**6.32** For a spontaneous process, if entropy and volume are constant, the internal energy of system must

(A) Increase (B) Decrease (C) Remain constant (D) Be zero.

**6.33** If a state function G is defined such as G = H – TS, then dG must decrease for a spontaneous process (involving only PV work) occuring at

(A) Constant volume and temperature (B) Constant pressure and temperature

(C) Constant volume and pressure (D) Constnat entropy and volume

**6.34** For an irreversible cyclic process $\oint \frac{dq}{T}$ of system is :

(A) Equal to zero (B) Greater than zero

(C) Less than zero (D) Equal to change in Gibb's energy.

**Comprehension # 5**

The contributions of both heat (enthalpy) and randomness (entropy) shall be considered to the overall spontaneity of a process. When deciding about the spontaneity of a chemical reaction or other process, we define a quantity called the Gibb's energy change ($\Delta G$).

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

where, $\Delta H$ = Enthalpy change ; $\Delta S$ = Entropy change ; T = Temperature in kelvin.

If $\Delta G < 0$, Process is spontaneous ; $\Delta G = 0$, Process is at equilibrium, $\Delta G > 0$, Process is non-spontaneous.

**6.35** For the change $H_2O$ (s), (273 K, 2 atm) $\longrightarrow$ $H_2O$ ($\ell$), (273K, 2 atm), choose the correct option.

(A) $\Delta G = 0$ (B) $\Delta G < 0$ (C) $\Delta G > 0$ (D) None

**6.36** 5 mol of liquid water is compressed from 1 bar to 10 bar at constant temperature. Change in Gibb's energy ($\Delta G$) in Joule is : [Density of water = 1000 kg/m$^3$].

(A) 18 (B) 225 (C) 450 (D) 900

**6.37** Quick lime (CaO) is produced by heating limestone ($CaCO_3$) to drive off $CO_2$ gas.

$CaCO_3$ (s) $\longrightarrow$ CaO (s) + $CO_2$ (g), $\Delta H^\circ$ = 180 KJ, $\Delta S^\circ$ = 150 J/K.

Assuming that variation of enthalpy change and entropy change with temperature to be negligible, choose the correct option :

(A) Decomposition of $CaCO_3$ (s) is never spontaneous.

(B) Decomposition of $CaCO_3$ (s) becomes spontaneous when temperature is less than 900°C.

(C) Decomposition of $CaCO_3$ (s) becomes non-spontaneous when temperature is greater than 1000°C

(D) Decomposition of $CaCO_3$ (s) becomes spontaneous when temperature is greater than 927°C.

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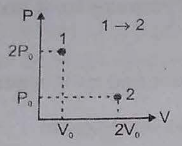
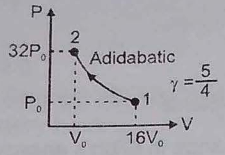
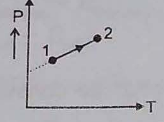
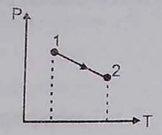
## SECTION - VI : MATRIX - MATCH TYPE

6.38

| Column-I<br>(For a definite amount of an ideal gas) | Column-II<br>(Enthalpy change / work done) |
|---|---|
| (A)  | (p) $\Delta H > 0$ |
| (B)  | (q) $\Delta H = 0$ |
| (C)  | (r) $W > 0$ |
| (D)  | (s) $W < 0$ |
| | (t) $\Delta E = 0$ |

6.39 Based on data given below, match column-I and column-II

$3X(g) \xrightarrow{250K, 1atm} X_3(g)$, $\Delta H = -200$ KJ/mol ; $\Delta S = -300$ J/K/mol

$X(\ell) \xrightarrow{1atm, 250K} X(g)$, $\Delta H_{vap} = 10$ KJ/mol

$X_3(\ell) \xrightarrow{500K, 1atm} X_3(g)$, $\Delta H_{vap} = 80$ KJ/mol

$X_3(g, 250\text{ K}, 1\text{ atm}) \longrightarrow X_3(g, 500\text{ K}, 1\text{ atm})$ $\Delta H = 100$ KJ/mol ; $\Delta S = 100$ J/K/mol ; $\Delta G = 60$ kJ/mol Normal boiling point of X = 250 K, normal boiling point of $X_3$ = 500 K.

Enthalpy change and entropy change of cooling $X_3(\ell)$ to lower temperature is negligible.

| Column-I | Column-II |
|---|---|
| (A) For $3X(\ell) \xrightarrow{250K, 1atm} X_3(\ell)$, $\Delta S$ in J/K/mol is | (p) 40 |
| (B) For $3X(\ell) \xrightarrow{250K, 1atm} X_3(\ell)$, $\Delta H$ in KJ/mol is | (q) – 150 |
| (C) For $3X(\ell) \xrightarrow{250K, 1atm} X_3(\ell)$, $\Delta G$ in KJ/mol is | (r) – 240 |
| (D) For $X(\ell) \xrightarrow{250K, 1atm} X(g)$, $\Delta S$ in J/K/mol is | (s) – 65 |
| | (t) 65 |

6.40

| Columm-I | Columm-II |
|---|---|
| (A) Reversible isothermal expansion of an ideal gas | (p) $w = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$ |
| (B) Reversible adiabatic compression of an ideal gas | (q) $PV^{\gamma}$ = constant |
| (C) Irreversible adiabatic expansion of an ideal gas | (r) $w = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$ |
| (D) Irreversible isothermal compression of an ideal gas | (s) $\Delta H = 0$ |

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**6.41**

| **Columm - I** | **Columm - II** |
|---|---|
| (A) Reversible adiabatic compression | (p) $\Delta S_{system} > 0$ |
| (B) Reversible vaporisation of liquid | (q) $\Delta S_{system} < 0$ |
| (C) $2N(g) \longrightarrow N_2(g)$ | (r) $\Delta S_{surrounding} < 0$ |
| (D) $MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$ | (s) $\Delta S_{surrounding} = 0$ |

**6.42** **Match the following :**

| **Column-I** | **Column–II** |
|---|---|
| (A) $\Delta H = q_p$ | (p) $\Delta H_f^\circ = 0$ |
| (B) Kirchhoff's equation | (q) A definite quantity |
| (C) $H^+(aq.)$ | (r) $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$ |
| (D) Spontaneous process | (s) $\Delta G > 0$ |
| | (t) $\Delta S^\circ_{Total} > 0$ |

