a K_a (ionisation constant) of 1.36×10^{-3}. Calculate boiling point of 0.01 M aqueous solution. K_b (molal elevation constant) = 0.51 K kg mol^{-1}, b.pt. (H_2O) = 100 °C. Assume 0.01 molar = 0.01 molal.

19. A solution of 6.2 g ethylene glycol in 55 g H_2O is cooled to –3.72 °C. The ice separated from solution is : [$K_f(H_2O)$ = 1.86 K molality^{-1}]

20. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is *(JEE Advanced 2014)*

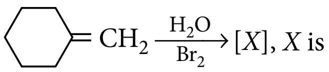
HALOALKANES AND HALOARENES

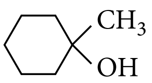
SECTION - I

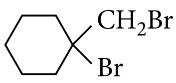
Only One Option Correct Type

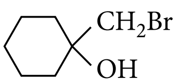
1. The synthesis of alkyl fluorides is best accomplished by
(a) Finkelstein reaction
(b) Swarts reaction
(c) free radical fluorination
(d) Sandmeyer's reaction. *(JEE Main 2015)*

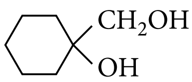
2. In the following reaction,



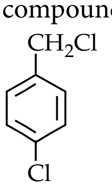
(a) 

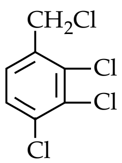
(b) 

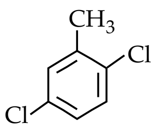
(c) 

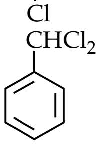
(d) 

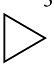
3. An aromatic compound $C_7H_6Cl_2$ (*A*), gives AgCl on boiling with alcoholic $AgNO_2$ solution and yields C_7H_7OCl on treatment with sodium hydroxide. (*A*) on oxidation gives monochlorobenzoic acid. The compound (*A*) is

(a) 

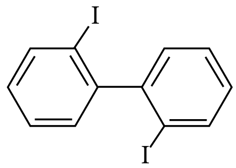
(b) 

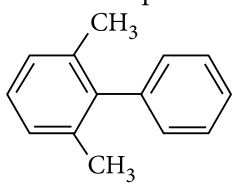
(c) 

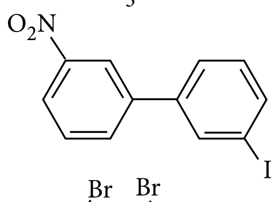
(d) 

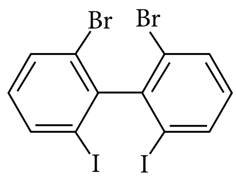
4. Which of the following reactions gives best yield of *n*-propylbromide?
(a) $CH_3CH_2CH_3 + Br_2 \xrightarrow{h\upsilon}$
(b) $CH_3CH{=}CH_2 + HBr \longrightarrow$
(c) $CH_3CH_2CH_2Cl + NaBr \xrightarrow{\text{acetone}, \Delta}$
(d)  $+ HBr \xrightarrow{\Delta}$

5. Which of the following biphenyls is optically active?

(a) 

(b) 

(c) 

(d) 

(NEET-Phase II 2016)

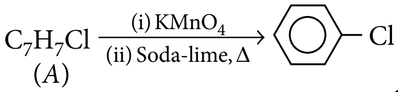
SECTION - II

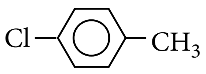
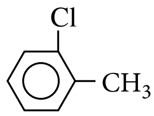
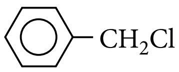
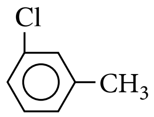
More than One Options Correct Type

6. Which of the following statements is/are correct?
(a) $CH_3CHClCH_3$ is a secondary alkyl halide.
(b) Acetylene is formed when $CH_2{=}CH{-}Cl$ is heated with water.
(c) Iodoform gives a precipitate with $AgNO_3$ solution on heating, whereas chloroform does not.
(d) Freon (CCl_2F_2) is prepared by the action of CCl_4 and SbF_3 in the presence of $SbCl_5$ as catalyst.

7. Pick out the correct equations.
(a) $CH_3CH{=}CH_2 + HCl \xrightarrow{\text{Peroxide}} CH_3CHClCH_3$
(b) $CH_3CH{=}CH_2 + HBr \longrightarrow CH_3CH_2CH_2Br$
(c) $CH_3CH{=}CH_2 + HI \xrightarrow{\text{Peroxide}} CH_3CHICH_3$
(d) $CH_3CH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CHBrCH_3$

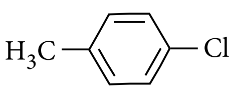
8. In the given reaction, compound (*A*) is



(a) 
(b) 
(c) 
(d) 

9. Which of the following compounds are chiral?
(a) 2-Chloropentane
(b) 1-Chloropentane
(c) 3-Chloro-2-methylpentane
(d) 1-Chloro-2-methylpentane

10. The IUPAC name(s) of the following compound is(are)



(a) 1-chloro-4-methylbenzene
(b) 4-chlorotoluene
(c) 1-methyl-4-chlorobenzene
(d) 4-methylchlorobenzene.

(*JEE Advanced 2017*)

SECTION - III

Assertion Reason Type

Assertion Reason type MCQs having only one option correct. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

11. Assertion : S_N2 reaction of CH_3-Br is faster in DMSO than in H_2O.
Reason : DMSO has greater capability to solvate nucleophile.

12. Assertion : Benzyl chloride is more reactive than *p*-chlorotoluene towards aqueous NaOH.
Reason : The C — Cl bond in benzyl chloride is more polar than C — Cl bond in *p*-chlorotoluene.

13. Assertion : 1, 2-dichloroethane is optically active.
Reason : Meso compound is optically active.

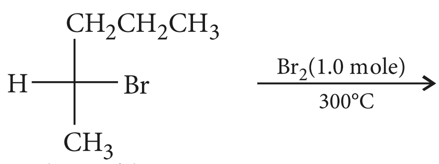
(*AIIMS 2012*)

SECTION - IV

Numerical Value Type

14. How many of the following alkenes on addition of HBr would give the same product in presence or absence of peroxide?
Propene, 1-butene, 2-butene, 3-hexene,
2, 3-dimethyl-2-butene, 1, 2-dimethylcyclohexene,
1,4-dimethyl-2-cyclohexene,
3,4-dimethyl-3-hexene, cyclohexene

15. In the following monobromination reaction, the number of possible chiral products is



(1.0 mole)
(Enantiomerically pure)

(*JEE Advanced 2016*)

SOLUTIONS

SOLUTIONS

1. (c) : $\pi = CRT \qquad C = \pi/RT$

$$C = \frac{0.821}{0.0821 \times 300} = 0.033\ \text{M}$$

2. (c)

3. (a) : $P = 120X_A + 138$; $P = (p_A^\circ - p_B^\circ)X_A + p_B^\circ$
If $X_A = 0$, then pure *B* is present. $\therefore\ p_B^\circ = 138$
If $X_A = 1$, then pure *A* is present.
$\therefore\ p_A^\circ = 120 + 138 = 258$

4. (c) : $\pi_{Na_2SO_4} = \pi_{Glucose}$
$CRT(1 + 2\alpha) = CRT$
$0.004\ (1 + 2\alpha) = 0.01 \quad \therefore\ \alpha = 0.75 = 75\%$

5. (d): $\dfrac{P^\circ - P_s}{P^\circ} = \dfrac{w_2 M_1}{w_1 M_2}$

Given : $P^\circ = 185$ torr, $w_1 = 100$ g, $w_2 = 1.2$ g, $P_s = 183$ torr
$M_1 = M_{CH_3COCH_3} = 58\ \text{g mol}^{-1}$

$$\frac{185 - 183}{185} = \frac{1.2 \times 58}{100 \times M_2}$$

$$\Rightarrow\ M_2 = \frac{1.2 \times 58 \times 185}{100 \times 2}$$

$= 64.38 \approx 64\ \text{g mol}^{-1}$

6. (b,c,d) **7. (a, b)**

8. (b, c) : $M_{Na_2CO_3} = \frac{5.3}{106} \times \frac{1000}{100} = \frac{1}{2} = 0.5$

$N_{Na_2CO_3} = 0.5 \times 2 = 1.0$

$M_{H_2C_2O_4.2H_2O} = \frac{6.3}{126} \times \frac{1000}{100} = \frac{1}{2} = 0.5$

$N_{H_2C_2O_4.2H_2O} = 0.5 \times 2 = 1$

Both solutions have same molarity and normality.

9. (a,b,d) : When $CHCl_3$ and $(CH_3)_2CO$ are mixed, the hydrogen bonding takes places between the two molecular species due to which the escaping tendency of either of the liquid molecules become less. Consequently, the boiling point of solution increases.

10. (a, b) : $CCl_4 + CH_3OH$ and $CS_2 + (CH_3)_2CO$ (A–B interactions are weaker than A–A and B–B interactions) shows positive deviation from Raoult's law. Benzene and toluene form an ideal solution. Phenol + aniline (A–B interactions are stronger than A–A and B–B interactions) shows negative deviation from Raoult's law.

11. (a): $\Delta T_b = K_b \times m$

K_b = molal elevation constant

$$\lim_{m \to 0} \left(\frac{\Delta T_b}{m}\right) = K_b$$

12. (c) : $\Delta T_b = m \times K_b$; $K_b = 0.52°\ mol^{-1}\ kg$

$0.52 = 0.52 \times m \Rightarrow m = 1$

$$\frac{w}{m \times W} = 1 \Rightarrow \frac{w}{m} = 1 \times 1000 = 1000$$

$$n = \frac{w}{m} = 1000\ ;\ N_{(solvent)} = \frac{W}{M} = \frac{1000}{18}$$

Mole fraction (X_A)

$$= \frac{n}{N+n} = \frac{1000}{\frac{1000}{18} + 1000} = \frac{1000 \times 18}{1000 + 18 \times 1000} = 0.947$$

13. (d): $\Delta T_f = K_f \times m = 2 \times \frac{0.1}{0.9 \times 46} \times 1000$

or $\Delta T_f = 4.83$ K

Freezing point of solution M,

$T_f' = T_f^\circ - \Delta T_f = 155.7 - 4.83 = 150.9$ K

14. (b): Total vapour pressure,

$P = p_A^\circ X_A$ (Here, solute is non-volatile)

$P = 40 \times 0.9 = 36$ mm of Hg

15. (a) **16. (a)**

17. (a): This is according to Henry's law which states that the solubility of a gas in given volume of a liquid at a particular temperature is directly proportional to the pressure of gas above the liquid. *i.e.*, $m \propto p$ or $m = K_H p$, where K_H = Henry's constant.

