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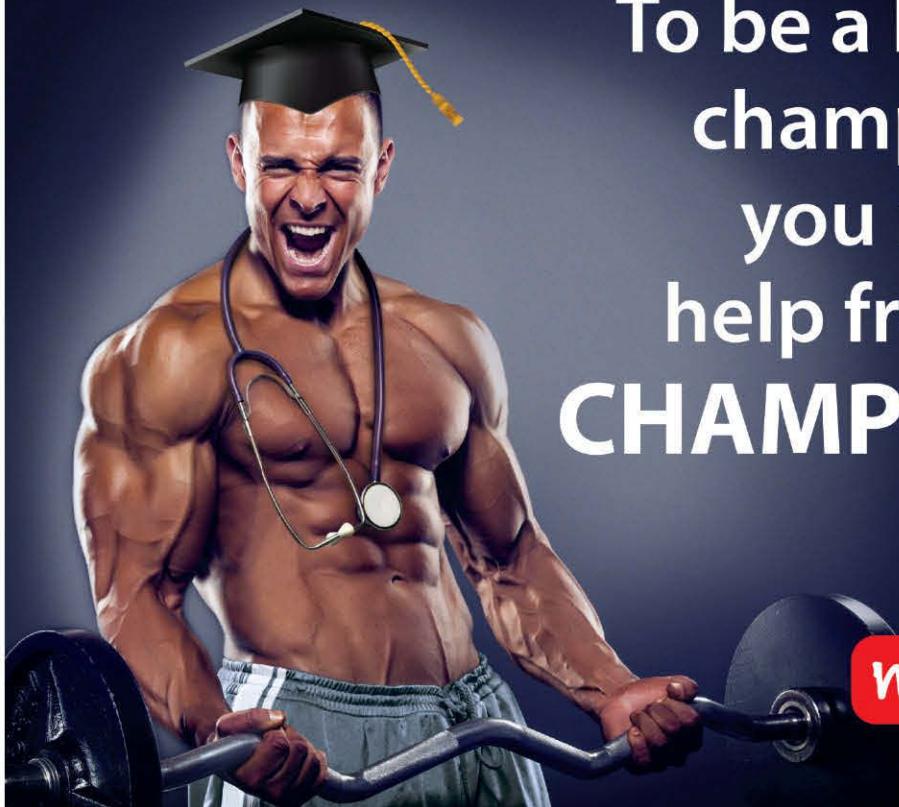
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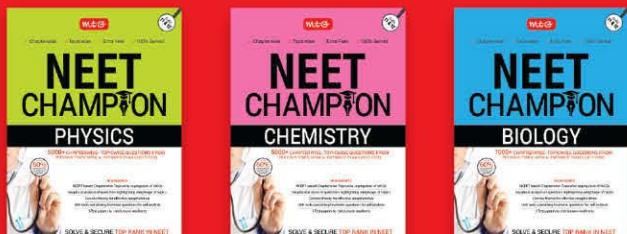
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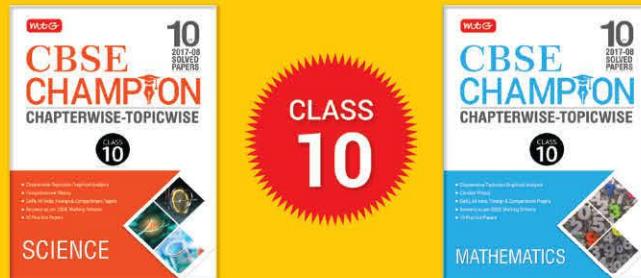
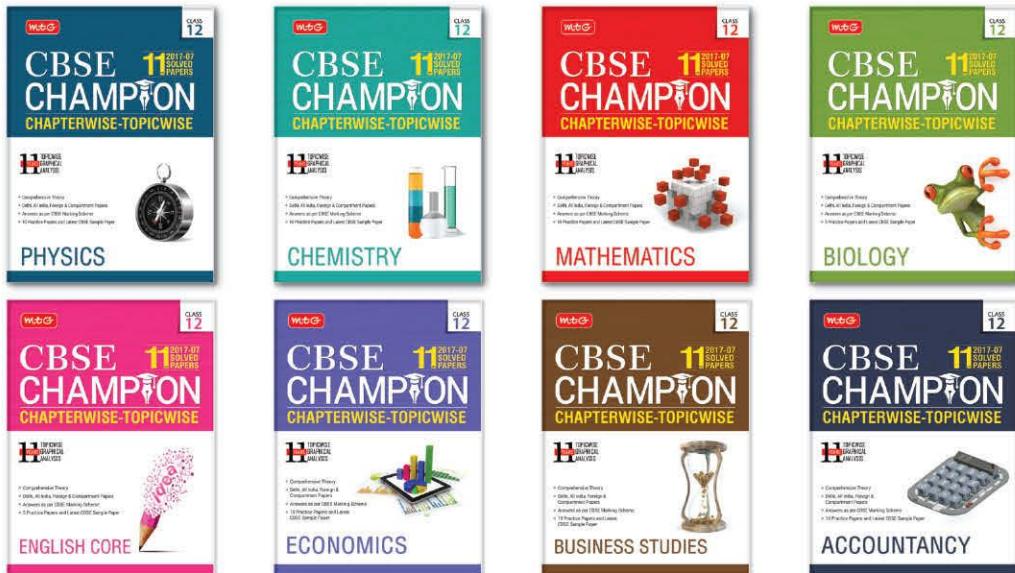
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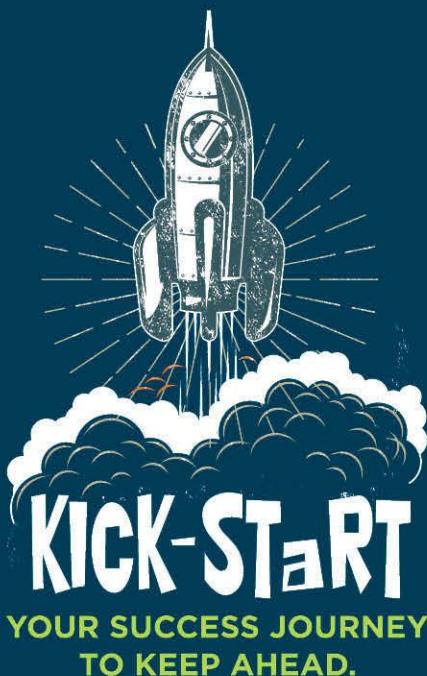
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# CHEMISTRY

## today



Volume 26

No. 9

September 2017

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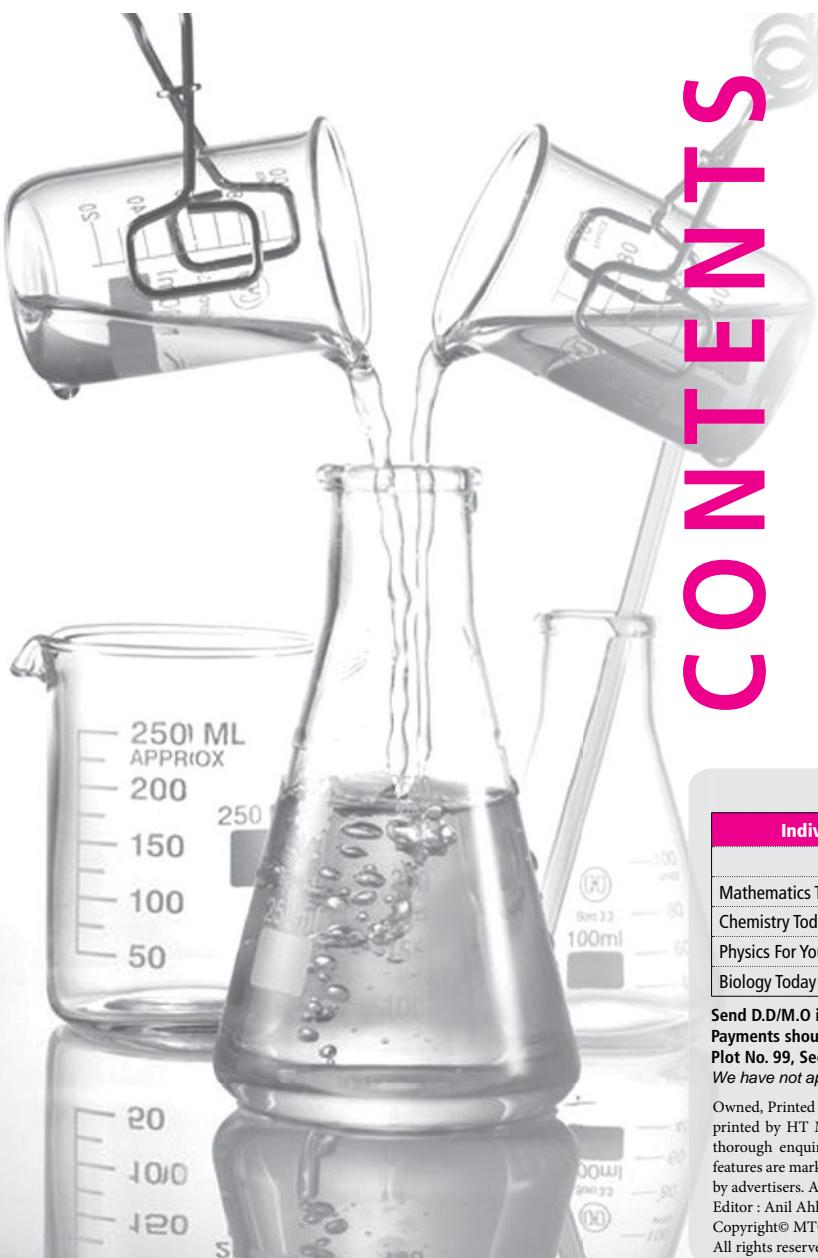
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# NEET | JEE ESSENTIALS

Class  
XI

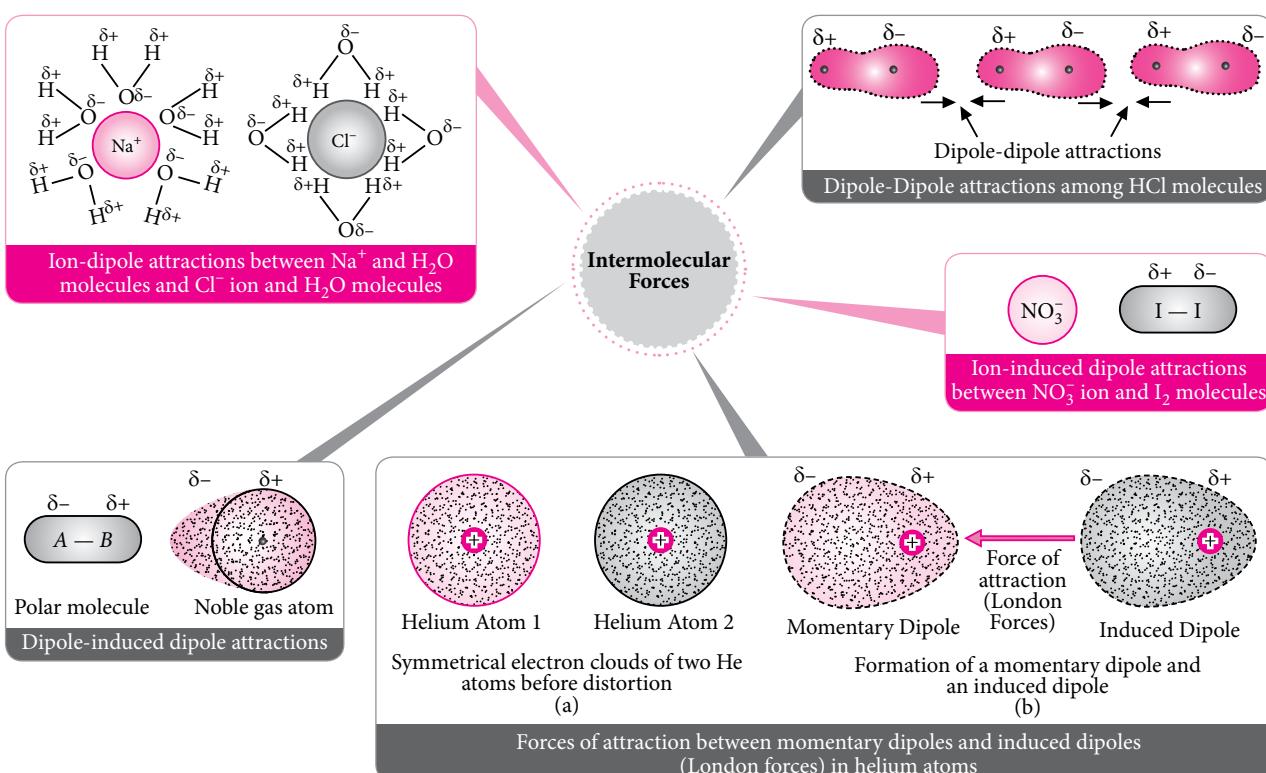
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## Unit 3

### States of Matter : Gases & Liquids | Thermodynamics

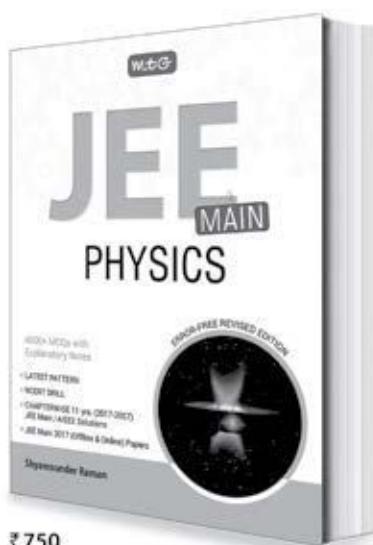
#### STATES OF MATTER : GASES & LIQUIDS

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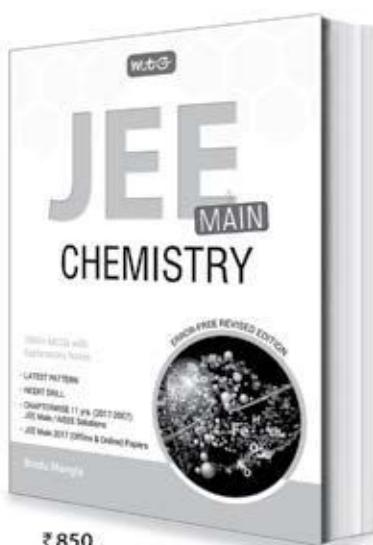


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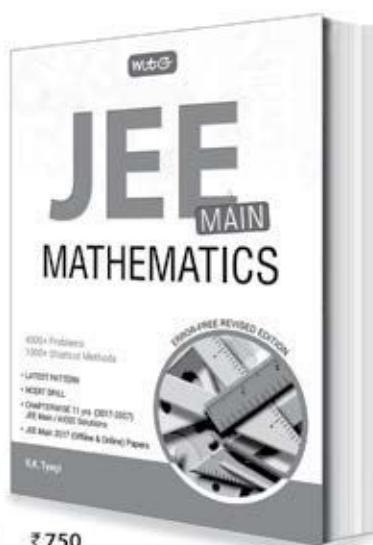
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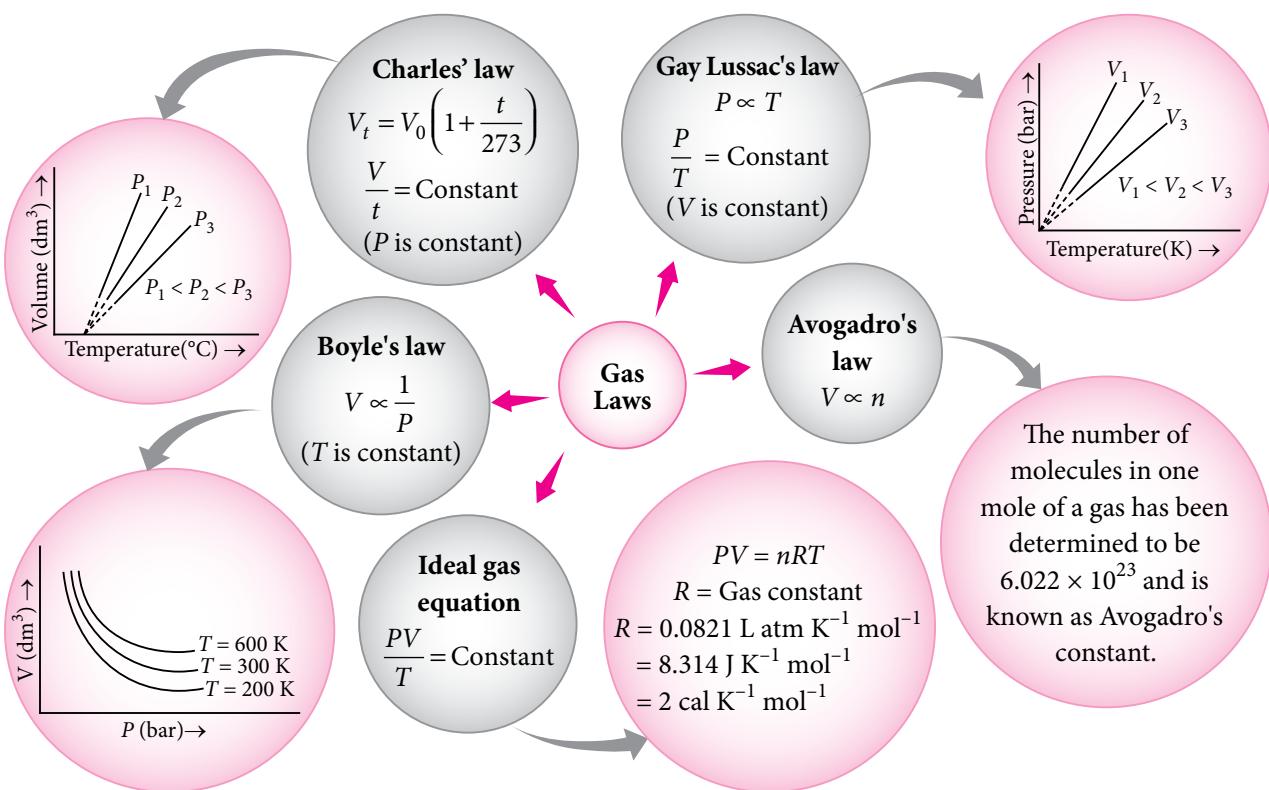
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## DALTON'S LAW OF PARTIAL PRESSURES

- The total pressure exerted by a mixture of two or more non-reacting gases enclosed in a vessel is equal to the sum of the individual partial pressures which each gas would exert when present alone in the same vessel at the same temperature.

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n$$

$$P_1 = x_1 P_{\text{total}}$$

$x_1$  = Mole fraction of the gas 1.

## GRAHAM'S LAW OF DIFFUSION / EFFUSION

- Under similar conditions of temperature and pressure, the rates of diffusion/effusion of different gases are inversely proportional to the square root of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

where  $d_1, d_2$  are densities of two gases.

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{T_1 d_2}{T_2 d_1}} = \sqrt{\frac{T_1 M_2}{T_2 M_1}}$$

## KINETIC MOLECULAR THEORY OF GASES

- The molecules are separated from one another by large distances.
- Molecular collisions are perfectly elastic.
- There are no forces of interactions between the molecules.
- Kinetic gas equation,  $PV = \frac{1}{3} mn\bar{u}^2$

where,  $P$  = Pressure exerted by the gas,

$m$  = Mass of each molecule of gas,

$n$  = Total number of molecules of the gas present in volume  $V$ ,

$\bar{u}$  = Root mean square speed of the gas

$$K.E., E_k = \frac{3}{2} nRT$$

$$\text{Average kinetic energy}, \bar{E}_k = \frac{1}{2} m\bar{u}^2 = \frac{3}{2} \frac{RT}{N_A}$$

where,  $N_A$  = Avogadro's constant

- The average kinetic energy of gas molecules is directly proportional to the absolute temperature of the gas.
- All gases are made up of a very large number of molecules.

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*Sanjay Shankar says, "Awesome book!! Everything is just perfect and the collaboration of the 11<sup>th</sup> and 12<sup>th</sup> std. just made it easier for us and with this less price. I will definitely recommend this book for every NEET preparing student."*

*Shweta says, "Must read for good score in NEET. Many questions in NEET are from this book in last 3 years. It also covers outside NCERT topics. Nice book."*

*Vijay says, "This book is ideal for practising MCQs (chapterwise). It appreciably covers all the important as well as less important questions. HOTS and sample question papers are provided as well. No demerits of the book can be listed. Though, it is not light weighted and thus cannot be carried, you wouldn't get bored revising each chapter from the revision section and then answering the questions. The language is appropriate and lucid as well as easy to understand."*

*S J. Uday says, "It is an awesome book. Firstly I was scared how it will be, but after having it, I was amazed. One must have this book who is interested in going for the NEET examination."*

*Sonal Singh says, "Book is very good. As it contains all the topicwise questions from every topic of NCERT, one can develop a question solving ability and also understand the basic concepts".*

*Sunehri says, "This book contains over 150 MCQs in each chapter, has categories like MCQs, NCERT, HOTS based questions, AIIMS assertion reasoning questions. Every chapter gives a short summary of chapter. Great book for entrance exams like NEET, AIIMS etc."*

*Prashant says, "The book is really awesome. It makes you cover up whole NCERT in a simple way. Solving the problems can increase your performance in exam. I would suggest each & every NEET candidate to solve the book. The book is also error free; not like other publications books which are full of errors."*

*Arka says, "It is a nice question bank of NCERT. I think it is the best of its kind. The book is a must to prepare for NEET."*



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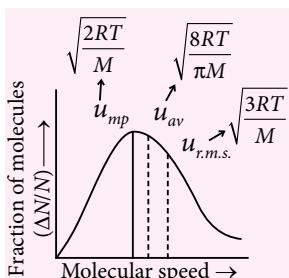
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## MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

- The plot between the fraction of molecules ( $\Delta N/N$ ) possessing particular speeds against their corresponding speeds at a particular temperature is known as Maxwell's distribution curve.

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



## DEVIATION FROM IDEAL GAS BEHAVIOUR

- Real gases do not follow ideal gas equation perfectly at all conditions of temperatures and pressures.
- $\frac{PV}{nRT} = Z$  = Compressibility factor
  - For an ideal gas,  $Z = 1$
  - For a real gas :
    - $Z > 1$  (Positive deviation)
    - $Z < 1$  (Negative deviation)
- Equation of state for real gases (van der Waals' equation) :**

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

where,  $a$  and  $b$  are van der Waals' constants.

## LIQUEFACTION OF GASES

- Gases can be liquefied by decreasing temperature or increasing pressure.
- Critical pressure** : The minimum pressure required to liquefy a gas at its critical temperature.

$$P_c = \frac{a}{27b^2}$$



### New state of matter !

A new form of matter, a supersolid, which combines the properties of solids with those of superfluids. By using lasers to manipulate a superfluid gas known as Bose-Einstein condensate was coaxed into a quantum phase of matter that has a rigid structure-like a solid and can flow without viscosity (like superfluids).

- Critical volume** : Volume occupied by one mole of a gas at its critical temperature and pressure.

$$V_c = 3b$$

- Critical temperature** : A temperature above which a gas cannot be liquefied however high pressure may be applied on the gas.

$$T_c = \frac{8a}{27Rb}$$

## LIQUID STATE OF MATTER

- Liquids have definite volumes but not definite shapes.

### Properties of Liquid State

- Boiling point** : Temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.
- Surface tension** : Force per unit length acting perpendicular to the tangential line drawn at the surface of liquid is known as surface tension.

#### (Surface Tension)

Surface tension causes

Rise of a liquid in a capillary tube.

Spherical shape of a drop

Liquid wet things.

Unit :  $N\ m^{-1}$  or  $dyne\ cm^{-1}$

Surface tension decreases with increase in temperature.

Greater the molecular forces, higher is the surface tension.

- Viscosity** : Internal resistance to the flow in liquids.

$$F = \eta A \frac{dv}{dx}, \text{ where, } A = \text{Area},$$

$\frac{dv}{dx}$  = Velocity gradient,

$\eta$  = Coefficient of viscosity,

## THERMODYNAMICS

- A specified part of the universe which is under thermodynamic consideration is called the system.

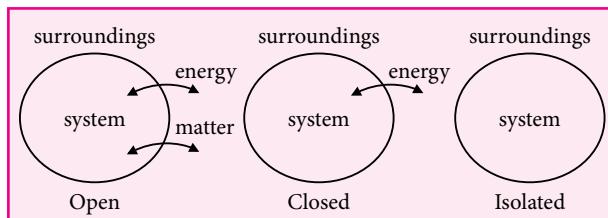
### THERMODYNAMICS TERMS

- Extensive properties** : Properties of the system whose value depends upon the amount or size of the substance present in the system e.g., Gibbs free energy, enthalpy, entropy, internal energy, etc.
- Intensive properties** : Properties of the system whose value is independent of the amount or size of the substance present in the system but depends only upon the nature of the substance e.g., temperature, pressure, viscosity, etc.
- State function** : A physical quantity is said to be a state function if its value depends only upon the

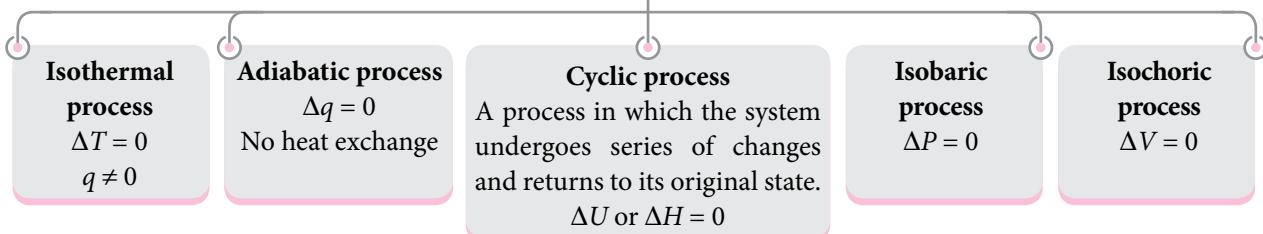
state of the system and is independent of the path by which the state is reached e.g., volume, temperature, internal energy, enthalpy.

- Path function** : A physical quantity is a path function if it depends upon the path by which the change is brought about e.g., work and heat.

### Different Types of Systems



### Types of Processes



### FIRST LAW OF THERMODYNAMICS

Energy can neither be created nor destroyed, although it can be converted to one form to another form. The total energy of the universe remains constant.

$$\Delta U = q + w$$

where,  $\Delta U$  = Change in internal energy;

$q$  = heat change;  $w$  = work done

#### Sign Conventions

$q = +ve$  (when heat is absorbed by the system)

$q = -ve$  (heat is evolved by the system)

$w = +ve$  (work is done on the system)

$w = -ve$  (work is done by the system)

#### Work

- For isothermal reversible expansion,

$$q = -w = p_{ext} (V_f - V_i)$$

$$= nRT \ln \frac{V_f}{V_i}$$

$$= 2.303 nRT \log \frac{V_f}{V_i}$$

$$= 2.303 nRT \log \frac{P_i}{P_f}$$

- For adiabatic reversible process,  $q = 0$

$$\Delta U = w_{ad} = nC_v \Delta T = \frac{nR}{\gamma - 1} \Delta T$$

**Enthalpy change ( $\Delta H$ )**  
Heat absorbed or evolved ( $\Delta H$ ) during a reaction at constant pressure.

**Internal energy change ( $\Delta U$ )**  
The change in internal energy ( $\Delta U$ ) is the heat absorbed or evolved at constant volume.

$$\Delta H = \Delta U + P\Delta V$$

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

$$\Delta n_g = \text{change in number of gaseous moles}$$

## HEAT CAPACITY

It is the amount of heat required to raise the temperature of the system through  $1^\circ\text{C}$

$$C = q/\Delta T$$

Heat capacity at constant volume ( $C_v$ )  
 $C_v = 3R/2$  (For monoatomic gas)  
 $C_v = 5R/2$  (For diatomic gas)

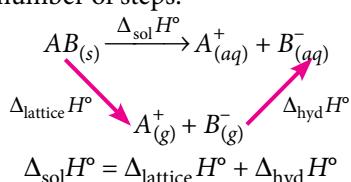
Heat capacity at constant pressure ( $C_p$ )  
 $C_p = 5R/2$  (For monoatomic gas)  
 $C_p = 7R/2$  (For diatomic gas)

$$C_p/C_v = \gamma$$

$$C_p = C_v + nR$$

## HESS'S LAW

- The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.



- Enthalpy of reaction = (Sum of bond enthalpies of reactants) – (Sum of bond enthalpies of products)
- Enthalpy of reaction = (Sum of enthalpies of products) – (Sum of enthalpies of reactants)

## ENTROPY

- The property of a system which measures the degree of disorder or randomness in the system.

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

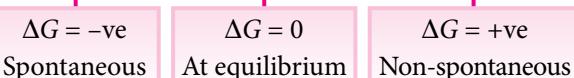
$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

- For isothermal process,  $\Delta S_t = nC_v \ln \frac{V_2}{V_1} = nC_p \ln \frac{P_1}{P_2}$
- For isochoric process,  $\Delta S_v = nC_v \ln \frac{T_2}{T_1}$
- For isobaric process,  $\Delta S_p = nC_p \ln \frac{T_2}{T_1}$
- $\Delta_{\text{fusion}}S^\circ = \frac{\Delta_{\text{fusion}}H^\circ}{T_f}; \Delta_{\text{vap}}S^\circ = \frac{\Delta_{\text{vap}}H^\circ}{T_b}$
- Second law of thermodynamics :** The entropy of the universe is continuously increasing in the course of every spontaneous change.

## GIBBS FREE ENERGY

- $G = H - TS$ , where,  $G$  = Gibbs free energy
- $\Delta G = \Delta H - T\Delta S$
- Units :** kJ/mol, J/mol
- $\Delta G^\circ = \sum \Delta_f G^\circ_{(\text{products})} - \sum \Delta_f G^\circ_{(\text{reactants})}$
- $\Delta G^\circ = -2.303 RT \log K_{\text{eq}}$
- $\Delta G = RT \ln \frac{V_1}{V_2} = RT \ln \frac{P_2}{P_1}$

### Gibbs Free Energy



- If  $\Delta H = +ve; \Delta S = +ve \Rightarrow \Delta G = -ve$  if  $T\Delta S > \Delta H$  (At high temperature)
- If  $\Delta H = -ve, \Delta S = +ve \Rightarrow \Delta G = -ve$  (at all temperatures)
- If  $\Delta H = -ve, \Delta S = -ve \Rightarrow \Delta G = -ve$  if  $\Delta H > T\Delta S$  (at low temperature)

## THIRD LAW OF THERMODYNAMICS

- At absolute zero, the entropy of a perfectly crystalline substance is taken as zero.  $S_0 = 0$
- The most important application of the third law of thermodynamics is that it helps in the calculation of the absolute entropies of the substances at room temperature (or at any temperature  $T$ ). These determinations are based upon the heat capacity measurements.
- Residual entropy :** The entropy possessed by a substance at absolute zero is called its residual entropy.



# SPEED PRACTICE

- 1.** The heat of combustion of benzene in a bomb calorimeter (*i.e.* at constant volume) was found to be  $3263.9 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . Calculate the heat of combustion of benzene (in  $\text{kJ mol}^{-1}$ ) at constant pressure.  
 (a)  $-3263.9$       (b)  $-3267.6$   
 (c)  $-3260.2$       (d)  $+436.1$
- 2.** Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?  
 (a)  $3/8$       (b)  $1/2$   
 (c)  $1/8$       (d)  $1/4$
- (NEET Phase-I 2016)**
- 3.** Calculate the heat required to raise the temperature of  $60.0 \text{ g}$  of aluminium from  $35$  to  $55^\circ\text{C}$ . (Molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ ).  
 (a)  $1.07 \text{ kJ}$       (b)  $1.57 \text{ kJ}$   
 (c)  $1.07 \text{ J}$       (d)  $1.57 \text{ J}$
- 4.** A gaseous mixture of  $2$  moles of *A*,  $3$  moles of *B*,  $5$  moles of *C* and  $10$  moles of *D* is contained in a vessel. Assuming that gases are ideal and the partial pressure of *C* is  $1.5 \text{ atm}$ , the total pressure is  
 (a)  $3 \text{ atm}$       (b)  $6 \text{ atm}$   
 (c)  $9 \text{ atm}$       (d)  $15 \text{ atm}$
- 5.** The heat of reaction,  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$ , at  $27^\circ\text{C}$  was found to be  $-21.976 \text{ kcal}$ . What will be the heat of the reaction at  $50^\circ\text{C}$ ? (The molar heat capacities at constant pressure for nitrogen, hydrogen and ammonia are  $6.8$ ,  $6.77$  and  $8.86 \text{ cal mol}^{-1}$  degree $^{-1}$  respectively.)  
 (a)  $-22.192 \text{ kcal}$       (b)  $-24.132 \text{ kcal}$   
 (c)  $-21.760 \text{ kcal}$       (d)  $-21.976 \text{ kcal}$
- 6.** What will be the pressure of the gaseous mixture when  $0.5 \text{ L}$  of  $\text{H}_2$  at  $0.8 \text{ bar}$  and  $2.0 \text{ L}$  of oxygen at  $0.7 \text{ bar}$  are introduced in  $1 \text{ L}$  vessel at  $27^\circ\text{C}$ ?  
 (a)  $1.8 \text{ bar}$       (b)  $0.4 \text{ bar}$   
 (c)  $1.4 \text{ bar}$       (d)  $1.5 \text{ bar}$
- 7.** Calculate  $\Delta H$  at  $85^\circ\text{C}$  for the reaction,  
 $\text{Fe}_2\text{O}_{3(s)} + 3\text{H}_{2(g)} \longrightarrow 2\text{Fe}_{(s)} + 3\text{H}_2\text{O}_{(l)}$ . Given :  $\Delta H^\circ_{(298 \text{ K})} = -33.29 \text{ kJ/mol}$  and  

Substance	$\text{Fe}_2\text{O}_{3(s)}$	$\text{Fe}_{(s)}$	$\text{H}_2\text{O}_{(l)}$	$\text{H}_{2(g)}$
$C_p^\circ (\text{J/K-mol})$	103.8	25.1	75.3	28.8
(a)	-28.14 kJ / mol	(b)	35.9 kJ / mol	
(c)	-303.29 kJ / mol	(d)	-25.1 kJ / mol	
- 8.** The average energy per molecule of a gas at a given temperature  $T$ , is given by  
 (a)  $\frac{3}{2}RT$       (b)  $\sqrt{\frac{3RT}{M}}$   
 (c)  $\sqrt{\frac{8(R/N_A)T}{\pi M}}$       (d)  $\frac{3}{2}\left(\frac{R}{N_A}\right)T$
- 9.** What will be the entropy change for the reaction,  
 $2\text{H}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{H}_2\text{O}_{(l)}$  at  $300 \text{ K}$ ? (Standard entropies of  $\text{H}_{2(g)}$ ,  $\text{O}_{2(g)}$  and  $\text{H}_2\text{O}_{(l)}$  are  $126.6$ ,  $201.20$  and  $68.0 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively.)  
 (a)  $-318.4 \text{ J K}^{-1} \text{ mol}^{-1}$       (b)  $318.4 \text{ J K}^{-1} \text{ mol}^{-1}$   
 (c)  $31.84 \text{ J K}^{-1} \text{ mol}^{-1}$       (d) None of these
- 10.** For a given reaction,  $\Delta H = 35.5 \text{ kJ mol}^{-1}$  and  $\Delta S = 83.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . The reaction is spontaneous at (Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature.)  
 (a)  $T > 425 \text{ K}$       (b) all temperatures  
 (c)  $T > 298 \text{ K}$       (d)  $T < 425 \text{ K}$
- (NEET 2017)**
- 11.** Given :  $\text{C} + 2\text{S} \longrightarrow \text{CS}_2 ; \Delta H = 117 \text{ kJ mol}^{-1}$   
 $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2 ; \Delta H = -393 \text{ kJ mol}^{-1}$   
 $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \Delta H = -297 \text{ kJ mol}^{-1}$   
 The heat of combustion of  $\text{CS}_2$  to form  $\text{CO}_2$  and  $\text{SO}_2$  is  
 (a)  $-1104 \text{ kJ mol}^{-1}$       (b)  $1104 \text{ kJ mol}^{-1}$   
 (c)  $+ 807 \text{ kJ mol}^{-1}$       (d)  $-807 \text{ kJ mol}^{-1}$
- 12.** Calculate the root mean square speeds of nitrogen at N.T.P.  
 (a)  $493 \times 10^4 \text{ m/s}$       (b)  $493.13 \text{ m/s}$   
 (c)  $493 \times 10^2 \text{ m/s}$       (d)  $493 \times 10^3 \text{ m/s}$



$$(c) \Delta S = nRT \ln\left(\frac{P_f}{P_i}\right)$$

$$(d) \Delta S = RT \ln\left(\frac{P_i}{P_f}\right)$$

(NEET Phase-II 2016)

27. The specific heat of a gas at constant volume is 0.075 cal/g-K. Predict the atomicity of the gas. (Molar mass of gas is 40 g mol<sup>-1</sup>.)