**6.43** Match the column.

| **Column-I** | **Column-II** |
|---|---|
| (A) Perfectly crystalline solid | (p) $\Delta H_{sys} = 0$ |
| (B) Reversible cyclic process | (q) $\lim_{T \to 0} S \to 0$ |
| (C) Irreversible cyclic process | (r) $\Delta S_{surrounding} = 0$ |
| (D) Any adiabatic process | (s) $\Delta U_{sys} = 0$ |
| | (t) net heat change is zero |

**6.44**

| **Columm - I** | **Columm - II** |
|---|---|
| (A) $C\text{ (s, graphite)} + O_2(g) \longrightarrow CO_2(g)$ | (p) $\Delta H^\circ_{combustion}$ |
| (B) $C\text{(s, graphite)} \longrightarrow C(g)$ | (q) $\Delta H^\circ_{formation}$ |
| (C) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ | (r) $\Delta H^\circ_{atomization}$ |
| (D) $CH_4(g) \longrightarrow C(g) + 4H(g)$ | (s) $\Delta H^\circ_{sublimation}$ |

## SECTION - VI : INTEGER TYPE

**6.45** Only $N_2$, CO and $CO_2$ gases remain after 0.72 gm of carbon is treated with one litre of air at 27°C and 4.92 atm pressure. Assume air composition $O_2 = 20\%$, $N_2 = 79\%$ and $CO_2 = 1\%$ (by volume). The heat evolved (in Kcal) under constant pressure is :

Given : $C + O_2 \longrightarrow CO_2, \quad \Delta H = -100$ Kcal/mol

$C + \frac{1}{2}O_2 \longrightarrow CO, \quad \Delta H = -25$ Kcal/mol

**6.46** A horizontal piston-cylinder arrangement is placed in a constant temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m³.

(a) The external force on the piston is reduced gradually, allowing the gas to expand until its volume doubles. Calculate the work done by the gas in moving the external force.

(b) How much work would be done if the same expansion is carried out by removing a part of the external force suddenly. Also calculate % efficiency of this process as compared with the reversible process (% of reversible work).

Take $\ell n2 = 0.7$.

Report your answer as (% efficiency × 0.7).

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**6.47** It is known that entropy of neutralisation of a strong acid and strong base is – 13.68 kcal/mol. If enthalpy of neutralisation of $N_2H_4$ (hydrazine) with strong acid is equal to – 11.68 kcal/mol, then enthalpy of the reaction

$N_2H_4 + H_2O \longrightarrow N_2H_5^+(aq) + OH^-(aq)$ in Kcal/mol is :

**6.48** The magnitude of work done (in kcal) when 120 gm of Mg (s) is reacted with excess of hydrochloric acid in an open vessel at 27°C is.

**6.49** For the synthesis of ammonia at 300 K :

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Calculate the value of $\Delta G°$ in Kcal and give your answer in magnitude by using the following data :

| | $N_2$ | $H_2$ | $NH_3$ |
|---|---|---|---|
| $\Delta H°_f$ (Kcal/mole) | 0 | 0 | –10 |
| S° (Cal/K-mole) | 40 | 30 | 45 |

**6.50** Calculate the pH at which the following conversion(reaction) will be at equilibrium in basic medium

$I_2(s) \rightleftharpoons I^-(aq) + IO_3^-(aq)$

when the equilibrium concentrations at 300 K are $[I^-] = 0.10$ M and $[IO_3^-] = 0.10$ M

{Given that $\Delta G_f^0(I^-,aq) = -50$ kJ/mole, $\Delta G_f^0(IO_3^-,aq) = -123.5$ kJ/mole, $\Delta G_f^0(H_2O, \ell) = -233$ kJ/mole,

$\Delta G_f^0(OH^-,aq) = -150$ kJ/mole, Ideal gas constant = $R = \frac{25}{3}$ Jmole$^{-1}$K$^{-1}$, $\log_e 10 = 2.3$,

**6.51** Reaction of gaseous fluorine ($F_2$) with compound X yields a single product Y, whose mass precent composition is 61.7% F and 38.3% Cl. Calculate $\Delta_r H°$ (in kJ/mol ) for the synthesis of Y using following information

$2ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g) \qquad \Delta H° = 205.6$ kJ

$2ClF_3(g) + 2O_2(g) \longrightarrow Cl_2O(g) + 3OF_2(g) \qquad \Delta H° = 533.0$ kJ

$\Delta_f H°(OF_2, g) = 24.7$ kJ/mol

**6.52** The heat of combustion of ethene gas is 330 Kcal mol$^{-1}$ calculate $>C=C<$ bond energy( in kcal/mol) assuming that bond energy of C–H bond is 93.6 Kcal mol$^{-1}$

Given : $\Delta H°_f$ for $CO_2(g)$ and $H_2O(\ell)$ are –94.2 and –61 Kcal mol$^{-1}$ respectively. Heat of atomisation of carbon and hydrogen are 150 and 51.5 Kcal mol$^{-1}$ respectively.

**6.53** 1 mole of an ideal gas, initially at 400 K and 10 atm is first expanded at constant pressure till the volume is doubled. Then the gas is made to undergo an isochoric process, in which its temperature is found to decrease. In the last final step, gas was compressed reversibly and adiabatically to initial state. Determine the net work involved in this cyclic process (in terms of R). Given, $C_V$ for gas = 1.5 R, $(4)^{-1/3} = 0.63$.

If $|W| = 2R \times z$, report your answer as z.

**6.54** Heat of hydrogenation of cyclohexene to cyclohexane is –28.6 kcal/mol. The observed heat of hydrogenation of benzene to cyclohexane is –49.8 kcal/mol Calculate the resonance energy of benzene in kcal/mole.

**6.55** 1 mol of a liquid of molar volume 100 mL is kept in an adiabatic container under a pressure of 1 bar. The pressure is steeply increased to 100 bar. Under this constant pressure of 100 bar, the volume of the liquid decreases by 1 mL. Calculate $\Delta U$ of the process. **[JEE 2004]**

## TOPIC
## 7

# SOLID STATE

## SECTION - I : STRAIGHT OBJECTIVE TYPE

7.1 In an ionic solid $r_{(+)} = 1.6$ Å and $r_{(-)} = 1.864$ Å. Use the radius ratio rule to determine the edge length of the cubic unit cell in Å.