18. (100.007): $Cl{-}CH_2COOH \rightleftharpoons Cl{-}CH_2COO^- + H^+$

van't Hoff factor, $i = (1 + \alpha)$

Using Ostwald's dilution law of weak electrolyte

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.36 \times 10^{-3}}{0.01}} = 0.37$$

$\therefore\ i = (1 + \alpha) = 1.37$

Hence, elevation in b.pt. $(\Delta T)_b = i K_b m$

$1.37 \times 0.51 \times 0.01 = 0.007°$

hence, b.pt. of solution $T = T_0 + \Delta T_b$

$= 100 + 0.007° = 100.007$ °C

19. (5): Mass of solute (w_2) = 6.2 g

$\Delta T_f = 3.72$ °C

Molecular mass of solute $(CH_2OH)_2 = 62$

$$M_2 = \frac{1000 \times K_f \times w_2}{w_1 \times \Delta T_f}$$

$$w_1 = \frac{1000 \times K_f \times w_2}{M_2 \times \Delta T_f} = \frac{1000 \times 1.86 \times 6.2}{62 \times 3.72} = 50\ g$$

Ice that will separate out = 55 – 50 = 5 g

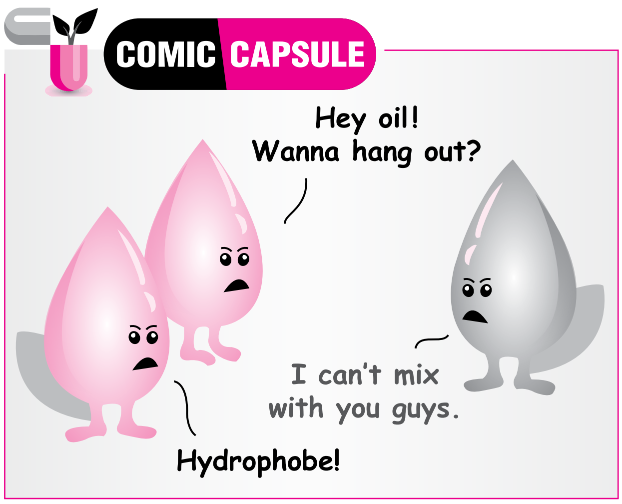
20. (2): $MX_2 \rightleftharpoons M_2^+ + 2X^-$

$(1 - \alpha) \quad \alpha \quad 2\alpha$

$i = 1 - \alpha + \alpha + 2\alpha$

$i = 1 + 2\alpha$ $(\because \alpha = 0.5)$

$i = 1 + 2 \times 0.5 = 2$

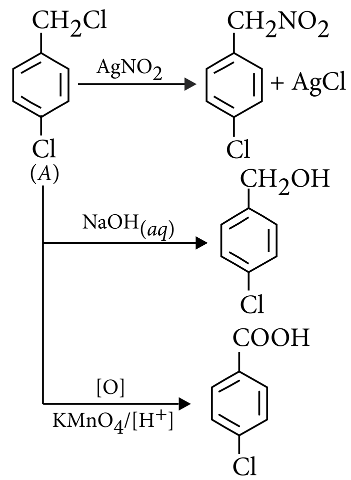


HALOALKANES AND HALOARENES

1. **(b):** Alkyl fluorides are more conveniently prepared indirectly by heating suitable chloro or bromoalkanes with inorganic fluorides, such as AsF_3, SbF_3, CoF_3, AgF, Hg_2F_2, etc.
$CH_3Br + AgF \longrightarrow CH_3F + AgBr$
This reaction is called Swarts reaction.

2. **(c)**

3. **(a):**



Monochlorobenzoic acid

4. **(d):** Being strained cyclopropane ring readily opens up to form only *n*-propylbromide. In contrast, reaction (a) gives a mixture of *n*-propyl bromide and isopropyl bromide, reaction (b) gives isopropyl bromide while reaction (c) does not occur at all.

5. **(d):** *o*-Substituted biphenyls are optically active as both the rings are not in one plane and their mirror images are non-superimposable.

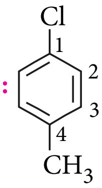
6. **(a,c,d) :** Vinyl chloride ($CH_2{=}CH{-}Cl$) does not undergo dehydrochlorination on boiling with water to produce acetylene.

7. **(a,c) :** Addition of HCl and HI to propene occurs in accordance with Markovnikov's rule even in presence of peroxide. Therefore, option (a) and (c) are correct.

8. **(a,b,d) :** *o*-, *m*- and *p*-chlorotoluenes on oxidation will first form their corresponding chlorobenzoic acids which upon subsequent decarboxylation with sodalime will give chlorobenzene. In contrast, benzyl chloride on oxidation will give benzoic acid which upon decarboxylation will give benzene.

9. **(a,c,d) :** As $CH_3CH_2CH_2CH_2CH_2Cl$ does not have a chiral carbon and hence is not optically active while all others have chiral carbon atoms and hence are optically active.
$CH_3-{}^*CHCl-CH_2CH_2CH_3$,
$ClCH_2-{}^*CH(CH_3)CH_2CH_2CH_3$
$CH_3-CH(CH_3)-{}^*CH(Cl)-CH_2CH_3$

10. **(a,b) :**



1-chloro-4-methylbenzene or 4-chlorotoluene

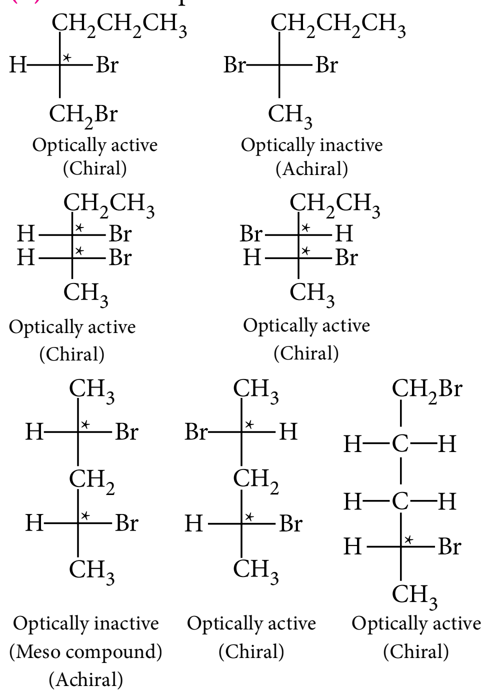
11. **(c):** S_N2 reactions are faster in aprotic solvents like DMSO.

12. **(a)**

13. **(d) :** $\overset{1}{C}H_2(Cl)-\overset{2}{C}H_2(Cl)$
Since, it has no chiral carbon, it is optically inactive. Meso compounds are optically inactive.

14. **(7):** Only symmetrical alkenes give the same product in presence or absence of peroxides. Here, only unsymmetrical alkenes are propene and 1-butene while all the remaining seven are symmetrical alkenes.

15. **(5):** Total five products are formed.



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CLASS XII

CBSE DRILL

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2018-19.

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 12 are short answer questions and carry 2 marks each.
(iv) Q. no. 13 to 24 are also short answer questions and carry 3 marks each.
(v) Q. no. 25 to 27 are long answer questions and carry 5 marks each.
(vi) Use log tables if necessary, use of calculators is not allowed.

Time Allowed : 3 hours | Maximum Marks : 70

The *d*- and *f*-Block Elements | Coordination Compounds

1. What is meant by chelate effect?

2. Calculate the overall complex dissociation equilibrium constant for $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for the complex if 2.1×10^{13}.

3. Name two coordination compounds which are biologically important.

4. $NH_2.NH_2$ although possesses two electron pairs for donation but not acts as chelating agent.

5. In a transition series, as the atomic number increases, paramagnetism first increases to the maximum and then decreases. Why?

6. Explain the following observations :
(i) Many of the transition elements are known to form interstitial compounds.
(ii) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).

7. Which of the following ions are expected to be coloured and why? Explain.
Cu^+, Fe^{2+}, Mn^{2+}, Cr^{3+}, Sc^{3+}, Ti^{4+}

8. Name the type of isomerism exhibited by the following compounds :
(i) $[Cr(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$
(ii) $[Co(py)_2(H_2O)_2Cl_2]Cl$ and $[Co(py)_2(H_2O)Cl_3]H_2O$
(iii) $[Pt(NH_3)_4Br_2]Cl_2$ and $[Pt(NH_3)_4Cl_2]Br_2$
(iv) $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

9. The sum of first and second ionisation energies and those of third and fourth ionisation energies of nickel and platinum are given below :

	$IE_1 + IE_2$ (kJ mol^{-1})	$IE_3 + IE_4$ (kJ mol^{-1})
Ni :	2.49×10^3	8.80×10^3
Pt :	2.66×10^3	6.70×10^3

Taking these values into account, answer the following :
(i) The most common oxidation state for Ni and Pt.
(ii) The name of the metal which can form compounds in +4 oxidation state more easily, and why?

OR

When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow coloured compound (*A*) is obtained which on acidification with dilute sulphuric acid gives a compound (*B*). Compound (*B*) on reaction with KCl forms a orange coloured crystalline compound (*C*). Identify the compound *A*, *B* and *C* and write the chemical reactions involved.

10. The hexaaquomanganese (II) ion contains five unpaired electrons while hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

11. Answer the following :

(i) Why are Sm^{2+}, Eu^{2+} and Yb^{2+} good reducing agents?

(ii) Can lanthanum ($Z = 57$) exhibit +4 oxidation state?

12. With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

13. A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms (*A*) and (*B*). The form (*A*) reacts with $AgNO_3$ to give a white precipitate, which is readily soluble in dilute aqueous ammonia, whereas (*B*) gives a pale yellow precipitate, soluble in concentrated ammonia. Identify (*A*) and (*B*) and write all the chemical equations.

14. For M^{2+}/M and M^{3+}/M^{2+} systems, the $E°$ values for some metals are as follows :

Cr^{2+}/Cr	–0.9 V	Cr^{3+}/Cr^{2+}	–0.4 V
Mn^{2+}/Mn	–1.2 V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	–0.4 V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon :

(i) The stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+}.

(ii) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

15. (*A*), (*B*) and (*C*) are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex (*A*) does not react with concentrated H_2SO_4, whereas complexes (*B*) and (*C*) lose 6.75% and 13.5% of their original weight respectively, on treatment with concentrated H_2SO_4. Identify (*A*), (*B*) and (*C*) and explain.