- (a) 1 (b) 2  
(c) 3 (d) None of these

28. When the temperature is increased, surface tension of water

- (a) increases  
(b) decreases  
(c) remains constant  
(d) shows irregular behaviour.

29. If an endothermic reaction occurs spontaneously at constant temperature  $T$  and pressure  $P$ , then which of the following is true?

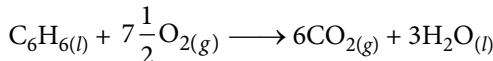
- (a)  $\Delta G > 0$  (b)  $\Delta H < 0$   
(c)  $\Delta S > 0$  (d)  $\Delta S < 0$

30. 22 g solid CO<sub>2</sub> or dry ice is enclosed in a bottle of one litre properly closed. If temperature of bottle is raised to 25 °C to sublime all the CO<sub>2</sub>, the pressure in bottle is

- (a) 13.23 atm (b) 12.23 atm  
(c) 11.23 atm (d) 14.23 atm

### SOLUTIONS

1. (b) : The reaction is



In this reaction, O<sub>2</sub> is the only gaseous reactant and CO<sub>2</sub> is the only gaseous product.

$$\therefore \Delta n_g = n_p - n_r = 6 - 7\frac{1}{2} = -\frac{3}{2}$$

Given :  $\Delta U$  (or  $q_v$ ) = -3263.9 kJ mol<sup>-1</sup>

$$T = 25^\circ\text{C} = 298 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = \frac{8.314}{1000} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \therefore \Delta H \text{ (or } q_p) &= \Delta U + \Delta n_g RT \\ &= -3263.9 - \frac{3}{2} \times \frac{8.314}{1000} \times 298 \\ &= -3263.9 - 3.7 = -3267.6 \text{ kJ mol}^{-1} \end{aligned}$$

2. (c) : Let the number of moles of each gas =  $x$

$$\text{Fraction of hydrogen escaped} = \frac{1}{2}x$$

$$\frac{r_{\text{O}_2}}{r_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{O}_2}}} \Rightarrow \frac{n_{\text{O}_2}/t}{\frac{x}{2}/t} = \sqrt{\frac{2}{32}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$\Rightarrow \frac{n_{\text{O}_2}/t}{\frac{x}{2}/t} = \frac{1}{4} \Rightarrow n_{\text{O}_2} = \frac{1}{8}x$$

Hence, fraction of oxygen escaped =  $\frac{1}{8}$

3. (a) : Mass of aluminium,  $m = 60.0 \text{ g}$   
Rise in temperature,  $\Delta t = (328 \text{ K} - 308 \text{ K}) = 20 \text{ K}$   
Molar heat capacity,  $C_m = 24 \text{ J K}^{-1} \text{ mol}^{-1}$

$$Q = \frac{C_m \times m \times \Delta t}{M}$$

$$\text{Molar mass of Al} = 27 \text{ g mol}^{-1}$$

$$\text{Heat required} = \frac{60 \times 24 \times 20}{27} \text{ J} = 1066.7 \text{ J} \approx 1.07 \text{ kJ}$$

4. (b) : Mole fraction of C ( $x_C$ )

$$= \frac{\text{Moles of C}}{\text{Total moles in the mixture}} = \frac{5}{2+3+5+10} = \frac{5}{20} = \frac{1}{4}$$

$$\therefore p_C = P_{\text{total}} \times x_C$$

where,  $p_C$  = Partial pressure of C

$$\therefore P_{\text{total}} = 1.5 \times 4 = 6 \text{ atm}$$

5. (a) :  $\Delta H = -21.976 \text{ kcal}$

$$\text{Here, } T_2 = 273 + 50 = 323 \text{ K}$$

$$T_1 = 273 + 27 = 300 \text{ K}$$

$$\Delta T = (T_2 - T_1) = (323 - 300) \text{ K} = 23 \text{ K}$$

$\Delta C_p$  = Sum of heat capacities of products

$$\begin{aligned} &\quad - \text{Sum of heat capacities of reactants} \\ &= (2 \times 8.86) - [6.8 + (3 \times 6.77)] \\ &= 17.72 - (6.8 + 20.31) = -9.39 \text{ cal degree}^{-1} \\ &= -9.39 \times 10^{-3} \text{ kcal degree}^{-1} \end{aligned}$$

Substituting these values in Kirchhoff's equation, we get

$$\begin{aligned} \Delta H_2 &= \Delta H_1 + (T_2 - T_1)\Delta C_p \\ &= -21.976 + [23 \times (-9.39 \times 10^{-3})] \\ &= -21.976 + (-0.216) \\ &= -22.192 \text{ kcal} \end{aligned}$$

6. (a) : Applying ideal gas equation :  $pV = nRT$

For H<sub>2</sub> gas,

$$0.8 \times 0.5 = n_{\text{H}_2} \cdot RT \Rightarrow n_{\text{H}_2} = \frac{0.8 \times 0.5}{RT} = \frac{0.4}{RT}$$

For O<sub>2</sub> gas,

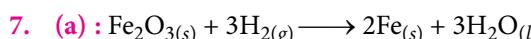
$$0.7 \times 2.0 = n_{\text{O}_2} \cdot RT \Rightarrow n_{\text{O}_2} = \frac{0.7 \times 2.0}{RT} = \frac{1.4}{RT}$$

When gas mixture is introduced in 1 L vessel, then

$$p \cdot V = (n_{H_2} + n_{O_2}) RT$$

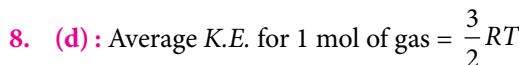
$$p \times 1 = \left( \frac{0.4}{RT} + \frac{1.4}{RT} \right) RT$$

$$\therefore p = 0.4 + 1.4 = 1.8 \text{ bar}$$



$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p$$

$$\begin{aligned} \therefore \Delta C_p &= \Sigma C_p (\text{products}) - \Sigma C_p (\text{reactants}) \\ &= (2 \times 25.1 + 3 \times 75.3) - (103.8 + 3 \times 28.8) \\ &= 276.1 - 190.2 = 85.9 \text{ J/K} = 85.9 \times 10^{-3} \text{ kJ/K} \\ \therefore \frac{\Delta H_{(358 \text{ K})} - (-33.29)}{358 - 298} &= 85.9 \times 10^{-3} \\ \Delta H_{358 \text{ K}} &= -28.14 \text{ kJ/mol} \end{aligned}$$



$$\text{Average K.E. for 1 molecule} = \frac{3}{2} \frac{RT}{N_A}$$

$$\begin{aligned} 9. (a) : \Delta S_{\text{reaction}} &= \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}} \\ &= 2 \times S_{H_2O} - [2 \times S_{H_2} + S_{O_2}] \\ &= 2 \times 68 - [2 \times 126.6 + 201.20] \\ &= -318.4 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

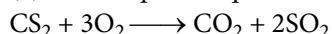


$$\Delta G < 0 \text{ i.e., } \Delta H - T\Delta S < 0$$

$$T > \frac{\Delta H}{\Delta S}$$

$$T > \left( \frac{35.5 \times 1000}{83.6} = 424.6 \approx 425 \text{ K} \right)$$

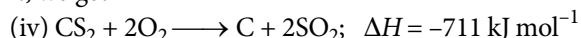
$$\therefore T > 425 \text{ K}$$



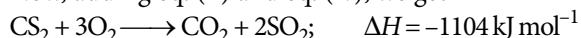
Given :

- (i)  $\text{C} + 2\text{S} \longrightarrow \text{CS}_2; \quad \Delta H = 117 \text{ kJ mol}^{-1}$
- (ii)  $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2; \quad \Delta H = -393 \text{ kJ mol}^{-1}$
- (iii)  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2; \quad \Delta H = -297 \text{ kJ mol}^{-1}$

Multiplying eq. (iii) by 2 and subtract eq. (i) from it, we get



Now, adding eq. (ii) and eq. (iv), we get



$$P = 760 \text{ mmHg} = 101325 \text{ N m}^{-2}$$

$$V = 22.4 \text{ L} = 0.0224 \text{ m}^3$$

$$M = 28 \text{ g/mol or } 0.028 \text{ kg/mol}$$

Putting these values in the equation,

$$u = \sqrt{\frac{3PV}{M}}$$

$$u = \sqrt{\frac{3 \times 101325 \times 0.0224}{0.028}} = 493.13 \text{ m s}^{-1}$$

13. (d) : For an irreversible process (work is being done by the system),  $(dG)_{T, P} = -\text{ve}$  and  $(dS)_{V, U} = +\text{ve}$ .

$$14. (d) : \because \frac{r_1}{r_2} = \frac{v/t_1}{v/t_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{500 \text{ mL}}{0.5 \text{ h}} = \sqrt{\frac{M_{\text{SO}_2}}{M_{\text{He}}}} = \sqrt{\frac{64}{4}} = 4$$

$$\therefore t_2 = 4 \text{ h}$$

$$15. (c) : q = C \times \Delta t = 30 \times 4 = 120 \text{ kJ}$$

Enthalpy of combustion of 4 g of graphite = -120 kJ

Enthalpy of combustion of 1 mole of graphite

$$= -\frac{12}{4} \times 120 = -360 \text{ kJ mol}^{-1}$$

$$16. (c) : c_{rms} = \sqrt{\frac{3RT}{M}}$$

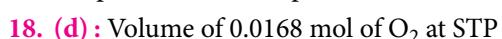
$$\frac{c_{rms(\text{H}_2)}}{c_{rms(\text{N}_2)}} = \sqrt{\frac{T_{(\text{H}_2)}}{M_{(\text{H}_2)}} \times \frac{M_{(\text{N}_2)}}{T_{(\text{N}_2)}}}$$

$$\sqrt{7} = \sqrt{\frac{T_{(\text{H}_2)}}{T_{(\text{N}_2)}} \times \frac{28}{2}} \Rightarrow \frac{T_{(\text{H}_2)}}{T_{(\text{N}_2)}} = \frac{1}{2}$$

$$2T_{(\text{H}_2)} = T_{(\text{N}_2)}$$

$$\therefore T_{(\text{H}_2)} < T_{(\text{N}_2)}$$

17. (b) : Real gases show ideal behaviour at high temperature and low pressure.



$$= 0.0168 \times 22400 \text{ mL} = 376.3 \text{ mL}$$

$$V_1 = 376.3 \text{ mL}, P_1 = 760 \text{ mmHg}, T_1 = 273 \text{ K}$$

$$V_2 = 428 \text{ mL}, P_2 = ?, T_2 = 298 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \frac{760 \times 376.3}{273} = \frac{P_2 \times 428}{298}$$

$$\Rightarrow P_2 = 729.4 \text{ mmHg}$$

$$\therefore \text{Pressure of water vapour} = 754 - 729.4 = 24.6 \text{ mmHg}$$

19. (c)

$$20. (c) : \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow P_2 = \frac{P_1 V_1 T_2}{T_1 V_2} \quad \dots(i)$$

Substituting values in eq. (i),

$$p_2 = (0.75 \text{ N m}^{-2}) \frac{V_1}{(3V_1)} \frac{(2T_1)}{T_1}$$

$$p_2 = 0.5 \text{ N m}^{-2}$$

- 21. (a) :** The entropy change at the melting point of a substance is given by

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{\text{melting}}}$$

$$\begin{aligned}\therefore T_{\text{melting}} &= \frac{\Delta H_{fus}}{\Delta S_{fus}} \\ &= \frac{7.25 \text{ kJ mol}^{-1}}{0.007 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 1035.7 \text{ K}\end{aligned}$$

Hence, the melting point of KCl is 1035.7 K

$$\begin{aligned}\text{22. (a) : } \bar{c} : \bar{c} : c &= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \\ &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224\end{aligned}$$

**23. (d)**

**24. (b)**

$$\text{25. (c) : } \Delta H = \Delta U + \Delta n_g RT$$

$$\therefore \Delta n_g = \frac{1}{2} - 0 = \frac{1}{2}$$

$$\therefore \Delta H = \Delta U + \frac{1}{2} RT$$

$$\therefore \Delta H > \Delta U$$

- 26. (b) :** For an ideal gas undergoing reversible expansion, when temperature changes from  $T_i$  to  $T_f$  and pressure changes from  $p_i$  to  $p_f$ ,

$$\Delta S = nC_p \ln \frac{T_f}{T_i} + nR \ln \frac{p_i}{p_f}$$

For an isothermal process,  $T_i = T_f$  so,  $\ln 1 = 0$

$$\therefore \Delta S = nR \ln \frac{p_i}{p_f}$$

$$\text{27. (a) : } C_v = 0.075 \times 40 = 3 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$C_p - C_v = R$$

$$\Rightarrow C_p - 3 = 2 \Rightarrow C_p = 5 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.66$$

Thus, the gas is monoatomic.

- 28. (b) :** The decrease in surface tension with increase in temperature is due to the fact that with the

increase in temperature, the kinetic energy of the molecules increases and hence, the intermolecular attraction between the molecule decreases.

- 29. (c) :**  $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$   
 $\Delta S > 0$ , for spontaneous process.

- 30. (a) :**  $w = 22 \text{ g}$ ;  $V = 1 \text{ litre}$ ,  $T = 298 \text{ K}$

$$\begin{aligned}PV &= \frac{w}{M} RT \quad (\text{Molar mass of CO}_2 = 44 \text{ g mol}^{-1}) \\ P_{\text{CO}_2} \times 1 &= \frac{22}{44} \times 0.0821 \times 298 \\ \therefore P_{\text{CO}_2} &= 12.23 \text{ atm} \\ \therefore P_{\text{in bottle}} &= P_{\text{CO}_2} + P_{\text{atm}} \\ &= 12.23 + 1 = 13.23 \text{ atm}\end{aligned}$$

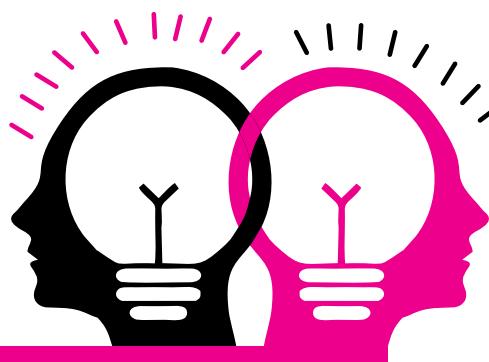


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# EXAMINER'S MIND CLASS XI



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI.

This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

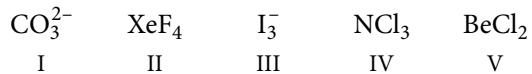
<b>Section - I</b>	Q. 1 to 10 Only One Option Correct Type MCQs.
<b>Section - II</b>	Q. 11 to 13 More than One Options Correct Type MCQs.
<b>Section - III</b>	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
<b>Section - IV</b>	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
<b>Section - V</b>	Q. 20 to 22 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.
<b>Section - VI</b>	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

## CHEMICAL BONDING AND MOLECULAR STRUCTURE

### SECTION - I

#### Only One Option Correct Type

- Which of the following has highest bond angle?  
 (a)  $\text{NO}_2^+$  (b)  $\text{NO}_2$  (c)  $\text{NO}_2^-$  (d)  $\text{NO}_3^-$
- In  $\text{PO}_4^{3-}$  ion, the formal charge on the oxygen atom of P—O bond is  
 (a) +1 (b) -1 (c) -0.75 (d) +0.75
- The ionic bond  $A^+ B^-$  is formed when  
 (1) I.E. of A is low (2) E.A. of B is high  
 (3) lattice energy of AB is high  
 (4) lattice energy of AB is low.  
 (a) 1 and 2 (b) 1, 2 and 3  
 (c) 3 only (d) 4 only
- Which of the following compounds/ions has V-shape?  
 (a)  $\text{SF}_5^-$  (b)  $\text{SF}_4$  (c)  $\text{OSF}_4$  (d)  $\text{SF}_2$
- In which one of the following species the central atom has the type of hybridisation which is not the same as in the other three?  
 (a)  $\text{SbCl}_5^{2-}$  (b)  $\text{PCl}_5$  (c)  $\text{SF}_4$  (d)  $\text{I}_3^-$
- The correct increasing order of s-character (in percentage) in the hybrid orbitals in the given molecules/ions is (assume all hybrid orbitals are exactly equivalent) :



- (a) II < III < IV < I < V (b) II < IV < III < V < I  
 (c) III < II < I < V < IV (d) II < IV < III < I < V

- In  $\text{ICl}_2^+$ ,  $\text{ICl}_2^-$ , and  $\text{ICl}_4^-$ , sum of the bond pairs and lone pairs on each iodine atom are respectively  
 (a) 2, 2 and 4 (b) 2, 3 and 2  
 (c) 4, 5 and 4 (d) 4, 5 and 6
- Which of the following molecules is formed by p-p overlapping?  
 (a)  $\text{F}_2$  (b)  $\text{H}_2\text{O}$  (c)  $\text{HCl}$  (d)  $\text{NH}_3$
- In  $\text{XeF}_2$  molecule, the angle between two lone pair orbitals is  $\alpha$ , the angle between lone pair orbital and bond pair orbital is  $\beta$  and the angle between two bond pair orbitals is  $\gamma$  then, which one is correct order of angle?  
 (a)  $\alpha = \beta = \gamma$  (b)  $\alpha > \beta > \gamma$   
 (c)  $\gamma > \beta > \alpha$  (d)  $\gamma > \alpha > \beta$
- Which one of the following properties is not shown by  $\text{NO}_2$ ?  
 (a) Its bond order is 2.5.  
 (b) It is diamagnetic in gaseous state.  
 (c) It is a neutral oxide.  
 (d) It combines with oxygen to form nitrogen dioxide.

## SECTION - II

### More than One Options Correct Type

11. According to VBT in  $\text{XeF}_2$ , Xe uses five  $sp^3d$  hybridised orbital for molecule formation. Select correct statement for  $\text{XeF}_2$ .
- (a) Three  $sp^3d$  orbitals are used for covalent bonding with F.
  - (b) Three  $sp^3d$  orbitals occupy lone pairs of Xe.
  - (c) Two  $sp^3d$  orbitals are used for covalent bonding with F.
  - (d) Two  $sp^3d$  orbitals are occupied by lone pairs of Xe.
12. Which statements are correct for  $AB_x$  type molecule?
- (a) If the electronegativity of central atom decreases, the bond angle decreases.
  - (b) If the size of central atom increases, the bond angle decreases.
  - (c) If the electronegativity of atom B decreases, the bond angle increases.
  - (d) If the electronegativity of atom B decreases, the bond angle decreases.
13. Which of the following statements are not correct?
- (a) Hybrid orbitals form stronger bonds than  $p$ -orbitals.
  - (b) Excitation of electron is essential for hybridisation.
  - (c) Boiling point of  $\text{H}_2\text{O}$  is more than  $\text{H}_2\text{S}$ .
  - (d) Resonance plays an important role in molecular orbital theory.

## SECTION - III

### Paragraph Type

#### Paragraph for Questions 14 and 15

Hydrogen bonding originates from the dipole-dipole interaction between H-atom and any of the other atom like F, O, N and in some cases with Cl atom also. There are two types of H-bonding i.e.; intermolecular and intramolecular H-bonding.

14. Which of the following molecules does not consist of intramolecular H-bonding?
- (a) Chloral
  - (b) Chloral hydrate
  - (c) *o*-Hydroxybenzaldehyde
  - (d) *o*-Chlorophenol
15. Which of the following statements is incorrect?
- (a) Boiling point of  $\text{H}_2\text{O}_2$  is greater than that of  $\text{H}_2\text{O}$ .
  - (b) Ethylene glycol is less viscous than glycerol.

- (c) *o*-Nitrophenol can be separated from its *m*- and *p*-isomers using its steam volatile property.
- (d) In ice, each 'O' atom is tetrahedrally arranged by four H-atoms which are all equidistant.

#### Paragraph for Questions 16 and 17

The VSEPR model considers double and triple bonds to have slightly greater repulsive effects than single bonds because of the repulsive effect of  $\pi$ -electrons. Consider molecule  $(\text{CH}_3)_2\text{C} = \text{CH}_2$  for given questions :

16. Which type of overlapping is not observed in the given molecule?
- (a)  $sp^3-s$
  - (b)  $sp^2-s$
  - (c)  $sp-s$
  - (d)  $sp^2-sp^2$
17. Select which has the largest bond angle in the given molecule.
- (a)  $\text{CH}_3-\text{C}-\text{CH}_3$
  - (b)  $\text{H}_3\text{C}-\text{C}\equiv\text{C}$
  - (c)  $\text{H}-\text{C}-\text{H}$
  - (d) All are same.

## SECTION - IV

### Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	<b>List I (Species)</b>	<b>List II (Properties)</b>
A.	$\text{O}_2^{2-}$	P. Isoelectronic with $\text{N}_2$
B.	CO	Q. Fractional bond order
C.	$\text{NO}^+$	R. Paramagnetic
D.	$\text{He}_2^+$	S. Diamagnetic

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
(a)	P	R, S	Q, P	P, S
(b)	Q, P	S	P, S	R, S
(c)	S	P, S	P, S	Q, R
(d)	R	R, S	S	P, Q

19. Match the List I with List II and select the correct answer using the codes given below the lists :

	<b>List I</b>	<b>List II</b>
(P)	$\text{CH}_4$	1. Linear molecule
(Q)	$\text{BeCl}_2$	2. Tetrahedral molecule
(R)	$\text{H}_2\text{O}$	3. Pyramidal molecule
(S)	$\text{NH}_3$	4. V-shaped molecule

	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(a)	2	1	4	3
(b)	2	3	4	1
(c)	1	2	3	4
(d)	2	3	1	4

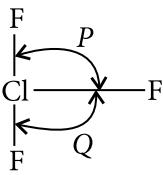
**SECTION - V****Assertion Reason Type**

- 20.** Assertion :  $C_2H_2$  molecule is linear.

Reason : In  $C_2H_2$ , carbon atoms remain unhybridised.

- 21.** Assertion :  $H_2$  molecule is more stable than  $HeH$  molecule.

Reason : The antibonding electron in the molecule destabilises  $HeH$ .



- 22.** Assertion : In  $ClF_3$  molecule,  $P = Q \neq 90^\circ$

**Reason :** The molecule is slightly bent T-shaped and there is repulsion between lone pairs of electrons.

**SECTION - VI****Integer Value Correct Type**

- 23.** How many of the following compounds violate octet rule?



- 24.** A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1.0 Å,  $1/x$  of an electronic charge 'e' exists on each atom. The value of  $x$  is

- 25.** The number of dative bonds in sulphuric acid molecule is

**HYDROGEN****SECTION - I****Only One Option Correct Type**

- 1.** Which one of the following processes will produce permanent hard water?

- (a) Addition of  $Na_2SO_4$  to water
- (b) Saturation of water with  $CaCO_3$
- (c) Saturation of water with  $MgCO_3$
- (d) Saturation of water with  $CaSO_4$

- 2.** Reaction between following pairs will produce hydrogen except

- (a)  $Cu + HCl$
- (b)  $Fe + H_2O_{(steam)}$
- (c)  $Mg + H_2O$  (hot)
- (d)  $Na + Alcohol$ .

- 3.** Protium, deuterium, tritium differ in

- (a) number of protons and physical properties
- (b) atomic number and chemical properties
- (c) number of neutrons and physical properties
- (d) number of neutrons and chemical properties.

- 4.** Moist hydrogen peroxide cannot be dried over conc.  $H_2SO_4$  because

- (a) it is oxidised by  $H_2SO_4$
- (b) it is reduced by  $H_2SO_4$
- (c) it can catch fire
- (d) all of these.

- 5.** Which of the following equations depicts reducing nature of  $H_2O_2$ ?

- (a)  $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$
- (b)  $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$
- (c)  $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$
- (d)  $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

- 6.** Heavy water is manufactured

- (a) by repeated electrolysis of water with 3% aqueous  $NaOH$
- (b) by electrolysis of water containing heavy hydrogen dissolved in it
- (c) by combination of hydrogen and heavier isotope of oxygen
- (d) none of the above.

- 7.** Which of the following explanations justifies for not placing hydrogen in either the group of alkali metals or halogens?

- (a) Hydrogen is much lighter than alkali metals or halogens.
- (b) Hydrogen atom does not contain any neutron.
- (c) The ionization energy of hydrogen is too high for group of alkali metals and too low for halogen group.
- (d) Hydrogen can form compounds with almost all other elements.

- 8.** The freezing point of heavy water is

- (a)  $-3.82^\circ C$
- (b)  $3.82^\circ C$
- (c)  $0^\circ C$
- (d)  $-10^\circ C$

- 9.** Water softening by Clark's process involves use of

- (a) calcium carbonate
- (b) sodium carbonate
- (c) potash alum
- (d) calcium hydroxide.

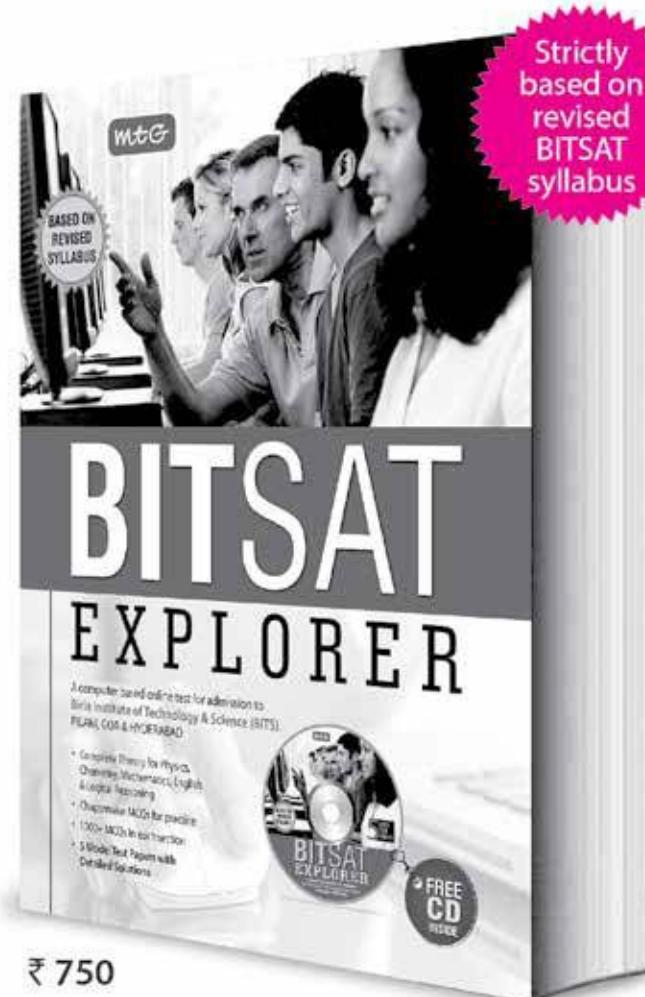
- 10.** Which is false about  $H_2O_2$ ?

- (a) It can act as both oxidising and reducing agent.
- (b) Two —OH bonds lie in the same plane.
- (c) It is pale blue liquid.
- (d) It can be oxidised by  $O_3$ .

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## SECTION - II

### More than One Options Correct Type

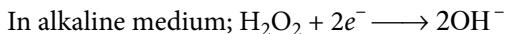
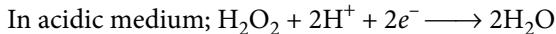
11. Which of the following statements are correct?
- (a) Metallic hydrides are deficient of hydrogen.
  - (b) Metallic hydrides conduct heat and electricity.
  - (c) Ionic hydrides do not conduct electricity in solid state.
  - (d) Ionic hydrides are very good conductors of electricity in solid state.
12. Which of the following statements are correct?
- (a) Dissociation of  $H_2$  molecules is an endothermic process.
  - (b) Hydrogen at the moment of liberation is more active.
  - (c) Atomic hydrogen is powerful reducing agent.
  - (d) Ordinary hydrogen is an oxidising agent.
13. Which of the following statements are correct about 6.8% strength of  $H_2O_2$ ?
- (a) Its normality is 4 N.
  - (b) Its molarity is 2 M.
  - (c) Its volume strength is 22.4 V.
  - (d) Volume strength =  $11.2 \times M$ .

## SECTION - III

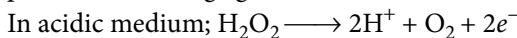
### Paragraph Type

#### Paragraph for Questions 14 and 15

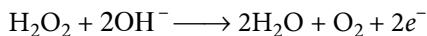
Hydrogen peroxide is a powerful oxidising agent, both in the acidic and alkaline medium.



Hydrogen peroxide acts as a reducing agent towards powerful oxidising agents.



In alkaline medium, however, its reducing nature is more effective.

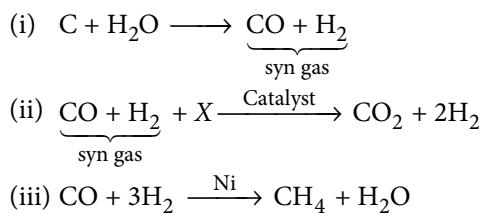


14. On addition of  $H_2O_2$  to acidified  $KMnO_4$ ,  $KMnO_4$  gets decolourised due to
- (a) oxidation of  $KMnO_4$
  - (b) reduction of  $KMnO_4$
  - (c) both oxidation and reduction
  - (d) none of these.

15. In which of the following reactions,  $H_2O_2$  acts as an oxidising agent?
- (a)  $2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$
  - (b)  $IO_4^- + H_2O_2 \longrightarrow IO_3^- + H_2O + O_2$
  - (c)  $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$
  - (d)  $2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

## Paragraph for Questions 16 and 17

Formation of methane from syn gas is represented by the following equations :



16. X in reaction (ii) refers to
- (a) liquid water
  - (b) steam
  - (c) oxygen
  - (d) carbon monoxide.

17. Hydrogen prepared by above method is passed over Ni catalyst
- (a) to remove traces of CO
  - (b) to prepare  $H_2O$
  - (c) to prepare  $CH_4$
  - (d) to separate  $H_2$  from water gas.

## SECTION - IV

### Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

#### List I

(P) Synthesis gas

(Q) Dihydrogen

(R) Heavy water

(S) Hydrogen

peroxide

#### List II

1. Forms stoichiometric compounds with s-block elements

2. Prolonged electrolysis of water

3. Mixture of CO and  $H_2$

4.  $Zn + NaOH$

5. Oxidising agent and/or Reducing agent

#### P Q R S

(a) 1, 2 3 4, 5 1, 2

(b) 3 1, 4, 5 2 5

(c) 1, 2 3, 4 1, 5 4

(d) 1, 3 2, 3 4 5

19. Match the List I with List II and select the correct answer using the codes given below the lists :

#### List I

(P) Ionic hydride

(Q) Electron deficient hydride

(R) Hydrolith

(S) Covalent hydride

#### List II

1.  $LiH$

2.  $CaH_2$

3.  $AlH_3$

4.  $SiH_4$

P	Q	R	S
(a) 1	2,3	3	1, 4
(b) 2,3	1	2	1, 4
(c) 1, 2	3	2	3, 4
(d) 3,4	3	2	1, 2

### SECTION - V

#### Assertion Reason Type

**20. Assertion :** *Para*-hydrogen with lower energy is favoured at high temperature.

**Reason :** The thermal conductivity of *para*-hydrogen is lesser than that of *ortho*-hydrogen.

**21. Assertion :** Permanent hardness of water is removed by treatment with washing soda.

**Reason :** Washing soda reacts with soluble magnesium and calcium sulphates to form insoluble carbonates.

**22. Assertion :** The colour of old lead paintings can be restored by washing with dilute solution of  $H_2O_2$ .

**Reason :** Black lead sulphide is oxidised by  $H_2O_2$  to white lead sulphate.

### SECTION - VI

#### Integer Value Correct Type

**23.** Half litre each of three samples of  $H_2O_2$  labelled 10 vol, 15 vol, 20 vol are mixed and then diluted with 1700 mL of water. Calculate relative strength of resultant  $H_2O_2$  solution.

**24.** Calculate the degree of hardness of a sample of water containing 6 mg of  $MgSO_4$  per kg of water.

**25.** What is the sum of protons, electrons and neutrons in the heaviest isotope of hydrogen?

### SOLUTIONS

#### CHEMICAL BONDING AND MOLECULAR STRUCTURE

**1. (a) :**  $NO_2^+$  has linear geometry and therefore, bond angle is highest ( $180^\circ$ ).

**2. (c) :** In  $PO_4^{3-}$  ion, formal charge on each O-atom of P—O bond

$$= \frac{\text{Total charge}}{\text{Number of O-atoms}} = -\frac{3}{4} = -0.75$$

**3. (b)**

**4. (d) :**  $SF_2$  has  $sp^3$  hybridisation and 'V' shape due to the presence of two lone pairs on sulphur.

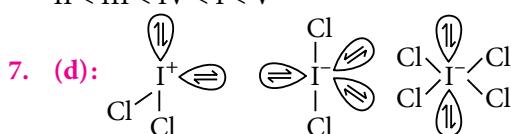
**5. (a) :**  $SbCl_5^{2-}$  has  $sp^3d^2$  hybridisation while all other species involve  $sp^3d$  hybridisation.

**6. (a) :**

Species	Hybridisation
$CO_3^{2-}$	$sp^2$
$XeF_4$	$sp^3d^2$
$I_3^-$	$sp^3d$
$NCl_3$	$sp^3$
$BeCl_2$	$sp$

Therefore, the correct increasing order of percentage of *s*-character is :

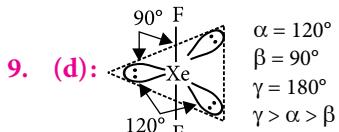
II < III < IV < I < V



So, total number of lone pairs and bond pairs in  $ICl_2^+$  = 2 + 2 = 4

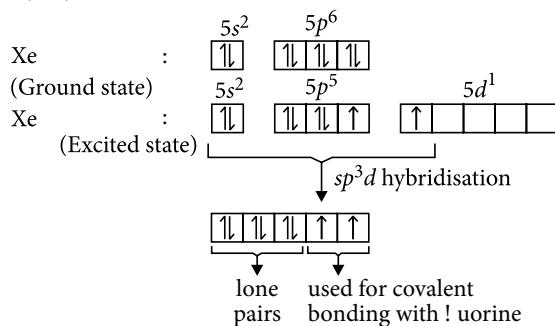
in  $ICl_2^-$  = 3 + 2 = 5 and  $ICl_4^-$  = 2 + 4 = 6

**8. (a) :**  $F_2$  is formed by *p-p* overlapping whereas,  $H_2O$ ,  $HCl$  and  $NH_3$  are formed by *s-p* overlapping.



**10. (b) :** NO is paramagnetic in gaseous state due to the presence of one unpaired electron.

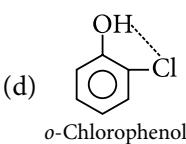
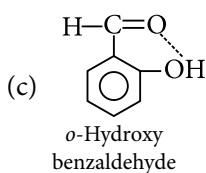
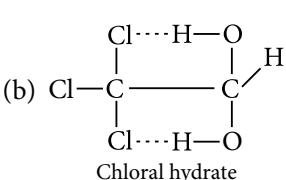
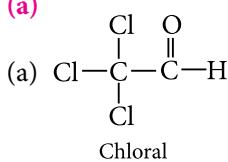
**11. (b,c) :**



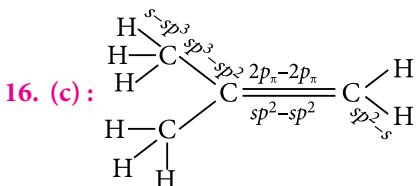
**12. (a, b, c)**

**13. (b, d) :** Excitation of electron is not essential for hybridisation, vacant orbitals can also participate in hybridisation. Resonance has no role in M.O. theory.