(A) 4 (B) $2\sqrt{3}$ (C) $3\sqrt{3}$ (D) $\frac{4}{\sqrt{3}}$

7.2 A crystal is made of particle X, Y & Z. X forms FCC packing, Y occupies all octahedral voids of X and Z occupies all tetrahedral voids of X, if all the particles along one body diagonal are removed then the formula of the crystal would be -

(A) $XYZ_2$ (B) $X_2YZ_2$ (C) $X_8Y_4Z_5$ (D) $X_5Y_4Z_8$

7.3 Diamond has face-centred cubic lattice. There are two atoms per lattice point, with the atoms at (000) and $\left(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}\right)$ coordinates. The ratio of the carbon-carbon bond distance to the edge of the unit cell is:

(A) $\sqrt{\frac{3}{16}}$ (B) $\sqrt{\frac{1}{4}}$ (C) $\frac{1}{4}$ (D) $\frac{1}{\sqrt{2}}$

7.4 In hexagonal close packing of sphere in three dimensions.

(A) In one unit cell there are 12 octahedral voids and all are completely inside the unit cell.

(B) In one unit cell there are six octahedral voids and all are completely inside the unit cell.

(C) In one unit cell there are six octahedral void and of which three are completely inside the unit cell and other three are partially inside the unit cell.

(D) In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell.

7.5 If the anions (A) form hexagonal close packing and cations (B) occupy only 2/3rd octahedral voids in it, then the general formula of the compound is :

(A) AB (B) $A_3B_2$ (C) $A_2B$ (D) $AB_2$

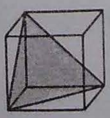
7.6 A transition metal M can exist in two oxidation states +2 and +3. It forms an oxide whose experimental formula is given by $M_xO$ where $x < 1$. Then the ratio of metal ions in +3 state to those in +2 state in oxide is given by :

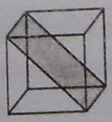
(A) $\frac{1-x}{1+x}$ (B) $1 + 2x$ (C) $1 + \frac{x}{2}$ (D) $\frac{2(1-x)}{3x-2}$

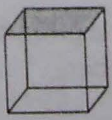
7.7 Analysis show that nickel oxide consist of nickel ion with 96% ions having $d^8$ configuration and 4% having $d^7$ configuration. Which amongst the following best represents the formula of the oxide.

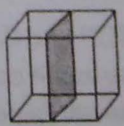
(A) $Ni_{1.02}O_{1.00}$ (B) $Ni_{0.96}O_{1.00}$ (C) $Ni_{0.98}O_{0.98}$ (D) $Ni_{0.98}O_{1.00}$

7.8 In an f.c.c. crystal, which of the following shaded planes contains the following type of arrangement of atoms?

(A)


(B)


(C)


(D)


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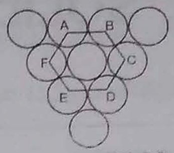
7.9 The percentage packing efficiency of the two dimensional arrangement of sphere for plane ABCDEF shown below is :

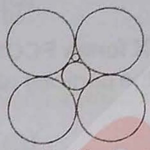


(A) 90.64% (B) 74.05% (C) 68.02% (D) 78.54%

7.10 **Consider the following statements and arrange in the order of true/false as given in the codes.**

**$S_1$ :** One type of unit cells are possible for the crystallaographic dimensions as $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$.

**$S_2$ :** In the configuration shown the size of the smallest circle is $\left(\frac{2}{\sqrt{3}} - 1\right)$ times the size of the biggest circles.



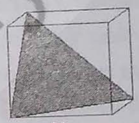
**$S_3$ :** Number of next neighbours of $Cs^+$ ion in CsCl structure is 6 $Cs^+$ ions.

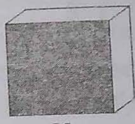
**$S_4$ :** A crystal has A ions at the cube corners and B ions at the edge centres. The coordination numbers of A and B are respectively 6 and 2.

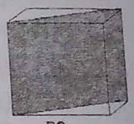
(A) TTTT (B) FFTT (C) FTFT (D) FFFF

## SECTION - II : MULTIPLE CORRECT ANSWER TYPE

7.11 Following three planes( $P_1$, $P_2$, $P_3$) in an FCC unit cell are shown. Consider the following statements and choose the correct option that follow :


P1


P2


P3

(A) $P_1$ contains no three dimensional voids.

(B) $P_2$ contains only octahedral voids.

(C) $P_3$ contains both octahedral and tertahedral voids.

(D) All are true

7.12 In a AB unit cell (Rock salt type) assuming $A^+$ forming FCC :

(A) The nearest neighbour of $A^+$ is six $B^-$ ion. (B) The nearest neighbour of $B^-$ is six $A^+$ ion.

(C) The second neighbour of $A^+$ is twelve $A^+$. (D) The packing fraction of AB crystal is 0.79.

7.13 In the fluorite structure if the radius ratio is $\left(\sqrt{\frac{3}{2}} - 1\right)$, how many ions does each cation touch ?

(A) 4 anions (B) 12 cations (C) 8 anions (D) No cations

7.14 The co-ordination number of FCC structure for metals is 12, since

(A) Each atom touches 4 others in same layer, 3 in layer above and 3 in layer below.

(B) Each atom touches 4 others in same layer, 4 in layer above and 4 in layer below.

(C) Each atom touches 6 others in same layer, 3 in layer above and 3 in layer below.

(D) Each atom touches 3 others in same layer, 6 in layer above and 6 in layer below.

7.15* Select the correct statement(s) related to hexagonal close packing of identical spheres in three dimensions:

(A) In one unit cell there are 12 octahedral voids and all are completely inside the unit cell

(B) In one unit cell there are six octahedral voids and all are completely inside the unit cell.

(C) In one unit cell there are six octahedral void and out of which three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell

(D) Co-ordination number of every sphere is 12 in hcp lattice.

7.16 The HCP and CCP structure for a given element would be expected to have :

(A) The same co-ordination number. (B) The same density.

(C) The same packing fraction. (D) All the above.

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## SECTION - III : ASSERTION AND REASON TYPE

7.17 **STATEMENT-1 :** An important feature of Fluorite structures is that cations being large in size occupy FCC lattice points whereas anions occupy all the tetrahedral voids giving the formula unit $AB_2$ (A : cation, B : anion).