16. $\underset{\text{(Colourless liquid)}}{MCl_4} \xrightarrow[H_2O]{Zn,\ \Delta} \underset{\text{Purple coloured compound}}{(A)}$

$MCl_4 \xrightarrow{\text{moist air}} \underset{\text{White fumes}}{(B)}$

Identify (*A*), (*B*) and MCl_4. Also explain colour difference between MCl_4 and (*A*).

17. Draw the structures of optical isomers of each of the following complex ions :
$[Cr(C_2O_4)_3]^{3-}$, $[PtCl_2(en)_2]^{2+}$, $[Cr(NH_3)_2Cl_2(en)]^{+}$

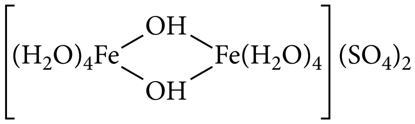
18. (i) Why *d*-block elements exhibit more oxidation states than *f*-block elements?

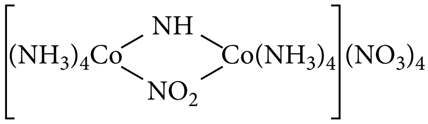
(ii) The enthalpies of atomization of the transition metals are high. Explain.

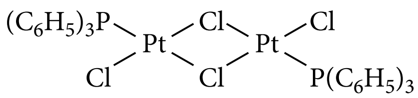
(iii) What is the equivalent mass of $KMnO_4$ when it acts as an oxidising agent in acidic medium?

19. Write the IUPAC name of the given complex along with its hybridisation and structure.
$K_2[Cr(NO)(NH_3)(CN)_4]$, $\mu = 1.73$ B.M.

20. Write the IUPAC name of

(i) 

(ii) 

(iii) 

21. For Mn^{3+} ion, the electron pairing energy *P* is 28000 cm^{-1}, Δ_o values for the complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are 21000 cm^{-1} and 38500 cm^{-1} respectively. Do these complexes have high spin or low spin complexes? Also write the configurations corresponding to these states.

OR

Why is dilute sulphuric acid and not dilute HCl or HNO_3 used to acidify a permanganate solution in volumetric analysis?

22. Explain the following :

(i) Low spin octahedral complexes of nickel are not known.

(ii) π-complexes are known for transition elements only.

(iii) CO is a stronger ligand than NH_3 for many metals.

23. $CoSO_4Cl.5NH_3$ exists in two isomeric forms '*A*' and '*B*'. Isomer '*A*' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer '*B*' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$. Answer the following questions.

(i) Identify '*A*' and '*B*' and write their structural formulae.

(ii) Name the type of isomerism involved.

(iii) Give the IUPAC name of '*A*' and '*B*'.

24. Write the chemical reactions involved in developing of a black and white photographic film. An aqueous $Na_2S_2O_3$ solution is acidified to give a milky white turbidity. Identify the product and write the balanced chemical reaction for it.

25. **(i)** What are the different oxidation states exhibited by the lanthanoids?

(ii) What happens when

(a) potassium ferricyanide is added to ferrous sulphate?

(b) excess of potassium iodide is added to mercuric chloride?

(c) green vitriol is strongly heated?

(d) silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium?

OR

Explain the following giving suitable reason :

(i) Yellow coloured aqueous solution of sodium chromate changes to orange red when CO_2 is passed under pressure.

(ii) Green solution of potassium manganate, K_2MnO_4, turns purple when CO_2 is circulated.

(iii) Ce^{3+} can be easily oxidised to Ce^{4+}.

(iv) $E°$ for Mn^{3+}/Mn^{2+} couple is more positive than for Fe^{3+}/Fe^{2+} couple.

(v) $Lu(OH)_3$ is a weaker base than $La(OH)_3$.

26. Explain why :

(i) $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic.

(ii) A solution of $[Ni(H_2O)_6]^{2+}$ is green but $[Ni(CN)_4]^{2-}$ is colourless.

(iii) The low spin tetrahedral complexes are rarely observed.

OR

(i) $[Ni(Cl)_2(P(CH_3)_3)_2]$ is a paramagnetic complex of Ni(II). Analogous Pd(II) complex is diamagnetic. How many geometrical isomers will be possible for Ni(II) and Pd(II) complexes? Also explain their magnetic behaviour.

(ii) How is the stability of a coordination compound in solution decided? How is the dissociation constant of a complex defined?

27. **(i)** **(a)** Out of the ions Ag^+, Co^{2+} and Ti^{4+} which will be coloured in aqueous solution?

(b) If each one of the above ionic species is placed in a magnetic field, how will they respond and why?

(ii) Explain the following :

(a) Acidified $K_2Cr_2O_7$ solution truns green when sodium sulphite is added.

(b) A ferrous salt decolourises acidified $KMnO_4$ solution.

OR

(i) What is Lanthanoid contraction? Write down its two consequences?

(ii) Explain :

(a) Why is europium (II) more stable than cerium (II)?

(b) Why is +3 oxidation state of gadolinium ($Z = 64$) and lutetium ($Z = 71$) especially stable?

SOLUTIONS

1. When a di– or polydentate ligand uses its two or more donor atoms to bind a single metal ion. It is said to be a chelate ligand. Chelating ligands form more stable complexes than monodentate analogs. This is called chelating effect.

2. Overall equilibrium dissociation constant (K)

$$= \frac{1}{\beta_4} = \frac{1}{2.1\times10^{13}} = 4.76\times10^{-14}$$

3. Haemoglobin (an Fe complex) and chlorophyll (a Mg complex).

4. $\ddot{N}H_2—\ddot{N}H_2$ have two donor atoms, it can form three membered ring which is very strained, thus it can not act as chelating agent.

5. Paramagnetism depends upon the number of unpaired electrons. As the atomic number increases in a transition series, the number of unpaired electrons first increases to a maximum and then decreases, so also the paramagnetism.

6. **(i)** Transition metals form a large number of interstitial compounds because small atoms of certain non-metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals.

(ii) As we move along transition metal series from left to right (*i.e.*, Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium to copper increases.

7. Any ion of transition elements which possesses unpaired *d*-electrons, (*d*-*d* transition is possible) shows a characteristic colour.

Ion	Configuration	Ion	Configuration
Cu^+	$3d^{10}$ (Colourless)	Fe^{2+}	$3d^6$ (Coloured)
Sc^{3+}	$3d^0$ (Colourless)	Mn^{2+}	$3d^5$ (Coloured)
Ti^{4+}	$3d^0$ (Colourless)	Cr^{3+}	$3d^3$ (Coloured)

8. **(i)** Coordination isomerism
(ii) Hydrate isomerism
(iii) Ionisation isomerism **(iv)** Linkage isomerism

9. **(i)** For nickel, +2 is the common oxidation state because the sum $(IE_1 + IE_2)$ for Ni has lower value than Pt. For platinum, +4 is the common oxidation state as the sum of $(IE_1 + IE_2 + IE_3 + IE_4)$ for Pt has lower value then Ni.
(ii) Platinum can form compounds in +4 oxidation state easily as the sum of $(IE_1 + IE_2 + IE_3 + IE_4)$ energies is lower for Pt than for Ni.

OR

$$4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow \underset{(A)}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$$

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow \underset{(B)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{(C)}{K_2Cr_2O_7} + 2NaCl$$

10. Mn in +2 oxidation state has the electronic configuration $3d^5$. H_2O is a weak ligand. In presence of H_2O molecules, the distribution of electrons is $t_{2g}^3\, e_g^2$, *i.e.*, all the electrons are unpaired.
CN^- is a strong ligand. In its presence, the distribution of electrons is $t_{2g}^5\, e_g^0$, *i.e.*, one unpaired electron is present.

11. **(i)** The most stable oxidation state of lanthanides in +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of one electron and hence, act as reducing agents.

(ii) La^{3+} has a stable configuration of an inert gas $[(Xe)5d^0 6s^0]$. To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence, La^{4+} does not exist.

12. **Structure :** All the lanthanoids are silvery white soft metals. Hardness of lanthanoids increases with increasing atomic number.
All actinoid metals are silvery in appearance but display a variety of structures. The structural variability is due to irregularities in metallic radii which are greater than that of lanthanoids.
Chemical reactivity : Earlier members of lanthanoid series are quite reactive similar to calcium but with increasing atomic number they behave more like aluminium. Actinoids are highly reactive in finely divided state.

13. Complex, $Cr(NH_3)_4Cl_2Br$, has two isomers. Since, coordination number of Cr is six, the two forms may be represented in the following way :

$$\underset{(A)}{[Cr(NH_3)_4ClBr]Cl} \qquad \underset{(B)}{[Cr(NH_3)_4Cl_2]Br}$$

$$\underset{(A)}{[Cr(NH_3)_4ClBr]Cl} + AgNO_3 \longrightarrow [Cr(NH_3)_4ClBr]NO_3 + \underset{\text{White ppt.}}{AgCl\downarrow}$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$\underset{(B)}{[Cr(NH_3)_4Cl_2]Br} + AgNO_3 \longrightarrow [Cr(NH_3)_4Cl_2]NO_3 + \underset{\text{Pale yellow}}{AgBr\downarrow}$$

$$AgBr + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{Ag(NH_3)_2Br} + 2H_2O$$

14. As $E^\circ_{Cr^{3+}/Cr^{2+}}$ is negative (–0.4 V), this means Cr^{3+} ions in solution cannot be reduced to Cr^{2+} easily, *i.e.*, Cr^{3+} ions are very stable. As $E^\circ_{Mn^{3+}/Mn^{2+}}$ is more positive (+1.5 V) as compared to $E^\circ_{Fe^{3+}/Fe^{2+}}$ (+0.8 V), Mn^{3+} ions can easily be reduced to Mn^{2+} ions in comparison to Fe^{3+} ions. Thus, the relative stability of these ions is : $Mn^{3+} < Fe^{3+} < Cr^{3+}$
(ii) Oxidation potentials for Cr, Mn and Fe will be +0.9 V, +1.2 V and +0.4 V. Thus, the ease of getting oxidised will be in the order, Mn > Cr > Fe.

15. (*A*) $[Cr(H_2O)_6]Cl_3$ (Violet)
(*B*) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (Green)
(*C*) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (Dark green)
Compound (*A*) contains six water molecules as coordinated water and thus, does not lose H_2O on treatment with H_2SO_4. Compound (*B*) contains five water molecules as coordinated water and one molecule as lattice water which is taken out by H_2SO_4, showing loss of 18 g out of 266.5 g *i.e.*, 6.75% loss. Similarly, compound (*C*) contains four coordinated water molecules and two molecules of lattice water which are taken out by H_2SO_4 to show a loss of 13.5%.