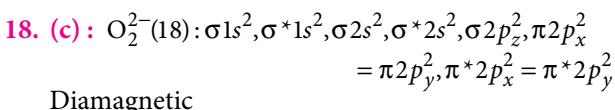
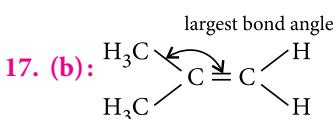
14. (a)



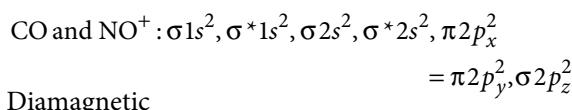
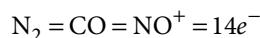
15. (d)



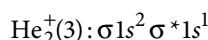
There is no  $sp-s$  overlapping.



$$B.O. = \frac{N_b - N_a}{2} = \frac{10 - 8}{2} = 1$$



$B.O. = \frac{10 - 4}{2} = 3$



Paramagnetic

$B.O. = \frac{2 - 1}{2} = \frac{1}{2}$

19. (a) : (P)  $\rightarrow$  2 :  $CH_4$  is  $sp^3$  hybridised so, it is tetrahedral molecule.

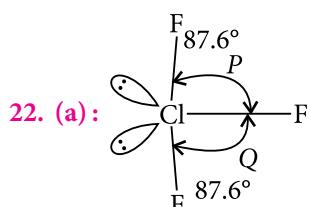
(Q)  $\rightarrow$  1 :  $BeCl_2$  is  $sp$  hybridised, hence linear in shape.

(R)  $\rightarrow$  4 :  $H_2O$  is  $sp^3$  hybridised, but due to the presence of lone pairs, it is V-shaped.

(S)  $\rightarrow$  3 :  $NH_3$  is  $sp^3$  hybridised, but due to the presence of one lone pair of electrons, its shape is pyramidal.

20. (c) : In  $C_2H_2$ , C atom is  $sp$ -hybridised. Thus, linear in shape.

21. (a) : Bond order of  $H_2 = 1$  (2 electrons;  $\sigma 1s^2$ ). Bond order of  $HeH = 0.5$  (3 electrons,  $\sigma 1s^2, \sigma^* 1s^1$ ). Greater the bond order of molecule, more stable the molecule. Hence,  $H_2$  is more stable than  $HeH$ .

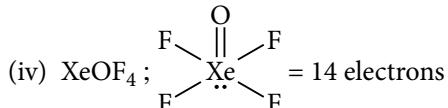


due to  $lp - lp$  repulsion

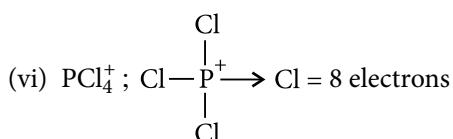
23. (5) : (i)  $BrF_5 = 12$  electrons

(ii)  $SF_6 = 12$  electrons

(iii)  $IF_7 = 14$  electrons



(v)  $ClF_2^-$  ;  $[F-\ddot{Cl}-F]^- = 10$  electrons



Hence, except  $PCl_4^+$  all five molecules violate octet rule.

24. (4) : Partial charge =  $\frac{\text{Dipole moment}}{\text{Bond distance}}$

$$= \frac{1.2 \times 10^{-18} \text{ esu.cm}}{1.0 \times 10^{-8} \text{ cm}} = 1.2 \times 10^{-10} \text{ esu}$$

The fraction of an electronic charge is

$$\frac{1.2 \times 10^{-10}}{4.8 \times 10^{-10}} = \frac{1}{4} \quad \therefore \text{Value of } x = 4$$

25. (2)

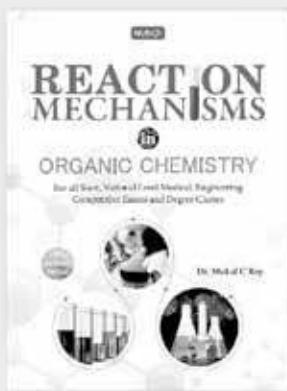
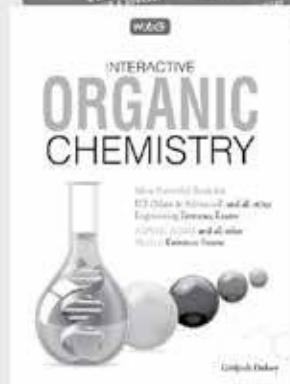
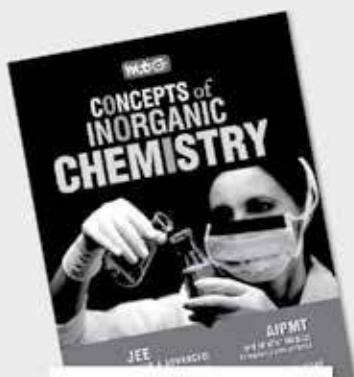
## HYDROGEN

1. (d) : Permanent hardness of water is due to the presence of soluble chlorides and sulphates of calcium and magnesium.

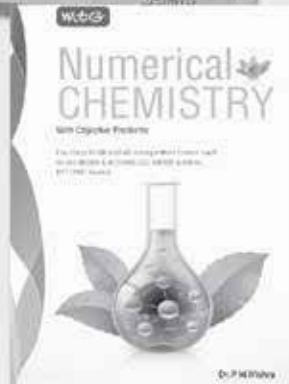
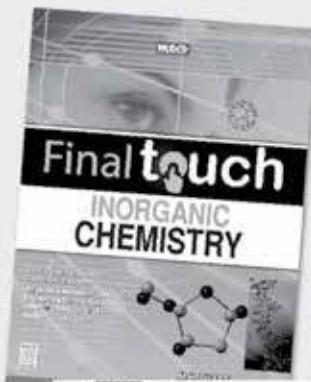
2. (a) : (a)  $Cu + HCl \longrightarrow$  No reaction

(b)  $3Fe + 4H_2O \xrightarrow{\text{Steam}} Fe_3O_4 + 4H_2$   
Ferrous ferric oxide

## Master Resource Books in Chemistry



These books comprehensively cover all topics, concepts and techniques to prepare students for all the competitive exams. i.e. JEE (Main & Advanced), PET, NEET, AIIMS and JIPMER.



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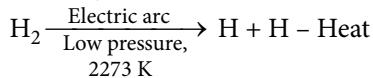
- (c)  $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$   
 (d)  $2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2$
3. (c)
4. (a):  $H_2SO_4$  acts as an oxidising agent and decomposes  $H_2O_2$ .  
 $H_2O_2 + [O] \rightarrow H_2O + O_2$
5. (b): When  $H_2O_2$  behaves as a reducing agent, it evolves molecular oxygen during the reaction. Therefore, only in option (b), it behaves as a reducing agent.
6. (a): Heavy water is manufactured by repeated electrolysis of water (containing a little NaOH).
7. (c): Hydrogen has ionization energy value which is too high as compared to alkali metals and too low as compared to halogens and thus, cannot be placed in any of these two groups.

8. (b) 9. (d)

10. (b): The two O-H bonds are in different planes due to repulsion between different bonding and antibonding orbitals.

11. (a, b, c)

12. (a, b, c) : Compounds which undergo reduction on heating with  $H_2$  are reduced by atomic H at ordinary temperature.



The H so produced is very reactive and its life is only one-third of a second.

13. (a, b, c, d) :

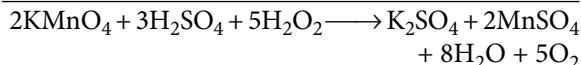
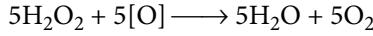
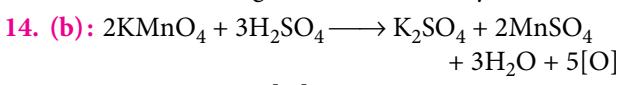
$$\text{Volume strength} = 5.6 \times \frac{\text{Percentage strength}}{\text{eq. wt. of } H_2O_2} \times 10 \\ = 5.6 \times \frac{6.8}{17} \times 10 = 22.4 \text{ V}$$

$$(a) \text{ Normality} = \frac{\text{Volume strength}}{5.6} = 4 \text{ N}$$

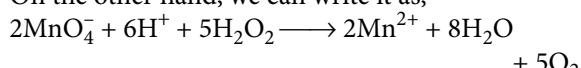
$$(b) \text{ Molarity} = \frac{\text{Volume strength}}{11.2} = 2 \text{ M}$$

$$(c) \text{ Volume strength} = 22.4 \text{ V}$$

$$(d) \text{ Volume strength} = 11.2 \times \text{molarity} = 22.4 \text{ V}$$



On the other hand, we can write it as,



15. (a):  $2I^- \rightarrow I_2$ , hence  $H_2O_2$  acts as an oxidising agent.

16. (b): Water gas is mixed with steam, producing  $CO_2$ .

17. (a): The hydrogen manufactured by the given method is utilised for synthesis of  $NH_3$  in which  $CO$  acts as a poison for catalyst. Thus, Ni is used to remove traces of  $CO$ .

18. (b) 19. (c)

20. (d): *Para*-hydrogen with lower energy is favoured at low temperature.

The thermal conductivity of *para*-hydrogen is 50% greater than that of *ortho*-hydrogen.

21. (a) 22. (a)

23. (7): Volume strength of  $H_2O_2 = 5.6 \times N$

$$10 \text{ vol. } H_2O_2 = \frac{10}{5.6} \text{ N } H_2O_2$$

$$15 \text{ vol. } H_2O_2 = \frac{15}{5.6} \text{ N } H_2O_2$$

$$20 \text{ vol. } H_2O_2 = \frac{20}{5.6} \text{ N } H_2O_2$$

As 500 mL of each is mixed then total volume of mixture = 1500 mL

Also this is diluted with 1700 mL, so total volume becomes 3200 mL

$$N \times 3200 = \frac{10 \times 500}{5.6} + \frac{15 \times 500}{5.6} + \frac{20 \times 500}{5.6}$$

$$\text{or } N_{H_2O_2} = \frac{500 \times 45}{5.6 \times 3200} = 1.255 \text{ N}$$

∴ Volume strength of  $H_2O_2 = 1.255 \times 5.6 = 7.03 \approx 7$

24. (5): 1 g-mole or 120 g  $MgSO_4 \equiv 1 \text{ g-mole}$   
 or 100 g  $CaCO_3$

$$6 \times 10^{-3} \text{ g } MgSO_4 = \frac{100 \times 6 \times 10^{-3}}{120} \\ = 5 \times 10^{-3} \text{ g of } CaCO_3$$

Thus, 1000 g of water contains  $MgSO_4$  equivalent to

$$5 \times 10^{-3} \text{ g of } CaCO_3 = \frac{5 \times 10^{-3}}{1000} \times 10^6$$

$10^6$  g of water will contain = 5 g of  $CaCO_3$

∴ Hardness of given water sample = 5 ppm

25. (4): Tritium T or  ${}^3_1H$ , the heaviest isotope of hydrogen has 1 proton, 2 neutrons and 1 electron. Hence, sum of protons, neutrons and electrons is 4.





# YOUR WAY CBSE XI

CHAPTERWISE PRACTICE PAPER : STATES OF MATTER | THERMODYNAMICS



Series 3

Time Allowed : 3 hours

Maximum Marks : 70

## 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 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

1. Under what conditions  $q$  and  $w$  become state functions?
2. What would have happened to the gas if the molecular collisions were not elastic?
3. The  $C_p$  and  $C_v$  of a gas are 20.834 and  $12.520 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. What is the atomicity of the gas?
4. How is the mole fraction of a gas component related to its partial pressure and the total pressure?
5. What is residual entropy?
6. Acetic acid (ethanoic acid) and hydrochloric acid react with KOH solution. The enthalpy of neutralisation of ethanoic acid is  $-55.8 \text{ kJ mol}^{-1}$  while that of hydrochloric acid is  $-57.1 \text{ kJ mol}^{-1}$ . Why are these two values different?
7. (a) Why does sharp glass edge become smooth on heating it upto its melting point in a flame? Explain which property of liquids is responsible for this phenomenon.  
(b) Which two other properties of liquids can be explained on the basis of the above property?
8. Distinguish between the total kinetic energy of a molecule and its translational kinetic energy. For what type of gas molecules these two are same?
9. (a) Define Charles' law.  
(b) What is the coefficient of volume expansion of a gas?
10. What do you understand by the term 'absolute zero temperature'? What is its significance?

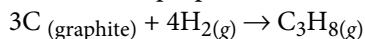
## OR

How does the magnitude of the enthalpy change depend on the strength of the intermolecular interaction for the substances undergoing phase changes? Explain with example.

11. Which of the following processes are accompanied by an increase of entropy?  
(a) Dissolution of iodine in a solvent.  
(b) HCl is added to  $\text{AgNO}_3$  solution and precipitate of  $\text{AgCl}$  is obtained.  
(c) A partition is removed to allow the gases to mix.

12. 20% of  $\text{N}_2\text{O}_4$  molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture.

13. Calculate the standard Gibbs energy change for the formation of propane at 298 K.



$$\Delta_f H^\circ \text{ for propane, } \text{C}_3\text{H}_8\text{(g)} = -103.8 \text{ kJ mol}^{-1}$$

$$(\text{Given : } S_m^\circ [\text{C}_3\text{H}_8\text{(g)}] = 270.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_m^\circ \text{ (graphite)} = 5.70 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{and } S_m^\circ [\text{H}_2\text{(g)}] = 130.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

14. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

15. 1 Litre flask containing  $\text{NH}_3\text{(g)}$  at 2.0 atm at 200 K is connected by a narrow tube of negligible volume to another 800 mL flask containing  $\text{HCl}\text{(g)}$  at 8.0 atm at 200 K. The two gases react according to equation :  $\text{NH}_3\text{(g)} + \text{HCl}\text{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$ ;  $\Delta H = -43 \text{ kJ/mol}$ . If heat capacity of  $\text{HCl}\text{(g)}$  is  $20 \text{ J K}^{-1} \text{ mol}^{-1}$ , determine the heat produced, final temperature and final pressure inside the flask. (The heat capacity of flask and volume of solid  $\text{NH}_4\text{Cl}$  in flask is negligible.)

16. (a) (i) How many calories are required to heat 100 g of copper ( $s = 0.092 \text{ cal/g/K}$ ) from 10 to 100°C?

(ii) The same quantity of heat as in (i) is added to 100 g of aluminium ( $s = 0.217 \text{ cal/g/K}$ ) at 10°C. Which gets hotter, the copper or aluminium?

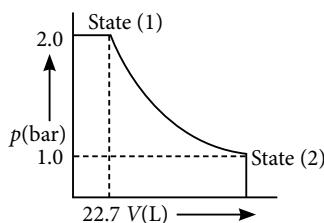
(b) How much heat is required to change 10 g ice at 0°C to steam at 100°C ? Latent heat of fusion and vaporization for  $\text{H}_2\text{O}$  are 80 cal/g and 540 cal/g respectively. Specific heat of water is 1 cal/g.

17. A student forgot to add the reaction mixture to the round bottom flask at 27°C but put it on the flame. After a lapse of time, he realised his mistake, using a pyrometer he found the temperature of the flask was 477°C. What fraction of air would have been expelled out?

### OR

The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15 g of aluminium reacts?

18. (a) 1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.  
(b) A certain volume of dry air at NTP is expanded reversibly to four times its volume isothermally. Calculate the final pressure.



19. A sample of 0.16 g  $\text{CH}_4$  was subjected to combustion at 27°C in a bomb calorimeter. 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 calorimeter system is  $17.7 \text{ kJ K}^{-1}$  and  $R$  is  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

20. Give reasons for the following :

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

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

21. Calculate the rise in temperature when a gas, for which  $\gamma = 1.5$ , is compressed to 27 times its original pressure, assuming the initial temperature to be 27°C.

22. (a) Calculate the maximum efficiency of an engine operating between 100°C and 25°C.

(b) Same mass of diamond and graphite (both being carbon) are burnt in oxygen. Will the heat produced be same or different? Why?

23. Sejal asked Saloni that why people are undergoing medical check up before going on Amarnath Yatra. Saloni explained the reason to Sejal and Sejal got satisfied, meanwhile Rishabh told that liquid boils at lower temperature at a hill station than in a plane area.

(a) What reason was explained by Saloni to satisfy Sejal?

(b) Why does liquid boil at lower temperature at hills stations?

(c) What values are associated with Saloni?

(d) What is critical temperature?

24. Nitrogen molecule ( $\text{N}_2$ ) has radius of about 0.2 nm. Assuming that nitrogen molecule is spherical in shape, calculate

- (a) volume of a single molecule of  $\text{N}_2$ .  
 (b) the percentage of empty space in one mole of  $\text{N}_2$  gas at S.T.P.

**OR**

- (a) When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why?  
 (b) Determine the value of  $\Delta H$  and  $\Delta U$  for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water behaves as an ideal gas and heat of evaporation of water is 540 cal  $\text{g}^{-1}$ .

25. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg  $\text{m}^{-3}$ . The vapours effuse through a small hole at a rate of 1.33 times faster than oxygen under the same conditions :

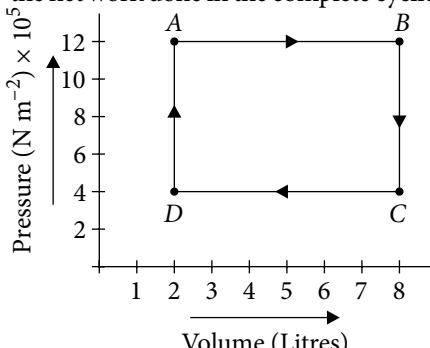
- (a) Determine : (i) molecular weight, (ii) molar volume, (iii) compressibility factor ( $Z$ ) of the vapours, (iv) Which forces among gas molecules are dominating, the attractive or the repulsive?  
 (b) If the vapours behave ideally at 1000 K, determine the average translational kinetic energy of a molecule.

**OR**

Two moles of a perfect gas undergo the following process :

- (a) A reversible isobaric expansion from (1 atm, 20 L) to (1 atm, 40 L).  
 (b) A reversible isochoric change of state from (1 atm, 40 L) to (0.5 atm, 40 L).  
 (c) A reversible isothermal compression from (0.5 atm, 40 L) to (1 atm, 20 L).  
 (i) Sketch with labels each of the process on the same  $P$ - $V$  diagram.  
 (ii) Calculate the total work ( $w$ ) and the total heat change ( $q$ ) involved in the above process.  
 (iii) What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process?

26. (a) The figure given below represents  $P$ - $V$  diagrams of different stages of a thermodynamic process. Calculate the work done in each stage and also the net work done in the complete cyclic process.



- (b) Give a statement which includes the main ideas of the first law and second law of thermodynamics.

**OR**

- (a) The composition of the equilibrium mixture ( $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ ), which is attained at 1200°C, is determined by measuring the rate of effusion through a pin hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (atomic weight of Kr is 84).  
 (b) The compression factor (compressibility factor) for 1 mol of a van der Waals' gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant  $a$ .

### SOLUTIONS

1. In a thermodynamically reversible process, on every collision, there would have been loss of energy. As a result, the molecules would have slowed down and ultimately settle down. The gas pressure would have gradually become zero.
2.  $\gamma = \frac{C_p}{C_v} = \frac{20.834}{12.520} = 1.66$   
 Therefore, the gas is monoatomic.
4. Mole fraction, is equal to the partial pressure divided by the total pressure.

$$x_i = \frac{P_i}{P_{\text{total}}}$$

5. The entropy possessed by a substance at absolute zero is called residual entropy.
6. Ethanoic acid is a weak acid while hydrochloric acid is strong acid (completely ionized). The enthalpy of neutralisation of weak acid (ethanoic acid) and strong base (KOH) is numerically less than  $-57.1 \text{ kJ mol}^{-1}$  (heat of neutralisation of strong acid and strong base) because the ionization of ethanoic acid is not complete in solution and some energy is utilised for dissociating acid molecules.
7. (a) On heating the glass, it melts and takes up rounded shape at the edges which has minimum surface area. This is due to the property of surface tension of liquids.  
 (b) The following two properties of liquids can be explained on the basis of surface tension :  
 (i) Capillary action of water.  
 (ii) Spherical shape of small droplets.

8. The total kinetic energy of a molecule includes the translational kinetic energy, rotational kinetic energy and vibrational kinetic energy.

For monoatomic gases, both rotational and vibrational kinetic energies are zero. Therefore, for these gases, total kinetic energy is equal to translational kinetic energy.

9. (a) Charles' law states that "The volume of a given amount of a gas at constant pressure varies directly with its absolute temperature.

$$V \propto T \text{ (pressure is constant)}$$

(b) According to Charles' law,

$$V_t = V_0 \left(1 + \frac{t}{273}\right) = V_0 (1 + \alpha t)$$

$$\alpha = \frac{1}{273} = \text{Coefficient of volume expansion}$$

here,  $V_0$  = Volume at  $0^\circ\text{C}$  and  $V_t$  = Volume at  $t^\circ\text{C}$

10. According to Charles' law, if a gas is cooled to  $-273^\circ\text{C}$ , its volume becomes zero as

$$\text{Volume at } -273^\circ\text{C} = V_0 \left(1 - \frac{273}{273}\right) = 0$$

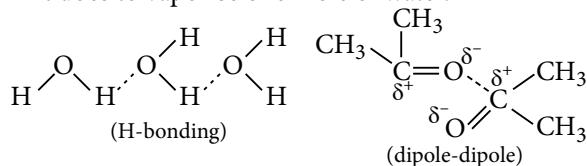
where,  $V_0$  = Volume at  $0^\circ\text{C}$

This means that  $-273^\circ\text{C}$  should be the lowest temperature because any further cooling would lead to a volume less than zero or negative volume which is meaningless. Therefore, this temperature is termed as absolute zero temperature. But volume never approaches zero at  $-273^\circ\text{C}$  because all gases condense to liquid or solid before the attainment of this temperature.

### OR

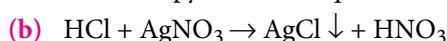
The magnitude of the enthalpy change depends directly on the strength of the intermolecular interaction.

For example, intermolecular hydrogen bonding between water molecules lead to large attractive intermolecular energy holding water molecules tightly in liquid phase. For an organic liquid such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mole of acetone than it does to vaporise one mole of water.



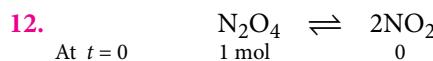
11. (a) Entropy is increased because solid iodine is converted into liquid phase (solution).

Order of entropy : Gases > liquids > solids



In this reaction, liquid HCl is mixed with the solution of AgNO<sub>3</sub> and the formation of AgCl(ppt.) occurs, hence entropy is decreased.

- (c) Entropy is increased because after removing the partition both the gases will mix and move upto larger space, thus the randomness of the molecules will increase.



At equilibrium    (1 - 0.2) mol        0.4

Total moles = 0.8 + 0.4 = 1.2

$$PV = nRT$$

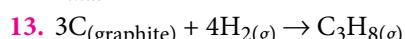
$$1 \times V = 1.2 \times 0.0821 \times 300 \quad (\because P = 760 \text{ torr} = 1 \text{ atm})$$

$$V = 29.556 \text{ L}$$

$$d_{\text{N}_2\text{O}_4} = \frac{m}{V} = \frac{0.8 \times 92}{29.556} = 2.490$$

$$d_{\text{NO}_2} = \frac{m}{V} = \frac{0.4 \times 46}{29.556} = 0.6225$$

$$d_{\text{mix}} = 2.490 + 0.6225 = 3.1125 \text{ g/L}$$



$$\Delta_r H^\circ = \Delta_f H^\circ (\text{C}_3\text{H}_8) - \{3\Delta_f H^\circ (\text{C}) + 4\Delta_f H^\circ (\text{H}_2)\}$$

$$= -103.8 - 0 - 0 = -103.8 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = S_m^\circ (\text{C}_3\text{H}_8) - \{3S_m^\circ (\text{C}) + 4S_m^\circ (\text{H}_2)\}$$

$$= 270.2 - \{3 \times 5.70 + 4 \times 130.7\}$$

$$= 270.2 - 539.9 = -269.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$= -103.8 - 298 \times (-269.7 \times 10^{-3}) = -23.43 \text{ kJ mol}^{-1}$$

14. The two conditions under which heat becomes independent of path are

(i) when volume remains constant

(ii) when pressure remains constant.

(i) At constant volume : By first law of thermodynamics,

$$\Delta U = q + w \quad \text{or} \quad q = \Delta U - w$$

$$w = -P\Delta V \quad \therefore \quad q = \Delta U + P\Delta V$$

But as volume remains constant,  $\Delta V = 0$

$$\therefore q_v = \Delta U$$

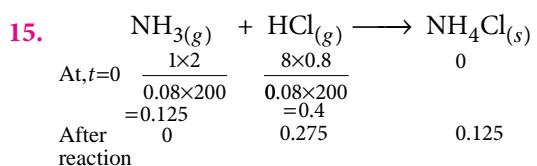
As  $\Delta U$  is a state function. Hence,  $q_v$  is a state function.

(ii) At constant pressure :  $q_p = \Delta U + P\Delta V$

$$\text{But } \Delta U + P\Delta V = \Delta H$$

$$\therefore q_p = \Delta H$$

As  $\Delta H$  is a state function, therefore,  $q_p$  is a state function.



Thus, heat produced during reaction,

$$Q = n_{\text{NH}_4\text{Cl}} \times \Delta H = 0.125 \times 43 \times 10^3 = 5375 \text{ J}$$

∴ During the formation of 1 mole  $\text{NH}_4\text{Cl}_{(s)}$ , heat produced is  $\Delta H$ . Because this heat is used to increase the temperature of HCl in both the flasks.

Thus,  $Q = n \times C_v \times \Delta T$

$$5375 = 0.275 \times 20 \times \Delta T \Rightarrow \Delta T = 977.27 \text{ K}$$

$$\therefore T_f = 200 + 977.27 = 1177.27 \text{ K}$$

$$\text{and } P_f = \frac{nRT_f}{V} = \frac{0.275 \times 0.0821 \times 1177.27}{1.8} = 14.76 \text{ atm} \quad (\text{Here, } V = 1 + 0.8 = 1.8 \text{ L})$$

16. (a) (i)  $\Delta H = ms \Delta T$

$$= (0.092 \text{ cal/g/K}) (100 \text{ g}) [(373 - 283) \text{ K}] = 828 \text{ cal}$$

(ii) Since the specific heat capacity of copper is less than that of aluminium, less heat is required to raise the temperature of a mass of copper by 1 K than is required for an equal mass of aluminium. Hence, the copper gets hotter.

(b) Total heat absorbed

$$\begin{aligned} &= \Delta H_{\text{fusion}} + \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}} \\ &= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200 \text{ cal} \end{aligned}$$

17. Suppose the number of moles of gas present at  $27^\circ\text{C}$  in flask of volume  $V$  at pressure  $P$  is  $n_1$ , then assuming ideal gas behaviour,

$$PV = n_1 R \times 300 \quad \dots(i)$$

Suppose,  $n_2$  = number of moles at  $477^\circ\text{C}$ , then

$$PV = n_2 R \times 750 \quad \dots(ii)$$

From eq. (i) and eq. (ii), we get

$$n_2 = \frac{300}{750} \times n_1 = 0.4 n_1$$

∴ 0.6 moles have been expelled out.

**OR**

The reaction between aluminium and caustic soda is  
 $2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2$

$$2 \times 27 = 54 \text{ g} \quad 3 \times 22.4 \text{ L}$$

$$= 54 \text{ g} \quad \text{at STP}$$

∴ 54 g of Al produces  $\text{H}_2$  at S.T.P. =  $3 \times 22.4 \text{ L}$

0.15 g of Al will produce  $\text{H}_2$  at S.T.P.

$$= \frac{3 \times 22.4}{54} \times 0.15 = 0.186 \text{ L}$$

Applying ideal gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \frac{1 \times 0.186}{273} = \frac{0.987 \times V_2}{293}$$

$$V_2 = \frac{293}{0.987} \times \frac{1 \times 0.186}{273} = 0.2030 \text{ L} = 203 \text{ mL}$$

18. (a) It is clear from the figure that the process has been carried out in infinite steps and therefore, it is an isothermal reversible expansion process.

$$\begin{aligned} w &= -2.303 nRT \log \frac{V_2}{V_1} = -2.303 nRT \log \frac{P_1}{P_2} \\ &= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log 2 \\ &= -1717.6 \text{ J} \end{aligned}$$

- (b) At constant temperature,

$$\begin{aligned} P_1 V_1 &= P_2 V_2 \\ P_2 &= \frac{P_1 V_1}{V_2} = \frac{1 \times V_1}{4V_1} = 0.25 \text{ atm} \end{aligned}$$

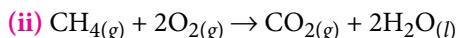
19. (i) Heat of combustion at constant volume,

$\Delta U$  = Heat capacity of calorimeter system ×

$$\text{rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{6}{0.6} = 8$$

$$\Delta U = -885 \text{ kJ mol}^{-1}$$



$$\Delta n_g = 1 - 3 = -2, T = 300 \text{ K},$$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Heat of combustion at constant pressure,

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

$$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$$

$$= -889.988 \text{ kJ mol}^{-1}$$

20. (a) At 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.

- (b) In summer, due to higher temperature, the average kinetic energy of the air molecules inside the tyres 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.

**21.** From adiabatic gas equation,  $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{\gamma-1}$

Given that,  $\gamma = 1.5$ ,  $P_2/P_1 = 27$ ,  $T_1 = 300$  K

Substituting the values,

$$\left(\frac{300}{T_2}\right)^{1.5} = \left(\frac{1}{27}\right)^{1.5-1}$$

After taking log on both sides,

$$1.5(\log 300 - \log T_2) = 0.5(\log 1 - \log 27)$$

$$\log 300 - \log T_2 = -\frac{0.5 \log 27}{1.5}$$

$$\log T_2 = \log 300 + 0.33 \log 27$$

$$= 2.477 + 0.4723 = 2.9493$$

$$\therefore T_2 = \text{antilog } 2.9493 = 889.81$$

$$= (889.81 - 273)^\circ\text{C} = 616.81^\circ\text{C}$$

Hence, the rise in temperature

$$= 616.81 - 27 = 589.81^\circ\text{C}$$

**22. (a)** Efficiency =  $\frac{T_2 - T_1}{T_2}$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$\text{Efficiency} = \frac{373 - 298}{373} = \frac{75}{373} = 0.0 = 0 \%$$

**(b)** Heat evolved will be different. This is because they have different crystal structures.

**23. (a)** At higher altitude, atmospheric pressure is low, so generally people have difficulty in breathing therefore, people must need to undergo for medical check-up before going on Amarnath Yatra.

**(b)** At higher altitude, atmospheric pressure is low. Therefore, the liquid boils at lower temperature.

**(c)** Knowledge, health concern.

**(d)** When density of liquid and vapours become the same, the clear boundary between liquid and vapours disappears. This temperature is called critical temperature.

**24. (a)** The volume of a sphere =  $\frac{4}{3}\pi r^3$

where,  $r$  is the radius of the sphere.

For  $\text{N}_2$  molecule,

$$r = 0.2 \text{ nm} = 0.2 \times 10^{-9} \text{ m} = 2 \times 10^{-8} \text{ cm}$$

$$\begin{aligned} \text{Volume of a molecule of } \text{N}_2 &= \frac{4}{3} \times \frac{2}{7} \times (2 \times 10^{-8})^3 \text{ cm}^3 \\ &= 3.35 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

**(b)** To calculate the empty space, let us first find the total volume of 1 mole ( $6.02 \times 10^{23}$  molecules) of  $\text{N}_2$ .

$$\begin{aligned} \text{Volume of } 6.02 \times 10^{23} \text{ molecules of } \text{N}_2 \\ = 3.35 \times 10^{-23} \times 6.02 \times 10^{23} = 20.17 \text{ cm}^3 \end{aligned}$$

Now, volume occupied by 1 mole of gas at S.T.P.  
 $= 22.4 \text{ litre} = 22400 \text{ cm}^3$

$$\begin{aligned} \text{Empty volume} &= \text{Total volume of gas} - \\ &\quad \text{Volume occupied by molecules} \\ &= (22400 - 20.17) \text{ cm}^3 \\ &= 22379.83 \text{ cm}^3 \end{aligned}$$

$$\therefore \text{Percentage empty space} = \frac{\text{Empty space}}{\text{Total volume}} \times 100 = \frac{22379.83}{22400} \times 100 = 99.9 \%$$

Thus, 99.9% of space of 1 mole of  $\text{N}_2$  at S.T.P is empty.

## OR

**(a)** In an ideal gas, there are no intermolecular forces of attraction and therefore, no force opposes the expansion in vacuum. Hence, no energy is required to overcome these forces. Moreover, when a gas expands against vacuum, work done is zero because  $p_{\text{ext}} = 0$ . Therefore, internal energy of the system does not change, i.e., there is no absorption or evolution of heat.

**(b)** Total heat change,

$$\Delta H = 90.0 \times 540 = 48600 \text{ cal}$$

$$\text{Now, } \Delta H = \Delta U + P\Delta V$$

$$\text{Here, } \Delta V = (V_{\text{vapour}} - V_{\text{liquid}}) = V_{\text{vapour}}$$

(Vol. of liquid is negligible as compared to volume of vapour)

$$\Delta H = \Delta U + PV_{\text{vapour}} = \Delta U + nRT$$

$$n = \frac{90}{18} = 5 \text{ mol}, R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}, T = 373 \text{ K}$$

$$\therefore \Delta H = \Delta U + 5 \times 2 \times 373$$

$$\Delta H = \Delta U + 3730; \quad \Delta U = \Delta H - 3730$$

$$= 48600 - 3730 = 44870 \text{ cal}$$

$$\text{(a) (i)} \quad \frac{r_{\text{vapour}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{vapour}}}}; \quad 1.33 = \sqrt{\frac{32}{M_{\text{vapour}}}}$$

$$M_{\text{vapour}} = 18.1$$

$$\text{(ii) Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$$

$$= \frac{18.1}{0.36 \times 10^3} = 50.27 \times 10^{-3} \text{ m}^3 / \text{mol}$$

(iii) Compressibility factor,

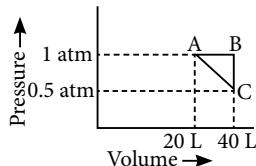
$$Z = \frac{PV}{RT} = \frac{101325 \times 50.27 \times 10^{-3}}{8.314 \times 500} = 1.225$$

(iv)  $Z > 1$ , shows that repulsive forces are dominant.

(b) Translational K.E. per molecule  $= \frac{3}{2} \times \frac{R}{N_A} \times T$   
 $= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 1000 = 2.07 \times 10^{-20} \text{ J}$

OR

(i)  $AB \rightarrow$  Isobaric process  
 $BC \rightarrow$  Isochoric process  
 $CA \rightarrow$  Isothermal compression



(ii) Total work  $= w_{AB} + w_{BC} + w_{CA}$

$$\begin{aligned} w &= -P \times (V_2 - V_1) + 0 + 2.303 nRT \log(V_2/V_1) \\ &= -1 \times (40 - 20) + 0 + 2.303 P_1 V_1 \times \log(40/20) \\ &\quad [nRT = P_1 V_1] \\ &= -20 + 2.303 \times (20) \log \frac{40}{20} \\ &= -20 + (2.303)(20)(0.301029) \\ &= -20 + 13.86539574 = -6.13 \text{ L atm} \\ &= \frac{6.13 \times 8.314 \text{ J}}{0.0821} = -620.76 \text{ J} \\ w &= q = -620.76 \text{ J} \end{aligned}$$

(iii) In cyclic process :

$$\Delta U = 0, \Delta H = 0 \text{ and } \Delta S = 0$$

26. (a) Process  $A \rightarrow B$  (expansion),  $P = 12 \times 10^5 \text{ N m}^{-2}$ ,  
 $\Delta V = 8 - 2 = 6 \text{ L} = 6 \times 10^{-3} \text{ m}^3$   
 $\therefore$  Work done  $= -P\Delta V = -(12 \times 10^5) \times (6 \times 10^{-3}) \text{ J}$   
 $= -7200 \text{ J}$

Process  $B \rightarrow C$ , No change in volume, i.e.,  $\Delta V = 0$

$$\therefore \text{Work done} = 0$$

Process  $C \rightarrow D$  (contraction),  $\Delta V = 8 - 2 = 6 \text{ L}$   
 $= 6 \times 10^{-3} \text{ m}^3, P = 4 \times 10^5 \text{ N m}^{-2}$

$$\therefore \text{Work done} = P\Delta V = (4 \times 10^5) (6 \times 10^{-3}) = 2400 \text{ J}$$

Process  $D \rightarrow A$ , No change in volume, i.e.,  $\Delta V = 0$

$$\therefore \text{Work done} = 0$$

$\therefore$  Net work done in the complete cyclic process

$$= -7200 + 2400 \text{ J} = -4800 \text{ J}$$

-ve sign shows that net work has been done by the gas.