**STATEMENT-2 :** There are 6 cations and 12 anions per FCC unit cell of the Fluorite structure.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

7.18 **Statement--1 :** In ZnS zinc blende structure $Zn^{2+}$ form FCC while alternate tetrahedral voids are occupied by $S^{2-}$.

**Statement--2 :** Positions of $Zn^{2+}$ and $S^{2-}$ in zinc blende structure are similar.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

7.19 **Statement--1 :** The ratio of $Zn^{2+}$ and $F^-$ per unit cell of ZnS and $CaF_2$ is 1 : 2.

**Statement--2 :** In ZnS, $Zn^{2+}$ ions occupy alternate tetrahedral voids and in $CaF_2$, $F^-$ ions occupy all the tetrahedral voids of FCC unit cell.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

7.20 **STATEMENT-1 :** In NaCl crystal each $Na^+$ ion is touching 6 $Cl^-$ ions but these $Cl^-$ ions do not touch each other.

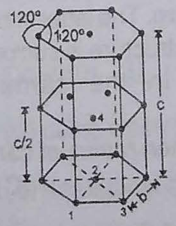
**STATEMENT-2 :** The radius ratio $r_{Na^+}/r_{Cl^-}$ is greater than 0.414, required for exact fitting.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

## SECTION - IV : COMPREHENSION TYPE

### Paragraph for Question Nos. 52 to 53

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.



7.21 The volume of this HCP unit cell is :

(A) $12\sqrt{2}\ r^3$ (B) $24\sqrt{2}\ r^3$ (C) $16\sqrt{2}\ r^3$ (D) $\frac{64}{3\sqrt{3}}\ r^3$

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**7.22** In hcp lattice, if a plane is drawn parallel to layers A and B, at a distance $\frac{c}{8}$ above the layer B, it passes through centres of x tetrahedral and y octahedral voids. A plane parallel to layer A, at a distance $\frac{c}{8}$ just below it passes through centres of p tetrahedral and q octahedral voids. Find (x + y + p + q). c is the cell parameter of hcp lattice, the vertical edge length.

(A) 10 (B) 9 (C) 6 (D) 14

**Comprehension # 1**

When an atom or an ion is missing from its normal lattice site, a lattice vacancy (Schottky defect) is created. In stoichiometric ionic crystals, a vacancy of one ion has to be accompanied by the vacancy of the oppositely charged ion in order to maintain electrical neutrality.

In a Frenkel defect an ion leaves its position in the lattice and occupies an interstitial void. This is the Frenkel defect commonly found along with the Schottky defects and interstitials. In pure alkali halides, Frenkel defects are not found since the ions cannot get into the interstitial sites. Frenkel defects are found in silver halides because of the small size of the $Ag^+$ ion. Unlike Schottky defects, Frenkel defects do not change the densiy of the solids. In certain ionic solids (e.g. AgBr) both Schottky and Frenkel defects occur.

The defects discussed above do not disturb the stoichiometry of the crystalline material. There is large variety of non-stoichiomertic inorganic solids which contain an excess or deficiency of one of the elements. Such solids showing deviations from the ideal stoichiometric composition form an important group of solids. For example in the vanadium oxide, $VO_x$, x can be anywhere between 0.6 and 1.3. There are solids which are difficult to prepare in the stoichiometric composition. Thus, the ideal composition in compounds such as FeO is difficult to obtain (normally we get a composition of $Fe_{0.95}O$ but it may range from $Fe_{0.93}O$ to $Fe_{0.96}O$). Non-stoichiometric behaviour is most commonly found for transition metal compounds though is also known for some lanthanoids and actinoids.

Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstitially, giving rise to electrons trapped in the neighbourhood. the enhanced electrical conductivity of the non-stoichiometric ZnO arises from these electrons.

Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of the alkali metal vapour. When the metal atoms deposit on the surface they diffuse into the crystal and after ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy. Electrons trapped in anion vacancies are referred to as F-centres ( from Farbe the German word for colour) that gives rise to interesting colour in alkali halides. Thus, the excess of potassium in KCl makes the crystal appear violet and the excess of lithium in LiCl makes it pink.

**7.23** The type of semiconductor shown by crystal capable of showing Schottky defect, will be.

(A) p - type (B) n - type (C) both (D) None

**7.24** Which of the following is most appropriate cystal to show Frenkel defect.

(A) CsCl (B) NaCl (C) AgBr (D) $CaCl_2$

**7.25** In the crystal of $Fe_{0.93}O$, the percentage of Fe(III) will be

(A) 15% (B) 85% (C) 30% (D) 78%

**Comprehension # 2**

Only those atoms which form four covalent bonds produce a repetitive three dimesional structure using only covalent bonds, e.g., diamond structure. The latter is based on a **FCC** lattice where lattice points are occupied by carbon atoms. Every atom in this structure is surrounded tetrahedrally by four others. Germanium, silicon and grey tin also crystallize in the same way as diamond. (Given : $N_A = 6 \times 10^{23}$, sin 54°44′ = 0.8164).

**7.26** If edge length of the cube is 3.60Å, then radius of carbon atom is

(A) 0.78 Å (B) 0.92 Å (C) 0.64 Å (D) 0.35 Å.

**7.27** If the edge length is 3.60Å, density of diamond crystal is

(A) 3.92 gm/cc (B) 2.40 gm/cc (C) 3.37 gm/cc (D) 2.58 gm/cc.

**7.28** Total number of diamond unit cells in 1.2 gm of diamond sample is

(A) $6.0 \times 10^{21}$ (B) $6.0 \times 10^{22}$ (C) $7.5 \times 10^{21}$ (D) $5.0 \times 10^{22}$.