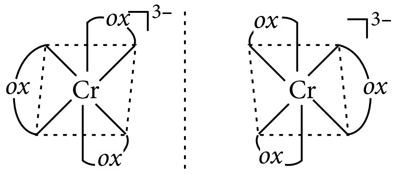
16. M = Ti; $A = [Ti(H_2O)_6]Cl_3$; B = HCl

$$TiCl_4 \xrightarrow{\text{Zn, heat}} TiCl_3 \xrightarrow{H_2O} \underset{\text{(Purple coloured)}}{\underset{A}{[Ti(H_2O)_6]Cl_3}}$$

$$TiCl_4 + \underset{\text{From moist air}}{H_2O} \rightarrow TiOCl_2 + \underset{\text{(White fumes)}}{\underset{B}{2HCl}}$$

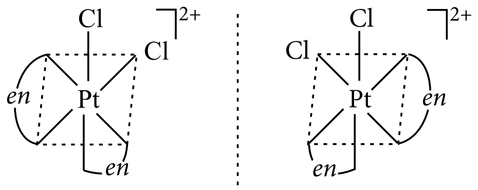
$TiCl_4$ is colourless because in $Ti^{4+}(3d^0)$ *d-d* transition is not possible. In $TiCl_3$ *i.e.*, Ti^{3+} $(3d^1)$ *d-d* transition is possible. Ti^{3+} absorbs greenish yellow component of white light and in its aqueous solution its colour is purple.

17. $[Cr(C_2O_4)]^{3-}$:



dextro Mirror *laevo*

$[PtCl_2(en)_2]^{2+}$:



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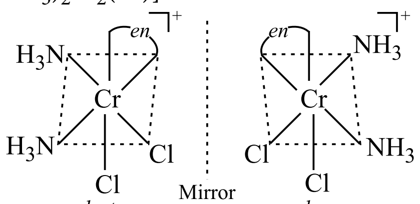
$[Cr(NH_3)_2Cl_2(en)]^+$:



dextro *laevo*

18. (i) All transition elements except the first and the last member in each series show a large number of variable oxidation states. This is because difference of energy in the $(n-1)d$ and ns orbitals is very little. Hence, electrons from both the energy levels can be used for bond formation.

(ii) As transition metals have a large number of unpaired electrons in the d-orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.

(iii) Oxidising action of $KMnO_4$ in acidic medium is represented as :

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

or $\quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Eq. mass of $KMnO_4$

$$= \frac{\text{Molecular mass}}{\text{Number of electrons gained per molecule}} = \frac{158}{5} = 31.6$$

19. The spin magnetic moment (μ) of complex = 1.73 B.M.

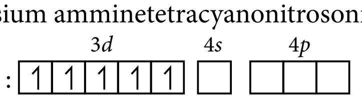
$\sqrt{n(n+2)} = 1.73$ or $n \simeq 1$

This indicates that in the complex, chromium has one unpaired electron *i.e.*, Cr^+. Thus, the ligand NO is uni- positively charged.

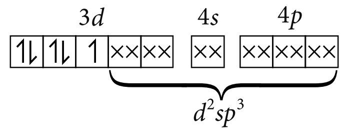
IUPAC name :

Potassium amminetetracyanonitrosoniumchromate(I).

$[Cr^+]$:



Cr^+ in complex :



Hybridisation = d^2sp^3 Shape = Octahedral

20. (i) O.N. of Fe = $0 + x - 1 - 1 + x + 0 - 4 = 0$

$\Rightarrow \quad 2x - 6 = 0 \Rightarrow x = +3$

Name : μ-Di-hydroxobis (tetraaquairon(III)) sulphate

(ii) O.N. of Co = $0 + x - 1 - 1 + x + 0 - 4 = 0$

$\Rightarrow \quad 2x - 6 = 0 \Rightarrow x = +3$

Name : μ-Amido-μ-nitritobis(tetraamminecobalt(III)) nitrate

(iii) O.N. of Pt = $0 - 1 + x - 1 - 1 + x + 0 - 1 = 0$

$\Rightarrow \quad 2x - 4 = 0 \Rightarrow x = +2$

Name : *trans*-Di-μ-chloridobis(chloridotriphenyl-phosphineplatium(II)

21. For $[Mn(H_2O)_6]^{3+}$ ion, $\Delta_o < P$ (Δ_o = 21000 cm^{-1}, P = 28000 cm^{-1}). Hence, this is a high spin complex (pairing up of electron will not take place.) Mn in $[Mn(H_2O)_6]^{3+}$ is present as Mn^{3+} ion. Mn^{3+} ion is d^4 system, its configuration is $t_{2g}^3e_g^1$.

For $[Mn(CN)_6]^{3-}$ ion, $\Delta_o > P$ (Δ_o = 38500 cm^{-1}, P = 28500 cm^{-1}.) Hence, paring of electron will take place and the $[Mn(CN)_6]^{3-}$ is low spin complex. Mn in $[Mn(CN)_6]^{3-}$ is present as Mn^{3+} ion which is d^4 system, its configuration is $t_{2g}^4e_g^0$.

OR

This is because oxygen produced from $KMnO_4$ + dil. H_2SO_4 is used only for oxidising the reducing agent. Moreover, H_2SO_4 does not give any oxygen of its own to oxidise the reducing agent.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

Reducing agent + [O] $\longrightarrow$ Oxidised product

When HCl is used, the oxygen produced from $KMnO_4$ is partly utilised to oxidise HCl and Cl_2 is produced.

$$2KMnO_4 \longrightarrow K_2O + 2MnO + 5[O]$$
$$K_2O + 2HCl \longrightarrow 2KCl + H_2O$$
$$MnO + 2HCl \longrightarrow MnCl_2 + H_2O$$
$$2HCl + [O] \longrightarrow H_2O + Cl_2$$

And when HNO_3 is used, it itself acts as an oxidising agent and partly oxidises the reducing agent.

22. (i) Nickel, in +2 oxidation state, has $3d^8$ configuration, mainly forms octahedral complexes. In presence of strong field ligand also it has two unpaired electrons in e_g orbital. Hence, it does not form low spin octahedral complexes.

(ii) The transition metals/ions have empty *d*-orbitals into which the electron pairs can be donated by ligands containing π-electrons.

(iii) CO is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π-bond with metal through back donation.

23. '*A*' gives precipitate with $AgNO_3$, so in it Cl is present outside the coordination sphere. '*B*' gives precipitate with $BaCl_2$, so in it SO_4^{2-} is present outside the coordination sphere.

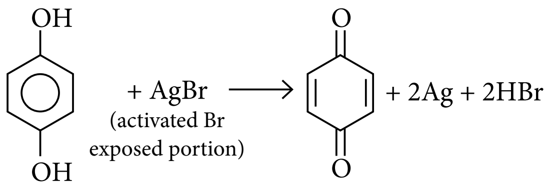
(i) *A* – $[Co(NH_3)_5SO_4]Cl$, *B* – $[Co(NH_3)_5Cl]SO_4$

(ii) Ionisation isomerism

(iii) [*A*] : Pentaamminesulphatocobalt(III) chloride

[*B*] : Pentaamminechloridocobalt(III) sulphate

24. Following reactions occur when a black and white photographic film is developed.



$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$
(Unexposed)

$$Na_2S_2O_3 + 2H^+ \longrightarrow 2Na^+ + H_2SO_3 + S\downarrow$$
(Colloidal sulphur)

25. (i) All the lanthanoids predomi-nantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g. $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$, $Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

(ii) (a) Ferrous ion is first oxidised to ferric ion while ferricyanide ion is reduced to ferrocyanide ion. Then, ferric ions react with ferrocyanide ions to form potassium ferric ferrocyanide (Turnbull's blue).

$$Fe^{2+} + [Fe(CN)_6]^{3-} \longrightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$$
$$K^+ + Fe^{3+} + [Fe(CN)_6]^{4-} \longrightarrow KFe[Fe(CN)_6]$$

(b) First scarlet precipitate is formed which then dissolves in excess of potassium iodide forming a complex.

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$
$$HgI_2 + 2KI \longrightarrow K_2HgI_4$$
(colourless)

(iv) When heated strongly, a mixture of gases (SO_2 and SO_3) is evolved and a red residue, Fe_2O_3 is formed.

$$\underset{\text{Green vitriol}}{FeSO_4 \cdot 7H_2O} \xrightarrow[-7H_2O]{300\,°C} \underset{\text{White}}{2FeSO_4} \xrightarrow[\text{temp.}]{\text{High}} Fe_2O_3 + SO_2 + SO_3$$

(v) AgCl dissolves in NaCN forming a complex. The addition of zinc precipitates silver.

$$AgCl + 2NaCN \longrightarrow Na[Ag(CN)_2] + NaCl$$
$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

OR

(i) On passing CO_2, H^+ ions are formed which are responsible for conversion of chromate into dichromate.

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$
$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange red}}{Cr_2O_7^{2-}} + H_2O$$

(ii) CO_2 gives H^+ ions which are responsible for conversion of manganate to permanganate.

$$CO_2 + H_2O \rightleftharpoons 2H^+ + CO_3^{2-}$$
$$\underset{\text{Green}}{3MnO_4^{2-}} + 4H^+ \longrightarrow \underset{\text{Purple}}{2MnO_4^-} + MnO_2 + 2H_2O$$

(iii) Ce^{3+} has the configuration $4f^1 5d^0 6s^0$. It can easily lose an electron to acquire more stable configuration ($4f^0 5d^0 6s^0$, *i.e.*, configuration of inert gas).

$$Ce^{3+} \longrightarrow Ce^{4+} + e^-$$

(iv) $E°$ for Mn^{3+}/Mn^{2+} couple is more positive than for Fe^{3+}/Fe^{2+} couple because Mn^{2+} state is more stable than Mn^{3+} state. Thus, the reduction is spontaneous.

$$Mn^{3+}(3d^4, 4s^0) + e^- \longrightarrow Mn^{2+}(3d^5, 4s^0)$$

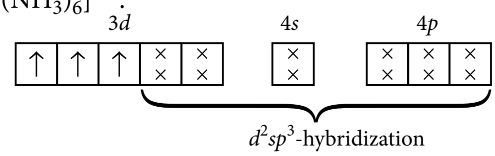
For Fe^{3+}/Fe^{2+} couple, $Fe^{3+}(3d^5, 4s^0)$ is more stable than $Fe^{2+}(3d^6, 4s^0)$. Thus, the reduction is non-spontaneous.

(v) In the lanthanide series, the size of the M^{3+} ion decreases from La^{3+} to Lu^{3+}. Thus, the covalent nature of $Lu(OH)_3$ increases (Fajan's rule). Hence, $Lu(OH)_3$ is weaker base than $La(OH)_3$.

26. (i) The oxidation state of Cr in the compelx is +3.