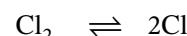
(b) The energy of the universe is constant, whereas the entropy of the universe is continuously increasing and tends to maximum.

OR

(a) According to Graham's law of diffusion

$$\frac{r_{\text{mix}}}{r_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{mix}}}} \Rightarrow 1.16 = \sqrt{\frac{84}{M_{\text{mix}}}}$$

$$\therefore M_{\text{mix}} = 62.425$$



$$\begin{array}{lll} \text{Initial mole} & 1 & 0 \\ \text{Final mole} & 1-x & 2x \end{array}$$

$$\text{Total moles} = 1 - x + 2x = 1 + x$$

$$\therefore M_{\text{mix}} = \frac{2x(3.5) + (1-x) \times 7}{1+x} = 6.4$$

$$\frac{7}{1+x} = 6.4$$

$$x = 0.1373 = 13.7\% \text{ dissociated}$$

(b) For 1 mol of a gas, the van der Waals' equation is

$$\left( p + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

Ignoring  $b$ , we get (given volume of gas molecule is negligible)

$$\left( p + \frac{a}{V_m^2} \right) V_m = RT \Rightarrow pV_m + \frac{a}{V_m} = RT$$

$$\frac{pV_m}{RT} + \frac{a}{V_m RT} = 1 \Rightarrow Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_m RT} \quad \dots(i)$$

$$Z = \frac{pV_m}{RT} = 0.5 \Rightarrow V_m = \frac{0.5 RT}{p}$$

$$\text{Now, from eq. (i), } 0.5 = 1 - \frac{a}{(0.5 RT / p) RT}$$

$$a = (0.5) \left( \frac{0.5 RT}{p} \right) RT = 0.25 \frac{R^2 T^2}{p}$$

Substituting the given values, we get

$$a = (0.25) \left[ \frac{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})^2 (273 \text{ K})^2}{100 \text{ atm}} \right]$$

$$= 1.2528 \text{ L}^2 \text{ atm mol}^{-2}$$



# MPP-5 | MONTHLY Practice Problems

Class XI

This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

## Equilibrium

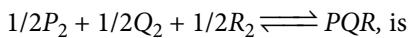
Total Marks : 120

**NEET / AIIMS**

**Only One Option Correct Type**

- Vapour density of  $\text{PCl}_5$  at  $200^\circ\text{C}$  is 70. Determine the degree of dissociation of  $\text{PCl}_5$  at this temperature.  
 (a) 48.9% (b) 57.9% (c) 38.8% (d) 46.1%
- Starting with 1 mol of  $\text{O}_{2(g)}$  and 2 mol of  $\text{SO}_{2(g)}$  the equilibrium for the formation of  $\text{SO}_{3(g)}$  was established at a certain temperature. If  $V$  is the volume of the vessel and  $2x$  is the number of moles of  $\text{SO}_{3(g)}$  present, the equilibrium constant will be  
 (a)  $\frac{x^2V}{(1-x)^3}$  (b)  $\frac{4x^2V}{(2-x)(1-x)}$   
 (c)  $\frac{(1-x)^3}{2V}$  (d)  $\frac{x^2V}{(2-x)(1-x)V}$
- Which one of the following solutions will have pH close to unity?  
 (a) 100 mL of M/10 HCl + 100 mL of M/10 NaOH  
 (b) 55 mL of M/10 HCl + 45 mL of M/10 NaOH  
 (c) 10 mL of M/10 HCl + 90 mL of M/10 NaOH  
 (d) 75 mL of M/5 HCl + 25 mL of M/5 NaOH
- When different types of salts have nearly same solubility product constant ( $K_{sp}$ ) which is lesser than  $K_{sp}$  value of one salt, then the most soluble salt is the one  
 (a) which produces maximum number of ions  
 (b) which produces minimum number of ions  
 (c) which produces more charge on ion  
 (d) none of these.
- Consider the following reactions in which all the reactants and the products are in gaseous state :  
 $2PQ \rightleftharpoons P_2 + Q_2 ; K_1 = 2.5 \times 10^5$   
 $PQ + 1/2R_2 \rightleftharpoons PQR ; K_2 = 5 \times 10^{-3}$   
 The value of  $K_3$  for the equilibrium :

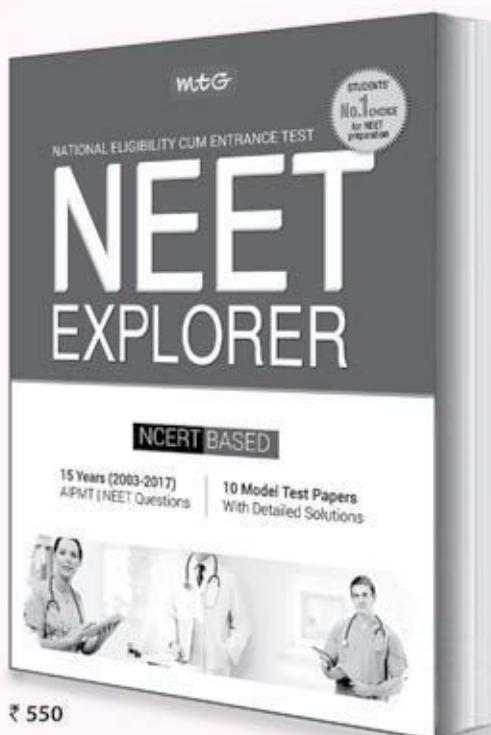
Time Taken : 60 Min.



- (a)  $2.5 \times 10^{-3}$  (b)  $2.5 \times 10^3$   
 (c)  $1.0 \times 10^{-5}$  (d)  $5.0 \times 10^3$

- The following equilibrium is established when hydrogen chloride is dissolved in acetic acid,  
 $\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$   
 The set that characterises the conjugate acid-base pairs is  
 (a) ( $\text{HCl}$ ,  $\text{CH}_3\text{COOH}$ ) and ( $\text{CH}_3\text{COOH}_2^+$ ,  $\text{Cl}^-$ )  
 (b) ( $\text{HCl}$ ,  $\text{CH}_3\text{COOH}_2^+$ ) and ( $\text{CH}_3\text{COOH}$ ,  $\text{Cl}^-$ )  
 (c) ( $\text{CH}_3\text{COOH}_2^+$ ,  $\text{HCl}$ ) and ( $\text{Cl}^-$ ,  $\text{CH}_3\text{COOH}$ )  
 (d) ( $\text{HCl}$ ,  $\text{Cl}^-$ ) and ( $\text{CH}_3\text{COOH}_2^+$ ,  $\text{CH}_3\text{COOH}$ )
- One mole of  $\text{N}_2\text{O}_4(g)$  at  $300\text{ K}$  is kept in a closed container under one atmosphere. It is heated to  $600\text{ K}$  when 20% by mass of  $\text{N}_2\text{O}_4(g)$  decomposes to  $\text{NO}_{2(g)}$ . The resultant pressure is  
 (a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm
- A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionisation constant of pyridine.  
 (a)  $1.8 \times 10^{-9}$  (b)  $2.1 \times 10^{-8}$   
 (c)  $1.5 \times 10^{-9}$  (d)  $1.0 \times 10^{-9}$
- For a reaction  $2A + B \rightleftharpoons C + D$ , the value of  $K_p$  will be :  
 (a)  $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{V_P}{RT^2}$  (b)  $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{P}{RT}$   
 (c)  $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{RT^2}{V_P}$  (d)  $K_p = \frac{n_C n_D}{n_A^2 n_B} \frac{V_P}{RT}$
- The equilibrium constant for the following reaction,  
 $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_{2(g)}$  is  $K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$

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- 10 Model Test Papers based on latest NEET syllabus
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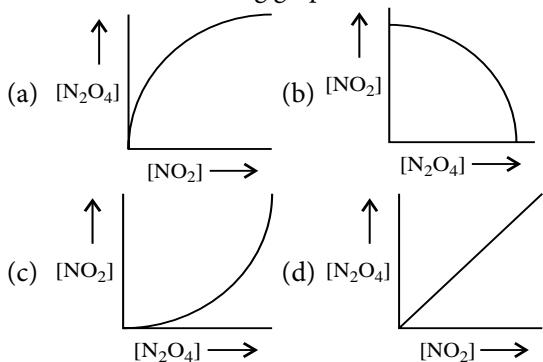


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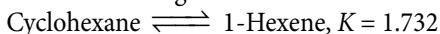
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Which of the following graphs is correct?



11. For the following isomerisation reaction :



Which of the following statements holds good at point 'A'?

- (a)  $Q > K$
- (b)  $Q < K$
- (c)  $Q = K = 1$
- (d)  $Q = K = 1.732$

12. The decreasing base strength of



- (a)  $\text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{HC}\equiv\text{C}^- > \text{OH}^-$
- (b)  $\text{HC}\equiv\text{C}^- > \text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{OH}^-$
- (c)  $\text{OH}^- > \text{NH}_2^- > \text{HC}\equiv\text{C}^- > \text{CH}_3\text{CH}_2^-$
- (d)  $\text{NH}_2^- > \text{HC}\equiv\text{C}^- > \text{OH}^- > \text{CH}_3\text{CH}_2^-$

#### Assertion & Reason Type

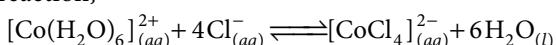
**Directions :** In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (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 :**  $K_p$  can be equal to or less than or even greater than the value of  $K_c$ .

$$\text{Reason : } K_p = K_c (RT)^{\Delta n}$$

14. **Assertion :** On cooling a freezing mixture, colour of the mixture turns to pink from deep blue for a reaction,



**Reason :** Reaction is endothermic so on cooling, the reaction moves to backward direction.

15. **Assertion :** Common salt is added during manufacturing of soap.

**Reason :** Common salt helps in the formation of soap.

#### JEE MAIN / JEE ADVANCED

##### Only One Option Correct Type

16. The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reactions :  $X \rightleftharpoons{} 2Y$  and  $Z \rightleftharpoons{} P + Q$ , respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is  
 (a) 1 : 9 (b) 1 : 36 (c) 1 : 1 (d) 1 : 3

17. Which of the following is not correct about the percentage ionisation of  $\text{BOH}$ ?

$$(a) \frac{K_w[\text{H}^+]}{K_b + K_w} \quad (b) 100 \times \sqrt{\frac{K_b}{C}}$$

$$(c) \frac{100}{1 + 10^{(pK_b - pOH)}} \quad (d) \frac{K_b \times 100}{K_b + \text{OH}^-}$$

18. The pH of pure water at  $25^\circ\text{C}$  and  $35^\circ\text{C}$  are 7 and 6 respectively. The heat of formation of water from  $\text{H}^+$  and  $\text{OH}^-$  is  
 (a) 84.551 kcal mol $^{-1}$  (b) -84.551 kcal mol $^{-1}$   
 (c) 74.551 kcal mol $^{-1}$  (d) -74.551 kcal mol $^{-1}$

19. Ammonia under a pressure of 15 atm at  $27^\circ\text{C}$  is heated to  $347^\circ\text{C}$  in a closed vessel in the presence of a catalyst. Under the conditions,  $\text{NH}_3$  is partially decomposed according to the equation,  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ . The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atm. Calculate the percentage of  $\text{NH}_3$  actually decomposed.  
 (a) 65% (b) 61.3% (c) 62.5% (d) 64%

##### More than One Options Correct Type

20. When two reactants, A and B are mixed to give two products, C and D, the reaction quotient, (Q) at the initial stages of the reaction  
 (a) is zero (b) decreases with time  
 (c) is independent of time (d) increases with time.

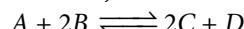
21. Which of the following are heterogeneous systems?  
 (a) Ice  $\rightleftharpoons$  Water (b) Water  $\rightleftharpoons$  Liquid  
 (c) S<sub>Rhombic</sub>  $\rightleftharpoons$  S<sub>Monoclinic</sub>  
 (d) C<sub>Diamond</sub>  $\rightleftharpoons$  C<sub>Amorphous</sub>

22. A reaction  $\text{S}_{8(g)} \rightleftharpoons 4\text{S}_{2(g)}$  is carried out by taking 2 moles of  $\text{S}_{8(g)}$  and 0.2 mole of  $\text{S}_{2(g)}$  in a reaction vessel of 1 litre at  $627^\circ\text{C}$ . Which of the following are correct if  $K_c = 6.30 \times 10^{-6}$ ?  
 (a) Reaction quotient is  $8 \times 10^{-4}$   
 (b) Reaction proceeds in backward direction  
 (c)  $K_p = 2.55 \text{ atm}^3$   
 (d) Reaction proceeds in forward direction

23. The solubility of a sparingly soluble salt  $A_xB_y$  in water at  $25^\circ\text{C} = 1.4 \times 10^{-4}$  M. The solubility product is  $1.1 \times 10^{-11}$ . The possibilities are  
 (a)  $x = 1, y = 2$       (b)  $x = 2, y = 1$   
 (c)  $x = 1, y = 3$       (d)  $x = 3, y = 1$

#### Integer Answer Type

24. In the study of reaction,



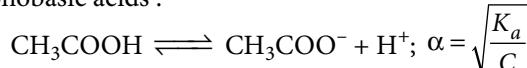
A and B were mixed in a reaction vessel at  $300\text{ K}$ . The initial concentration of B was 1.5 times the initial concentration of A. After the equilibrium has been attained, the equilibrium concentrations of A and D were equal. The value of equilibrium constant at  $300\text{ K}$  is

25. In 1 L saturated solution of  $\text{AgCl}$  [ $K_{sp(\text{AgCl})} = 1.6 \times 10^{-10}$ ], 0.1 mol of  $\text{CuCl}$  [ $K_{sp(\text{CuCl})} = 1 \times 10^{-6}$ ] is added. The resultant concentration of  $\text{Ag}^+$  in the solution is  $1.6 \times 10^{-x}$ . The value of  $x$  is  
 26. A mixture of  $\text{N}_2$  and  $\text{H}_2$  in the molar ratio 1 : 3 attains equilibrium when 50% of mixture has reacted. If  $P$  is the total pressure of the mixture, the partial pressure of  $\text{NH}_3$  formed is  $P/y$ . The value of  $y$  is

#### Comprehension Type

The concentration of hydrogen ion is a measure of acidity or alkalinity of a solution.

For monobasic acids :



where,  $K_a$  = Dissociation constant of acid

$C$  = Molarity of acid

$$[\text{H}^+] = C\alpha, [\text{H}^+] = \sqrt{K_a C}$$

pH of a weak acid can be calculated using  $[\text{H}^+]$  by any of above methods.

$$[\text{H}^+]_{\text{Total}} = \sqrt{C_1 K_{a_1} + C_2 K_{a_2}} \quad (\text{when two weak acids are mixed})$$

$[\text{H}^+]$  of polyprotic acid (Weak,  $\text{H}_3\text{A}$ ) (has dissociation constants  $K_{a_1} \gg K_{a_2} \gg K_{a_3}$ ) ; will be contributed by first dissociation at the most.

27. What will be the sulphide ion concentration of a dilute solution that has been saturated with 0.1 M

$\text{H}_2\text{S}$  if the pH of the solution is 3?  
 (Given :  $K_{a_1} = 1 \times 10^{-7}$ ;  $K_{a_2} = 1.3 \times 10^{-13}$ )

- (a)  $1.25 \times 10^{-11}$       (b)  $1.3 \times 10^{-13}$   
 (c)  $1.45 \times 10^{-9}$       (d)  $1.3 \times 10^{-15}$

28. The pH of 0.01 M  $\text{HCOOH}$  ( $K_a = 1.4 \times 10^{-4}$ ) will be  
 (a) 2.928      (b) 3.296      (c) 4.962      (d) 5.926

#### Matrix Match Type

29. Match the Column I with Column II and choose the correct option using the codes given below.

##### Column I

##### (Salt)

- (A) Zirconium phosphate  
 (B) Aluminium phosphate  
 (C) Calcium phosphate  
 (D) Sodium phosphate

##### Column II

##### (Solubility product)

- (p)  $27 S^4$   
 (q)  $108 S^5$   
 (r)  $6912 S^7$   
 (s)  $S^2$

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

30. Match the Column I with Column II and choose the correct option using the codes given below.

##### Column I

##### (Salt)

- (A)  $\text{NaCl}$

##### Column II

##### (Degree of hydrolysis)

$$(p) h = \sqrt{\frac{K_w}{C \cdot K_b}}$$

- (B)  $\text{CH}_3\text{COONa}$

$$(q) h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

- (C)  $\text{NH}_4\text{Cl}$

(r) No hydrolysis

- (D)  $\text{CH}_3\text{COONH}_4$

$$(s) h = \sqrt{\frac{K_w}{C \cdot K_a}}$$

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



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## SELF CHECK



#### Check your score! If your score is

> 90%

**EXCELLENT WORK !** You are well prepared to take the challenge of final exam.

90-75%

**GOOD WORK !**

You can score good in the final exam.

74-60%

**SATISFACTORY !**

You need to score more next time.

< 60%

**NOT SATISFACTORY!** Revise thoroughly and strengthen your concepts.

# NEET|JEE ESSENTIALS

Class  
XII

Maximise your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

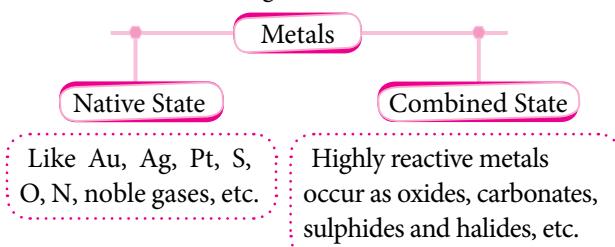
## Unit 3

### General Principles and Processes of Isolation of Elements | *p*-Block Elements (Group 15 to 18)

#### GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

##### GENERAL INTRODUCTION

The percentage of different elements in the earth crust are : O - 49%, Si - 26%, Al - 7.5%, Fe - 4.2%, Ca - 3.2%, Na - 2.4%, K - 2.3%, Mg - 2.5%, H - 1%

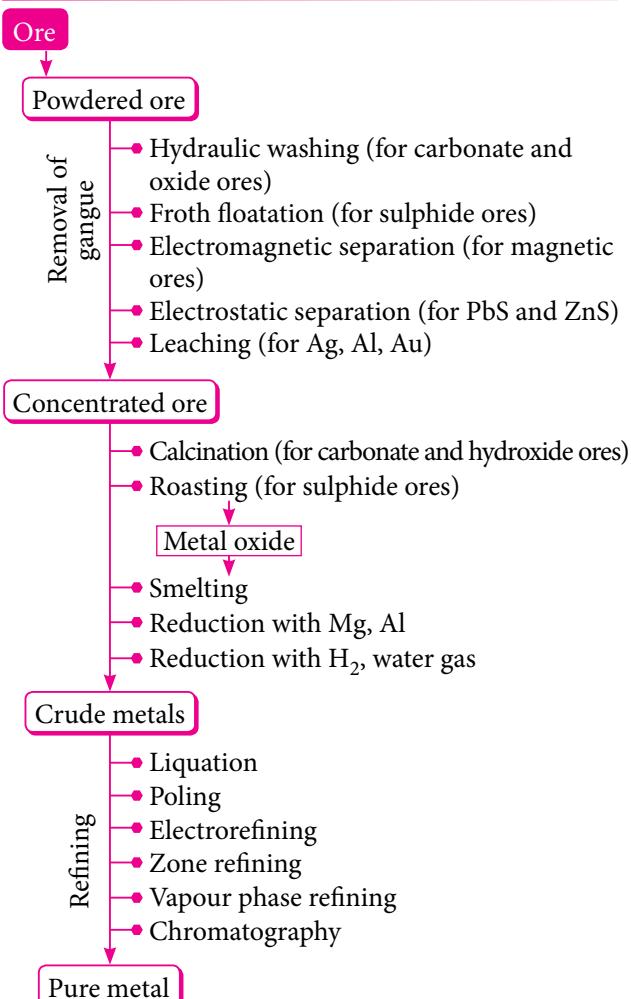


##### ORES / MINERALS

Combined state	Element	Ore/mineral
Oxides	Fe	Haematite ( $\text{Fe}_2\text{O}_3$ ) Magnetite ( $\text{Fe}_3\text{O}_4$ ) Limonite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) Chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ )
	Al	Bauxite ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ) Diaspore ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) Corundum ( $\text{Al}_2\text{O}_3$ )
	Zn	Zincite ( $\text{ZnO}$ )

Copper	Cu	Cuprite ( $\text{Cu}_2\text{O}$ )
Carbonates	Ca	Calcite ( $\text{CaCO}_3$ )
	Mg	Magnesite ( $\text{MgCO}_3$ )
	Cu	Malachite [ $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ]
	Zn	Calamine ( $\text{ZnCO}_3$ )
	Fe	Siderite ( $\text{FeCO}_3$ )
Sulphides	Fe	Iron pyrite ( $\text{FeS}_2$ )
	Cu	Copper glance ( $\text{Cu}_2\text{S}$ )
	Hg	Cinnabar ( $\text{HgS}$ )
	Zn	Zinc blende ( $\text{ZnS}$ )
	Pb	Galena ( $\text{PbS}$ )
	Ag	Argentite or Silver glance ( $\text{Ag}_2\text{S}$ )
Halides	Na	Common salt or Rock salt ( $\text{NaCl}$ )
	Al	Cryolite ( $\text{Na}_3\text{AlF}_6$ )
	K, Mg	Carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ )
	Ag	Horn silver ( $\text{AgCl}$ )

## EXTRACTION OF METALS

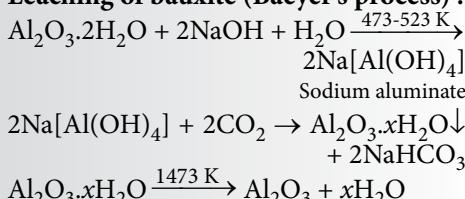


## Conversion of ore into metal oxide

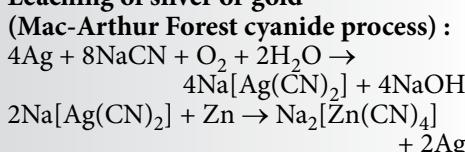
### Calcination

- Heating of ore below its fusion temperature in absence of air.
- For carbonate and hydroxide ores.
- In reverberatory furnace. e.g.,  $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2 \uparrow$

### Leaching of bauxite (Baeyer's process) :



### Leaching of silver or gold



### Roasting

- Ore is heated in presence of air.
  - For sulphide ores.
  - In reverberatory or blast furnace.
- e.g.,  $2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2 \uparrow$

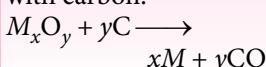
## Reduction of metallic oxide to free metal

### Pyrometallurgy

Heating of metal oxide with a suitable reducing agent.

### Smelting

Reduction of oxides with carbon.



### Self reduction (Auto-reduction)

Sulphide ores of less electropositive metals like Hg, Pb, Cu, etc. are heated in air.

### By aluminium (Goldschmidt alumino thermite process)

Reduction of metal oxide to metal by aluminium powder.  $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

### Electrolytic reduction

The oxides, hydroxides or chlorides of highly electropositive metals like Na, K, Mg, Ca and Al are extracted by electrolytic method, in their fused state. Electrolysis of this method is based on equation  $\Delta G^\circ = -nFE^\circ$ .

## CONCENTRATION OF ORE

### Froth floatation

- Based on preferential wetting of ore particles by oil (pine oil).
- Ore particles become light and form froth.
- Froth can be stabilised by stabilisers (aniline or cresols).

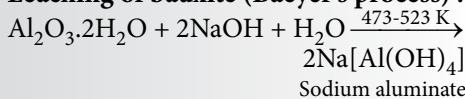
### Electromagnetic separation

- Conveyor belt moving over two rollers, one of which is magnetic in nature.
- Magnetic ores are attracted by the magnetic roller.

### Leaching

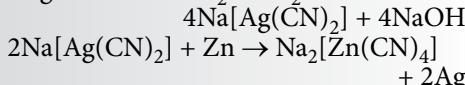
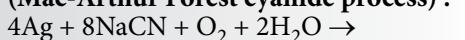
- It involves the treatment of the powdered ore with a suitable reagent so as to make it soluble while impurities remain insoluble.

### Leaching of bauxite (Baeyer's process) :



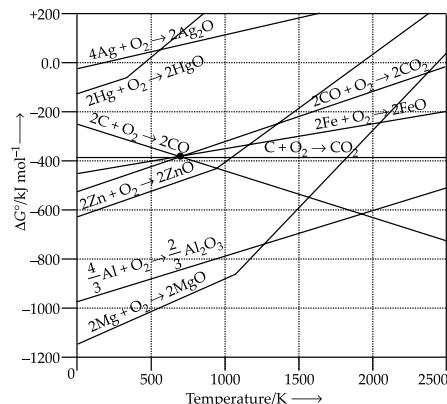
### Leaching of silver or gold

### (Mac-Arthur Forest cyanide process) :



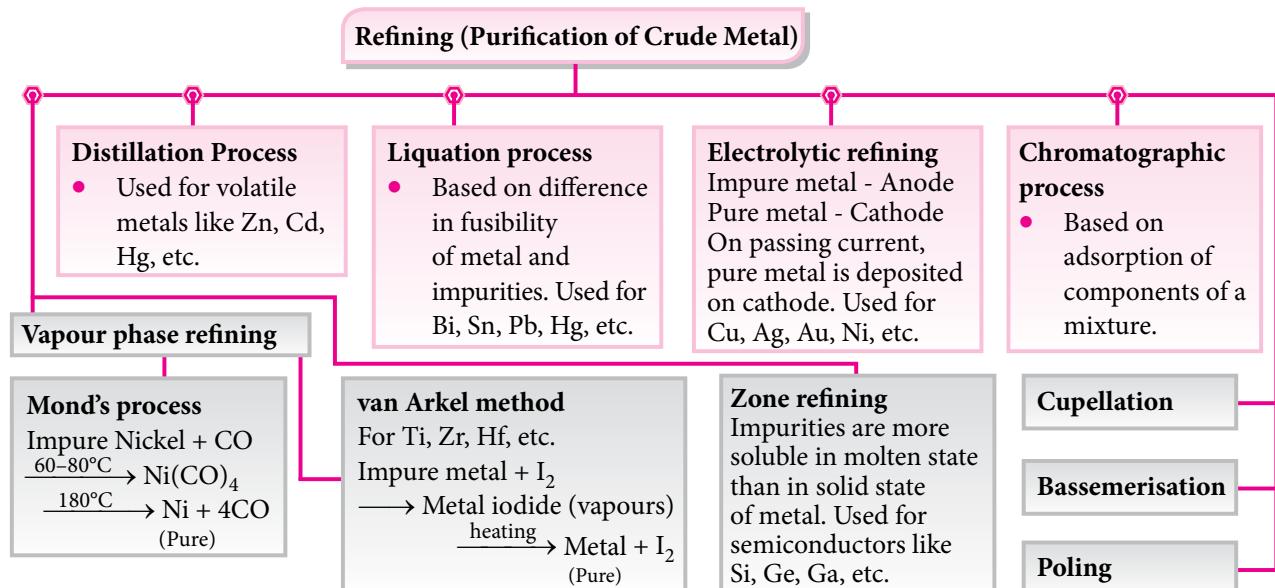
## THERMODYNAMIC PRINCIPLES IN EXTRACTION OF METALS

- The free energy change ( $\Delta G$ ), occurring during the reduction processes help in deciding the suitable method for reduction, is given by  $\Delta G = \Delta H - T\Delta S$ ; where,  $\Delta H$  = enthalpy change;  $\Delta G$  = Gibbs free energy change;  $T$  = temperature;  $\Delta S$  = entropy change.
- Greater the negative value of  $\Delta G$ , higher is the reducing power of an element.
- For the reduction of a metal oxide with a reducing agent, the plot of  $\Delta G^\circ$  vs temperature is studied, which is called Ellingham diagram.

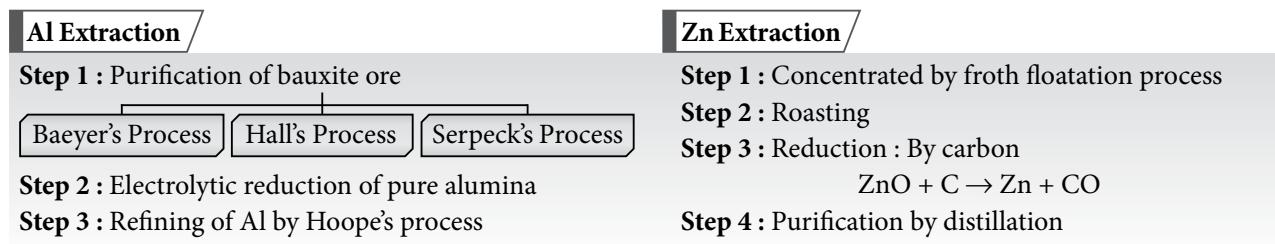


## CHARACTERISTICS OF ELLINGHAM DIAGRAM

- $\Delta G^\circ$  becomes more positive when temperature increases, i.e., stability of oxides decreases.
- A metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e., the metals for which the free energy of formation ( $\Delta G^\circ$ ) of their oxides is more negative can reduce those metal oxides which has less negative  $\Delta G^\circ$ . Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.
- CO is more effective reducing agent below 1073 K and above 1073 K coke is more effective reducing agent, e.g., CO reduces  $Fe_2O_3$  below 1073 K but above it, coke reduces  $Fe_2O_3$ .



## Extraction of Al and Zn



### Perovskite solar cells !

A perovskite is an unique crystal structure, consisting of formamidinium with multiple cations and mixed halide anions. A perovskite solar cell (PSC) is a type of solar cell, which includes the perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide based material, as the light harvesting active layer. These solar cells not only show relatively high photovoltaic energy conversion efficiencies (above 22%), but can be also easily fabricated using cheap inorganic-organic perovskite compounds.

## p-BLOCK ELEMENTS (GROUP 15 TO 18)

### Group-15

**Electronic configuration :**  $ns^2np^3$ ; ( $n = 2$  to  $6$ )  
**Metallic nature :** Increases with increase in atomic number.  
**Ionic/Atomic radii :** Increase down the group.  
**Ionisation energy :** Decreases down the group. For an element;  $I.E._1 < I.E._2 < I.E._3$   
**Allotropy :** All elements except N and Bi, show allotropy.  
**Oxidation states :** +3 and +5; N and P also show (-3) oxidation state.  
**Electronegativity :** Decreases down the group.

### Group-16

**Electronic configuration :**  $ns^2np^4$ ; ( $n = 2$  to  $6$ )  
**Metallic nature :** Increases with increase in atomic number.  
**Ionic/Atomic radii :** Smaller than group-15 elements and increase down the group.  
**Ionisation energy :** Lower than group-15 elements (due to half filled configuration of group-15 elements) and increases down the group.  
**Allotropy :** All elements exhibit allotropy.  
**Electronegativity :** Higher than group-15 elements and decreases down the group. O is second most electronegative element.  
**Oxidation states :** +2, +4  
Oxygen commonly shows -2 oxidation state.

### Group-17

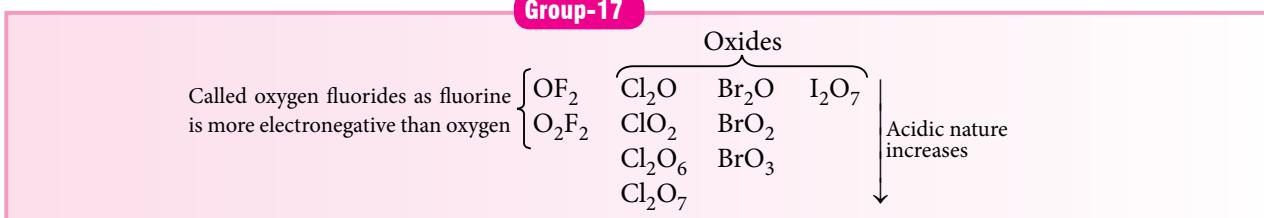
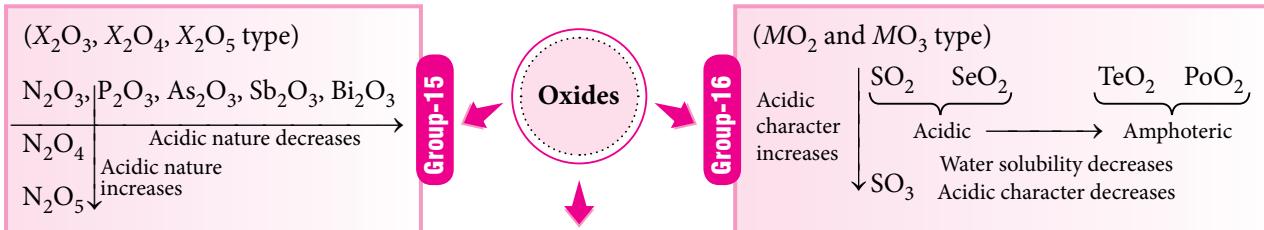
**Electronic configuration :**  $ns^2np^5$ ; ( $n = 2$  to  $6$ )  
**Oxidising nature :** Standard reduction potential of halogens are positive and decreases from fluorine to iodine.  
 $F_2$  is strongest oxidising agent while  $I_2$  is the weakest.  
**Ionic/Atomic radii :** Halogens have lowest atomic radii in their respective period which increase down the group.  
**Ionisation energy :** They have very high ionisation energy and decreases down the group.  
**Electronegativity :** Halogens are highly electronegative.  
**Oxidation states :** F (-1 only)  
Cl, Br, I show -1, +1, +3, +5, +7 oxidation states.

### PHYSICAL PROPERTIES

### Group-18

**Electronic configuration :**  $ns^2np^6$ ; ( $n = 2$  to  $6$ ), (stable, fully filled, very less reactive).  
**Atomic radii :** Exceptionally high as atomic radii correspond to van der Waals' radii.  
**Ionisation enthalpy :** High value due to stable fully filled configuration.  
**Adsorption over charcoal :** Except helium, these gases can be adsorbed by coconut charcoal at suitable temperatures.

## CHEMICAL PROPERTIES



**Oxyacids**

Group-15			
Oxyacids of N	$H_2N_2O_2 (+1)$ (Hyponitrous acid)	$HNO_2 (+3)$ (Nitrous acid)	$HNO_3 (+5)$ (Nitric acid)
Oxyacids of P	$H_3PO_2 (+1)$ (Monobasic) Phosphinic acid	$H_3PO_3 (+3)$ (Dibasic) Orthophosphorous acid	$H_4P_2O_6 (+4)$ (Tetrabasic) Hypophosphoric acid
	$H_3PO_4 (+5)$ (Tribasic) Orthophosphoric acid	$HPO_3 (+5)$ (Monobasic) Metaphosphoric acid	$H_4P_2O_7 (+5)$ (Tetrabasic) Pyrophosphoric acid
Oxyacids of As and Bi	$H_3AsO_3 (+3)$ Arsenious acid	$H_3AsO_4 (+5)$ Arsenic acid	$HBiO_3 (+5)$ Metabismuthic acid

Group-16			
Oxyacids of S	$H_2SO_3 (+4)$ (Dibasic) Sulphurous acid	$H_2SO_4 (+6)$ (Dibasic) Sulphuric acid	$H_2S_2O_3 (+6, -2)$ (Dibasic) Thiosulphuric acid
$H_2S_2O_7 (+6)$ (Dibasic) Pyrosulphuric acid	$H_2S_2O_6 (+6)$ (Dibasic) Dithionic acid	$H_2S_2O_8 (+6)$ (Dibasic) Peroxodisulphuric acid	$H_2SO_5 (+6)$ (Dibasic) Peroxomonosulphuric acid

Group-17				
Oxyacids of F	$HOF (+1)$ (Hypofluorous acid)	—	—	—
Oxyacids of Cl	$HOCl (+1)$ (Hypochlorous acid)	$HClO_2 (+3)$ Chlorous acid	$HClO_3 (+5)$ Chloric acid	$HClO_4 (+7)$ Perchloric acid
Oxyacids of Br	$HOBr (+1)$ (Hypobromous acid)	—	$HBrO_3 (+5)$ Bromic acid	$HBrO_4 (+7)$ Perbromic acid
Oxyacids of I	$HOI (+1)$ Hypoiodous acid	—	$HIO_3 (+5)$ Iodic acid	$HIO_4 (+7)$ Periodic acid

### Hydrides

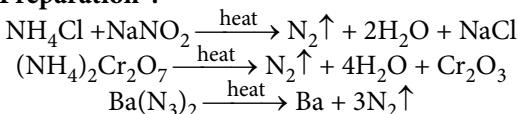
NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	BiH <sub>3</sub>
H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te	
HF	HCl	HBr	HI	

Bond length increases  
Thermal stability decreases  
Acidic strength increases  
Reducing nature increases

### IMPORTANT COMPOUNDS

#### Dinitrogen (N<sub>2</sub>)

##### Preparation :



Properties : Colourless, odourless, tasteless, non-toxic, unreactive due to triple bond; N≡N.