## SECTION - V : MATRIX - MATCH TYPE

**7.29** Match List I with List II and select the correct answer using the code given below the lists :

| **List-I** | **List-II** |
|---|---|
| (A) For Ionic solid $\frac{r_+}{r_-} = 0.51$ | (p) Anion-anion contact present, cation lies in octahedral void |
| (B) For Ionic solid $\frac{r_+}{r_-} = 0.414$ | (q) Anion-anion contact missing, cation lies in tetrahedral void |
| (C) For Ionic solid $\frac{r_+}{r_-} = 0.4$ | (r) Anion-anion contact missing, cation lies in cubical void |
| (D) For ionic solid $\frac{r_+}{r_-} = 0.9$ | (s) Anion-anion contact missing, cation lies in octahedral voids |

**7.30**

| **Column-I**<br>**(Arrangenment in unit cell, radius ratio in higher limit)** | **Column-II**<br>**(Coordination number of cation : Anion)** |
|---|---|
| (A) Cations in CCP and anions in alternate tetrahedral voids | (p) Ratio of number of cation to anion in one unit cell is 1 : 1 |
| (B) Cations in simple cubic and anions in the body centre. | (q) Ratio of coordination number of cation to anion is 1 : 1. |
| (C) Anions in CCP and cations in all tetrahedral voids. | (r) Ratio of number of cation to anion just touching each other is not 1. |
| (D) Cations in CCP and anions in all octahedral voids | (s) Number of next neighbours of ion is greater than 10. |
| | (t) Effective number of formula units = 4 |

**7.31** **Column-I** and **Column-II** contains four entries each. Entries of **Column-I** are to be matched with some entries of **Column-II**. One or more than one entries of **Column-I** may have the matching with the same entries of **Column-II**.

| **Column-I (Bravais Lattice(s))** | **Column-II [Crystal system]** |
|---|---|
| (A) Primitive, face centered, body centered, end centered | (p) Cubic |
| (B) Primitive, face centered, body centered | (q) Orthorhombic |
| (C) Primitive, body centered | (r) Hexagonal |
| (D) Primitive only | (s) Tetragonal |

**7.32**

| **Column - I** | **Column - II** |
|---|---|
| (A) 74% occupancy of space | (p) cubic close packing of identical spheres. |
| (B) Coordination number = 6 | (q) hexagonal close packing of identical spheres. |
| (C) 68% occupancy of space | (r) body centred cubic packing of identical spheres. |
| (D) Coordination number = 12 | (s) simple cubic packing of identical spheres. |
| | (t) AB AB AB ....... type of close packing of identical spheres. |

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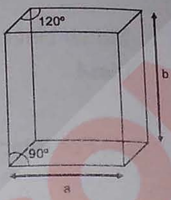
## SECTION - VI : INTEGER TYPE



7.33 $A_2B$ molecule (molar mass = 259.8 g/mol) crystallises in a hexagonal lattice as shown. Density of crystal is 5 g/cm³. If $a = 5\overset{0}{A}$ and $b = 8\overset{0}{A}$, then number of molecules contained in given unit cell are:

7.34 $N_A$ spheres of radius 'R' are melted in $x \times N_A$ smaller spheres, so that when fcc lattice is generated from smaller spheres the edge length is formed to be $2^{5/6}R$. Find x.

7.35 Total number of faces in a truncated octahedron = x
Total number of faces in a truncated tetrahedron = y
Then x + y is :

7.36 An ionic compound MCl is simultaneously doped with $10^{-6}$ mole% $NCl_2$ and $10^{-7}$ mole% $RCl_3$. Calculate the concentration of cationic vacancies x. Express your answer as $\frac{x}{9} \times 10^{14}$.

(take N & R = divalent & trivalent cations)

7.37 Let 'a' be the sum of oxidation number of N atom in products X, Y, Z, W, U, V, T. Find $\frac{a}{2}$.

$HNO_2 \longrightarrow HNO_3 + H_2O + X \quad \Rightarrow \quad NH_4Cl + NaNO_2 \longrightarrow Y + H_2O + NaCl$

$Ba(N_3)_2 \longrightarrow Ba + Z \quad \Rightarrow \quad NH_4NO_3 \xrightarrow{\Delta} W + H_2O$

$HNO_3 + P_4O_{10} \longrightarrow HPO_3 + U \quad \Rightarrow \quad Cu + HNO_3\,(conc.) \longrightarrow Cu(NO_3)_2 + V + H_2O$

$I_2 + HNO_3\,(conc.) \longrightarrow HIO_3 + T + H_2O$

7.38 Ionic solid $B^+A^-$ crystallizes in rock salt type of structure. 1.296 gm ionic solid salt $B^+A^-$ is dissolved in water to make one litre solution. The pH of the solution is measured to be 6.0. If the value of face diagonal in the unit cell of $B^+A^-$ be $600\sqrt{2}$ pm. Calculate the density of ionic solid in gm/cc. [T = 298 K, $K_b$ for BOH is $10^{-5}$, (Avogadro Number = $6.0 \times 10^{23}$)]

7.39 Consider the arrangement of circles of equal radii with their centres arranged as per the 2-dimensional lattice defined by $a = b$, $\theta = 60°$ such that each circle is touching all its nearest neighbours. If all the void areas present are additionally occupied by smaller circles of relevant size so that the void circles are just contacting their neighbours find the packing efficiency of the configuration in percent.

7.40 In F.C.C. arrangement of identical spheres, distance between two nearest octahedral void is 8.51Å. The distance between two nearest tetrahedral voids would be ?

**7.41** The face diagonal length of FCC cubic cell is $660\sqrt{2}$ pm. If the radius of the cation is 110 pm, What should be the radius of the anion following radius ratio rules

**7.42** How many of the following ionic compounds have coordination number of either cation or anion equal to 6 or more :

$ZnS$, $KCl$, $K_2O$, $CsBr$, $NaBr$, $CaF_2$

**7.43** A cube-shaped crystal of an alkali metal, 1.62 mm on an edge, was vaporized in a 500.0 mL evacuated flask. The pressure of the resulting vapour was 12.5 mm of Hg at 802°C. The structure of the solid metal is known to be body-centered cubic. What is the atomic radius of the metal atom in picometers ?

(R = 0.082 lt-atm/mol-K)

(The radii of metals atoms are Li=152 pm, Na=186pm, K = 227 pm, Rb = 248 pm)

**7.44** A solid cube of edge length = 25.32 mm of an ionic compound which has NaCl type lattice is added to 1kg of water. The boiling point of this solution is found to be 100.52°C (assume 100% ionisation of ionic compound). If radius of anion of ionic solid is 200 pm then calculate radius of cation of solid in pm (picometer).