Cr^{3+} : Ar$[3d]^3$

$[Cr(NH_3)_6]^{3+}$:

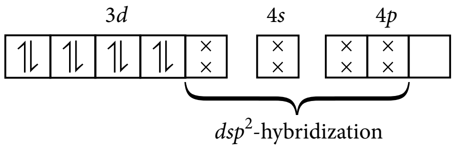


Three unpaired electrons are present, hence it is paramagnetic.

The oxidation state of Ni in the complex is +2.

Ni^{2+} : $[Ar]3d^8$

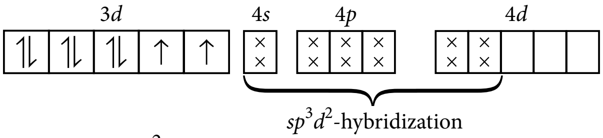
$[Ni(CN)_4]^{2-}$:



As CN^- is a strong ligand, unpaired electrons are paired up, hence it is diamagnetic.

(ii) H_2O is a weak ligand hence, $[Ni(H_2O)_6]^{2+}$ is a outer-orbital complex. The complex has two unpaired electrons. The *d-d* transition is possible. Hence, the compound is coloured.

$[Ni(H_2O)_6]^{2+}$:



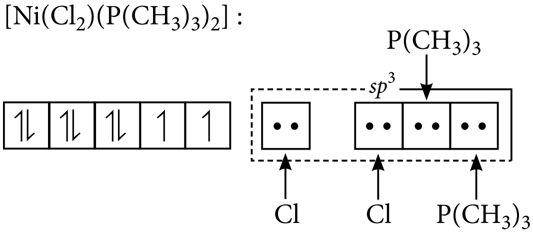
In $[Ni(CN)_4]^{2-}$: CN^- is a strong ligand. The unpaired electrons are paired up. No unpaired electrons are present, *i.e.*, *d-d* transition is not possible, hence the complex is colourless.

(iii) In tetrahedral coordination entity formation, the *d*-orbital splitting is smaller. Consequently, the orbital splitting energies are not sufficiently large to force pairing and therefore, low spin configurations are rarely observed.

OR

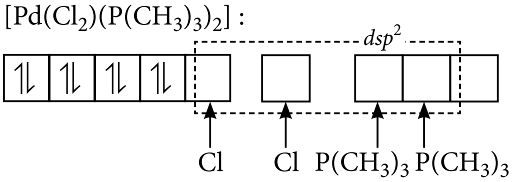
(i) In both Ni(II) and Pd(II), there is d^8 configuration. In Ni(II), value of crystal field splitting energy is less than Pd(II). So in Ni(II) pairing is less favoured in Pd(II), all electrons are paired.

$[Ni(Cl_2)(P(CH_3)_3)_2]$:

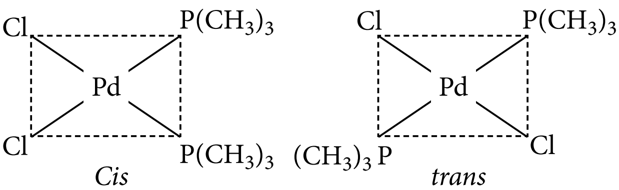


Geomtry is tetrahedral, so only one isomer will be possible.

$[Pd(Cl_2)(P(CH_3)_3)_2]$:



So, it has square planar structure *i.e.*, MA_2B_2 type and will exist as *cis* and *trans* isomer.



Cis *trans*

(ii) The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant for the association, quantitatively expresses the stability.

The instability constant or dissociation constant of coordination compound is defined as the reciprocal of the formation constant.

27. (i) (a) The ionic species which possesses unpaired electron or electrons in $(n-1)d$-subshell will show colour. Out of the ions $Ag^+(4d^{10})$, $Co^{2+}(3d^7)$ and $Ti^{4+}(3d^0)$, Co^{2+} will be coloured as it contains three unpaired electrons, Ag^+ and Ti^{4+} will be colourless.

(b) When placed in magnetic field, Co^{2+} will be attracted because it is paramagnetic due to unpaired electrons. Ag^+ and Ti^{4+} ions will be repelled by the magnetic field as they are diamagnetic.

(ii) (a) Na_2SO_3 is a reducing agent. It reduced acidified $K_2Cr_2O_7$ to chromic sulphate which is green in colour.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + 3Na_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + 4H_2O$$

(b) Ferrous salt acts as a reducing agent. It reduces acidified $KMnO_4$ into $MnSO_4$ and K_2SO_4 which form colourless solution, *i.e.*, decolourisation of $KMnO_4$ solution takes place.

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

OR

(i) Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

Consequences of lanthanoid contraction :

(a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.

(b) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. *e.g.*, atomic radii of zirconium(Zr) is same as that of hafnium Hf.

(ii) (a) Europium (II) has electronic configuration $[Xe]4f^7 5d^0$ while cerium (II) has electronic configuration $[Xe]\ 4f^1\ 5d^1$. In Eu^{2+}, 4*f* subshell is half filled and 5*d*-subshell is empty. Since half filled and completely filled electronic configurations are more stable, hence Eu^{2+} ions is more stable than Ce^{2+}.

(b) This is because gadolinium in +3 state has half filled 4*f*-subshell ($4f^7$) and lutetium in +3 state has completely filled 4*f*-subshell which are very stable configurations.

◈◈

Class XII

MONTHLY TUNE UP!

PRACTICE PROBLEMS

These practice problems enable you to self analyse your extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Performance analysis table given at the end will help you to check your readiness.

- General Principles and Processes of Isolation of Elements
- Surface Chemistry

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

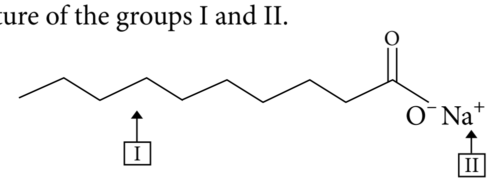
Only One Option Correct Type

1. $Fe(OH)_3$ is positively charged colloid. The most effective electrolyte causing coagulation would be
(a) $K_3[Fe(CN)_6]$ (b) KBr
(c) K_2SO_4 (d) $C_2O_4^{2-}$

2. Scheelite ($CaWO_4$) is an ore of tungsten, which contain tungstate ion. Tungstate ion is also present in
(a) limonite (b) dolomite
(c) wolframite (d) siderite.

3. Physical adsorption of a gaseous species may change to chemical adsorption with
(a) decrease in temperature
(b) increase in temperature
(c) increase in surface area of adsorbent
(d) decrease in surface area of adsorbent.

4. The cleansing action of soap is the result of the dual nature of the groups I and II.



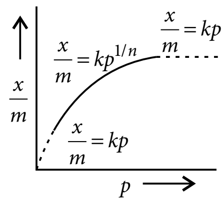
I and II are

	I	II
(a)	hydrophilic	hydrophobic
(b)	hydrophilic	hydrophilic
(c)	hydrophobic	hydrophilic
(d)	hydrophobic	hydrophobic

5. Given below, catalyst and corresponding process/reaction are matched. The mismatch is
(a) $[RhCl(PPh_3)_3]$: hydrogenation
(b) $TiCl_4 + Al(C_2H_5)_3$: polymerization
(c) V_2O_5 : Haber-Bosch process
(d) Nickel : hydrogenation.

6. Among the following statements, the incorrect one is
(a) calamine and siderite are carbonate ores.
(b) argentite and cuprite are oxide ores.
(c) zinc blende and pyrites are sulphide ores.
(d) malachite and azurite are ores of copper.

7. Which one is not correct about Freundlich isotherm?



(a) $n = \frac{1}{\tan\theta}$ at average pressure
(b) $\theta = 45°$ at low pressure
(c) $\theta = 45°$ at high pressure
(d) None of these

8. From the given reduction processes :
$A : Fe_2O_3 + C \rightarrow Fe$; $B : ZnO + C \rightarrow Zn$
$C : PbO + C \rightarrow Pb$; $D : WO_3 + C \rightarrow W$
The correct processes are
(a) A, B, C and D (b) B, C
(c) A, B, C (d) B, D

9. Spiegel (or spiegeleisen), used in the manufacture of steel by the Bessemer process, is an alloy of
(a) iron, chromium and carbon
(b) iron, nickel and carbon
(c) iron, tungsten and carbon
(d) iron, manganese and carbon.

10. A black mineral on roasting breaks up into two compounds *A* and *B* with the liberation of gas *C*. When air is passed through the molten mixture of *A* and *B*, *B* converts into oxide that can be reduced by air. The mineral is
(a) chalcocite (b) feldspar
(c) chalcopyrite (d) pyrargyrite.

11. The formula of azurite is
(a) $CuCO_3.Cu(OH)_2$ (b) $2CuCO_3.Cu(OH)_2$
(c) $CuCO_2.Cu(OH)_2$ (d) $CuSO_4.Cu(OH)_2$

12. The isoelectric point of a colloidally dispersed material is the pH value at which
(a) the dispersed phase migrate in an electric field
(b) the dispersed phase does not migrate in an electric field
(c) the dispersed phase has pH equal to 7
(d) the dispersed phase has pH equal to zero.

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion**: Alcohols are dehydrated to hydrocarbons in the presence of acidic zeolites.
Reason : Zeolites are porous catalysts.

14. **Assertion** : Magnesium is extracted by the electrolysis of fused mixture of $MgCl_2$, NaCl and $CaCl_2$.
Reason : Calcium chloride acts as a reducing agent.

15. **Assertion :** Extraction of iron metal from iron oxide ore is carried out by heating with coke.
Reason : The reaction $Fe_2O_{3(s)} \rightarrow Fe_{(s)} + 3/2O_{2(g)}$ is a spontaneous process.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. Copper is extracted from its ore copper pyrites through the scheme given below :

$$\text{Copper pyrites} \xrightarrow{\text{Roasting}} X + Y + SO_2\uparrow$$
$$\text{Molten matte slag} \xleftarrow[\text{Powdered Coke + Flux}]{\text{Smelting}}$$
$$\xrightarrow{\text{Bessemerisation}} \text{Crude copper metal}$$

The compounds *X* and *Y* are respectively.
(a) Cu_2S and FeO (b) Cu_2S and Fe_2O_3
(c) Cu_2S and FeS (d) CuS + FeS

17. In an absorption experiment a graph between log *x*/*m* versus log *P* was found to be linear with a slope of 45° the intercept of the log *x*/*m* was found to be 0.3010. Calculate the amount of gas adsorbed per gram of charcoal under a pressure of 0.6 bar.
(a) 0.6 (b) 1.8 (c) 1.2 (d) 6.3

18. For the coagulation of 200 mL of As_2S_3 solution, 10 mL of 1 M NaCl is required. What is the coagulating value of NaCl?
(a) 200 (b) 100 (c) 50 (d) 25

19. Gold number is defined as the mass of protective colloidal solution which will just prevent the coagulation of *x* mL of a given gold solution on adding *y* mL of *z*% NaCl solution. *x*, *y* and *z* are respectively
(a) 10, 1, 10 (b) 1, 1, 1
(c) 10, 10, 10 (d) 1, 1, 10

More than One Options Correct Type

20. The incorrect statements are
(a) for coagulation of As_2S_3 sol, +ve ions are effective
(b) for coagulation of aluminium hydroxide sol Ba^{2+} ions are more effective than Na^+
(c) cellulose solution is an example of multimolecular colloid system
(d) colloidal sol of metals such as gold, silver etc are prepared by Bredig's arc method.