Uses : For manufacturing of HNO<sub>3</sub>, NH<sub>3</sub>, etc.

#### Ammonia (NH<sub>3</sub>)

##### Preparation : By Haber's process,



Properties : Its aqueous solution is basic in nature.



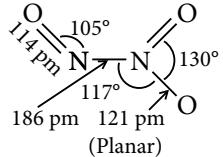
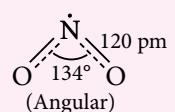
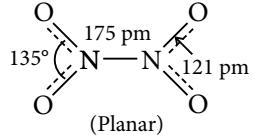
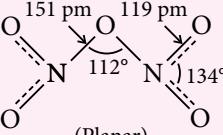
Uses : For manufacturing of nitrogenous fertilizers, HNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, etc.

### ABNORMAL BEHAVIOUR

N, O and F show different properties than their respective period elements due to

- small size
- high electronegativity
- absence of vacant d-orbitals.

### Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N <sub>2</sub> O	$\begin{array}{c} \text{N} \swarrow \text{O} \\   \\ \text{N}=\text{N} \end{array} \longleftrightarrow \begin{array}{c} \text{N}=\text{N} \\   \\ \text{N} \swarrow \text{O} \end{array}$	N≡N—O 113 pm 119 pm (Linear)
NO	$\begin{array}{c} \text{N} \swarrow \text{O} \\   \\ \text{N}=\text{O} \end{array} \longleftrightarrow \begin{array}{c} \text{N}=\text{O} \\   \\ \text{N} \swarrow \text{O} \end{array}$	:N=O: 115 pm (Linear)
N <sub>2</sub> O <sub>3</sub>	$\begin{array}{c} \text{O} \cdot \text{N} \swarrow \text{N} \cdot \text{O} \\    \quad    \\ \text{N} \text{—} \text{N} \end{array} \longleftrightarrow \begin{array}{c} \text{O} \cdot \text{N} \swarrow \text{N} \cdot \text{O} \\    \quad    \\ \text{N} \text{—} \text{N} \end{array}$	 114 pm 121 pm 186 pm (Planar)
NO <sub>2</sub>	$\begin{array}{c} \text{N} \swarrow \text{O} \\   \\ \text{N}=\text{O} \end{array} \longleftrightarrow \begin{array}{c} \text{N} \swarrow \text{O} \\   \\ \text{N}=\text{O} \end{array}$	 120 pm 134° O (Angular)
N <sub>2</sub> O <sub>4</sub>	$\begin{array}{c} \text{O} \cdot \text{N} \swarrow \text{N} \cdot \text{O} \\    \quad    \\ \text{N} \text{—} \text{N} \end{array} \longleftrightarrow \begin{array}{c} \text{O} \cdot \text{N} \swarrow \text{N} \cdot \text{O} \\    \quad    \\ \text{N} \text{—} \text{N} \end{array}$	 175 pm 135° O 121 pm (Planar)
N <sub>2</sub> O <sub>5</sub>	$\begin{array}{c} \text{O} \cdot \text{N} \swarrow \text{N} \cdot \text{O} \\    \quad    \\ \text{N} \text{—} \text{N} \end{array} \longleftrightarrow \begin{array}{c} \text{O} \cdot \text{N} \swarrow \text{N} \cdot \text{O} \\    \quad    \\ \text{N} \text{—} \text{N} \end{array}$	 151 pm 119 pm 112° O 134° O (Planar)

# CONCEPT MAP

## CLASS XI

## Titrimetric / Volumetric Analysis

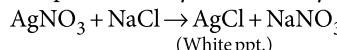
Titrimetric analysis has a wide applications in the various fields. It is used to determine the acid content of alcoholic beverages, calcium content in dairy products, total water hardness, vitamin C in fruit juices, etc.

### Simple Titration

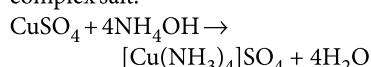
- Acid-base titration :** The concentration of an acid is estimated by adding a solution of standard base. The equivalence point is detected by adding a few drops of suitable indicator to the acid solution.

- Redox titration :** The concentration of oxidant is estimated by adding reductant or vice versa. For example,  $\text{Fe}^{2+}$  ions can be estimated by titrating against acidified  $\text{KMnO}_4$  solution.

- Precipitation titration :** Cations and anions combine to form a compound of very low solubility.



- Complexometric titration :** Titrate combines with the titrant to form a complex salt.



### If a mixture of $\text{NaOH}$ & $\text{NaHCO}_3$ is taken

- Equivalents of  $\text{NaOH}$  = equivalents of  $\text{HCl}$  required upto phenolphthalein end point.
- Equivalents of  $\text{NaHCO}_3$  = equivalents of  $\text{HCl}$  required from phenolphthalein to methyl orange end point.

### If a mixture of $\text{Na}_2\text{CO}_3$ & $\text{NaHCO}_3$ is taken

- $\frac{1}{2}$  Equivalents of  $\text{Na}_2\text{CO}_3$  ( $n = 2$ ) = equivalents of  $\text{HCl}$  required upto phenolphthalein end point.
- $\frac{1}{2}$  Equivalents of  $\text{Na}_2\text{CO}_3$  ( $n = 2$ ) + equivalents of  $\text{NaHCO}_3$  ( $n = 1$ ) initially = Equivalents of  $\text{HCl}$  required from phenolphthalein end point to methyl orange end point.

### Back Titration

Reactant A of known concentration is titrated with reactant B ( $V_1$  litre) of known concentration.

Equivalents of B reacted with A =  $N_1 V_1$ . In another flask, reactant C of unknown concentration is reacted with A and excess of A is titrated with B ( $V_2$  litre).

Equivalents of B reacted with excess of A =  $N_1 V_2$ .

Equivalents of pure C =  $N_1 V_1 - N_1 V_2$

$$\text{Moles of pure C} = \frac{N_1 V_1 - N_1 V_2}{n}$$

### Here, n-factor

For acids,  $n$  = basicity of acid

For bases,  $n$  = acidity of base

In case of redox reactions :

$$n\text{-factor} = \frac{\text{change in oxidation number per molecule}}{\text{total number of electrons transferred per mole}}$$

$$\text{Mass of pure C} = \frac{N_1 V_1 - N_1 V_2}{n} \times \text{Molar mass of C}$$

$$\% \text{ Purity of C} = \frac{N_1 V_1 - N_1 V_2}{n} \times \frac{\text{Molar mass of C}}{w} \times 100$$

where,  $N_1$  = Normality of B,  
 $w$  = Mass of C

In the given calculation, we have taken alkali mixture of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  but other alkali mixtures can also be taken.

### If a mixture of $\text{NaOH}$ , $\text{Na}_2\text{CO}_3$ & $\text{NaHCO}_3$ is taken

- Equivalents of  $\text{NaOH} + \frac{1}{2}$  equivalents of  $\text{Na}_2\text{CO}_3$  ( $n = 2$ ) = Equivalents of  $\text{HCl}$  required upto phenolphthalein end point
- $\frac{1}{2}$  equivalents of  $\text{Na}_2\text{CO}_3$  ( $n = 2$ ) + equivalents of  $\text{NaHCO}_3$  initially ( $n = 1$ ) = Equivalents of  $\text{HCl}$  required from phenolphthalein end point to methyl orange end point.

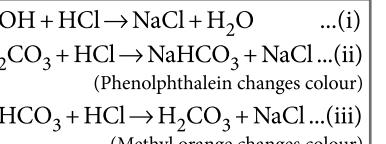
### Double Titration

The purpose of double titration is to determine the percentage composition of an alkali mixture or an acid mixture.

#### Process:

- Dissolve mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  in water to make alkaline solution, add two indicators phenolphthalein and methyl orange.
- Now this solution is titrated against HCl.

### Reactions Taking Place



### Calculations

#### At methyl orange end point:

- Moles of HCl consumed by  $\text{NaHCO}_3$  =  $M_1 V_2$  = Moles of  $\text{NaHCO}_3$  formed from  $\text{Na}_2\text{CO}_3$  = Moles of  $\text{Na}_2\text{CO}_3$  in the mixture
- Mass of  $\text{Na}_2\text{CO}_3$  in the mixture =  $M_1 V_2 \times 106$
- % of  $\text{Na}_2\text{CO}_3$  in mixture =  $\frac{M_1 V_2 \times 106}{w} \times 100$

#### At phenolphthalein end point:

- Moles of HCl used in eq. (i) =  $M_1 V_1 - M_1 V_2$  = Moles of  $\text{NaOH}$
- Mass of  $\text{NaOH}$  =  $(M_1 V_1 - M_1 V_2) \times 40$
- % of  $\text{NaOH}$  =  $\frac{(M_1 V_1 - M_1 V_2) \times 40}{w} \times 100$
- where,  $V_1$  = volume of HCl used when phenolphthalein changes colour,  $V_2$  = volume of HCl required from phenolphthalein colour change to methyl orange colour change
- $w$  = Mass of  $\text{Na}_2\text{CO}_3$ - $\text{NaOH}$  mixture

## Redox Reactions

Redox reactions are very important in day to day life, these found vast applications in photosynthesis, production of chemicals, extraction of metals, electrochemical cells and quantitative analysis. Some important reduction processes are discussed here.

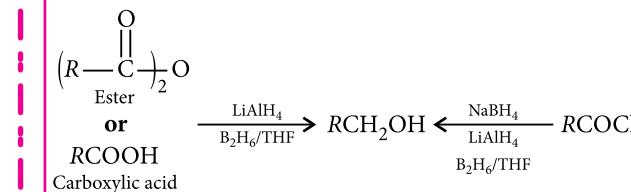
# CONCEPT MAP

## CLASS XII

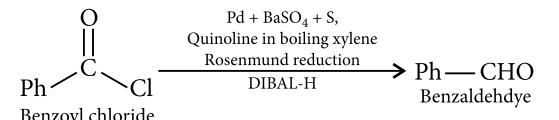
## Titrimetric / Volumetric Analysis

## Reduction Processes

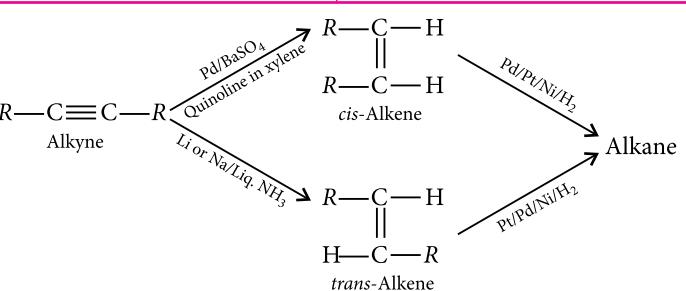
### Reduction to Alcohol



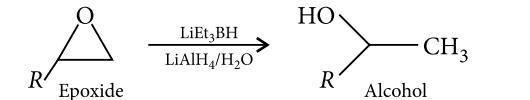
### Reduction of Benzoyl Chloride



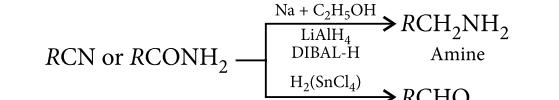
### Reduction of Unsaturated Compounds



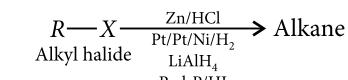
### Reduction of Epoxide



### Reduction of N-containing Compounds



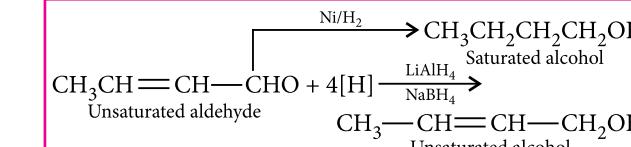
### Reduction of Halides



### Important Named Reduction Reagents and Reagents

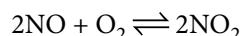
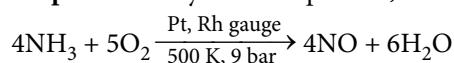
- $\text{Zn}-\text{Hg}/\text{H}_2\text{O} \Rightarrow$  Clemmensen reduction
- $\text{NH}_2-\text{NH}_2/\text{H}_2\text{O} \Rightarrow$  Wolff-Kishner reduction
- $\text{Al}(\text{O}-\text{CH}(\text{CH}_3)_2)_3 + \text{CH}_3\text{CH}-\text{CH}_3 \Rightarrow$  Meerwein-Ponndorf-Verley reduction (MPV Reduction)
- $\text{DIBAL-H} \Rightarrow$  Di-iso-butyl aluminium hydride (Highly reactive, hard to control, explodes on heating, grinding or on exposure to water)
- $\text{H}_2[\text{SnCl}_4] \Rightarrow$  Stephen's reduction (RCN to RCHO)
- $\text{Pd} + \text{BaSO}_4 + \text{quinoline in boiling xylene} \Rightarrow$  Lindlar's catalyst
- Reduction of alkynes to trans-alkene using Li, Na/Liq.  $\text{NH}_3$   $\Rightarrow$  Birch reduction

### Reduction of Unsaturated Aldehydes



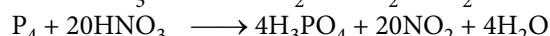
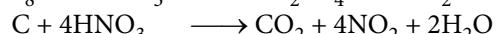
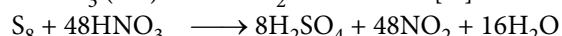
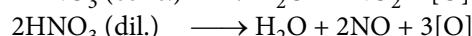
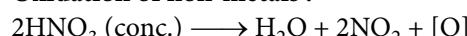
## Nitric Acid ( $\text{HNO}_3$ )

- Preparation :** By Ostwald process,



- Properties :** It is a strong oxidising agent as it decomposes to give nascent oxygen easily.

- Oxidation of non-metals :**

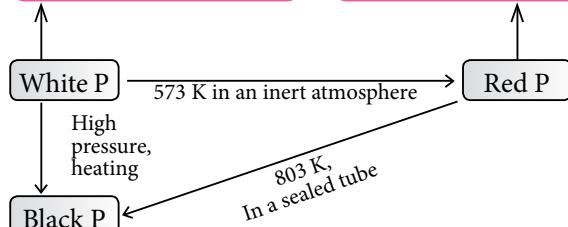


- The concentrated nitric acid renders metals like iron, cobalt, nickel, chromium, etc passive.
- Metal +  $\text{HNO}_3 \longrightarrow$  Metal nitrate + [H]
- Causes nitration of organic compounds.

## Phosphorus ( $\text{P}_4$ )

- Discrete tetrahedral
- Very reactive
- Translucent waxy solid

- Iron grey luster
- Less reactive than white P
- Polymeric structure ( $\text{P}_4$  units linked)



- Two forms
  - $\alpha$ -black P (at 803 K)
  - $\beta$ -black P (at 473 K)
- Very less reactive
- Opaque monoclinic or rhombohedral crystals

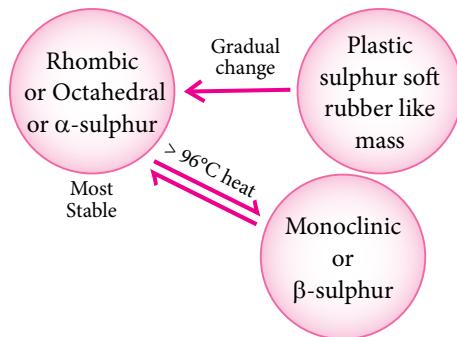
Oxygen	Ozone
$\ddot{\text{O}} = \ddot{\text{O}}$	$\begin{array}{c} & 1.278 \text{ \AA} \\ & \diagdown \\ \ddot{\text{O}} & \text{---} & \text{O} & \text{---} & \text{O} & \diagup \\ & \diagup & & & & \diagdown \\ & 1.278 \text{ \AA} & & & & 116.8^\circ & \ddot{\text{O}} \end{array}$
<b>Laboratory Preparation</b>	
$2\text{KClO}_3 \xrightarrow{420 \text{ K}} 2\text{KCl} + 3\text{O}_2$	$3\text{O}_2 \rightleftharpoons 2\text{O}_3$ – energy 5-10% ozone mixture is obtained, known as ozonised oxygen.
<b>Properties</b>	
$2\text{H}_2 + \text{O}_2 \xrightarrow[\text{or electric discharge}]{1073 \text{ K}} 2\text{H}_2\text{O}$ $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ $\text{P}_4 + 5\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$ $4\text{Al} + 3\text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3$	$\text{O}_3 + 2\text{H}^+ + 2e^- \longrightarrow \text{O}_2 + \text{H}_2\text{O}; E^\circ = +2.07 \text{ V}$ $2\text{HCl} + \text{O}_3 \longrightarrow \text{H}_2\text{O} + \text{Cl}_2 + \text{O}_2$ $\text{PbS} + 4\text{O}_3 \longrightarrow \text{PbSO}_4 + 4\text{O}_2$ $\text{I}_2 + \text{H}_2\text{O} + 5\text{O}_3 \longrightarrow 2\text{HIO}_3 + 5\text{O}_2$ Coloured substance + [O] $\longrightarrow$ Colourless substance (Bleaching action)



### van der Waals' forces !

Very weak van der Waals' forces between individual atoms are measured for the first time. Individual noble gas atoms were fixed within a molecular network and the interactions with a single xenon atom were determined that was positioned at the tip of an atomic force microscope. As expected, the forces varied according to the distance between the two atoms, but in some cases, the forces were several times larger than theoretically calculated.

## Allotropic Forms of Sulphur

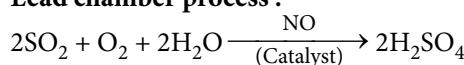


## INTERHALOGEN COMPOUNDS

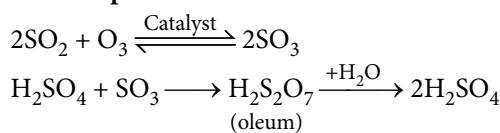
Type $XX'_1$ (Linear shape)	Type $XX'_3$ (T-shape)	Type $XX'_5$ (Square pyramidal shape)	Type $XX'_7$ (Pentagonal bipyramidal shape)
ClF	ClF <sub>3</sub>	ClF <sub>5</sub>	
BrF, BrCl	BrF <sub>3</sub>	BrF <sub>5</sub>	
ICl, IBr, IF	ICl <sub>3</sub> , IF <sub>3</sub>	IF <sub>5</sub>	IF <sub>7</sub>

## Sulphuric Acid

- Lead chamber process :

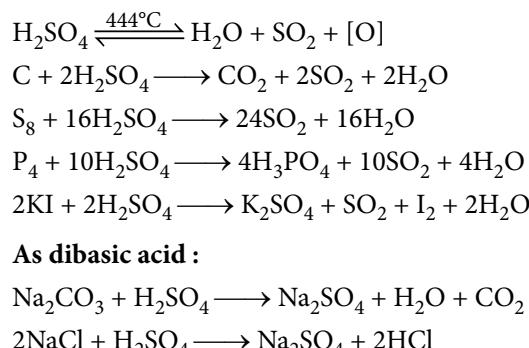


- Contact process :



- Properties

- As oxidising agent (due to nascent O) :



## Bleaching Powder ( $\text{CaOCl}_2 \cdot \text{H}_2\text{O}$ )

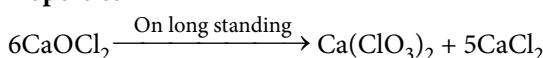
- Preparation :



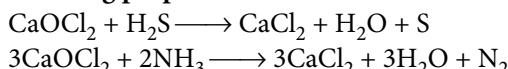
Dry slaked lime

Preparation is carried out in Hasenclever's plant and Beckmann's plant.

- Properties



- Oxidising properties :



- Bleaching action :

Coloured matter + [O]  $\longrightarrow$  Colourless product

## COMPOUNDS OF XENON

Molecule	Electron pairs	Hybridisation	Shape
XeF <sub>2</sub>	5	$sp^3d$	Linear
XeF <sub>4</sub>	6	$sp^3d^2$	Square planar
XeF <sub>6</sub>	7	$sp^3d^3$	Distorted octahedral
XeOF <sub>2</sub>	5	$sp^3d$	T-shape
XeOF <sub>4</sub>	6	$sp^3d^2$	Square pyramidal
XeO <sub>3</sub>	4	$sp^3$	Pyramidal
XeO <sub>2</sub> F <sub>2</sub>	5	$sp^3d$	See-saw
XeO <sub>4</sub>	4	$sp^3$	Tetrahedral

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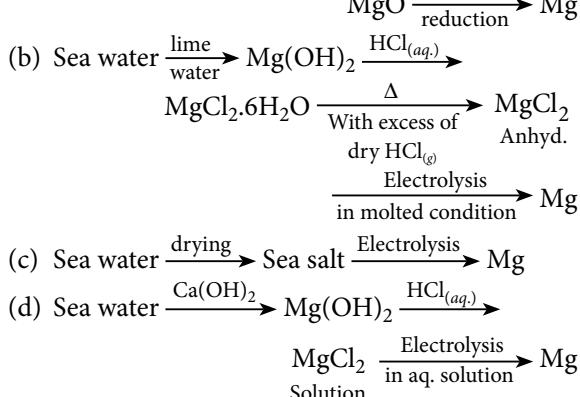
# SPEED PRACTICE

1. From the following information,  
 $X + H_2SO_4 \longrightarrow Y$  (a colourless and irritating gas)  
 $Y + K_2Cr_2O_7 + H_2SO_4 \longrightarrow$  green coloured solution  
Identify the pair X and Y.  
(a)  $Cl^-$ ,  $HCl$       (b)  $SO_3^{2-}$ ,  $SO_2$   
(c)  $S^{2-}$ ,  $H_2S$       (d)  $CO_3^{2-}$ ,  $CO_2$
  2. In the commercial electrochemical process for aluminium extraction, the electrolyte used is  
(a)  $Al(OH)_3$  in  $NaOH$  solution  
(b) an aqueous solution of  $Al_2(SO_4)_3$   
(c) a molten mixture of  $Al_2O_3$  and  $Na_3AlF_6$   
(d) a molten mixture of  $AlO(OH)$  and  $Al(OH)_3$
  3. Which of the following is correct statement?  
(a) Phosphates have no biological significance in humans.  
(b) Between nitrates and phosphates, phosphates are less abundant in earth's crust.  
(c) Between nitrates and phosphates, nitrates are less abundant in earth's crust.  
(d) Oxidation of nitrates is possible in soil.
  4. Composition of azurite mineral is  
(a)  $CuCO_3 \cdot CuO$   
(b)  $Cu(HCO_3)_2 \cdot Cu(OH)_2$   
(c)  $2CuCO_3 \cdot Cu(OH)_2$   
(d)  $CuCO_3 \cdot 2Cu(OH)_2$
  5. The number of  $S=O$  and  $S-OH$  bonds present in peroxodisulphuric acid and pyrosulphuric acid are respectively  
(a) (4 and 2) and (4 and 2)  
(b) (2 and 4) and (2 and 4)  
(c) (4 and 2) and (2 and 4)  
(d) (2 and 2) and (2 and 2)
- (JEE Main Online 2017)**
6. In the construction of aircrafts, an alloy, elektron is often used. Its composition is  
(a) 15% Mg and 85% Al  
(b) 95% Mg and 5% Zn  
(c) 95% Mg and 5% Al  
(d) 80% Al and 20% Zn

7. Which of the following is not correct?  
(a)  $3O_2 \xrightleftharpoons[\text{discharge}]{\text{Silent electric}} 2O_3$ ;  $\Delta H = -284.5 \text{ kJ mol}^{-1}$   
(b) Ozone undergoes addition reaction with unsaturated carbon compounds.  
(c) Sodium thiosulphate reacts with  $I_2$  to form sodium tetrathionate and sodium iodide.  
(d) Ozone oxidises lead sulphide to lead sulphate.
  8. The process is used to remove reducible oxides from metals. Molten impure metal is stirred by a wooden rods. The hydrocarbon gases reduce the oxides. The process is called  
(a) zone refining      (b) cupellation  
(c) poling      (d) leaching.
  9. Roasted copper pyrite on smelting with sand produces  
(a)  $FeSiO_3$  as fusible slag and  $Cu_2S$  as matte  
(b)  $CaSiO_3$  as infusible slag and  $Cu_2O$  as matte  
(c)  $Ca_3(PO_4)_2$  as fusible slag and  $Cu_2S$  as matte  
(d)  $Fe_3(PO_4)_2$  as infusible slag and  $Cu_2S$  as matte.
  10. The correct statement(s) about the oxoacids,  $HClO_4$  and  $HClO$ , is(are)  
(a) the conjugate base of  $HClO_4$  is weaker base than  $H_2O$   
(b) the central atom in both  $HClO_4$  and  $HClO$  is  $sp^3$  hybridized  
(c)  $HClO_4$  is formed in the reaction between  $Cl_2$  and  $H_2O$   
(d)  $HClO_4$  is more acidic than  $HClO$  because of the resonance stabilization of its anion.
- (JEE Advanced 2017)**
11. Hydrolysis of  $XeF_4$  and  $CaCN$  give respectively  
(a)  $XeO_3$  and  $CaCO_3$       (b)  $XeO_2$  and  $CaCN_2$   
(c)  $XeO_3$  and  $CaCN_2$       (d)  $XeOF_2$  and  $CaCO_3$
  12. Xenon hexafluoride reacts with potassium fluoride to yield  
(a)  $[XeF_4]^{2+} [KF_3]^{2-}$       (b)  $XeF_4$   
(c)  $[XeF_5]^+ [KF_2]^-$       (d)  $K^+[XeF_7]^-$

13. Pb, which is present as impurity in silver, is removed by  
 (a) Parke's process  
 (b) Pattinson process  
 (c) cupellation  
 (d) addition of Zn in molten silver.

14. Which of the following diagrams is correctly related to the extraction of Mg from sea water?  
 (a) Sea water  $\xrightarrow{\text{Na}_2\text{CO}_3}$   $\text{MgCO}_3 \xrightarrow{\text{Calcination}}$   
 $\text{MgO} \xrightarrow[\text{reduction}]{\text{Carbon}} \text{Mg}$



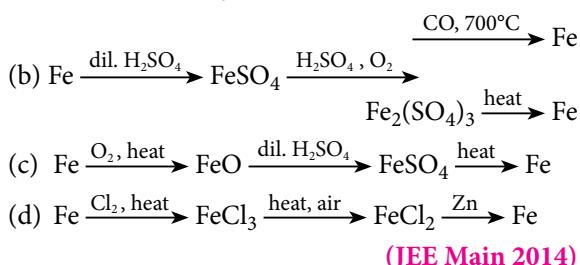
15. When copper is heated with conc.  $\text{HNO}_3$  it produces  
 (a)  $\text{Cu(NO}_3)_2$ , NO and  $\text{NO}_2$   
 (b)  $\text{Cu(NO}_3)_2$  and  $\text{N}_2\text{O}$   
 (c)  $\text{Cu(NO}_3)_2$  and  $\text{NO}_2$   
 (d)  $\text{Cu(NO}_3)_2$  and NO

(NEET 2016)

16. Out of  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_2\text{O}_6$ ,  $\text{H}_2\text{SO}_5$  and  $\text{H}_2\text{S}_2\text{O}_8$  peroxy acids are  
 (a)  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{S}_4\text{O}_6$       (b)  $\text{H}_2\text{S}_4\text{O}_6$ ,  $\text{H}_2\text{SO}_5$   
 (c)  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{S}_2\text{O}_8$       (d)  $\text{H}_2\text{S}_2\text{O}_3$  and  $\text{H}_2\text{S}_2\text{O}_8$

17. The process of pickling is to  
 (a) cover metal surface with a less reactive metal  
 (b) electroplate a metal with a non-metal  
 (c) cool a red hot steel by dipping it in oil  
 (d) remove layers of basic oxides from metal surface before electroplating.

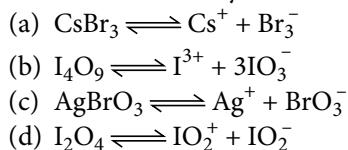
18. Which series of reactions correctly represents chemical relations related to iron and its compound?  
 (a)  $\text{Fe} \xrightarrow{\text{O}_2, \text{heat}} \text{Fe}_3\text{O}_4 \xrightarrow{\text{CO, } 600^\circ\text{C}} \text{FeO}$



(JEE Main 2014)

19. Pitch blende is  
 (a) ore of Ti      (b) ore of U  
 (c) ore of W      (d) ore of B.

20. Which is incorrectly matched?

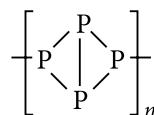


21. The chemical composition of slag formed during the smelting process in the extraction of copper is  
 (a)  $\text{Cu}_2\text{O} + \text{FeS}$       (b)  $\text{FeSiO}_3$   
 (c)  $\text{CuFeS}_2$       (d)  $\text{Cu}_2\text{S} + \text{FeO}$

22. The non-metal that does not exhibit positive oxidation state is  
 (a) chlorine      (b) iodine  
 (c) fluorine      (d) oxygen.

(JEE Main Online 2016)

23. Which of the following allotropic forms of phosphorus contain given structure?



- (a) White phosphorus      (b) Red phosphorus  
 (c) Black phosphorus      (d) Yellow phosphorus

24. Which of the following is correct?

- (a) Superphosphate is  $[3\text{Ca}(\text{H}_2\text{PO}_4)_2 + 7\text{CaSO}_4]$ .  
 (b) Triple superphosphate is  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .  
 (c) Both (a) and (b)  
 (d) None of these

25. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with

- (a) carbon monoxide      (b) copper (I) sulphide  
 (c) sulphur dioxide      (d) iron (II) sulphide.

(NEET 2015)

### MPP-5 CLASS XI

### ANSWER KEY

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

26. When an inorganic compound reacts with  $\text{SO}_2$  in aqueous medium produces (A). (A) on reaction with  $\text{Na}_2\text{CO}_3$  gives the compound (B) which with sulphur gives a substance (C) used in photography. The compound (C) is

(a)  $\text{Na}_2\text{S}_2\text{O}_3$       (b)  $\text{Na}_2\text{SO}_4$   
 (c)  $\text{Na}_2\text{S}$       (d)  $\text{Na}_2\text{S}_2\text{O}_7$

27. In which pair of ions both the species contain S — S bond?

(a)  $\text{S}_4\text{O}_6^{2-}, \text{S}_2\text{O}_3^{2-}$       (b)  $\text{S}_2\text{O}_7^{2-}, \text{S}_2\text{O}_8^{2-}$   
 (c)  $\text{S}_4\text{O}_6^{2-}, \text{S}_2\text{O}_7^{2-}$       (d)  $\text{S}_2\text{O}_7^{2-}, \text{S}_2\text{O}_3^{2-}$

(NEET 2017)

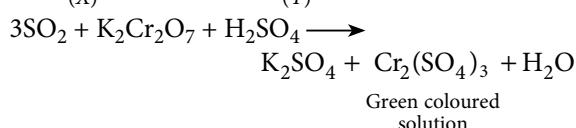
28. Compounds formed when the noble gases get entrapped in the cavities of crystal lattices of certain organic and inorganic compounds are known as  
 (a) interstitial compounds  
 (b) clathrates  
 (c) hydrates      (d) picrates.

29. Cassiterite is concentrated by  
 (a) levigation  
 (b) electromagnetic separation  
 (c) floatation  
 (d) liquefaction.

30. In which of the following reactions  $\text{HNO}_2$  acts as an oxidising agent?  
 (a)  $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{NO}_3^- + \text{H}_2\text{O}$   
 (b)  $\text{KI} + \text{H}_2\text{SO}_4 + \text{HNO}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{NO} + \text{I}_2 + \text{H}_2\text{O}$   
 (c)  $\text{Cl}_2 + \text{HNO}_2 \rightarrow \text{HCl} + \text{NO}_2$   
 (d)  $\text{O}_3 + \text{NO}_2^- + \text{H}^+ \rightarrow \text{O}_2 + \text{NO}_3^- + \text{H}_2\text{O}$

### SOLUTIONS

1. (b):  $\text{SO}_3^{2-} + 2\text{H}^+ \rightarrow \text{SO}_2 + \text{H}_2\text{O}$   
 $\quad \quad \quad (\text{X}) \quad \quad \quad (\text{Y})$

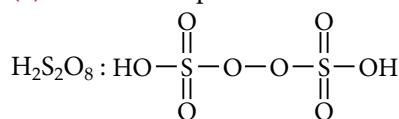


2. (c): The electrolysis of pure alumina faces some difficulties. Pure alumina is a bad conductor of electricity. The fusion temperature of pure alumina is about  $2000^\circ\text{C}$ . At this temperature, when electrolysis is carried out on the fused mass, the metal formed vaporises, as the boiling point of aluminium is  $1800^\circ\text{C}$ . These difficulties are overcome by using a mixture containing alumina, cryolite ( $\text{Na}_3\text{AlF}_6$ ), and fluorspar ( $\text{CaF}_2$ ).

3. (c): Between nitrates and phosphates, nitrates are more soluble in water and hence, are less abundant in earth's crust.

4. (c): Azurite is a basic copper carbonate ore having composition  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ .

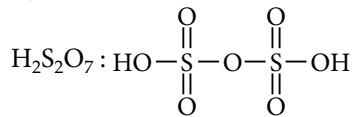
5. (a): Peroxodisulphuric acid :



No. of  $\text{S}=\text{O}$  bonds = 4

No. of  $\text{S}-\text{OH}$  bonds = 2

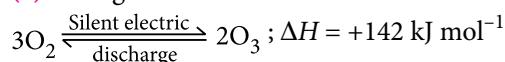
Pyrosulphuric acid :



No. of  $\text{S}=\text{O}$  bonds = 4 ; No. of  $\text{S}-\text{OH}$  bonds = 2

6. (c): Elektron is magnesium alloy containing 0% to 9.5% of some of the following elements in varying proportion aluminium (< 9.5%), yttrium (5.25%), silver (2.5%), etc.

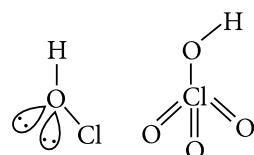
7. (a): The given reaction is endothermic.



8. (c)

9. (a): During smelting, silica combines with  $\text{FeO}$  to form fusible  $\text{FeSiO}_3$  slag and  $\text{Cu}_2\text{S}$  as matte.

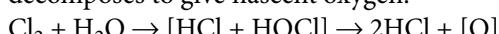
10. (a,b,d): Structures of  $\text{HClO}$  and  $\text{HClO}_4$  are :



- (a)  $\text{HClO}_4$  is a stronger acid than  $\text{H}_3\text{O}^+$ . Therefore, conjugate base of  $\text{HClO}_4$ , i.e.,  $\text{ClO}_4^-$ , is weaker base than  $\text{H}_2\text{O}$ .

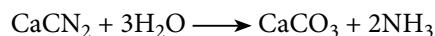
- (b) The hybridisation of central atom in both  $\text{HClO}$  and  $\text{HClO}_4$  is  $sp^3$ .

- (c) Reaction of  $\text{Cl}_2$  with water forms  $\text{HOCl}$  which decomposes to give nascent oxygen.

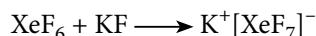


- (d)  $\text{HClO}_4$  is more acidic than  $\text{HClO}$  as  $\text{ClO}_4^-$  is more stable than  $\text{ClO}^-$  due to resonance.

11. (a):  $6\text{XeF}_4 + 12\text{H}_2\text{O} \xrightarrow[\text{hydrolysis}]{\text{Partial}} 2\text{XeO}_3 + 24\text{HF} + 4\text{Xe} + 3\text{O}_2$

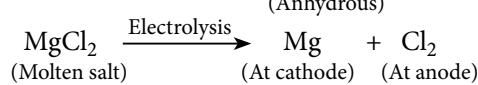
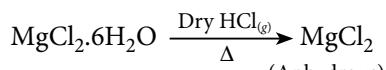
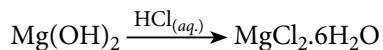
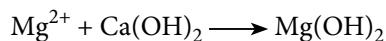


12. (d):  $\text{XeF}_6$  behaves as  $\text{F}^-$  acceptor to form fluorooanions.