($K_b$ of water = 0.52 K kg mole$^{-1}$, Avogadro's number, $N_A = 6 \times 10^{23}$, $(\sqrt[3]{75}) = 4.22$)

**7.45** 5.35 g of a salt ACl (of weak base AOH) is dissolved in 250 ml of solution. The pH of the resultant solution was found to be 4.85. Find the ionic radius of $A^+$ & $Cl^-$ if ACl forms CsCl type crystals having density 2.2g/cc. Given $K_b(AOH) = 2 \times 10^{-5}$, $\frac{r_+}{r_-} = 0.731$ for this unit cell.

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# TOPIC 8

# CHEMICAL EQUILIBRIUM

## SECTION - I : STRAIGHT OBJECTIVE TYPE

8.1 $N_2$ and $H_2$ are taken in 1 : 3 molar ratio in a closed vessel to attain the following equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Find $k_p$ for reaction at total pressure of 2P if $P_{N_2}$ at equilibrium is $\frac{P}{3}$

(A) $\frac{1}{3P^2}$ (B) $\frac{4}{3P^2}$ (C) $\frac{4P^2}{3}$ (D) None

8.2 The unit of equilibrium constant $K_C$ of a reaction is $mol^{-2}\ l^2$. For this reaction, the product concentration increases by -

(A) Increasing the pressure (B) Lowering the temperature

(C) Lowering the pressure (D) Both B and C

8.3 At 1400 K, $K_c = 2.5\times10^{-3}$ for the reaction $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$. A 10.0L reaction vessel at 1400 K contains 2.00 mole of $CH_4$, 3.0 mol of $CS_2$, 3.0 mole of $H_2$ and 4.0 mole of $H_2S$. Then

(A) This reaction is at equilibrium with above concentrations.

(B) The reaction will proceed in forward direction to reach equilibrium

(C) The reaction will proceed in backward direction to reach equilibrium

(D) The information is insufficient to decide the direction of progress of reaction

8.4 In a basic aqueous solution chloromethane undergoes a substitution reaction in which $Cl^-$ is replaced by $OH^-$ as.

$$CH_3Cl\ (aq) + OH^- \rightleftharpoons CH_3OH(aq) + Cl^-\ (aq)$$

The equilibrium constant of above reaction $K_c = 1 \times 10^{16}$. If a solution is prepared by mixing equal volumes of 0.1 M $CH_3Cl$ and 0.2 M NaOH (100% dissociated) then $[OH^-]$ concentration at equilibrium in mixture will be:

(A) 0.1 M (B) 0.5 M (C) 0.2 M (D) 0.05 M

8.5 $NH_4COONH_2\ (s) \rightleftharpoons 2NH_3(g) + CO_2(g)$.

If equilibrium pressure is 6 atm for the above reaction ; $K_p$ will be :

(A) 32 (B) 27 (C) 4/27 (D) 1/27

8.6 Equilibrium constant for the given reaction is $K = 10^{20}$ at temperature 300 K

$A(s) + 2B\ (aq.) \rightleftharpoons 2C\ (s) + D\ (aq.)$ $K = 10^{20}$

The equilibrium conc. of B starting with mixture of 1 mole of A and 1/3 mole/litre of B at 300 K is

(A) $\sim 4 \times 10^{-11}$ (B) $\sim 2 \times 10^{-10}$ (C) $\sim 2 \times 10^{-11}$ (D) $\sim 10^{-10}$

8.7 10 ℓt. box contain $O_3$ and $O_2$ at equilibrium at 2000 K. The $\Delta G° = -534.52$ kJ at 8 atm equilibrium pressure. The following equilibrium is present in the container

$2O_3(g) \rightleftharpoons 3O_2(g)$. The partial pressure of $O_3$ will be ( ln 10 = 2.3, R = 8.3 $Jmole^{-1}K^{-1}$):

(A) $8 \times 10^{-6}$ (B) $22.62 \times 10^{-7}$ (C) $9.71 \times 10^{-6}$ (D) $9.71 \times 10^{-2}$

8.8 The reactions

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$ and $COCl_2\ (g) \rightleftharpoons CO(g) + Cl_2\ (g)$

are simultaneously in equilibrium in an equilibrium box at constant volume. A few moles of CO(g) are later introduced into the vessel. After some time, the new equilibrium concentration of

(A) $PCl_5$ will remain unchanged (B) $Cl_2$ will be greater

(C) $PCl_5$ will become less (D) $PCl_5$ will become greater

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**8.9** For the chemical reaction,

$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$

the amount of $X_3Y$ at equilibrium is affected by :

(A) Temperature and pressure (B) Temperature only

(C) Pressure only (D) Temperature, pressure and catalyst

**8.10** What is the minimum mass of $CaCO_3$ (s), below which it decomposes completely, required to establish equilibrium in a 6.50 litre container for the reaction : [$K_c$ = 0.05 mole/litre]

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(A) 32.5 g (B) 24.6 g (C) 40.9 g (D) 8.0 gm

**8.11** The value of $k_p$ for the reaction at 27°C

$Br_2(\ell) + Cl_2(g) \rightleftharpoons 2BrCl(g)$

is '1 atm'. At equilibrium in a closed container partial pressure of BrCl gas is 0.1 atm and at this temperature the vapour pressure of $Br_2(\ell)$ is also 0.1 atm. Then what will be minimum moles of $Br_2(\ell)$ to be added to 1 mole of $Cl_2$, initially, to get above equilibrium situation :

(A) $\frac{10}{6}$ moles (B) $\frac{5}{6}$ moles (C) $\frac{15}{6}$ moles (D) 2 moles

**8.12** For an equilibrium $H_2O(s) \rightleftharpoons H_2O(\ell)$ which of the following statements is true.

(A) The pressure changes do not affect the equilibrium

(B) More of ice melts if pressure on the system is increased

(C) More of liquid freezes if pressure on the system is increased

(D) The pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system

## SECTION - II : MULTIPLE CORRECT ANSWER TYPE

**8.13** An arbitrary combound $P_2Q$ decomposes according to reaction :

$2P_2Q(g) \rightleftharpoons 2P_2(g) + Q_2(g)$

If one starts the decomposition reaction with 4 moles of $P_2Q$ and value of equilibrium constant $K_p$ is numerically equal to total pressure at equilibrium. Then which option is/are correct at equilibrium :

(A) moles of $n_{P_2Q} = n_{Q_2}$

(B) moles of $n_{P_2} = (8/3)$

(C) degree of dissociation is $\alpha = (2/3)$

(D) total number of moles of products ($P_2$ & $Q_2$) at equilibrium is 4

**8.14** Consider the following statements :

(I) An increase in pressure (caused by decrease in volume) at equilibrium results in increase in molar concentration of each gaseous substance involved.