21. Select the incorrect statements about Ellingham diagram.
(a) Theoretically, all oxides cannot be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained.
(b) Any metal will not reduce the oxide of other metals which lie above it in the Ellingham diagram.
(c) When temperature is raised, a point will be reached where the graph crosses the $\Delta_f G°$ line. Below this temperature, the free energy of formation of the oxide is negative, so the oxide is stable.
(d) According to Ellingham diagram, Al will not reduce MgO at temperature below 1350°C.

22. Which acts as negative catalyst?
(a) Tetraethyl lead as antiknock compound
(b) Phosphoric acid in decomposition of H_2O_2
(c) Ethanol in oxidation of chloroform
(d) Manganese dioxide in decomposition of H_2O_2

23. Select the correct statements.
(a) Based on reactivity series, occurence of certain elements takes place in native state.
(b) Cresol and aniline are called froth stabilizers in froth floatation process.
(c) Due to basic nature of oxides alkali metal oxides can not be reduced by carbon.
(d) Sulphide ores of Cu, Ag, Zn are concentrated by hydraulic washing.

Numerical Value Type

24. 1 g of charcoal adsorbs 100 mL 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.0×10^2 m^2.

25. The volume of nitrogen gas (measured at STP) required to cover a sample of silica gel with a mono-molecular layer is 129 cm^3/g of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies $16.2 \times 10^{-20} m^2$.

26. A solution of palmitic acid (M = 256) in benzene contains 4.24 g acid per litre. When this solution is dropped on the water surface, benzene evaporates and palmitic acid forms monomolecular film of solid type. If we wish to cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area occupied by one palmitic acid molecule may be taken to be 21×10^{-20} m^2.

Comprehension Type

The heating process for the extraction of elements are quite old but highly acceptable method for the extraction of elements. Because in this process the elements produced is in the highly pure state. Mostly As, Sb, Ni, Zr, B, etc., are prepared by this principle.

A number of metal sulphide are used which may be roasted first in air to partially convert them to the oxide, and then further roasted in the absence of air, causing self-reduction.

27. How is very pure Sb prepared from the impure Sb?

(a) $Sb(impure) + O_2 \longrightarrow Sb_2O_3 \xrightarrow{heat} Sb(pure)$

(b) $Sb(impure) + Cl_2 \longrightarrow SbCl_3 \xrightarrow{heat} Sb(pure)$

(c) $Sb+Zn+dil\ H_2SO_4 \longrightarrow SbH_3 \xrightarrow{heat} Sb(pure)$

(d) $Sb + Zn + dil\ HCl \longrightarrow SbH_3 \xrightarrow{heat} Sb(pure)$

28. $H_{2(g)}$ is not widely used as a reducing agent because

(a) H_2 decomposes to atomic hydrogen at higher temperature

(b) H_2 isomerises to *ortho* hydrogen at higher temperature

(c) many metal form hydrides at lower temperature

(d) there is also a risk of explosion from hydrogen and dioxygen in air.

Matrix Match Type

29. Match the Column-I with Column-II and choose the correct answer using the codes given below :

Column-I	Column-II
(A) Extracted by the reduction of ore by carbon	(p) Ag
(B) Extracted by the formation of soluble complex	(q) Zn
(C) Byproduct as anode mud of electrolytic refining of Cu	(r) Fe
(D) Metals involve in Parke's process	(s) Au

Codes :

	A	B	C	D
(a)	q, p	p, s	r	s
(b)	r	p	q	s
(c)	q, r	p, s	p, s	p, q
(d)	q, r	s	p, s	r

30. Match the Column-I with Column-II and choose the correct answer using the codes given below :

Column-I	Column-II
(A) Gold sol	(p) Bredig's arc method
(B) Purification of colloidal solution	(q) Negatively charged
(C) As_2S_3 sol	(r) Ultracentrifugation
(D) Zeta potential	(s) Electrokinetic potential
(E) Casein	(t) Double decomposition reaction
	(u) Protective colloid

Codes :

	A	B	C	D	E
(a)	q, r	p	r, u	s	t
(b)	r	p,q	q	s, t	u
(c)	s	q, t	p	r	t, u
(d)	p, q	r	q, t	s	u

Keys are published in this issue. Search now! ☺

CHECK YOUR PERFORMANCE

No. of questions attempted ......

No. of questions correct ......

Marks scored in percentage ......

If your score is

> 80%	Your preparation is going good, keep it up to get high score.
60-80%	Need more practice, try hard to score more next time.
<60%	Stress more on concepts and revise thoroughly.

CHEMISTRY MUSING

PROBLEM SET 62

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. K_p = 0.04 at 899 K for the equilibrium, $C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_{2(g)}$. If the reaction takes place in a flask at 4.0 atm pressure, what is the equilibrium concentration of C_2H_6?

(a) 4.9×10^{-2} mol/L (b) 6.2×10^{-2} mol/L
(c) 3.2×10^{-2} mol/L (d) 4.0×10^{-2} mol/L

2. Which the following is incorrect?

(a) First two nearest neighbour distances for *sc* lattice are, *a* and $\sqrt{2}a$ respectively.
(b) First two nearest neighbour distances for *bcc* lattice are, $\frac{\sqrt{3}a}{2}$ and *a* respectively.
(c) In ZnS (wurtzite), Zn^{2+} ions occupy lattice point while in ZnS (zinc blende), Zn^{2+} ions occupy alternate tetrahedral voids.
(d) In point defects, volume and geometry of the crystal do not change.

3. Which of the following sequences is correctly related to refining of gold?

(a) Treatment with KCN $\longrightarrow$ Precipitation of gold $\longrightarrow$ Electrolytic refining
(b) Cupellation $\longrightarrow$ Parting $\longrightarrow$ Miller's process $\longrightarrow$ Electrolytic refining
(c) Quenching $\longrightarrow$ Annealing $\longrightarrow$ Tempering $\longrightarrow$ Cascharding $\longrightarrow$ Nitriding
(d) Magnetic separation $\longrightarrow$ Self reduction $\longrightarrow$ Poling

4. Calculate the change in entropy when 350 g of water at 5 °C is mixed with 500 g of water at 80° C, assuming that the specific heat is 1.00 cal deg^{-1} g^{-1}.

(a) 4.0 cal deg^{-1} (b) 5.4 cal deg^{-1}
(c) 3.9 cal deg^{-1} (d) 4.5 cal deg^{-1}

5. $Xe_{(g)} + PtF_{6(g)} \longrightarrow A \xrightarrow[25\,°C]{PtF_6} B \xrightarrow[60\,°C]{PtF_6} C$

A, *B* and *C* respectively are

(a) $Xe^+[PtF_6]^-$, $[XeF]^+[Pt_2F_{11}]^-$, $[XeF]^+[Pt_3F_{16}]^-$
(b) $[XeF]^+[PtF_6]^-$, $[XeF]^+[Pt_2F_{11}]^-$, $[XeF]^+[Pt_3F_{16}]^-$
(c) $[XeF]^+[PtF_6]^-$, $[XeF_2]^+[Pt_2F_{11}]^-$, $[XeF_3]^+[Pt_3F_{16}]^-$
(d) $Xe^+[PtF_6]^-$, $[XeF]^+[PtF_6]^-$, $[XeF]^+[Pt_2F_{11}]^-$

JEE ADVANCED

6. 12 g of impure cyanogen undergoes hydrolysis by two different pathways :

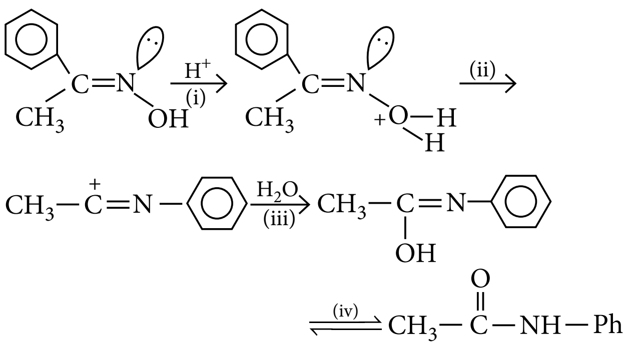
(i) $(CN)_2 + 4H_2O \rightarrow (NH_4)_2C_2O_4$
(ii) $(CN)_2 + 2H_2O \rightarrow NH_2CONH_2$

The same amount of urea was obtained when 11.52 g of pure ammonium carbonate was heated. If 20 mL of 1.6 M acidic $KMnO_4$ solution was required to completely oxidise $(NH_4)_2C_2O_4$ then which of the following statements is incorrect?

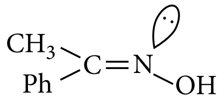
(a) % purity of cyanogen is 86.67%.
(b) % purity of cyanogen is 60.67%.
(c) % progress in case (i) is 40%.
(d) % progress in case (ii) is 60%.

COMPREHENSION

Beckmann rearrangement mechanism is given as :

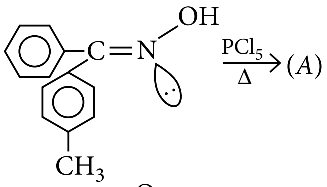


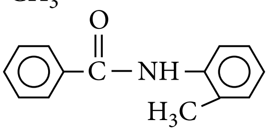
7. On treatment with H_2SO_4 followed by hydrolysis in acidic medium, the following compound gives

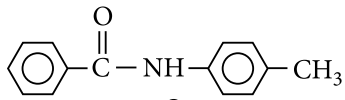


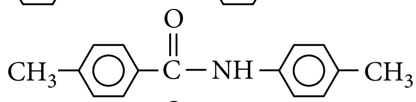
(a) CH_3-CO_2H, $Ph-NH_2$
(b) $Ph-CO_2H$, CH_3-CO_2H
(c) $Ph-CH_2-NH_2$, $Ph-CO_2H$
(d) CH_3-NH_2, $Ph-CO_2H$

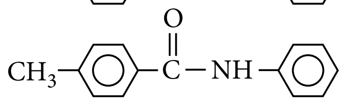
8. Identify the product *A*.