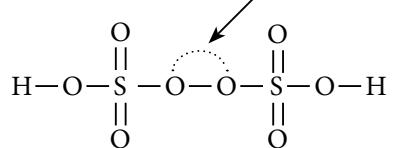
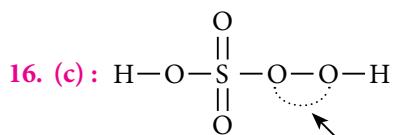
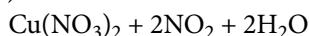


13. (c)

14. (b): Sea water contains  $Mg^{2+}$  ions.

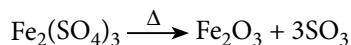


15. (c):  $Cu + 4HNO_3(\text{conc.}) \longrightarrow$



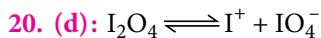
17. (d)

18. (a): Combustion of Fe to give  $Fe_3O_4$  which upon reduction with CO first gives  $FeO$  and finally Fe. Option (b) and (c) are wrong because  $FeSO_4$  and  $Fe_2(SO_4)_3$  on heating gives  $Fe_2O_3$ ,  $SO_2$ ,  $SO_3$  and not Fe.

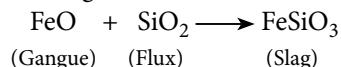


Option (d) is wrong because in presence of air, reduction of  $FeCl_3$  to  $FeCl_2$  cannot occur.

19. (b)



21. (b): When smelting is done in the blast furnace, most of the ferrous oxide is converted to ferric oxide. With silica, it forms ferrous silicate, which is the slag.



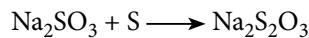
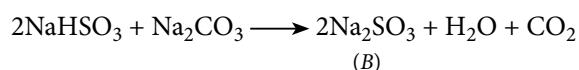
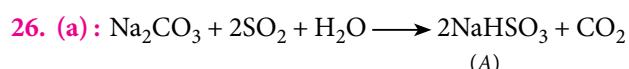
22. (c): Fluorine is the most electronegative element and it shows only -1 oxidation state.

23. (b): Polymeric form of  $\text{P}_4$  is red phosphorus.

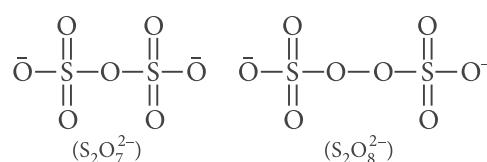
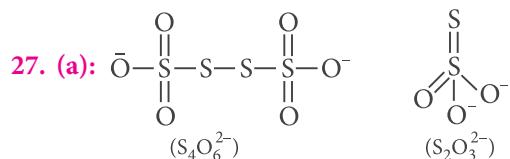
24. (c)



It is an example of auto-reduction.



(C)



28. (b)

29. (b): Cassiterite is tinstone ( $SnO_2$ ) which is non-magnetic and contains wolframite,  $FeWO_4$  (magnetic) impurities. These are separated by electromagnetic separation.

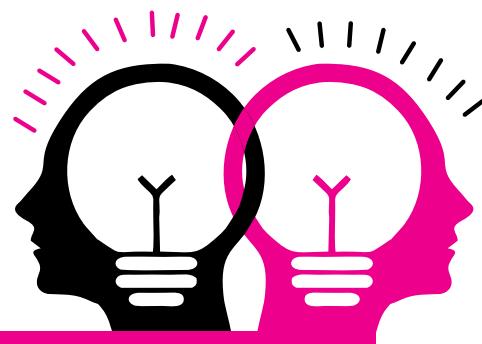
30. (b):  $HNO_2$  oxidises KI to iodine ( $I_2$ ).

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# EXAMiNER'S MiND CLASS XII



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.

This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

<b>Section - I</b>	Q. 1 to 10 Only One Option Correct Type MCQs.
<b>Section - II</b>	Q. 11 to 13 More than One Options Correct Type MCQs.
<b>Section - III</b>	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
<b>Section - IV</b>	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
<b>Section - V</b>	Q. 20 to 22 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.
<b>Section - VI</b>	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

## THE p-BLOCK ELEMENTS (GROUP 15 TO 18)

### SECTION - I

#### Only One Option Correct Type

- Under normal conditions, which of the following hydrides is non-combustible?  
 (a) NH<sub>3</sub> (b) PH<sub>3</sub> (c) AsH<sub>3</sub> (d) SbH<sub>3</sub>
- Aqueous solutions of hydrogen sulphide and sulphur dioxide when mixed together, yield  
 (a) sulphur and water  
 (b) sulphur trioxide and water  
 (c) hydrogen peroxide and sulphur  
 (d) hydrogen and sulphurous acid.
- Which among the following factors is most important in making fluorine the strongest oxidising agent?  
 (a) Electron affinity (b) Ionisation energy  
 (c) Hydration energy (d) Bond dissociation energy
- The heat of vaporisation, polarisation and solubility in water of noble gases are in the order  
 (a) He < Ne < Ar < Kr < Xe  
 (b) Xe < Kr < Ar < Ne < He  
 (c) He < Ne < Ar < Xe < Kr  
 (d) He < Ne ≈ Ar < Kr ≈ Xe

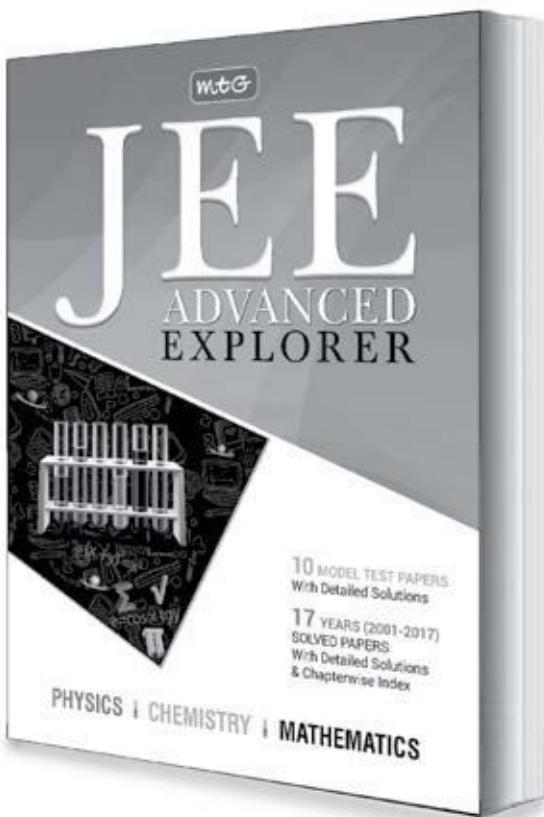
- Sodium hydroxide solution reacts with phosphorus to give phosphine. To bring about this reaction, we need  
 (a) white phosphorus and dil. NaOH  
 (b) white phosphorus and conc. NaOH  
 (c) red phosphorus and dil. NaOH  
 (d) red phosphorus and conc. NaOH.
- Which of the following properties of H<sub>2</sub>SO<sub>4</sub> in respective reaction is wrong?  

$$\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow{\text{H}_2\text{SO}_4} \text{CO} + \text{CO}_2 + \text{H}_2\text{O};$$
 H<sub>2</sub>SO<sub>4</sub> acts as dehydrating agent.  
 (b) Cu + 2H<sub>2</sub>SO<sub>4</sub> → CuSO<sub>4</sub> + 2H<sub>2</sub>O + SO<sub>2</sub>;  
 H<sub>2</sub>SO<sub>4</sub> acts as oxidising agent.  
 (c) Na<sub>2</sub>S + H<sub>2</sub>SO<sub>4</sub> → Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>S;  
 H<sub>2</sub>SO<sub>4</sub> acts as an acid.  
 (d) 2HBr + H<sub>2</sub>SO<sub>4</sub> → 2H<sub>2</sub>O + SO<sub>2</sub> + Br<sub>2</sub>;  
 H<sub>2</sub>SO<sub>4</sub> acts as reducing agent.
- A black compound of manganese reacts with a halogen acid to give greenish yellow gas. When excess of this gas reacts with NH<sub>3</sub> and unstable trihalide is formed. In this process, the oxidation state of nitrogen changes from  
 (a) -3 to +3 (b) -3 to 0  
 (c) -3 to +5 (d) 0 to -3

JEE (ADVANCED)



# Dry runs are here!



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8. The stability of interhalogen compounds follows the order  
 (a)  $\text{IF}_3 > \text{BrF}_3 > \text{ClF}_3$     (b)  $\text{BrF}_3 > \text{IF}_3 > \text{ClF}_3$   
 (c)  $\text{ClF}_3 > \text{BrF}_3 > \text{IF}_3$     (d)  $\text{ClF}_3 > \text{IF}_3 > \text{BrF}_3$
9. The reaction between  $\text{NH}_2^-$  and  $\text{N}_2\text{O}$  gives  
 (a)  $\text{NO}$     (b)  $\text{N}_2\text{O}_5$   
 (c)  $\text{NH}_2\text{NH}_2$     (d)  $\text{N}_3^-$
10. Which of the following statements regarding sulphur is incorrect?  
 (a)  $\text{S}_2$  molecule is paramagnetic.  
 (b) The vapour at  $200^\circ\text{C}$  consists mostly of  $\text{S}_8$  rings.  
 (c) At  $600^\circ\text{C}$  the gas mainly consists of  $\text{S}_2$  molecules.  
 (d) The oxidation state of sulphur is never less than +4 in its compounds.

### SECTION - II

#### More than One Options Correct Type

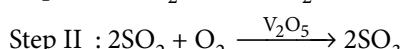
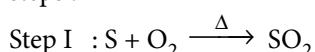
11. Which of the following statements are incorrect?  
 (a) Dry slaked lime reacts with  $\text{Cl}_2$  to give calcium chlorate.  
 (b) With excess chlorine ammonia forms nitrogen trichloride.  
 (c) Sulphur reacts with  $\text{Cl}_2$  to give  $\text{SCl}_4$ .  
 (d) With hot and conc.  $\text{NaOH}$ ,  $\text{Cl}_2$  gives sodium chlorate.
12. Which statements regarding argon in solid state are correct?  
 (a) Its atoms form a covalent network.  
 (b) The forces between the molecules are weak van der Waals' forces.  
 (c) Its molecules are monoatomic.  
 (d) It is good conductor of electricity.
13. Ammonia on reaction with hypochlorite anion can form  
 (a)  $\text{NO}$     (b)  $\text{NH}_4\text{Cl}$     (c)  $\text{N}_2\text{H}_4$     (d)  $\text{HNO}_2$

### SECTION - III

#### Paragraph Type

#### Paragraph for Questions 14 and 15

Industrially sulphuric acid is produced by the following steps :



Since the reaction between  $\text{SO}_3$  and  $\text{H}_2\text{O}$  is violent, therefore,  $\text{SO}_3$  is passed into 98%  $\text{H}_2\text{SO}_4$  to produce oleum ( $\text{H}_2\text{S}_2\text{O}_7$ ).

14. Pure  $\text{H}_2\text{SO}_4$  does not react with metal because  
 (a) pure  $\text{H}_2\text{SO}_4$  does not contain any water  
 (b) pure  $\text{H}_2\text{SO}_4$  acts as an oxidising agent  
 (c) pure  $\text{H}_2\text{SO}_4$  is strongly H-bonded  
 (d) pure  $\text{H}_2\text{SO}_4$  does not contain any  $\text{SO}_3$ .

15.  $\text{H}_2\text{SO}_4 + \text{PCl}_5 \longrightarrow (X) \xrightarrow{\text{H}_2\text{O}}$  two strong acids  
 Therefore (X) is  
 (a)  $\text{SO}_2\text{Cl}_2$     (b)  $\text{SOCl}$   
 (c)  $\text{ClSO}_3\text{H}$     (d)  $\text{POCl}_3$

#### Paragraph for Questions 16 and 17

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6.  $\text{XeF}_4$  reacts violently with water to give  $\text{XeO}_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

16. The structure of  $\text{XeO}_3$  is  
 (a) linear    (b) planar  
 (c) pyramidal    (d) T-shaped.
17.  $\text{XeF}_4$  and  $\text{XeF}_6$  are expected to be  
 (a) oxidising    (b) reducing  
 (c) unreactive    (d) strongly basic.

### SECTION - IV

#### Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

#### List I

- (P)  $\text{P}_4\text{O}_6$   
 (Q)  $\text{P}_4\text{O}_{10}$

#### List II

- (i) White crystalline solid  
 (ii) Waxy solid with garlic smell  
 (iii) Blue coloured liquid  
 (iv) Coordinate bonds

- (R)  $\text{N}_2\text{O}_3$

- (S)  $\text{N}_2\text{O}_5$

- (a) (P-i); (Q-ii, iv); (R-iii); (S-iv)

- (b) (P-ii); (Q-i, iv); (R-iii); (S-i, iv)

- (c) (P-i); (Q-i, iii); (R-iv); (S-i, ii, iii)

- (d) (P-ii); (Q-i, iii); (R-iv); (S-i)

19. Match the List I with List II and select the correct answer using the codes given below the lists :

#### List I

- (A) Helium

- (B) Argon

- (C) Neon

- (D) Xenon

- (a) A-q; B-s; C-p; D-r

- (c) A-r; B-q; C-s; D-p

#### List II

- (p) Ionisation energy comparable to  $\text{O}_2$

- (q) Provides inert atmosphere in metallurgy

- (r) Cryogenic

- (s) For advertising sign

- (b) A-q; B-p; C-s; D-r

- (d) A-r; B-s; C-q; D-p

SECTION - V

### **Assertion Reason Type**

- 20. Assertion :**  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  are tribasic acids as they contain three hydrogen atoms each.  
**Reason :** Both  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$  are reducing in nature.

**21. Assertion :** Reaction of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  in the presence of  $\text{Fe}_2\text{O}_3$  catalyst gives elemental sulphur.  
**Reason :** In this reaction  $\text{H}_2\text{S}$  is acting as a reducing agent.

**22. Assertion :**  $\text{HClO}_4$  is less acidic than  $\text{HBrO}_4$ .  
**Reason :**  $\text{HClO}_4$  ionises less in water than  $\text{HBrO}_4$ .

## **SECTION - VI**

## Integer Value Correct Type

23. What is the oxidation state of chlorine in  $\text{HClO}_4$ ?

24. Number of P—OH bonds present in pyrophosphoric acid is

25. Amongst the following, the maximum number of isoelectronic molecules/ions are

$\text{XeO}_3$ ,  $\text{BrO}_3^-$ ,  $\text{ClF}$ ,  $\text{XeF}_2$ ,  $\text{OF}_2$ ,  $\text{XeF}_4$ ,  $\text{ICl}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{IBr}_2^-$

## **ALCOHOLS, PHENOLS AND ETHERS**

SECTION - I

### **Only One Option Correct Type**

- 1.** When 2,3-dimethyl-2-butanol undergoes acid catalysed dehydration the minor product is  
(a) 2,3-dimethyl-1-butene  
(b) 2,3-dimethyl-2-butene  
(c) 3,3-dimethyl-1-butene  
(d) none of these.

**2.** What is the function of diethyl ether in Grignard reagent preparation?  
1. To act as catalyst  
2. To act as solvent  
3. To provide lone pair of electrons for coordination  
4. To act as an acid  
(a) 1,2      (b) 2,3      (c) 3,4      (d) 2,4

**3.** Which of the following is not true in case of reaction with heated copper at 300°C?  
(a) Phenol  $\longrightarrow$  Benzyl alcohol  
(b) Primary alcohol  $\longrightarrow$  Aldehyde  
(c) Secondary alcohol  $\longrightarrow$  Ketone  
(d) Tertiary alcohol  $\longrightarrow$  Olefin

**4.** The reaction of  $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_5-\text{OH}$  with HBr gives  
(a)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_5-\text{OH}$   
(b)  $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_5-\text{OH}$   
(c)  $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_5-\text{Br}$   
(d)  $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_5-\text{Br}$

5. For which of the following parameters the structural isomers  $C_2H_5OH$  and  $CH_3OCH_3$  would be expected to have same values? (Assume ideal behaviour)

  - Vapour pressure at the same temperature
  - Heat of vaporisation
  - Gaseous densities at the same temperature and pressure
  - Boiling points

6. Which of the following statements are correct?

  - Glycerol on reaction with oxalic acid at  $110^\circ C$  ( $383\text{ K}$ ) and followed by hydrolysis gives formic acid and glycerol.
  - Glycerol on reaction with oxalic acid at  $230^\circ C$  ( $503\text{ K}$ ) and followed by heating gives allyl alcohol.
  - Glycerol on oxidation with dil.  $HNO_3$  gives a mixture of glyceric and tartaric acid.
  - Glycerol on oxidation with conc.  $HNO_3$  gives glyceric acid.
  - I and II
  - I and III
  - III and IV
  - I, II, III, IV

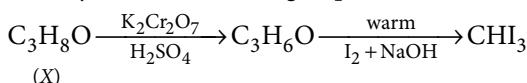
7. Isopropyl benzene is oxidised in the presence of air to give a compound 'A'. When compound 'A' is treated with dilute mineral acid, the aromatic product formed is

  - phenol
  - benzene
  - benzaldehyde
  - acetophenone.

8. Intramolecular rearrangement of phenyl acetate to give *o*- and *p*-hydroxyacetophenone in the presence of anhydrous  $AlCl_3$  is known as

  - Reimer-Tiemann reaction
  - Kolbe's reaction
  - Fries rearrangement
  - Claisen rearrangement.

9. Identify X in the following sequence :



- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (b)  $\text{CH}_3\text{CHOHCH}_3$   
 (c)  $\text{CH}_3\text{OCH}_2\text{CH}_3$  (d)  $\text{CH}_3\text{CH}_2\text{CHO}$

10. What amount of bromine will be required to convert 2 g of phenol into 2, 4, 6-tribromophenol?

- (a) 4.00 g (b) 6.00 g  
 (c) 10.08 g (d) 20.44 g

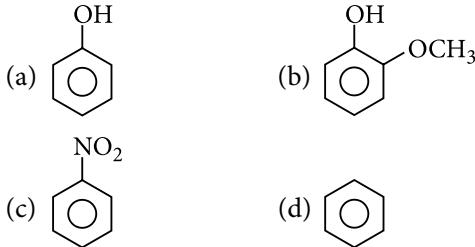
### SECTION - II

#### More than One Options Correct Type

11. Phenol is less acidic than

- (a) acetic acid (b) *p*-methoxyphenol  
 (c) *p*-nitrophenol (d) ethanol.

12. Which of the following compounds may undergo Reimer-Tiemann reaction?



13. Which of the following compounds will give a yellow precipitate with iodine and alkali?

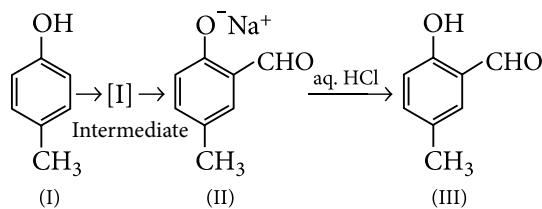
- (a) Acetophenone (b) Methyl acetate  
 (c) Acetamide (d) 2-Hydroxypropane

### SECTION - III

#### Paragraph Type

#### Paragraph for Questions 14 and 15

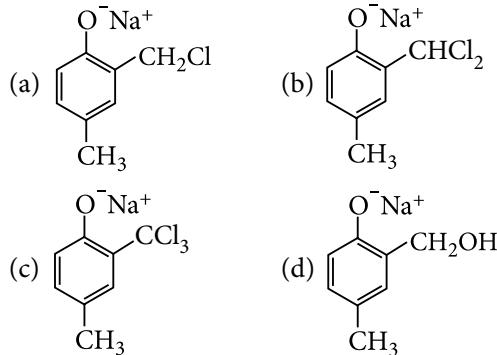
Reimer-Tiemann reaction introduces aldehyde group on to the aromatic ring of phenol, *ortho* to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of a substituted salicylaldehydes as depicted below.



14. Which one of the following reagents is used in the above reaction?

- (a) aq.  $\text{NaOH} + \text{CH}_3\text{Cl}$   
 (b) aq.  $\text{NaOH} + \text{CH}_2\text{Cl}_2$   
 (c) aq.  $\text{NaOH} + \text{CHCl}_3$   
 (d) aq.  $\text{NaOH} + \text{CCl}_4$

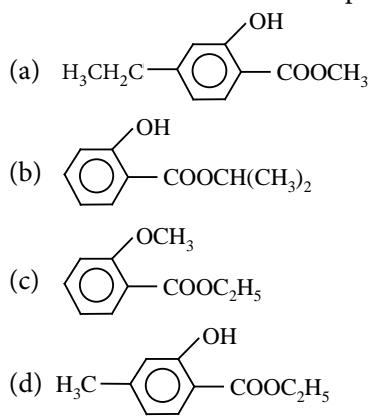
15. The structure of the intermediate (I) is



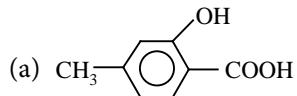
#### Paragraph for Questions 16 and 17

Compound (A),  $\text{C}_{10}\text{H}_{12}\text{O}_3$  is insoluble in water, dil.  $\text{HCl}$  and dilute aq.  $\text{NaHCO}_3$ . It is however soluble in dilute  $\text{NaOH}$ . A solution of (A) in dilute  $\text{NaOH}$  was boiled and the distillate collected in a solution of  $\text{NaOI}$ , where a yellow precipitate was formed. The alkaline residue in the distillation flask was acidified with dil.  $\text{H}_2\text{SO}_4$  to precipitate a solid (B), which was boiled, steam distilled and collected. The pure steam distilled product (B) was found to have the formula,  $\text{C}_7\text{H}_6\text{O}_3$  and it was dissolved in aq.  $\text{NaHCO}_3$  with effervescence.

16. The structural formula of compound (A) is



17. The structural formula of compound (B) is



- (b)
- (c)
- (d) none of these.

#### SECTION - IV

##### Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Compounds)		List II (Methods to distinguish)	
(P) Methanol and ethanol	1. Lucas reagent		
(Q) Phenol and cyclohexanol	2. Sodium metal		
(R) <i>n</i> -Butyl alcohol and <i>tert</i> -butyl alcohol	3. Iodoform test		
(S) Ethanol and diethyl ether	4. Ferric chloride		

P	Q	R	S
(a) 2	4	1	3
(b) 4	1	2	3
(c) 1	2	3	4
(d) 3	4	1	2

19. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Reaction)		List II (Product)	
(P) Reimer-Tiemann reaction	1. Benzoquinone		
(Q) Kolbe's reaction	2. Salicylaldehyde		
(R) Williamson synthesis	3. Salicylic acid		
(S) Oxidation of phenol	4. Ether		

#### SOLUTIONS

##### THE p-BLOCK ELEMENTS (GROUP 15 TO 18)

- (a)
- (a):  $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + 2\text{H}_2\text{O}$
- (c): Although both hydration energy and bond dissociation energy make  $\text{F}_2$  a strong oxidising agent but the effect of hydration energy is more important.
- (a)

P	Q	R	S
(a) 3	4	2	1
(b) 3	4	1	2
(c) 4	3	1	2
(d) 2	3	4	1

#### SECTION - V

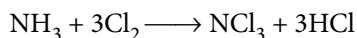
##### Assertion Reason Type

20. **Assertion :** Phenol is more reactive than benzene.  
**Reason:** In case of phenol, the intermediate carbocation is more resonance stabilised.
21. **Assertion :** The ease of dehydration of alcohols follows the order : Primary > Secondary > Tertiary.  
**Reason:** Dehydration proceeds through the formation of oxonium ions.
22. **Assertion :** *tert*-Butyl methyl ether is not prepared by the reaction of *tert*-butyl bromide with sodium methoxide.  
**Reason :** Sodium methoxide is a weak nucleophile.

#### SECTION - VI

##### Integer Value Correct Type

23. How many of structurally isomeric pentyl alcohols will give immediate turbidity in Lucas test?
- 24
- How many moles of HI consumed in above reaction?
25. How many of the following ethers cannot be prepared by Williamson's synthesis?  
 $\text{CH}_3\text{OCH}_2\text{CH}_3, \text{C}_6\text{H}_5\text{OCH}_3, \text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3, (\text{C}_6\text{H}_5)_2\text{O}, (\text{CH}_3)_3\text{COCH}_3, (\text{CH}_3)_3\text{COCH}_2\text{CH}_3, (\text{CH}_3)_3\text{COC(CH}_3)_3, (\text{C}_2\text{H}_5)_2\text{O}, \text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_5$



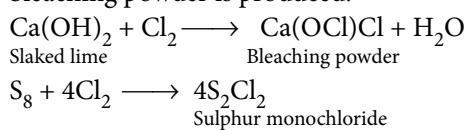
Oxidation state of N in  $\text{NH}_3$ (-3) and in  $\text{NCl}_3(+3)$ .

8. (a): The stability of interhalogens increases as the size difference and polarity of bond increases. Thus, the correct order of stability is  $\text{IF}_3 > \text{BrF}_3 > \text{ClF}_3$ .

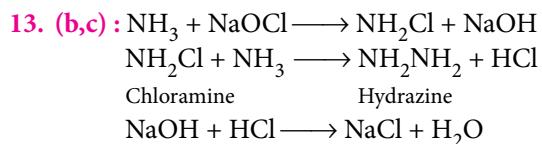


10. (d): The oxidation state of sulphur in its compounds varies from -2 to +6.

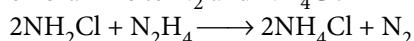
11. (a,c) : If chlorine is passed through dry slaked lime, bleaching powder is produced.



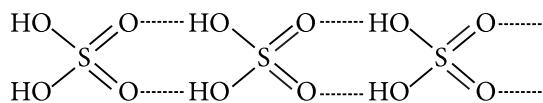
12. (b,c)



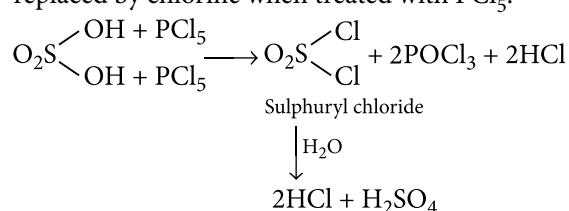
$2\text{NH}_3 + \text{NaOCl} \longrightarrow \text{NH}_2\text{NH}_2 + \text{NaCl} + \text{H}_2\text{O}$   
Hydrazine produced may be decomposed by chloramine to  $\text{N}_2$  and  $\text{NH}_4\text{Cl}$ .



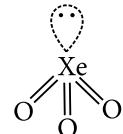
14. (c) : Pure  $\text{H}_2\text{SO}_4$  does not act as oxidising agent, because its molecules are associated due to strong hydrogen bonds.



15. (a) : Two hydroxyl groups of sulphuric acid can be replaced by chlorine when treated with  $\text{PCl}_5$ .

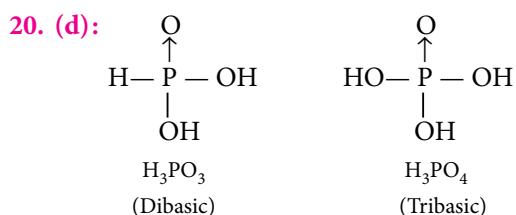


16. (c) : In  $\text{XeO}_3$  there are total of 4 electron pairs around central atom. Out of which 3 are bonding electron pairs and one is non-bonding electron pair. Thus, it has  $sp^3$  hybridisation and pyramidal shape.

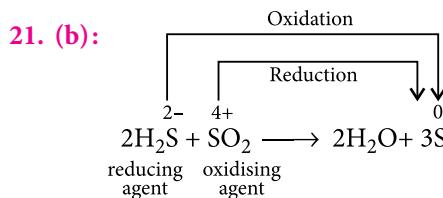


17. (a) : All the xenon fluorides are strongly oxidising.

18. (b)      19. (c)

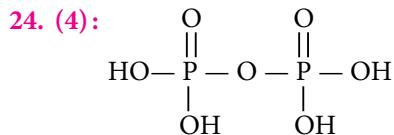


$\text{H}_3\text{PO}_3$  is reducing in nature but  $\text{H}_3\text{PO}_4$  is not a reducing agent as in  $\text{H}_3\text{PO}_4$ , phosphorus is in +5 oxidation state.



22. (d)

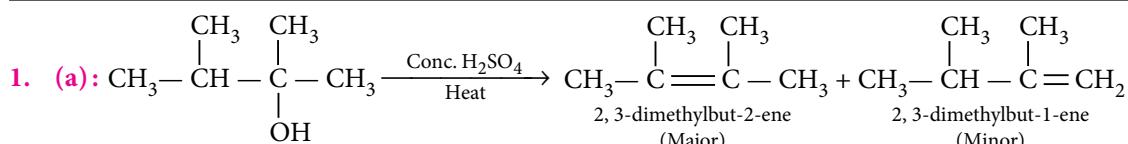
23. (7) : The oxidation state of Cl in  $\text{HClO}_4$  is +7.



4(P—O—H) bonds are present in pyrophosphoric acid.

25. (3) :  $\text{ClF}$  ( $17 + 9 = 26$ ),  $\text{OF}_2$  ( $8 + 2 \times 9 = 26$ ),  $\text{ClO}^-$  ( $17 + 8 + 1 = 26$ )

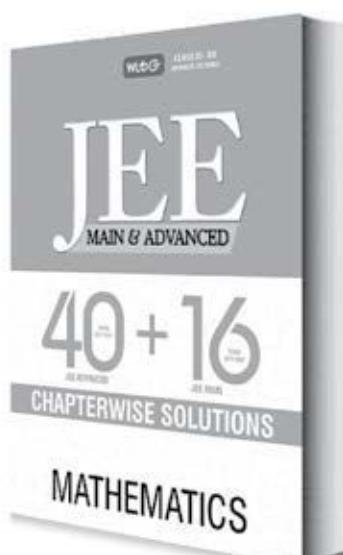
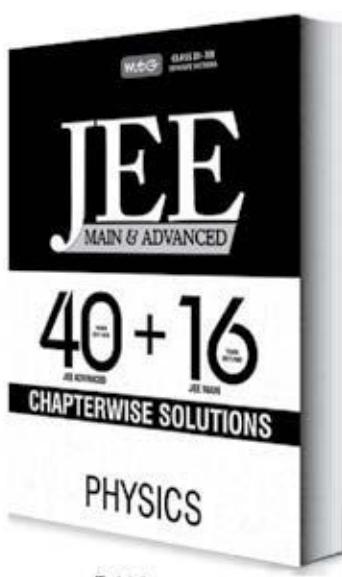
### ALCOHOLS, PHENOLS AND ETHERS



2. (b)

3. (a) : Phenol does not react with copper at  $300^\circ\text{C}$ .

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# YOUR WAY CBSE XII

## CHAPTERWISE PRACTICE PAPER : THE *d*- AND *f*-BLOCK ELEMENTS | COORDINATION COMPOUNDS

Time Allowed : 3 hours

Maximum Marks : 70

### 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 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carry 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

1. Why do Zr and Hf exhibit similar properties?
  2. Why is Ca-EDTA used for the treatment of lead poisoning?
  3. What properties of tungsten make it suitable for use as filaments in light bulbs?
  4. What is the coordination number of Fe in  $[\text{Fe}(\text{EDTA})]$ ?
  5. State the kind of isomerism possible for the following:  
(i)  $[\text{Cr}(\text{en})_3]^{3+}$   
(ii)  $[\text{Cr}(\text{NH}_3)_4(\text{Cl})(\text{Br})]\text{Br}$
  6. What will be the correct order of absorption of wavelength of light in the visible region for the complexes  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ?
  7. Write the formula of the oxo-metal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
  8. Specify the oxidation numbers of the metals in the following coordination entities :
  - (a)  $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$   
(b)  $[\text{PtCl}_4]^{2-}$   
(c)  $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$     (d)  $[\text{CoBr}_2(\text{en})_2]^+$
  9. Write the electronic configurations of the elements with the atomic numbers 61, 91, 101 and 109.
- OR**
- Write the chemical equations for the reactions of  $\text{Cr}_2\text{O}_7^{2-}$  with excess of (a)  $\text{Fe}^{2+}$  and (b)  $\text{SO}_3^{2-}$ .
10. Explain the crystal field splitting in square planar complexes.
  11. How would you account for the following?  
(i) The atomic radii of the third series of transition elements are virtually the same as those of the corresponding members of the second series.  
(ii) The  $E^\circ$  value for  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple is much more positive than that for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  couple or  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple.  
(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.
  12. Calculate the crystal field stabilisation energy of a  $d^8$  ion in a square planar field for both strong and weak field cases.

- 13.** (i) Why are  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{Yb}^{2+}$  good reducing agents?  
(ii) Can lanthanum ( $Z = 57$ ) exhibit +4 oxidation state?  
(iii) Why are +3 oxidation state of gadolinium ( $Z = 64$ ) and lutetium ( $Z = 71$ ) especially stable?
- 14.** Name the following compounds :  
(a)  $[\text{Co}(\text{en})_2(\text{CN})_2]\text{ClO}_3$   
(b)  $\text{K}_4[\text{Co}(\text{CN})_6]$   
(c)  $[\text{Ni}(\text{NH}_3)_6]_3 [\text{Co}(\text{NO}_2)_6]_2$
- 15.** Name the members of the lanthanoid series which exhibit + 4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements.
- 16.** Write the correct formulae for the following coordination compounds :  
(a)  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (violet, with 3 chloride ions/unit formula)  
(b)  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (light green colour, with 2 chloride ions/unit formula)  
(c)  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (dark green colour, with 1 chloride ion/unit formula)
- OR**
- For the square coplanar complex  $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{py}(\text{NO}_2)]^+$ , how many geometrical isomers are possible? Draw the structures of these isomers.
- 17.** What are interstitial compounds? Explain them with reference to transition metals and mention their two important properties.
- 18.** What can be inferred from the magnetic moment values of the following complex species?
- | Example                                       | Magnetic Moment (B.M.) |
|---|------------------------|
| (i) $\text{K}_4[\text{Mn}(\text{CN})_6]$      | 1.7                    |
| (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ | 4.9                    |
| (iii) $\text{K}_2[\text{MnCl}_4]$             | 5.9                    |
- 19.** Decide giving reasons which one will exhibit the property indicated in the given pair.  
(i)  $\text{Sc}^{3+}$  or  $\text{Cr}^{3+}$  : Paramagnetism  
(ii) V or Mn : More number of oxidation states  
(iii)  $\text{V}^{4+}$  or  $\text{V}^{5+}$  : Diamagnetism
- 20.** Discuss briefly giving an example in each case the role of coordination compounds in  
(i) biological systems (ii) medicinal chemistry  
(iii) analytical chemistry.
- 21.** Among lanthanoids,  $\text{Ln}(\text{III})$  compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.
- 22.** Draw geometrical isomers of the following :  
(a)  $[\text{CoCl}_2(\text{en})_2]^+$  (b)  $[\text{Co}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$   
(c)  $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+}$
- 23.** Raman after passing M.Sc. in Chemistry joined a textile factory as a junior scientist. He came to know that factory is using chlorine based bleaching agents for bleaching of textiles. Raman suggested the chief production manager of the factory to use potassium permanganate instead of chlorine for bleaching purpose.  
Now answer the following questions :  
(i) Which property of  $\text{KMnO}_4$  makes it a bleaching agent?  
(ii) Write reduction half reaction of  $\text{KMnO}_4$  in acidic medium.  
(iii) Why is  $\text{KMnO}_4$  better bleaching agent than chlorine?  
(iv) What value is associated with the suggestion of Raman?
- 24.** (a) Give the formula of each of the following coordination entities :  
(i)  $\text{Co}^{3+}$  ion is bound to one  $\text{Cl}^-$ , one  $\text{NH}_3$  molecule and two bidentate ethylene diamine (*en*) molecules.  
(ii)  $\text{Ni}^{2+}$  ion is bound to two water molecules and two oxalate ions.  
Write the name and magnetic behaviour of each of the above coordination entities.  
(b) Identify low spin and high spin complex out of these two.
- OR**
- Indicate the oxidation state, electronic configuration, coordination number and magnetic moment for each of the following complexes.
- (i)  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$   
(ii)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (iii)  $[\text{CrCl}_3(\text{py})_3]$   
(iv)  $\text{Cs}[\text{FeCl}_4]$  (v)  $\text{K}_4[\text{Mn}(\text{CN})_6]$
- 25.** (i) A black mineral (*A*) on treatment with dilute sodium cyanide solution in the presence of air gives a clear solution containing (*B*) and (*C*).  
(ii) The solution of (*B*) on reaction with zinc gives precipitate of metal (*D*).  
(iii) (*D*) dissolved in dil.  $\text{HNO}_3$  and the resulting solution gives a white precipitate of (*E*) with dil.  $\text{HCl}$ .