(II) An increase in pressure (caused by decrease in volume) at equilibrium results in increase in no. of moles of each gaseous substance involved.

(III) For the reaction $A(s) \rightleftharpoons B(g) + C(g)$ at constant temperature, total pressure at equilibrium (of B(g) & C(g)) is not affected by changing the volume of container.

(IV) $H_2O(\ell) \rightleftharpoons H_2O(g)$ on temperature increase, $K_r$ of this reaction is increased.

Tick the correct statement(s)

(A) (I) (B) (II) (C) (III) (D) (IV)

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**8.15** $CuSO_4 . 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$ $K_p = 10^{-10}$ (atm). $10^{-2}$ moles of $CuSO_4 . 5H_2O(s)$ is taken in a 2.5L container at 27°C then at equilibrium [Take : $R = \frac{1}{12}$ litre atm $mol^{-1}$ $K^{-1}$]

(A) Moles of $CuSO_4 . 5H_2O$ left in the container is $9 \times 10^{-3}$
(B) Moles of $CuSO_4 . 5H_2O$ left in the container is $9.8 \times 10^{-3}$
(C) Moles of $CuSO_4$ left in the container is $10^{-3}$
(D) Moles of $CuSO_4$ left in the container is $2 \times 10^{-4}$

**8.16** Solid ammonium carbamate, $NH_4CO_2NH_2(s)$, dissociates into ammonia and carbon dioxide when it evaporates as shown by

$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. If 0.1 atm of $CO_2$ is introduced after equilibrium is reached then :

(A) Final pressure of $CO_2$ will be less than 0.1 atm
(B) Final pressure of $CO_2$ will be more than 0.1 atm
(C) Pressure of $NH_3$ will decrease due to addition of $CO_2$
(D) Pressure of $NH_3$ will increase due to addition of $CO_2$

**8.17** 1 mole each of $N_2(g)$ and $O_2(g)$ are introduced in a 1L evacuated vessel at 523K and equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is established. The concentration of NO(g) at equilibrium :

(A) Changes on changing volume of the vessel.
(B) Changes on changing temperature.
(C) Changes on changing pressure.
(D) Remains same even when a platinum gauze is introduced to catalyse the reaction.

**8.18** 138 gm of $N_2O_4$ (g) is placed in 8.2L container at 300 K. The equilibrium vapour density of mixture was found to be 30.67. Then (R = 0.082 L atm $mol^{-1}$ $K^{-1}$)

(A) $\alpha$ = degree of dissociation of $N_2O_4 = 0.25$
(B) $K_p$ of $N_2O_4 \rightleftharpoons 2NO_2(g)$ will be 9 atm.
(C) Total pressure at equilibrium = 6.75 atm
(D) The density of equilibrium mixture will be 16.83 gm/litre.

**8.19** Consider two equilibrium $2Cl_2(g) + 2H_2O(g) \rightleftharpoons 4HCl(g) + O_2(g)$ and $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ simultaneously established in a closed vessel. When some amount of HCl is added at equilibrium, which of the following statements is/are correct :

(A) Amount of $N_2$ gas will increase.
(B) Amount of $O_2$ gas will increase.
(C) Amount of $O_2$ gas will decrease.
(D) Nothing can be said with certainty about amount of $O_2$ gas.

**8.20** In a closed jar having water vapours in equilibrium with liquid suddenly all the vapours of the jar is transferred to another identical jar and is subjected to compression. Assume initial temperature to be the same and negligible volume occupied by the liquid water. Select the observation in the record jar.

(A) Liquid water will start forming in the jar
(B) Vapour will undergo gradual compression without any condensation.
(C) Temperature of the vapour will increases.
(D) Final pressure will be the same as initial pressure.

**8.21** If two gases $AB_2$ and $B_2C$ are mixed the following equilibria are readily established

$AB_2(g) + B_2C(g) \rightarrow AB_3(g) + BC(g)$

$BC(g) + B_2C(g) \rightarrow B_3C_2(g)$

It the reaction is started only with $AB_2$ with $B_2C$ , then which of the following is necessarily true at equilibrium:

(A) $[AB_3]_{eq} = [BC]_{eq}$ (B) $[AB_2]_{eq} = [B_2C]_{eq}$ (C) $[AB_3]_{eq} > [B_3C_2]_{eq}$ (D) $[AB_3]_{eq} > [BC]_{eq}$

8.22 The following reaction attains equilibrium at high temperature.

$N_2(g) + 2H_2O(g) + \text{heat} \rightleftharpoons 2NO(g) + 2H_2(g)$

The yield of NO is affected by

(A) Increasing the nitrogen concentration (B) Decreasing the hydrogen concentration

(C) Compressing the reaction mixture (D) None of these

## SECTION - III : ASSERTION AND REASON TYPE

8.23 **Statement-1 :** Graphite can be converted into diamond by application of very high pressure and temperature, using a suitable catalyst.

**Statement-2 :** Graphite is thermodynamically more stable and less dense than diamond.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

8.24 **STATEMENT-1 :** $A(s) \rightleftharpoons B(g) + C(g)$ ; $Kp_1$

$X(s) \rightleftharpoons B(g) + Y(g)$ ; $Kp_2 = 3Kp_1$

Total pressure of B over the mixture of solid A and X is greater than pressure of B either over excess solid A or over excess solid X But less then their directly sumup value when excess of solid A and excess of solid X kept in different container.

**STATEMENT-2 :** In presence of each other, degree of dissociation of both solids decreases.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

8.25 **STATEMENT-1:** $Ag_2S + 4\,KCN \overset{O_2}{\rightleftharpoons} 2K[Ag(CN)_2] + K_2S$

**STATEMENT-2 :** The reaction is carried out in presence of air or $O_2$ so that $K_2S$ is oxidised to $K_2SO_4$ thereby shifting the equilibrium in forward direction.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

## SECTION - IV : COMPREHENSION TYPE

**Comprehension # 1**

### Le chatelier's principle

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way so as to minimise the effect of that change.