(a) 

(b) 

(c) 

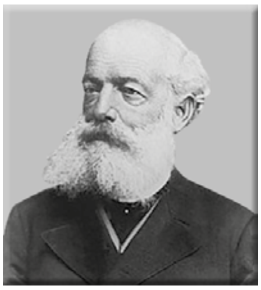
(d) 

INTEGER VALUE

9. Number of alloys that contain nickel among the following :
Solder, gunmetal, German silver, nichrome, Monel metal, constantan, bell metal, duralumin, type metal, invar, alnico.

10. The number of diamagnetic complexes among the following complexes are
$K_3[Fe(CN)_6]$, $[Co(NH_3)_6]Cl_3$, $Na_3[Co(ox)_3]$, $[Ni(H_2O)_6]Cl_2$, $K_2[Pt(CN)_4]$, $[Zn(H_2O)_6](NO_3)_2$

Scientist of the Month



Friedrich August Kekulé
(7 September, 1829 - 13 July, 1896)

He was a German organic chemist. From 1850s until his death, Kekulé was one of the most prominent chemists in Europe, especially in theoretical chemistry. He was the principal founder of the theory of chemical structure.

Early Life and Education

Kekulé was born in Darmstadt, the capital of the Grand Duchy of Hesse. After graduating from secondary school (the Grand Ducal Gymnasium in Darmstadt), in the fall of 1847 he entered the University of Giessen, with the intention of studying architecture. After hearing the lectures of Justus von Liebig in his first semester, he decided to study chemistry. Following four years of study in Giessen and a brief compulsory military service, he took temporary assistantships in Paris (1851–52), in Chur, Switzerland (1852–53), and in London (1853–55), where he was decisively influenced by Alexander Williamson. His Giessen doctoral degree was awarded in the summer of 1852.

In 1856 Kekulé became Privatdozent at the University of Heidelberg. In 1858 he was hired as professor at the University of Ghent, then in 1867 he was called to Bonn, where he remained for the rest of his career.

Contributions

- Kekulé's most famous work was on the structure of benzene. In 1865 Kekulé published a paper in French, suggesting that the structure contained a six-membered ring of carbon atoms with alternating single and double bonds.
- Basing his ideas on those of predecessors such as Williamson, Edward Frankland, William Odling, Auguste Laurent, Charles-Adolphe Wurtz and others, Kekulé was the principal formulator of the theory of chemical structure (1857–58). This theory proceeds from the idea of atomic valence, especially the tetravalence of carbon (which Kekulé announced late in 1857) and the ability of carbon atoms to link to each other to the determination of the bonding order of all of the atoms in a molecule.

Honors

- 1979 East German stamp of Kekulé, in honour of the sesquicentennial of his birth.
- In 1895 Kekulé was ennobled by Kaiser Wilhelm II of Germany, giving him the right to add "von Stradonitz" to his name, referring to a possession of his patrilineal ancestors in Stradonice, Bohemia. This title was used by his son, genealogist Stephan Kekulé von Stradonitz.
- Of the first five Nobel Prizes in Chemistry, Kekulé's students won three: van't Hoff in 1901, Fischer in 1902 and Baeyer in 1905.

ADVANCED CHEMISTRY BLOC

Scattering in Colloids and Gas Molecules

Mukul C. Ray, Odisha

Following the Mount Krakatoa volcanic eruption, in the year 1883, the moon appeared blue and sometimes green for several years. The whole world watched vivid red sunsets for years. Mount Krakatoa, Tambora, Gamkonora of Indonesia and closer areas have displayed some of the massive volcanic eruptions, the world has ever seen. Such eruptions besides causing severe damages to living beings of the archipelago had released several cubic kilometers of rocks and dusts to the atmosphere; the routine optical phenomena occurring in atmosphere was then all set to change.

If a homogeneous solution is observed in the direction of light it appears clear and when observed in a direction right angle to the direction of light, it appears perfectly dark. When light passes through a colloidal solution, scattering takes place. The scattered intensity being highest in the plane at right angle to the path of the light, the path of light becomes visible, particularly when viewed at right angle to the path of the light. This kind of scattering is the Rayleigh scattering. This effect was first noticed by Faraday but detailed studies were made by Tyndall giving it a name Tyndall effect. Scattering also occurs in solution but the amount of scattering is extremely weak. For Tyndall effect to take place, two conditions must be satisfied :

- The diameter of the particles of the dispersed phase must not be much smaller than the wavelength of the light used.
- The refractive indices of the dispersed phase and the dispersion medium must differ considerably.

Do you wonder what will happen when the refractive indices are equal? Insert a glass rod to Canada balsam, a plant product; the rod will disappear as both the glass and the Canada balsam have nearly equal refractive indices.

When the colloidal particles scatter light, they appear as bright self-luminescent particles. Have you ever noticed Sun beam coming from the window in the early morning lights up dust particle brightly? You observe the phenomenon best when you watch at right angle. Next time when you notice it, watch the particles carefully, each one behaves like a tiny bulb but when the same dust particle falls on the floor, it appears pale.

Rayleigh scattering is important in atmosphere, where scattering takes place by gas molecules. For Rayleigh scattering, the scattered energy in any direction is proportional to the inverse fourth power of the radiation wavelength. This shows that when the incident radiation covers a wavelength spectrum, the shorter wavelength radiation will be Rayleigh scattered with a strong preference.

Rayleigh scattering by molecules of the atmosphere accounts for the background of sky being blue and for the sun appearing red at the sunset. The blue portion of the incident sunlight is at the short wavelength end of the visible spectrum. Hence, it undergoes strong Rayleigh scattering into all directions, giving the sky its overall blue background. Without molecular scattering the sky would appear black except for the direct view of the sun. As the sun moves towards setting, the path length for direct radiation through the atmosphere becomes much longer than during middle of the day. In transversing this longer path, proportionately more of the short wavelength part of the visible radiation is scattered away. As a result, at the sunset the sun takes on a red colour. The longer wavelength red rays are able to penetrate the atmosphere along the path to the observer. If many dust particles are present, the sunset may be deep red.

With very different range of size of particles in the atmosphere, unusual scattering effect may be observed. Krakatoa eruption had fed such particles in the atmosphere changing the whole phenomenon of scattering. Similar incidents have also been reported, on September 26, 1950, a blue moon was observed in Europe believed due to finely dispersed smoke particles coming from a forest fire in Canada. A green moon was observed following the El Chichon eruption in Mexico in 1982.

There is another scattering called 'Mie (read as 'me') scattering' observed for particles similar in diameter as the wavelength of the light. Larger particles of the atmosphere are able to scatter light of all wavelengths of white light equally, a phenomenon called Mie scattering. This is the reason why lighter clouds appear white. When you are watching beautiful patches of white clouds against the clear blue sky, besides feeling delighted never forget you are watching Mie scattering and Rayleigh scattering together. If the cloud is thick, light cannot penetrate and it appears black.

(Mount Krakatoa incident had also exemplified optical phenomena "Bishop Ring".)

UNSCRAMBLE ME

Unscramble the words given in column I and match them with their explanations in column II.

Column I	Column II
1. NEILOVI	(a) A compound which is used to preserve the moisture content of material due to its hygroscopic nature.
2. NGAIMARER	(b) It is a violet variety of quartz. It is impure crystalline silica.
3. UTNOGLEJ	(c) Highly explosive. Formed from ethanoic acid, ethanoic anhydride and nitric acid.
4. TNTAMECHU	(d) It is a mineral silicate of magnesium and iron. The transparent form is used as a gem stone.
5. ITOAIRNLEUT	(e) The property of a crystal of having a different colour depending upon the direction of transmitted light through the crystal.
6. RTTYTSEMA	(f) A chemical which produces malformation, generally in the form of mutations or tumours.
7. SMIROHECOLP	(g) The process of separation of lyophillic sols into too immiscible liquid phases, each of which has a different concentration of the dispersed phase.
8. YNOIETCCL	(h) It is substituted food product like butter which is obtained from vegetable oils (Polyunsaturated fats).
9. VTINOERCCOAA	(i) It is the method of separating a material into fractions of various sizes by allowing it to settle against upward moving stream of fluid, generally air or water.
10. GNTREATOE	(j) It is rubber like material obtained from the tree Dyera costularia.

Readers can send their responses at editor@mtg.in or post us with complete address by 10th of every month to win exciting prizes. Winners' names will be published in next issue.

CHEMISTRY MUSING

SOLUTION SET 61

1. **(c) :** $XeO_3 + XeOF_4 \rightarrow 2XeO_2F_2$ (Xenon dioxydifluoride)

2. **(b) :** $b = 4V$

or $V = \frac{b}{4} = \frac{0.0318}{4} = 7.95 \times 10^{-3}$ L mol^{-1}

$= 7.95$ cm^3 mol^{-1}

$\therefore$ Volume occupied by one O_2 molecule

$= \frac{7.95}{6.02 \times 10^{23}} = 1.32 \times 10^{-23}$ cm^3

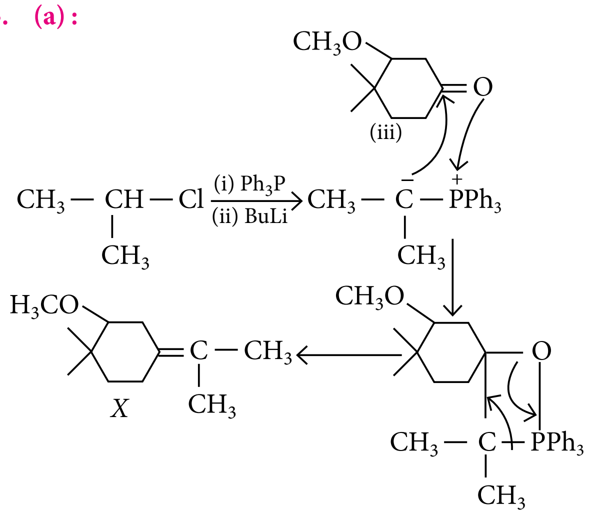
Considering the molecule to be spherical,

$\frac{4}{3}\pi r^3 = 1.32 \times 10^{-23}$ or $r^3 = 3.15 \times 10^{-24}$

$r = 1.466 \times 10^{-8}$ cm

$\therefore$ Diameter of oxygen molecule $= 2 \times r = 2 \times 1.466 \times 10^{-8}$ $= 2.932 \times 10^{-8}$ cm $= 2.932$ Å

3. **(a) :**



(Unstable)

4. **(a) :** The amount of energy released when 1 mol ($\approx 6.0 \times 10^{23}$ atoms) of Cl are converted to Cl^- ions is $\Delta_{eg}H$ of Cl atom.