- (iv) (E) on fusion with sodium carbonate gives (D).  
 (v) (E) dissolved in aqueous solution of ammonia giving a colourless solution of (F).

Identify A to F and give chemical equations involved.

### OR

- (a) First ionisation energy of copper is higher than those of alkali metals, while second and third ionisation energies are lower. Explain.  
 (b) A mixed oxide of iron and chromium,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  is fused with sodium carbonate in the presence of air to form a yellow compound (A). On acidification, the compound (A) forms an orange coloured compound (B) which is a strong oxidising agent. Identify  
 (i) the compounds (A) and (B)  
 (ii) write balanced chemical equations for each step.

26. (a) Arrange the following complexes in the increasing order of conductivity of their solutions :  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ ,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .  
 (b) Why do compounds having similar geometry have different magnetic moment?  
 (c)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is blue in colour while  $\text{CuSO}_4$  is colourless. Why?

### OR

- (a) Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?  
 (b) What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?  
 (c)  $\text{CoSO}_4\text{Cl} \cdot 5\text{NH}_3$  exists in two isomeric forms 'A' and 'B'. Isomer 'A' reacts with  $\text{AgNO}_3$  to give white precipitate, but does not react with  $\text{BaCl}_2$ . Isomer 'B' gives white precipitate with  $\text{BaCl}_2$  but does not react with  $\text{AgNO}_3$ . 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'.

### SOLUTIONS

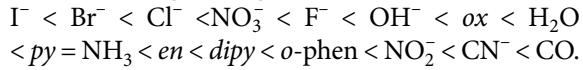
- Due to lanthanoid contraction, Zr and HF have nearly similar size i.e., Zr (160 pm), Hf (159 pm), thus, they exhibit similar properties.
- The complex of calcium with EDTA is used for the treatment of lead poisoning. Lead readily replaces calcium in the complex and lead-EDTA complex

thus formed is finally eliminated from the body through urine.

- High melting point ( $3410^\circ\text{C}$ ), moderate electrical resistance, low volatility, makes tungsten an important component in light bulbs.
- EDTA is a hexadentate ligand, thus coordination number of Fe is 6 in  $[\text{Fe}(\text{EDTA})]$ .
- (i) Optical isomerism  
 (ii) Geometrical isomerism

- As strength of ligand increases crystal field splitting energy (CFSE) increases.

Order of strength of ligands :



$$\text{Now, } \Delta E = \frac{hc}{\lambda}$$

So, as CFSE increases,  $\Delta E$  increases and  $\lambda$  decreases. Thus, the correct order of absorption of wavelength of light in the visible region is :



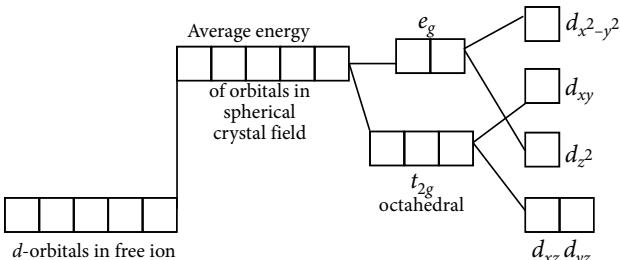
- $\text{ScO}_2^-$ ; Group number = Oxidation state of Sc = 3  
 $\text{TiO}_3^{2-}$  : Group number = Oxidation state of Ti = 4  
 $\text{VO}_3^-$  : Group number = Oxidation state of V = 5  
 $\text{Cr}_2\text{O}_7^{2-}$  : Group number = Oxidation state of Cr = 6  
 $\text{CrO}_4^{2-}$  : Group number = Oxidation state of Cr = 6  
 $\text{MnO}_4^-$  : Group number = Oxidation state of Mn = 7
- (a)  $x + (-1) = +2$  or  $x = +3$   
 (b)  $x + 4(-1) = -2$  or  $x = +2$   
 (c)  $x + 3(-1) = 0$  or  $x = +3$   
 (d)  $x + 2(-1) = +1$  or  $x = +3$
- Atomic number (61) =  ${}_{54}\text{[Xe]} 4f^5 6s^2$   
 Atomic number (91) =  ${}_{86}\text{[Rn]} 5f^2 6d^1 7s^2$   
 Atomic number (101) =  ${}_{86}\text{[Rn]} 5f^{13} 7s^2$   
 Atomic number (109) =  ${}_{86}\text{[Rn]} 5f^{14} 6d^7 7s^2$

### OR

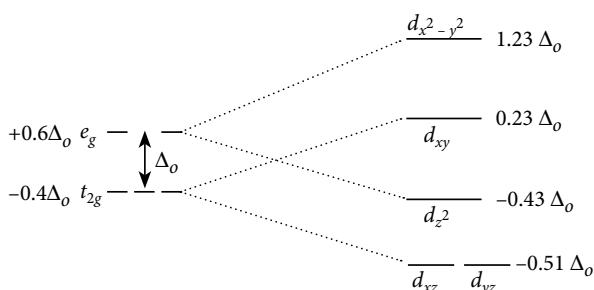
- (a)  $6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \longrightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$   
 (b)  $\text{Cr}_2\text{O}_7^{2-} + 3\text{SO}_3^{2-} + 8\text{H}^+ \longrightarrow 3\text{SO}_4^{2-} + 2\text{Cr}^{3+} + 4\text{H}_2\text{O}$

- The square planar arrangement can be derived from octahedral by removing two ligands from z-axis. On removing ligands from z-axis,  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals become more stable. As the lobes of  $d_{x^2-y^2}$  point towards the ligands, the orbital has highest energy and the lobes of  $d_{xy}$  orbital lie

between the ligands, it is thus next highest orbital in energy. The lobes of  $d_{xz}$  and  $d_{yz}$  are least affected as they lie out of the plane of the complex. The  $d_z^2$  orbital is somewhat affected by electrostatic field of the ligands.



- 11. (i)** The atomic radii of the third series of transition elements are virtually the same as those of the corresponding members of the second series due to lanthanoid contraction.
- (ii)**  $Mn^{3+}(3d^4)$  is less stable than  $Mn^{2+}(3d^5)$  which has stable half-filled configuration.  $Fe^{3+}$  is more stable than  $Fe^{2+}$  due to half-filled configuration.  $Cr^{3+}$  has stable  $t_{2g}^3$  configuration. So,  $E^\circ$  value for the  $Mn^{3+}/Mn^{2+}$  couple is much more positive.
- (iii)** The highest oxidation state of a metal is exhibited in its oxide or fluoride. Due to the high electronegativity and small size of oxygen and fluorine.
- 12.** The terms “strong field” for square planar complexes means that the splitting of the two highest orbitals is greater than the pairing energy. Thus, the strong and weak field configurations are



$$CFSE \text{ (for strong field)} = 4(-0.51\Delta_o) + 2(-0.43\Delta_o) + 2(0.23\Delta_o) + P = -2.44\Delta_o + P$$

$$CFSE \text{ (for weak field)} = 4(-0.51\Delta_o) + 2(-0.43\Delta_o) + 1(+0.23\Delta_o) + 1(+1.23\Delta_o) + P = -1.44\Delta_o + P$$

- 13. (i)** The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of electron and act as reducing agents.

- (ii)**  $La^{3+}$  has a stable configuration of an inert gas  $[Xe]5d^06s^0$ . 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.
- (iii)** This is because gadolinium in +3 oxidation state has half filled 4f-subshell ( $4f^{17}$ ) and lutetium in +3 state has completely filled 4f-subshell ( $4f^{14}$ ) which are very stable configurations.

- 14. (a)** Dicyanobis(ethylenediamine)cobalt(III) chloride
- (b)** Potassium hexacyanocobaltate(II)
- (c)** Hexaamminenickel(II) hexanitrocobaltate(III)

- 15.** +4 oxidation state : Cerium (Ce), Praseodymium (Pr), Terbium (Tb), Dysprosium (Dy)  
 +2 oxidation state : Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Thulium (Tm) and Ytterbium (Yb)  
 +4 and +2 oxidation states of lanthanoid elements arise mainly from the extra stability of empty, half-filled and fully-filled f-subshells. For example, Ce(IV) is  $4f^0$  and has noble gas configuration. Similarly, Tb (IV) and Eu (II) have  $4f^7$  configuration. Yb(II) has  $4f^{14}$  configuration.

- 16.** The given three coordination compounds are examples of special form of ionisation, called hydrate isomerism. Water can exist as a part of coordination entity or a part outside the coordination entity.

- (a)**  $[Cr(H_2O)_6]Cl_3$  : all three  $Cl^-$  ions are outside the coordination entity.
- (b)**  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$  : one  $Cl^-$  ion is part of coordination entity and two are outside of it.
- (c)**  $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$  : two  $Cl^-$  ions are part of coordination entity and one is present outside of it.

The  $Cl^-$  ions outside the coordination entity are ionisable and forms white precipitate with  $AgNO_3$  while  $Cl^-$  ions which are part of coordination entity are not ionisable.

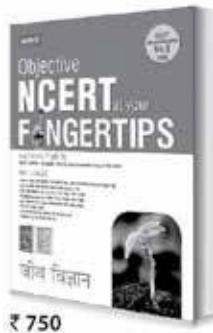
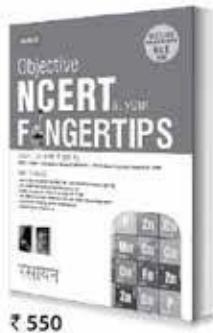
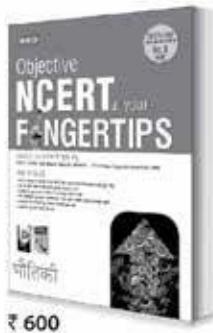
### OR

Three geometric isomers are possible for the given coordination compound. Any other possible configuration would merely be a rotation or reflection of one of these.

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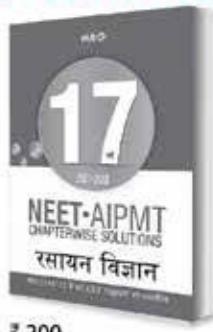
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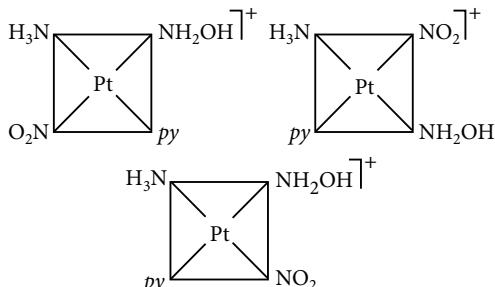
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**17.** Small atoms like B, C, N, etc., can occupy positions in the voids among the atoms of transition metals. Such combinations are termed as interstitial compounds. They are usually non-stoichiometric materials having formulae like  $VH_{0.56}$ ,  $TiH_{1.7}$ ,  $TiC$ , etc. Steel is an interstitial compound in which voids among iron atoms are occupied by carbon atoms.

Two important properties :

- (i) Transition metals become more harder and rigid.
- (ii) Melting points of interstitial compounds are higher than parent metals.

**18.** Calculate the magnetic moment by applying formula;  $\mu = \sqrt{n(n+2)}$

- (i) The magnetic moment of 1.7 B.M. corresponds to  $n = 1$ . Thus, in  $K_4[Mn(CN)_6]$  there is only one unpaired electron in  $3d$ -subshell. Thus, the distribution of five  $3d$ -electrons in Mn(II) is  $(t_{2g})^5$ .
- (ii) The magnetic moment of 4.9 B.M. indicates that there are four unpaired electrons in the complex. Thus, the six  $3d$ -electrons in Fe(II) are distributed as  $(t_{2g})^4 (e_g)^2$ .
- (iii) The magnetic moment of 5.9 B.M. indicates that there are five unpaired electrons in the complex. Hence, the five  $3d$ -electrons in Mn(II) are distributed as  $(t_{2g})^3 (e_g)^2$  in the given complex.

**19. (i)**  $Sc : [Ar]3d^14s^2, Sc^{3+} : [Ar] ;$

It has no unpaired electron.

$Cr : [Ar]3d^54s^1, Cr^{3+} : [Ar]3d^3 ;$

It has three unpaired electrons. Hence,  $Cr^{3+}$  is paramagnetic.

- (ii)  $V : [Ar]3d^34s^2, Mn : [Ar]3d^54s^2$ ; Mn exhibits more number of oxidation states.

The expected oxidation states in V are +2, +3, +4, +5.

The expected oxidation states in Mn are +2, +3, +4, +5, +6, +7.

- (iii)  $V^{4+} : [Ar]3d^1$ ; One unpaired electron
- $V^{5+} : [Ar]$ ; No unpaired electron

Hence,  $V^{5+}$  is diamagnetic in nature.

**20. (i)** Chlorophyll is a coordination compound of magnesium. Haemoglobin is a coordination compound of iron. Vitamin  $B_{12}$ , cyanocobalamin, the anti-pernicious anaemia factor, is a coordination compound of cobalt.

- (ii) There is growing interest in the use of chelate therapy in medicinal chemistry. Excess of copper and iron are removed by the chelating ligands *D*-penicillamine and desferrioxime *B* via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours e.g. *cis*-platin.

(iii) Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands) as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime),  $\alpha$ -nitroso- $\beta$ -naphthol, etc.

**21.** All lanthanoids exhibit a common stable oxidation state of +3. In addition, some lanthanoids show +2 and +4 oxidation states also in solution or in solid compounds. These are shown by those elements which by doing so attain the stable  $f^0$  (empty  $f$ -subshell),  $f^7$  (half filled  $f$ -subshell) and  $f^{14}$  (fully filled  $f$ -subshell) configurations.

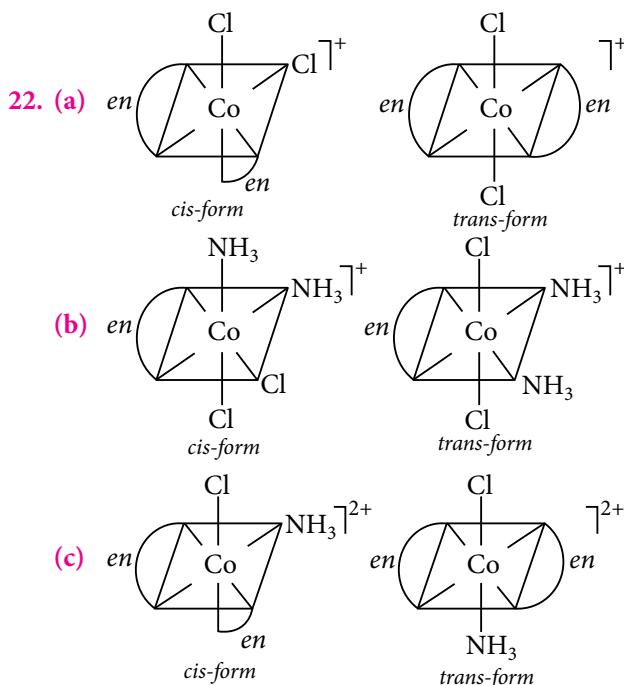
For example,

- (i) Ce and Tb exhibit +4 oxidation state. Cerium (Ce) and terbium (Tb) attain  $f^0$  and  $f^7$  configurations respectively when they get +4 oxidation states, as shown below :

$Ce^{4+} : [Xe]4f^0, Tb^{4+} : [Xe]4f^7$

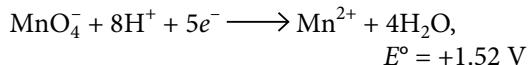
- (ii) Eu and Yb exhibit +2 oxidation state. Europium and ytterbium get  $f^7$  and  $f^{14}$  configurations in +2 oxidation states as shown below :

$Eu^{2+} : [Xe]4f^7, Yb^{2+} : [Xe]4f^{14}$



**23. (i)** Oxidising property of  $\text{KMnO}_4$  makes it a bleaching agent.

**(ii)** Reduction half reaction of  $\text{KMnO}_4$  in acidic medium

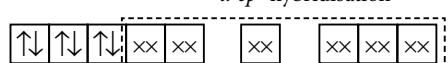
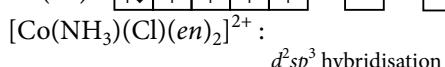
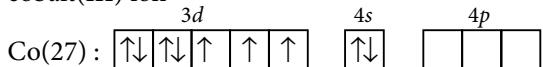


**(iii)** Chlorine may form some harmful compounds during bleaching of textiles. These compounds may cause water pollution whereas the bleaching by  $\text{KMnO}_4$  is harmless.

**(iv)** Self awareness and concern towards environment.

**24. (a) (i)**  $[\text{Co}(\text{NH}_3)(\text{Cl})(\text{en})_2]^{2+}$

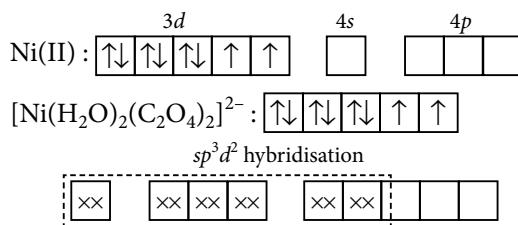
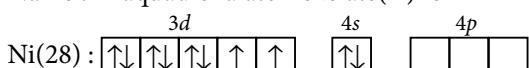
Name : Amminechloridobis(ethane-1, 2-diamine) cobalt(III) ion



Since there are no unpaired electrons, complex is diamagnetic.

**(ii)**  $[\text{Ni}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^{2-}$

Name : Diaquadioxalatonickelate(II) ion



The complex has two unpaired electrons and therefore, it will be paramagnetic.

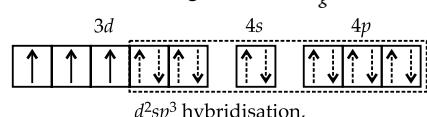
**(b)**  $[\text{Co}(\text{NH}_3)(\text{Cl})(\text{en})_2]^{2+}$  is low spin complex and  $[\text{Ni}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^{2-}$  is high spin complex.

**OR**

**(i)**  $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2].3\text{H}_2\text{O}$

Oxidation state = +3, coordination number = 6

Electronic configuration :  $t_{2g}^3$

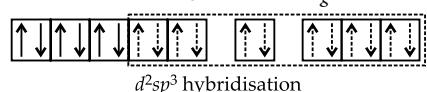


$$\mu = \sqrt{n(n+2)} = \sqrt{3 \times 5} = \sqrt{15} = 3.87 \text{ B.M.}$$

**(ii)**  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Oxidation state of Co = +3, coordination number = 6

Electronic configuration :  $t_{2g}^6$

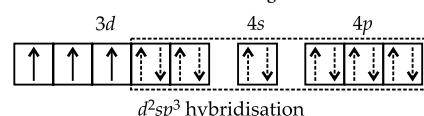


$$\mu = 0 \text{ B.M.}$$

**(iii)**  $[\text{CrCl}_3(\text{py})_3]$

Oxidation state = +3, coordination number = 6

Electronic configuration :  $t_{2g}^3$

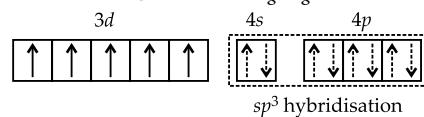


$$\mu = \sqrt{n(n+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

**(iv)**  $\text{Cs}[\text{FeCl}_4]$

Oxidation state = +3, coordination number = 4

Electronic configuration :  $t_{2g}^3 e_g^2$

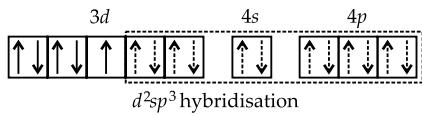


$$\mu = \sqrt{n(n+2)} = \sqrt{5 \times 7} = \sqrt{35} = 5.92 \text{ B.M.}$$

**(v)**  $\text{K}_4[\text{Mn}(\text{CN})_6]$

Oxidation state = +2, coordination number = 6

Electronic configuration :  $t_{2g}^5$

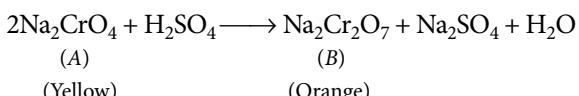
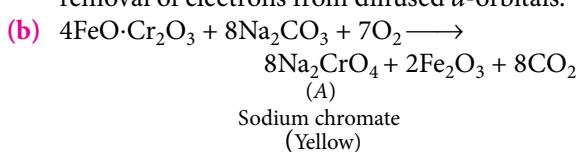


$$\mu = \sqrt{n(n+2)} = \sqrt{1 \times 3} = 1.732 \text{ B.M.}$$

25. (i)  $\text{Ag}_2\text{S} + 4\text{NaCN} + 2\text{O}_2 \longrightarrow 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{SO}_4$
- (ii)  $2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag} \downarrow$
- (iii)  $2\text{Ag} + 4\text{HNO}_3 \longrightarrow 2\text{AgNO}_3 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
- (iv)  $2\text{AgCl} + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{Ag} + 2\text{NaCl} + \text{CO}_2 + 1/2\text{O}_2$
- (v)  $\text{AgCl} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$
- Thus, A =  $\text{Ag}_2\text{S}$ ; B =  $\text{Na}[\text{Ag}(\text{CN})_2]$   
C =  $\text{Na}_2\text{SO}_4$ ; D = Ag; E = AgCl; F =  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

### OR

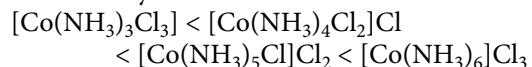
- (a) Copper has small size compared to alkali metals in their period. Its electronic configuration is  $[\text{Ar}]3d^{10}4s^1$ . As filled 3d-subshell is less effective in shielding than s- and p-subshells, so s-electron in copper is more tightly held by the nucleus than that in alkali metals. Hence, its first ionisation energy is higher than for alkali metals. However, second and third ionisation energy values of copper are lower as compared to those of alkali metals due to removal of electrons from diffused d-orbitals.



The compound (B) is oxidising agent.

26. (a) These complexes can ionise in solution as :
- $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  – does not ionise.
- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \longrightarrow [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$  (2 ions)
- $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \longrightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$  (4 ions)
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \longrightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$  (3 ions)

As the number of ions in solution increases, their conductivity also increases. Therefore, conductivity follows the order :



- (b) The compounds having similar geometry may have different number of unpaired electrons due to the presence of weak and strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and if CFSE is low, the complex will show high value of magnetic moment. For example, the  $[\text{CoF}_6]^{3-}$  is paramagnetic but  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic.
- (c) In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , water acts as ligand. As a result it causes crystal field splitting. Hence, d-d transition is possible in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and shows colour. In the anhydrous  $\text{CuSO}_4$  due to the absence of water (ligand), crystal field splitting is not possible and hence, no d-d transition occurs and shows no colour.

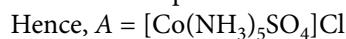
### OR

- (a) Lower wavelength is absorbed in octahedral complex than tetrahedral complex for the same metal and ligand. In tetrahedral coordination entity, formation of the d-orbital splitting is inverted and is smaller as compared to the octahedral field splitting. Thus, the energy of tetrahedral complex is smaller than compared to octahedral complex.  $\Delta_t = (4/9)\Delta_o$

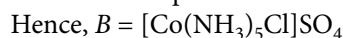
- (b) When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.



- (i) Isomer A reacts with  $\text{AgNO}_3$  but not with  $\text{BaCl}_2$ , it shows it has  $\text{Cl}^-$  ion outside the coordination sphere.



- Isomer B reacts with  $\text{BaCl}_2$  but not with  $\text{AgNO}_3$ , it shows it has  $\text{SO}_4^{2-}$  outside the coordination sphere.

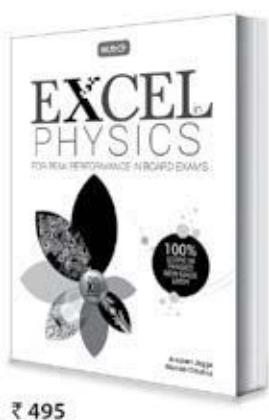


- (ii) Ionisation isomerism

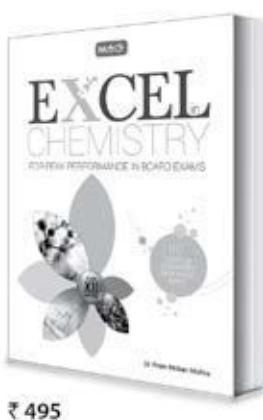
- (iii) A = Pentaamminesulphatocobalt(III) chloride and



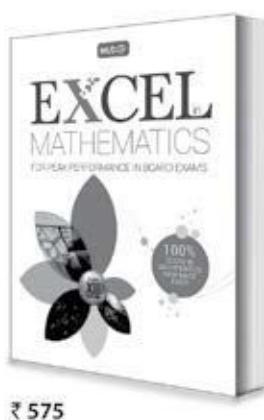
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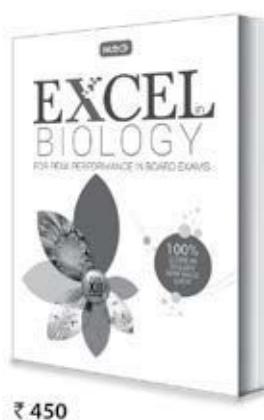
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# MPP-5 | MONTHLY Practice Problems

Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

## The *d*- and *f*- Block Elements | Coordination Compounds

Total Marks : 120

Time Taken : 60 Min.

NEET / AIIMS

Only One Option Correct Type

1. The basic character of the transition metal monoxides follow the order
  - (a) CrO > VO > FeO > TiO
  - (b) TiO > VO > CrO > FeO
  - (c) TiO > FeO > VO > CrO
  - (d) VO > CrO > TiO > FeO
2. Which of the following statements is correct?
  - (a) Geometrical isomerism is not observed in complexes of coordination number four having tetrahedral geometry.
  - (b) Square planar complexes generally do not show geometrical isomerism.
  - (c) The square planar complexes of general formulae  $Ma_3b$  or  $Mab_3$  exhibit *cis-trans* isomerism.
  - (d) The platinum glycinate complex,  $[Pt(\text{gly})_2]$  does not show geometrical isomerism.
3. There are three unpaired electrons in  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and calculated value of magnetic moment is 3.87 B.M which is quite different from the experimental value of 4.40 B.M. This is because of
  - (a) increase in number of unpaired electrons
  - (b) some contribution of the orbital motion of the electron to the magnetic moment
  - (c) change in orbital spin of the electron
  - (d) *d-d* transition.
4. In which of the following metal complexes, central metal atom have zero valency?
  - (a)  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
  - (b)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
  - (c)  $[\text{Ni}(\text{CO})_4]$
  - (d)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

5. If zinc pieces are added to  $\text{FeCl}_3$  solution, its colour changes from yellow to light green. It is because
  - (a)  $\text{FeCl}_3$  solution is acidic due to hydrolysis and zinc added produces nascent hydrogen causing reduction of  $\text{FeCl}_3$  to  $\text{FeCl}_2$
  - (b)  $\text{FeCl}_3$  solution is basic and zinc added produces  $\text{H}_2$  which reduces  $\text{FeCl}_3$  to  $\text{FeCl}_2$
  - (c) zinc oxidises  $\text{FeCl}_3$  to  $\text{FeCl}_2$
  - (d) none of the above is correct.
6. The two compounds pentaamminesulphato-cobalt(III) bromide and pentaamminesulphato-cobalt(III) chloride represent
  - (a) linkage isomerism
  - (b) ionisation isomerism
  - (c) coordination isomerism
  - (d) none of these.
7. Which compound is coloured due to charge transfer spectra?
  - (a)  $\text{K}_2\text{Cr}_2\text{O}_7$
  - (b)  $\text{KMnO}_4$
  - (c)  $\text{CrO}_3$
  - (d) All of these
8. Crystal field stabilisation energies of octahedral and tetrahedral complexes having high spin  $d^6$  configuration respectively are
  - (a)  $0.6 \Delta_o, 0.6 \Delta_t$
  - (b)  $0.4 \Delta_o, 0.4 \Delta_t$
  - (c)  $0.4 \Delta_o, 0.6 \Delta_t$
  - (d)  $0.6 \Delta_o, 0.4 \Delta_t$
9. Pick out the correct statements from the following :
  - (1) Cobalt(III) is more stable in octahedral complexes.
  - (2) Zinc forms coloured complexes.
  - (3) Most of the *d*-block elements and their compounds are ferromagnetic.
  - (4) Osmium shows +8 oxidation state.



## **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 :** KMnO<sub>4</sub> is stored in dark coloured bottles.

**Reason :** On heating with alkalies,  $\text{KMnO}_4$  is converted to manganate.

**14. Assertion :**  $\text{F}^-$  ion is a weak ligand and forms outer orbital complex.

**Reason :** F<sup>-</sup> ion cannot force the electrons of  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals of the inner shell to occupy  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  orbitals of the same shell.

**15. Assertion :** There is an increase in oxidation potential of  $\text{Fe}^{2+}$  when it combines with a ligand  $\text{CN}^-$ .  
**Reason :** Ionic activity of  $\text{Fe}^{2+}$  increases during complex formation of  $[\text{Fe}(\text{CN})_6]^{4-}$ .

JEE MAIN / JEE ADVANCED

## Only One Option Correct Type

16. A complex containing  $Mn^{2+}$  and  $Br^-$  ions was found to have a magnetic moment of 5.92 B.M. The

probable formula and geometry of the complex is most likely to be

- (a)  $[\text{MnBr}_4]^{2-}$ , tetrahedral
  - (b)  $[\text{MnBr}_6]^{3-}$ , octahedral
  - (c)  $[\text{MnBr}_4]^{2-}$ , square planar
  - (d)  $[\text{MnBr}_5]^{3-}$ , trigonal planar

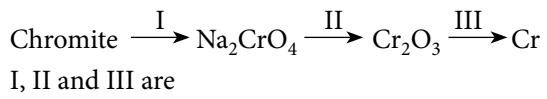
**17.** Which of the following orders are correct?



18. On treatment of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  with concentrated HCl, two compounds (I) and (II) having the same formula,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  are obtained, (I) can be converted into (II) by boiling with dilute HCl. A solution of (I) reacts with oxalic acid to form  $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  whereas (II) does not react. Choose the correct option from the following :

- (a) (I) *cis*, (II) *trans*; both tetrahedral
  - (b) (I) *cis*, (II) *trans*; both square planar
  - (c) (I) *trans*, (II) *cis*; both tetrahedral
  - (d) (I) *trans*, (II) *cis*; both square planar

19.  $\text{FeCr}_2\text{O}_4$  (chromite) is converted to Cr by the following steps :



I	II	III
(a) $\text{Na}_2\text{CO}_3/\text{air}, \Delta$	C	C
(b) $\text{NaOH}/\text{air}, \Delta$	$\text{C}, \Delta$	$\text{Al}, \Delta$
(c) $\text{NaOH}/\text{air}, \Delta$	$\text{C}, \Delta$	$\text{Mg}, \Delta$
(d) conc. $\text{H}_2\text{SO}_4, \Delta$	$\text{NH}_4\text{Cl}, \Delta$	C, $\Delta$

## More than One Options Correct Type

**20.**  $K_4[Fe(CN)_6]$  is used in the identification of



**21.** Mark the incorrect statements.

- (a) Potassium dichromate oxidises a secondary alcohol into a ketone.
  - (b) Potassium permanganate is a weaker oxidising agent than potassium dichromate.
  - (c) Potassium permanganate is a stronger oxidising agent than potassium dichromate.
  - (d) Potassium dichromate oxidises a secondary alcohol into a aldehyde.

22. In basic medium, the amount of  $\text{Ni}^{2+}$  in a solution can be estimated with the dimethylglyoxime reagent. The correct statements about the reaction and the product are

- (a) in ammoniacal solution,  $\text{Ni}^{2+}$  salts give cherry-red precipitate of nickel(II) dimethylglyoximate
- (b) two dimethylglyoximate units are bound to one  $\text{Ni}^{2+}$
- (c) in the complex, two dimethylglyoximate units are hydrogen bonded to each other
- (d) each dimethylglyoximate unit forms a six-membered chelate ring with  $\text{Ni}^{2+}$ .

23. When an acidified dichromate solution is shaken with a pinch of  $\text{Na}_2\text{O}_2$

- (a) a blue colouration is observed
- (b) orange red colouration finally changes to green
- (c) oxygen gas is evolved
- (d) bluish green precipitate is formed.

#### Integer Answer Type

24. The volume (in mL) of 0.1 M  $\text{AgNO}_3$  required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ , as silver chloride, is close to

25. Amongst the following, the number of metals which do not form amalgams is

- Ti, V, Cr Mn, Fe, Co, Ni, Pt, Cu, Zn

26. The complex,  $\text{Ca}_2[M(\text{CN})_6]$  has spin only magnetic moment 2.83 B.M. and the complex  $\text{K}_2[\text{MCl}_4]$  has spin only magnetic moment of 4.9 B.M. How many electrons are present in valence shell  $d$ -orbitals of the neutral gaseous atom  $M$ ?

#### Comprehension Type

The lanthanoids exhibit a principal oxidation state of +3. The +3 oxidation states in lanthanum, gadolinium and lutetium are stable because these ions have an empty, a half-filled and completely filled 4f-subshell respectively. But some of the lanthanoids exhibit different oxidation states.

27. Good oxidising agent out of the following lanthanoids is

- (a)  $\text{Ce}^{3+}$
- (b)  $\text{Sm}^{2+}$
- (c)  $\text{Ce}^{4+}$
- (d)  $\text{Eu}^{2+}$

28. For which of the following lanthanoids, +2 oxidation state exists in aqueous solution?

- (a) Ce, Yb, La
- (b) Ce, Eu, Ho
- (c) Er, Tb, Sm
- (d) Sm, Eu, Yb

#### Matrix Match Type

29. Match the magnetic moments listed in Column II with the electronic configurations of the complexes listed in Column I and choose the correct option using the codes given below.

##### Column I

- (A)  $d^3$  (octahedral)
- (B)  $d^5$  (octahedral, low spin)
- (C)  $d^6$  (octahedral, low spin)
- (D)  $d^6$  (octahedral, outer orbital)

##### Column II

- (p) 0.0 B.M.
- (q)  $2\sqrt{6}$  B.M.
- (r)  $\sqrt{15}$  B.M.
- (s)  $\sqrt{3}$  B.M.

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

30. Match the Column I with Column II and choose the correct option using the codes given below.

##### Column I

- (A) Aquated  $\text{Mn}^{2+}$  ion
- (B)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
- (C) Aquated  $\text{V}^{4+}$  ion
- (D) Anhydrous  $\text{CuSO}_4$

##### Column II

- (p) White
- (q) Blue
- (r) Pink
- (s) Green

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



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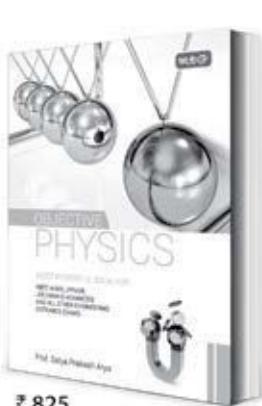
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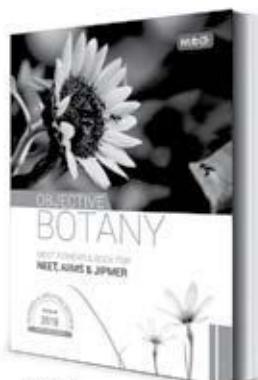
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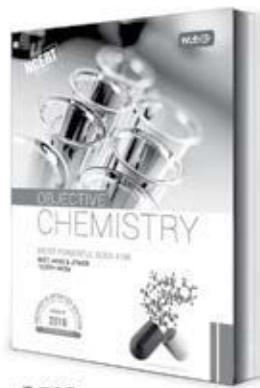
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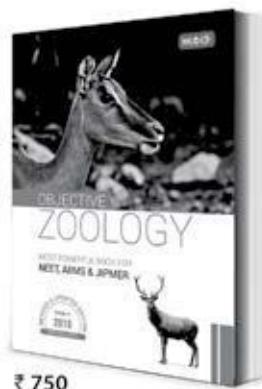
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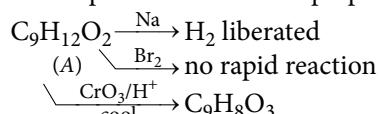


(d) I > IV

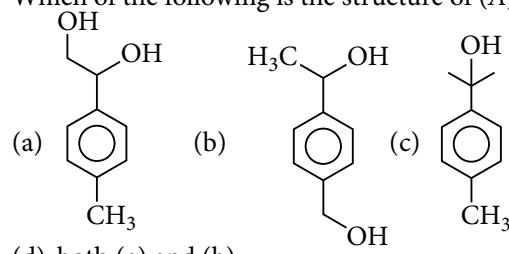
6. An optically active compound (A) of formula,  $C_9H_{12}O_2$  produced the following compound when refluxed with  $KMnO_4$ .