$\therefore \Delta_{eg}H$ of Cl atom $= \frac{-58 \times 10^{-10}\text{ J} \times 6 \times 10^{23}}{10^{12}}$

$= -3480$ J mol^{-1} $= -3.48$ kJ mol^{-1}

We know that, 1 eV atom^{-1} = 96.49 kJ mol^{-1}.

Therefore, $\Delta_{eg}H$ of Cl atom in eV is

$= \frac{-3.48}{96.49} = -0.036$ eV atom^{-1}

5. **(c)**

6. **(b) :** The given cell is

$Ag|Ag^+$ (satd. Ag_2CrO_4 soln.)$||Ag^+$ (0.1 M)$|Ag$

Right half-cell reaction : $(Ag^+)_R + e^- \rightarrow Ag$

Left half-cell reaction : $Ag \rightarrow (Ag^+)_L + e^-$

$(Ag^+)_R \rightarrow (Ag^+)_L$

$\therefore E_{cell} = -\frac{RT}{F} \ln \frac{[Ag^+]_L}{[Ag^+]_R}$

In the left half-cell, the concentration of Ag^+ will be related to the solubility product of Ag_2CrO_4 as shown in the following :

$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$

If x is the solubility of Ag_2CrO_4 in solution, then

$[Ag^+] = 2x$ and $[CrO_4^{2-}] = x$

and $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2x)^2(x)$ or $x = (K_{sp}/4)^{1/3}$

$[Ag^+]_L = 2x = 2(K_{sp}/4)^{1/3} = (2K_{sp})^{1/3}$

$\therefore \quad E_{cell} = -\frac{RT}{F} \ln \frac{(2K_{sp})^{1/3}}{[Ag^+]_R}$

Substituting the given data, we get

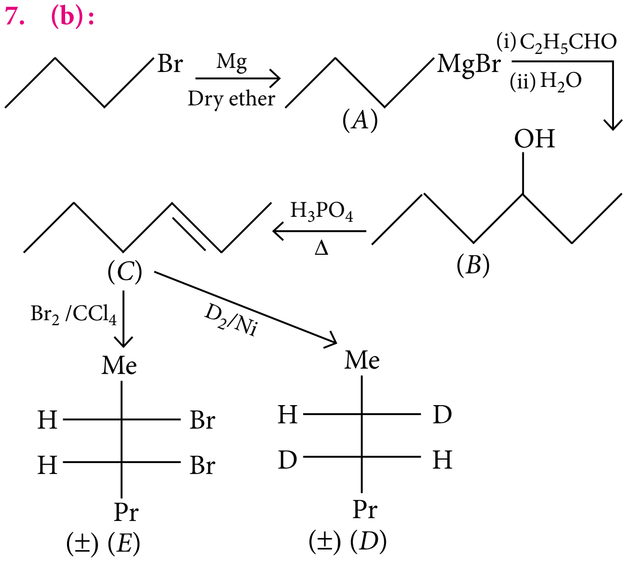
$\Rightarrow \quad 0.164 = -(0.059) \log \frac{(2K_{sp})^{1/3}}{(0.1)}$

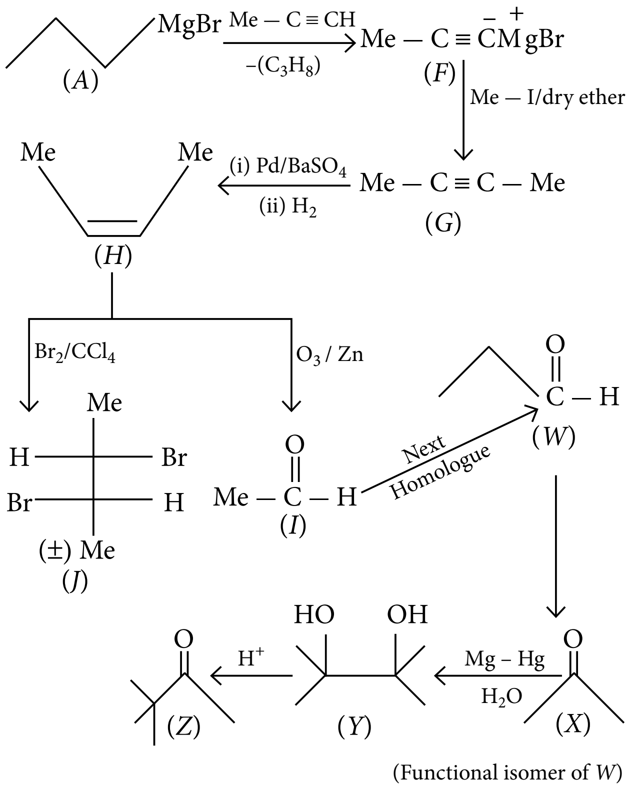
$\log (2K_{sp})^{1/3} = -\frac{0.164}{0.059} + \log 0.1 = -3.78$

$2K_{sp} = \text{antilog } (-3 \times 3.78) = 4.57 \times 10^{-12}$

$K_{sp} = 2.29 \times 10^{-12}$

7. **(b) :**





8. (d)

9. (2): Density $(\delta) = \dfrac{Z \times \text{mol.wt.}}{a^3 \times N_a}$

$$= \frac{4 \times 40}{(0.50 \times 10^{-7})^3 \text{cm}^3 \times 6 \times 10^{23}}$$

$$= \frac{160}{0.75 \times 10^2} = 2.133 \text{ g/cm}^3$$

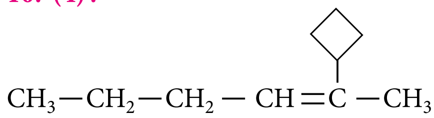
Due to Schottky defect density reduces by 0.25% :

$$\therefore \rho' = \rho\left(1 - \frac{0.25}{100}\right)$$

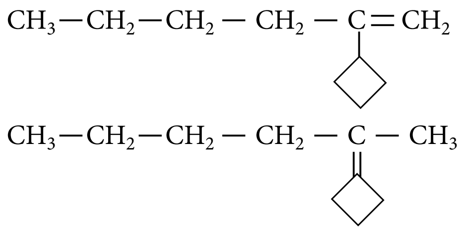
$$= 2.133 \text{ g/cm}^3 \left(1 - \frac{0.25}{100}\right)$$

$$= 2.133 \times 0.9975 = 2.127 \text{ g/cm}^3 \approx 2 \text{ g/cm}^3$$

10. (4):



$\Rightarrow$ 2 geometrical isomers



$\therefore$ Total number of alkene products = 4

3 AMAZING FACTS YOU MUST KNOW

1

The wallpaper in Napoleon's room was dyed with Scheele's Green, which contains copper arsenide. In 1893 the Italian biochemist Gosio found that dampening wallpaper containing Scheele's Green allowed a mold to convert the copper arsenide into poisonous arsenic vapour.

Although this may not have been the cause of Napoleon's death, it certainly can't have helped his health!

2

If you exposed a glass of water to space, it would boil rather than freeze. However, the water vapour would crystallize into ice afterward. When we talk about putting liquid water in the vacuum of space, we're talking about doing both things simultaneously: taking water from a temperature/pressure combination where it's stably a liquid and moving it to a lower pressure, something that makes it want to boil, and moving it to a lower temperature, something that makes it want to freeze.

So, it does both: first it boils and then it freezes! We know this because this is what used to happen when astronauts felt the call of nature while in space.

3

Fire typically spreads uphill more quickly than downhill. This is because temperature affects the rate of combustion. The region above a fire tends to be much hotter than the area below it, plus it may have a better supply of fresh air.

YOU ASK WE ANSWER

Do you have a question that you just can't get answered?
Use the vast expertise of our MTG team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough. The best questions and their solutions will be printed in this column each month.

1. Why radiation is harmful for humans?

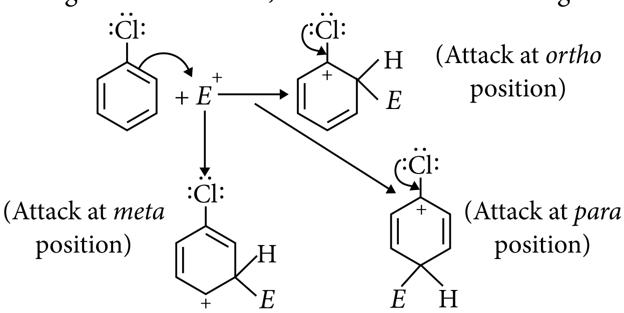
(Lakshay Sareen, Punjab)

Ans. Radiations are harmful or not, depend on the following points :
- How it is used?
- How strong it is?
- How often a person is exposed?
- What type of exposure occurs?
- How long exposure last?

Radiations are harmful because when they collide with molecules in living cells they can damage them. If the DNA in the nucleus of a cell is damaged, the cell may become cancerous. Then cell goes out of control, divides rapidly and causes serious health problems. The greater the dose of radiation a cell get, the greater the chance that the cell will become cancerous. However, very high doses of radiation can kill the cell completely. If use smartly, this property of radiations can be used to kill cancer cells and also harmful bacteria and other micro-organisms.

2. Why chlorine is deactivating but *ortho*, *para* directing group? *(Poulami Das)*

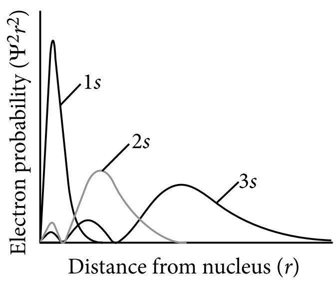
Ans. Chlorine shows –*I* effect as well as has three lone pairs of electrons. These three electron pairs can cause resonance in benzene ring. Chlorine withdraws electrons through inductive effect, thus it deactivates the ring.



The intermediate carbocation can be stabilised by resonance when the attack is on *ortho* or *para* position, thus chlorine is *ortho*, *para* directing group.

3. The probability density and probability distribution graphs of orbitals start more or less near $r = 0$ whether it is 2*s* or 1*s* or 2*p*. But 2*p* or 2*s* is not near the nucleus. So, how can the graphs start from near $r = 0$? Does the graphs mean that the orbitals are merging at nucleus? *(Subhadeep Mondal, West Bengal)*

Ans. Every orbital has origin from nucleus itself, however, probability of finding the electron decrease around nucleus as value of *n* increase but it could not be zero. In this plot of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as *n* increases, but the 2*s* and 3*s* orbitals have regions of significant electron probability at small values of *r*.



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