The original compound showed these properties also :



Which of the following is the structure of (A)?



## COMPREHENSION

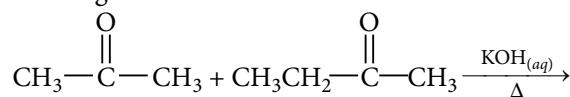
A yellow powder X is burnt in a stream of fluorine to obtain a colourless gas, Y which is thermally stable and chemically inert. Its molecule has octahedral geometry. Another colourless gas, Z with same constituent atoms as that of Y is obtained when sulphur dichloride is heated with sodium fluoride. Its molecule has trigonal bipyramidal geometry.

7. The yellow powder X is  
(a)  $K_2Cr_2O_7$       (b)  $FeCl_3$   
(c)  $K_2CrO_4$       (d) S

8. The colourless gases Y and Z respectively are  
(a)  $SF_4, SF_4$       (b)  $SF_6, SF_4$   
(c)  $NaF, SF_6$       (d)  $S_2F_2, NaF$

## INTEGER VALUE

9. Total number of aldol condensation products of the following reaction is



10. The reaction,  $\text{SO}_2\text{Cl}_2 \xrightarrow{k_1} \text{SO}_2 + \text{Cl}_2$   
 is a first order reaction with  $k_1 = 2.2 \times 10^{-5} \text{ sec}^{-1}$   
 at  $302^\circ\text{C}$ . The percentage of  $\text{SO}_2\text{Cl}_2$  that will get  
 decomposed in 90 minutes when the reaction is  
 carried out at  $302^\circ\text{C}$  is  $(8.2 + y)$ . The value of  $y$  is

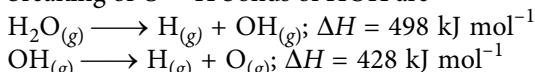
# JEE Advanced

## PRACTICE PROBLEMS

### SECTION 1 (Maximum Marks : 18)

This section contains 6 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.

1. The enthalpy changes at 298 K in successive breaking of O—H bonds of HOH are

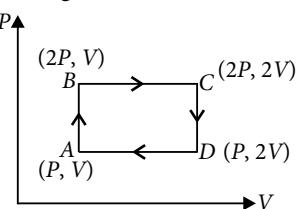


The bond enthalpy of O—H bond is

- (a) 498 kJ mol<sup>-1</sup>      (b) 463 kJ mol<sup>-1</sup>  
 (c) 428 kJ mol<sup>-1</sup>      (d) 70 kJ mol<sup>-1</sup>

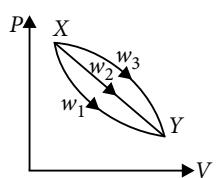
2. An ideal monoatomic gas is taken round the cycle ABCDA as shown in the figure. The work done during the cycle is

- (a)  $-PV$   
 (b)  $-2PV$   
 (c)  $-\frac{1}{2}PV$   
 (d) zero.



3. A given mass of gas expands from the state X to state Y by three paths 1, 2 and 3 as shown in the figure. If  $w_1$ ,  $w_2$  and  $w_3$  respectively be the work done by the gas along these three paths then

- (a)  $w_1 > w_2 > w_3$       (b)  $w_2 < w_1 < w_3$   
 (c)  $w_1 = w_2 = w_3$       (d)  $w_1 < w_2 < w_3$



4. Identify the reaction in which the heat liberated corresponds to the heat of formation ( $\Delta H$ ).

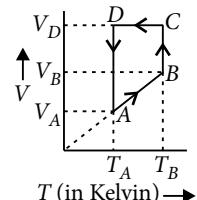
- (a)  $\text{C}_{(\text{diamond})} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + \text{heat}$   
 (b)  $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)} + \text{heat}$   
 (c)  $\text{C}_{(\text{diamond})} + 2\text{H}_{2(g)} \rightarrow \text{CH}_{4(g)} + \text{heat}$   
 (d)  $\text{S}_{(\text{rhombic})} + \text{O}_{2(g)} \rightarrow \text{SO}_{2(g)} + \text{heat}$

5. The entropy change in the fusion of one mole of a solid melting at 27°C is (latent heat of fusion = 2930 J mol<sup>-1</sup>)  
 (a) 9.77 J K<sup>-1</sup> mol<sup>-1</sup>      (b) 10.73 J K<sup>-1</sup> mol<sup>-1</sup>  
 (c) 2930 J K<sup>-1</sup> mol<sup>-1</sup>      (d) 108.5 J K<sup>-1</sup> mol<sup>-1</sup>

6. Two moles of a monoatomic ideal gas are taken through a cyclic process starting from A as shown in the figure. The volume ratios are  $\frac{V_B}{V_A} = 2$  and  $\frac{V_D}{V_A} = 4$ .

If the temperature  $T_A$  at A is 27 °C, calculate the total heat absorbed (in calories) in the cyclic process.

- (a) 1080      (b) 900      (c) 600      (d) 1200



### SECTION 2 (Maximum Marks : 08)

This section contains 2 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which one or more than one answer is correct. For each question you will be awarded 4 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marking in this section.

7. Five moles of an ideal gas at 293 K are expanded isothermally from an initial pressure of 0.4 kPa to a final pressure of 0.1 kPa against a constant external pressure of 0.1 kPa. Select the correct option(s).

- (a)  $q = 0$  and  $w \neq 0$   
 (b)  $q = 0$  and  $w = 0$   
 (c)  $\Delta E = 0$  and  $\Delta H \neq 0$   
 (d)  $\Delta E = 0$  and  $\Delta H = 0$

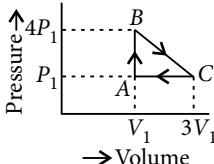
8. In an insulated container, 1 mole of a liquid (molar volume 100 mL) at 1 bar is steeply taken to 100 bar when volume of liquid decreases by 1 mL. Select the correct option(s).

- (a)  $\Delta U = 99 \text{ bar mL}$       (b)  $\Delta U = 100 \text{ bar mL}$   
 (c)  $\Delta H = 9900 \text{ bar mL}$       (d)  $\Delta H = 100 \text{ bar mL}$

### SECTION 3 (Maximum Marks : 24)

This section contains 6 integer type questions. Answers have to be given in between 0 to 9 in the form of nearest integer. Each question carries 4 marks if you have darkened the correct answer and no negative mark will be awarded for an incorrectly bubbled answer.

9. 3.5 g of a gas (mol. wt. = 28) was burnt in excess of oxygen at 298 K in a constant volume calorimeter. The temperature of the calorimeter was found to increase to 298.45 K. The enthalpy of combustion (in  $\text{kJ mol}^{-1}$ ) is (Heat capacity of calorimeter =  $2.5 \text{ kJ K}^{-1}$ )
10. The heat of formation of ethane is  $-19.46 \text{ kcal}$ . Bond energies of H—H, C—H and C—C bonds are 104.18, 99.0 and 80.0 kcal respectively. The heat of atomization of graphite can be expressed in scientific notation as  $p \times 10^q$  calories. Identify  $p$ .
11. For a hypothetical reaction,  $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$   $\Delta G^\circ$  and  $\Delta S^\circ$  are  $20 \text{ kJ/mol}$  and  $-20 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively at  $200 \text{ K}$ . If  $\Delta C_p$  is  $20 \text{ J K}^{-1} \text{ mol}^{-1}$  then  $\Delta H^\circ$  at  $400 \text{ K}$  is  $x$ . Find  $\frac{x}{4}$ ?
12. An ideal gas is taken around the cycle ABCA as shown in the figure. Work done in the cyclic process =  $xP_1V_1$ . What is the value of  $x$ ?
13. In a thermodynamic process, helium gas obeys the law  $\frac{T}{P^{2/5}} = \text{constant}$ . The heat given to  $n$  moles of He in order to raise the temperature from  $T$  to  $2T$  is



14. In the process :  
 $\text{H}_2\text{O}_{(s)} (-10 \text{ }^\circ\text{C}, 1 \text{ atm}) \rightarrow \text{H}_2\text{O}_{(l)} (10 \text{ }^\circ\text{C}, 1 \text{ atm})$   
 $C_p$  for ice =  $9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ,  
 $C_p$  for  $\text{H}_2\text{O}$  =  $18 \text{ cal deg}^{-1} \text{ mol}^{-1}$   
Latent heat of fusion of ice =  $1440 \text{ cal mol}^{-1}$  at  $0 \text{ }^\circ\text{C}$   
The entropy change for the above process will be

### SECTION 4 (Maximum Marks : 06)

This section contains 1 paragraph. Based upon paragraph, 2 multiple choice questions have to be answered. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.

#### PARAGRAPH

Chemical reactions can be viewed from a thermodynamic perspective. Change in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) are the two driving forces that determine whether a reaction is spontaneous. Gibbs free energy ( $\Delta G$ ) combines these two factors in one equation :

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

Compound	$\Delta H_f^\circ (\text{kJ/mol})$	$S^\circ (\text{J/mol-K})$
$\text{N}_{2(g)}$	0	192
$\text{H}_{2(g)}$	0	131
$\text{NH}_{3(g)}$	-46	192

15. What is the value of  $\Delta H^\circ$  for the reaction,  $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$ ?
  - (a) -46 kJ
  - (b) -92,000 J
  - (c) 0 J
  - (d) 138 kJ
16. What is  $\Delta S^\circ$  for the reaction,  $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$ ?
  - (a) -201 J/K
  - (b) -192 J/K
  - (c) -131 J/K
  - (d) 201 J/K

### SECTION 5 (Maximum Marks : 16)

This section contains 2 questions. Each question contains statements given in 2 columns. Statements in the first column have to be matched with statements in the second column. For each question in this section, you will be awarded 8 marks if you have darkened all the bubbles corresponding only to the correct answer and 2 marks for each row. No negative mark will be awarded for an incorrectly bubbled answer.

17. Match the Column I with Column II.

Column I	Column II
(A) $\text{Ice} \rightleftharpoons \text{H}_2\text{O}_{(l)}$	(p) $\Delta H = -\text{ve}$ , $\Delta S = +\text{ve}$ at room temperature $25 \text{ }^\circ\text{C}$
(B) $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{Ice}$	(q) $\Delta G = +\text{ve}$ at room temperature $25 \text{ }^\circ\text{C}$
(C) $2\text{O}_{3(g)} \rightarrow 3\text{O}_{2(g)}$	(r) $\Delta H = +\text{ve}$ , $\Delta S = -\text{ve}$
(D) $3\text{O}_{2(g)} \rightarrow 2\text{O}_{3(g)}$	(s) $\Delta G = -\text{ve}$
18. Match the Column I with Column II.

Column I	Column II
(A) $\text{Ice} \rightleftharpoons \text{Water}$ at $273 \text{ K}$	(p) $\Delta H < 0$ , $\Delta S < 0$
(B) $\text{NH}_{3(g)} + \text{HCl}_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$	(q) $\Delta G = 0$
(C) $2\text{NH}_{3(g)} \rightarrow 3\text{H}_{2(g)} + \text{N}_{2(g)}$	(r) $\Delta n > 0$ , $\Delta H > \Delta U$
(D) $\text{CO}_{2(g)} \rightarrow \text{Dry ice}$	(s) $\Delta n < 0$ , $\Delta H < \Delta U$

### ANSWER KEY

1. (b)
2. (a)
3. (d)
4. (d)
5. (a)
6. (d)
7. (d)
8. (b, c)
9. (9)
10. (2)
11. (5)
12. (3)
13. (0)
14. (6)
15. (b)
16. (a)
17. (A) - (s), (B) - (q), (C) - (p, s); (D) - (q, r)
18. (A) - (q), (B) - (p, s), (C) - (r); (D) - (p, s)

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# CONCEPT BOOSTER

Hi all!! Hope you all are doing well. This is the last part of the consecutive 'SHORTCUT OF INORGANIC CHEMISTRY' article. Inorganic Chemistry is endless but what I have tried is to give you an idea, how to read Inorganic Chemistry. Hope you liked it. Keep practicing harder and harder.

\*Arunava Sarkar

## HEATING EFFECTS

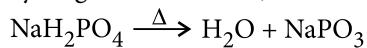
### HEATING EFFECT OF DICHROMATE SALTS



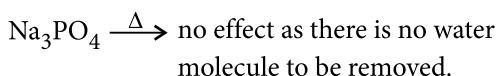
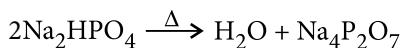
### HEATING EFFECT OF PHOSPHATE SALTS

**Shortcut :** Remove only water and if any gas is possible (like NH<sub>3</sub> but not O<sub>2</sub> and oxides of P) then that too.

- Now, phosphoric acid is H<sub>3</sub>PO<sub>4</sub>. So, the first salt that comes to our mind is NaH<sub>2</sub>PO<sub>4</sub> (one acidic hydrogen substitution). It is 1° phosphate salt.

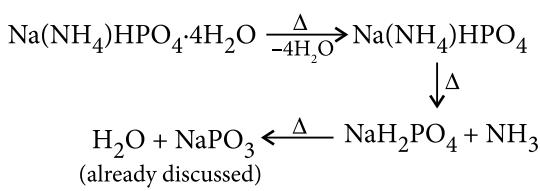
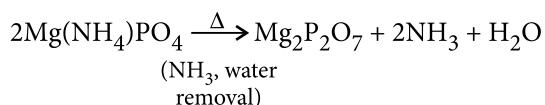


(Just remove H<sub>2</sub>O; don't think much.)



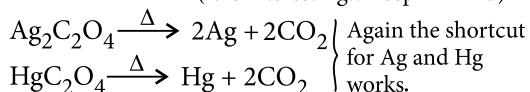
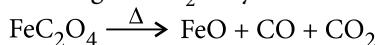
- Ammonium containing phosphate salts, of course evolve NH<sub>3</sub> along with water on heating.

For example,



### HEATING EFFECT OF OXALATE SALTS

- In general, more reactive metal's oxalate salts give both CO and CO<sub>2</sub> on heating whereas less reactive metals give CO<sub>2</sub> only.

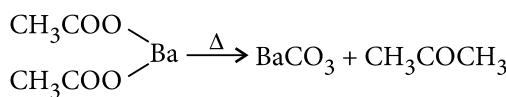
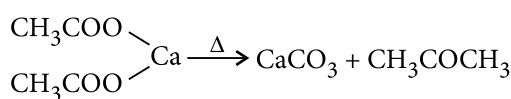


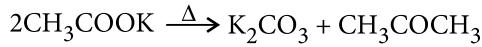
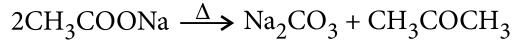
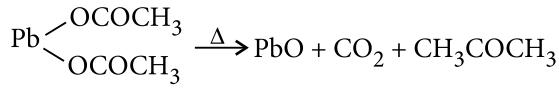
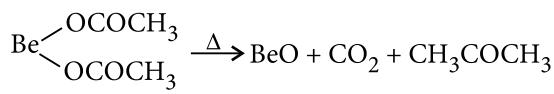
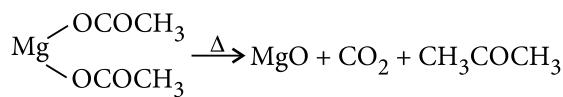
### HEATING EFFECT OF ACETATE SALTS

A few points must be remembered here :

- Formation of acetone is inevitable as this is a general method of preparation of acetone.
- Smaller alkaline earth metals like Be, Mg (first two in the group) cannot hold bigger CO<sub>3</sub><sup>2-</sup> tightly with them and they prefer to exist in the form of oxide. So, for them, metal oxide and CO<sub>2</sub> will be produced. But, for relatively larger metals like Ca, Ba, etc. carbonate salts will be produced.
- For alkali metals, carbonate salts are obtained.

Let us check :

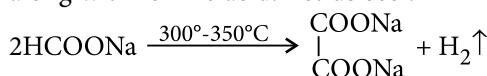




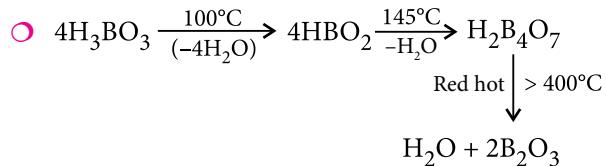
### HEATING EFFECT OF FORMATE SALTS

Three major points to be remembered :

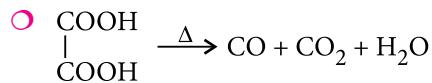
- Lower alkali metals give corresponding oxalates.
- Alkaline earth metals give formaldehyde (in general).
- Silver and mercury salts as usual give metal back along with formic acid. Let us see :



### HEATING EFFECT OF BORIC ACID



### HEATING EFFECT OF OXALIC ACID



### MPP-5 CLASS XII

### ANSWER KEY

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

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# ADVANCED CHEMISTRY BLOC

(AN INSIGHT TO MOT)

Mukul C. Ray, Odisha

## LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

The definition goes like this.

"The simplest trial functions that work reasonably well in molecular orbital theory turn out to be linear combination of atomic orbitals, or LCAO".

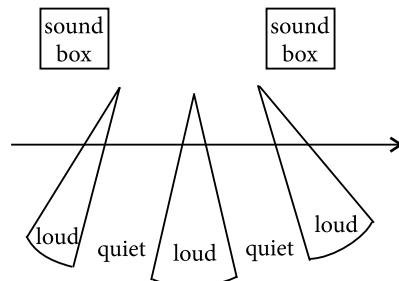
But what is the trial function? In molecular orbital theory (MOT), you actually do not solve Schrödinger ( $\ddot{o}$  is a German umlaut, read it as Schroedinger) equation. It's not that easy. Instead you use a trial function, an "educated guess" as to what the solution might be. Suppose you want to know the value of  $x$  in the equation,  $4x + 5 = 70$  without solving. Without solving you just guess a value of  $x$  and see how it works. In MOT, the estimating procedure is analogous. In order to determine how well a trial function for an orbital works in MOT, you calculate energy. Your trial wave function should try to approach as close as to the energy of the actual orbital. In MOT, the trial wave function for molecular orbitals are weighted linear sum of valence atomic orbitals of atoms in a molecule. When I say weighted that means you need not necessarily take equal contribution of atomic orbital wave functions of combining atoms.

Number of atomic orbitals combining is equal to the number of molecular orbitals formed. It's not new, I am sure, for you that atomic orbitals combine to give  $\sigma 1s$  and  $\sigma^*1s$ , former having lower energy and later higher energy than combining atomic orbitals.

In VBT, we treat electrons as if they reside in the atomic orbital. This is an over simplification. We tried in a better way in MOT. The bonding molecular orbital arises out of constructive interference between the atomic orbitals because both orbitals have the same

phase. The antibonding orbital arises out of destructive interference.

You can compare the situation like the following :



Say, you are walking along the arrow mark you will be able to notice remarkably neat pattern of alternating maxima and minima produced from two identical sources. This is superposition of waves from two loud speakers. The atomic orbital wave functions almost behave similarly.

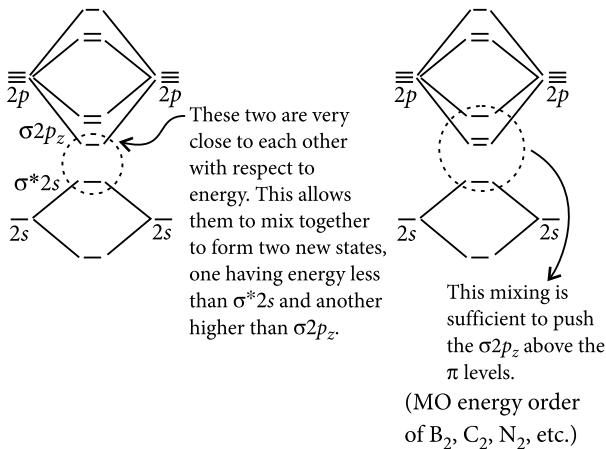
The key point to understand is that, every electron which enters a bonding molecular orbital stabilises the molecule or polyatomic ion and every electron which enters an antibonding molecular orbital destabilises it. The emphasis on electron pair has been removed. Also, an electron when removed from bonding orbital, destabilises the system and an electron when added to antibonding orbital also destabilises the system but adding an electron to antibonding orbital destabilises it more.

## Applications

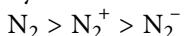
- Stability :  $H_2 > H_2^+ > H_2^-$

Even though the bond order of  $H_2^+$  and  $H_2^-$  are same,  $H_2^-$  is less stable. The paragraph just above explains this observation.

- For second period diatomic molecules, O<sub>2</sub> and F<sub>2</sub>, the sequence of energy of molecular orbital is ( $\sigma_{2s}$ ) ( $\sigma^*_{2s}$ ) ( $\sigma_{2p_z}$ ) ( $\pi_{2p_x} = \pi_{2p_y}$ ) ( $\pi^*_{2p_x} = \pi^*_{2p_y}$ ) ( $\sigma^*_{2p_z}$ ) It's simple to handle, O<sub>2</sub>, O<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup>, F<sub>2</sub>, etc. You just feel the electrons from lower end considering each molecular orbital takes maximum 2 electrons and for degenerate molecular orbital, Hund's rule is applicable.
- For second period diatomic molecules on the left of oxygen like B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, the energy sequence is slightly altered. The reason is that the energy gap between 2s and 2p is less in these atoms B, C, N, etc.

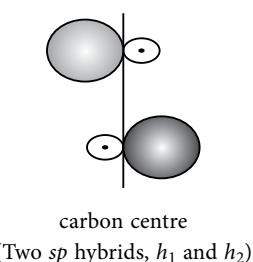


Also you must note the stability sequence :



The explanation is the same as for H<sub>2</sub><sup>+</sup> and H<sub>2</sub><sup>-</sup>.

- For CO, the two hybrid orbitals are directed at 180° to each other.

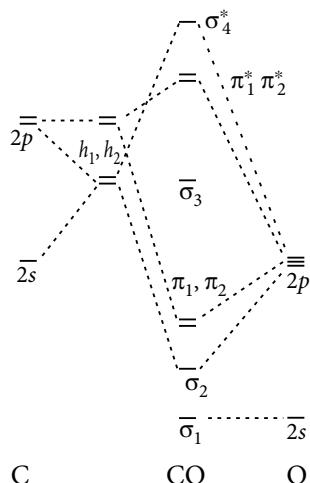


### Solution Senders of Chemistry Musing

#### Set - 49

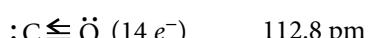
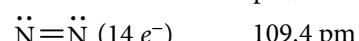
- Ravinder Kashapogu, Telangana
- Naveen Soni, Gujarat
- Akila Iyer, Bengaluru

One hybrid orbital is directed dimetrically opposite to the CO bonding region. Hence, it does not form bond but retains a pair of electron ( $\sigma_3$ ).

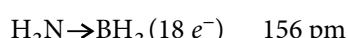


$\sigma_3$  is primarily of non-bonding nature. The pair of electrons present in  $\sigma_3$  is the carbon based lone pair, which is approximately 126 pm far from carbon in opposite direction to oxygen. This lowers the dipole moment of CO molecule significantly down to 0.112 D.

When CO ionises to CO<sup>+</sup>, the carbon-oxygen bond length decreases from 112.8 pm to 111.5 pm. Some author have an opinion that bond order has increased from 3 to 3.5 in CO<sup>+</sup>. But this is not very reasonable as second period elements can never form more than three bonds. (Though Re forms quadruple bond in Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> ion). The better explanation comes from VBT. A triple bond that has partial dative bond character develops pure covalent character in order to distribute the net positive charge on both the atoms. As an evidence, we can see that dative bonds are longer than isoelectronic covalent bonds. For example,



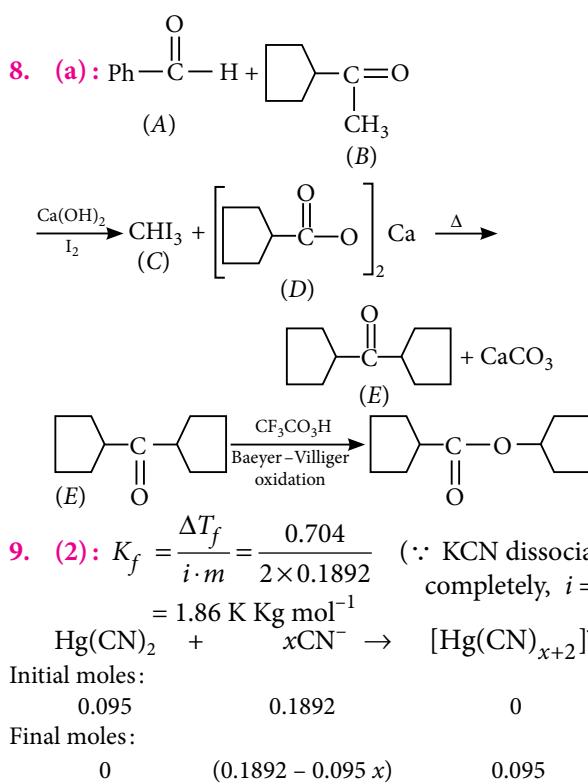
Also,



So, when the dative bond of CO changes to covalent bond in CO<sup>+</sup>, the bond length decreases.







$$\begin{aligned} &\text{Total molality after the addition of Hg(CN)}_2 \\ &= \text{molality of K}^+ + \text{molality of CN}^- \\ &\quad + \text{molality of } [\text{Hg(CN)}_{x+2}]^{x-} \end{aligned}$$

$$= 0.1892 + (0.1892 - 0.095x) + 0.095$$

$$= (0.4734 - 0.095x)$$

$$\text{Now, } K_f = \frac{\Delta T_f}{m} \Rightarrow 1.86 = \frac{0.53}{0.4734 - 0.095x}$$

$$x = 2.$$

10. (2) : The kinetic energy of the electron is provided by accelerating potential,

$$\begin{aligned} V &= \frac{h^2}{\lambda^2 \times 2 \times e \times m} \\ \lambda &= 8.7 \text{ pm} = 8.7 \times 10^{-12} \text{ m} \\ e &= 1.6 \times 10^{-19} \text{ C,} \\ m &= 9.1 \times 10^{-31} \text{ kg} \\ h &= 6.63 \times 10^{-34} \text{ J s} \\ V &= \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(8.7 \times 10^{-12} \text{ m})^2 \times 2 \times (1.6 \times 10^{-19} \text{ C}) \times 9.1 \times 10^{-31} \text{ kg}} \\ &= 1.99 \times 10^4 \text{ kg m}^2 \text{ s}^{-2} \text{ C} \approx 2 \times 10^4 \text{ V} \end{aligned}$$

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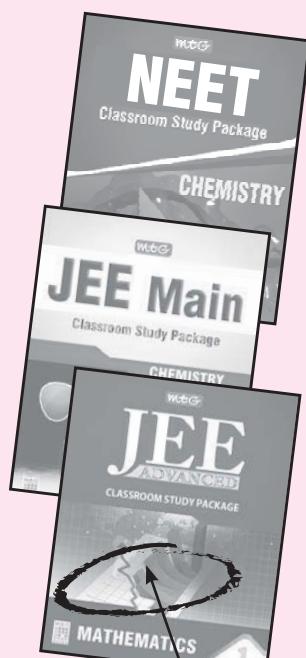
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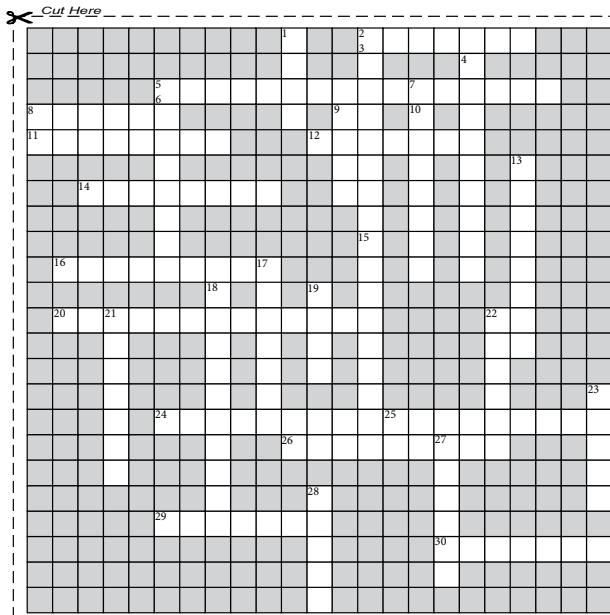
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## ACROSS

3. A mildly toxic, white crystalline organic compound belonging to the indole family. It occurs naturally in faeces and coal tar and has a strong faecal odour. (7)
6. An aminopyridine that functions as a centrally acting non-opioid analgesic that was originally used as an analgesic for acute and chronic pain. (10)
7. A gelatinous precipitate formed by coagulation of a sol. (6)
8. A German scientist who prepared almost perfectly semipermeable membrane using gelatinous copper ferrocyanide,  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ . (6)
11. Naturally occurring alloy of gold and silver (upto 45% Ag). It resembles pure gold in appearance. (8)
12. An atomic unit of energy which is equal to  $e^2/a_0$  (where  $e$  is the charge of an electron and  $a_0$  is the atomic unit of length). (7)
14. An arsenic derivative that causes blisters and used in chemical warfare. (8)
16. An instrument used to determine fermentation efficiency of yeast by measuring the amount of carbon dioxide produced from a given quantity of sugar. (9)
20. The action of heating a substance until it burns away rapidly. (12)
24. \_\_\_\_\_ law which expresses the dependence of a reaction enthalpy on temperature. (9)
25. A stable heterocyclic octacirculene based on thiophene. (9)
26. A polycyclic alkane with a structure similar to basket. (9)
29. Fraction which is defined as the mass defect divided by the mass number. (7)
30. A mineral deposit of gravel, sand and nitrates, found in dry areas of America. (7)

## DOWN

1. Small, granular, opaque diamonds, used as an abrasive in cutting tools. (4)
2. The contraction of a gel accompanied by the separating out of liquid. (9)
4. A technique in which a stable atom in a compound is replaced by its radioactive isotope. (9)
5. \_\_\_\_\_ include all quarks and leptons, as well as any composite particle made of an odd number of these, such as all baryons and many atoms and nuclei. (8)
9. A metal oxide obtained by heating an ore to high temperature in air. (4)



10. A reactor which produces more fissile nuclei than it consumes. (7)
13. A thermodynamic property of a real gas which is effective partial pressure. (8)
15. Polymethine fibre with elastic properties. (7)
17. Equation which gives relation between effect of temperature on surface tension. (6)
18. A mixture of two or more components that reaches an equilibrium temperature which is independent of the temperature of any of its components before they are mixed. (10)
19. The rule which is a practical aid for determining the configuration of chiral centers of amino acids. (4)
21. An organothiophosphate insecticide primarily used on corn. (7)
22. An analogue of pyrrole in which an arsenic atom replaces the nitrogen atom. (6)
23. The tendency of a solid material to move slowly or deform permanently under the influence of mechanical stress. (5)
27. A general name for alloys containing Al, Ni, Co and Fe, used as permanent magnets. (6)
28. A very hard natural form of silica, used for knife-edges of balances and in ornaments. (5)



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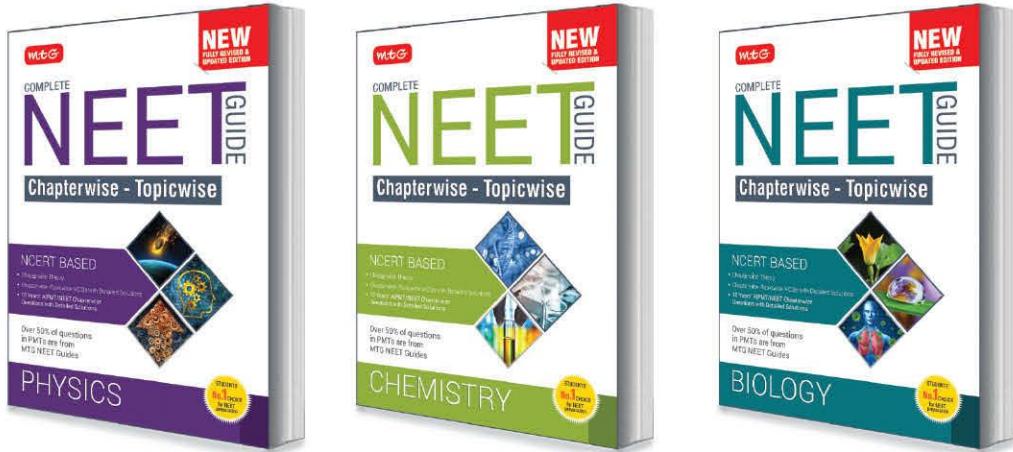
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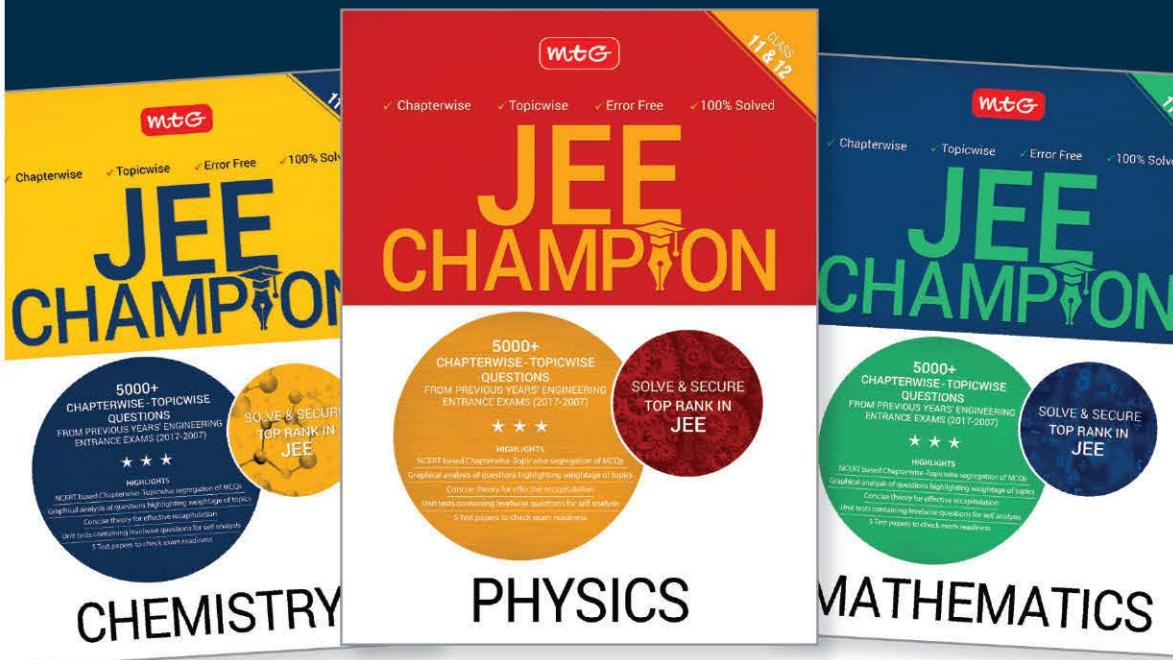
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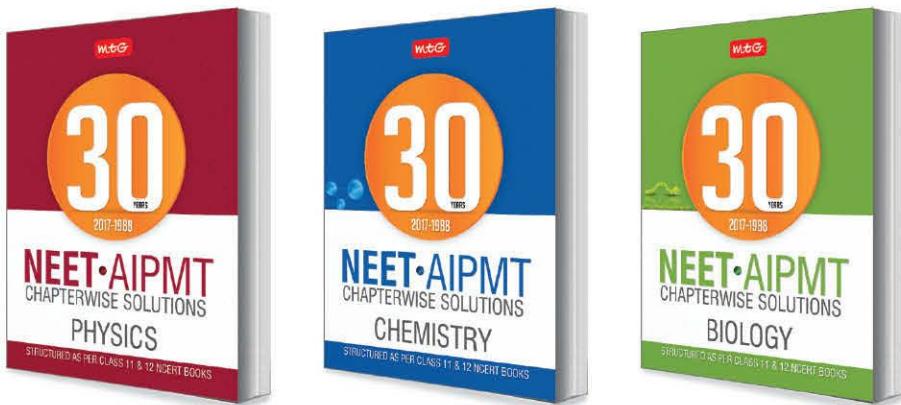
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