**Change of pressure :** If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more and the equilibirum will shift in the direction in which there is decrease in number of moles i.e., towards the direction in which there is decrease in volume.

**Effect of pressure on melting point :** There are two types of solids :

(a) Solids whose volume decreases on melting, e.g., ice, diamond, carborundum, magnesium nitride and quartz.

Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

The process of melting is facilitated at high pressure, thus melting point is lowered.

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(b) Solids whose volume increase on melting, e.g., Fe, Cu, Ag, Au, etc.
Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)
In this case the process of melting becomes difficult at high pressure; thus melting point becomes high.

(c) **Solubility of substances :** When solid substance are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).
$KCl + aq \rightleftharpoons KCl(aq) - heat$
In such cases, solubility increase with increase in temperature.
Consider the case of KOH; when this is dissolved, heat is evolved.
$KOH + aq \rightleftharpoons KOH(aq) + heat$
In such cases, solubility decrease with increase in temperature.

(d) **Solubility of gases in liquids :** When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

**Effect of temperature :** Le-Chatelier's principle predicts a system at equilibrium will tend to shift in the endothermic direction when temperature is raised, for then energy is absorbed as heat and the rise in temperature is opposed. Conversely, an equilibrium will shift in the exothermic direction if the temperature is lowered, for then that energy is released and the reduction in temperature is opposed. Van't Hoff equation shows the dependence of equilibrium constant K on temperature as:

$$\frac{d}{dT}\ell nK = \frac{\Delta H^\circ}{RT^2} \text{ or } \ell n\,K = \text{constant} - \frac{\Delta H^\circ}{R}\cdot\frac{1}{T}$$

**8.26** A gas 'X' when dissolved in water heat is evolved. Then solublity of 'X' will increase
(A) Low pressure, high temperature
(B) Low pressure, low temperature
(C) High pressure, high temperature
(D) High pressure, low temperature

**8.27** $Au(s) \rightleftharpoons Au(\ell)$
Above equilibrium is favoured at
(A) High pressure low temperature
(B) High pressure high temperature
(C) Low pressure, high temperature
(D) Low pressure, low temperature

**8.28** For the reaction $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$
If pressure is increased by reducing the volume of the container then
(A) Total pressure at equilibrium will change
(B) Concentration of all the component at equilibrium will not change
(C) Concentration of all the component at equilibrium will remain same
(D) Equilibrium will shift in the forward direction

**8.29** The plot of log K against $\frac{1}{T}$ is a straight line with positive slope (K being the equilibrium constant of a reaction), which of the following is then correct ?
(A) The reaction is endothermic in nature
(B) The reaction will be exothermic in nature
(C) The reaction goes to farther extent on raising the temperature
(D) None of these

## Comprehension # 3

For certain substances such as ammonium chloride, nitrogen peroxide, phosphorus pentachloride, etc. the measured densities are found to be less than those calculated from their molecular formula. The observed densities decrease towards a limit as the temperature is raised. This is due to the splitting of the molecules into simpler ones. The process is reversible and is called thermal dissociation.

Examples : $NH_4Cl \rightleftharpoons NH_3 + HCl$ $I_2 \rightleftharpoons 2I$
$N_2O_4 \rightleftharpoons 2NO_2$ $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

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With increase in the number of molecules, the volume increases (pressure remaining constant) and, in consequence, the density decreases. As the temperature rises, more and more dissociation takes place, and when practically complete dissociation occurs the density reaches its lowest limit. The extent of dissociation, i.e., the fraction of the total number of molecules which suffers dissociation is called the degree of dissociation. Gas density measurements can be used to determine the degree of dissociation. Let us take by general case where one molecule of a substance A splits up into n molecule of A on heating; i.e.,

$$A_n(g) \rightleftharpoons nA(g)$$

$t = 0$   $a$   $0$

$t = t_{eq}$   $a - x$   $n.x$   $\alpha = \frac{x}{a} \Rightarrow x = a\alpha.$

$a - a\alpha$   $n a \alpha$

Total no. of moles $= a - a\alpha + n a \alpha$

$= [1 + (n - 1)\alpha]\, a$

* Observed molecular weight or molar mass of the mixture

$$M_{mixture} = \frac{M_{A_n}}{[1+(n-1)\alpha]}, \; M_{A_n} = \text{Molar mass of gas } A_n$$

8.30 A sample of mixture of A(g), B(g) and C(g) under equilibrium has a mean molecular weight (observed) is 80. The equilibrium is $A(g) \rightleftharpoons B(g) + C(g)$
(mol. wt. = 100) (mol. wt. = 60) (mo. wt. = 40)

Find the degree of dissociation $\alpha$ for A(g).

(A) 0.25 (B) 0.5 (C) 0.75 (D) 0.8

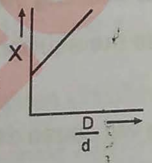
8.31 If the total mass of the mixture in the above case is 300 gm, the moles of C(g) present are.

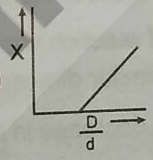
(A) $\frac{1}{4}$ mole (B) $\frac{4}{3}$ mole (C) $\frac{3}{4}$ mole (D) None

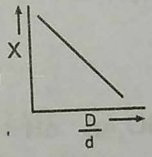
8.32 The $K_p$ for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 640 mm at 775 K. The percentage dissociation of $N_2O_4$ at equilibrium pressure of 160 mm is :

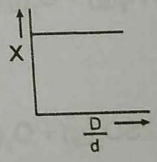
(A) 80 % (B) 30 % (C) 50 % (D) 70%

8.33 x (degree of dissociation) varies with $\frac{D}{d}$ in the above reaction according to :

(A)


(B)


(C)


(D)


8.34 The equation $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for :

(A) $A \rightleftharpoons nB/2 + nC/3$ (B) $A \rightleftharpoons nB/3 + (2n/3)C$

(C) $A \rightarrow (n/2)B + (n/4)C$ (D) $A \rightleftharpoons (n/2)B + C$

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## SECTION - V : MATRIX - MATCH TYPE

**8.35** **Match the following :**

| **Column I (Assume only reactant were present initially)** | **Column II** |
|---|---|
| (A) For the equilibrium $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$, if pressure is increased at equilibrium | (p) Forward shift |
| (B) For the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ volume is increased at equilibrium | (q) No shift in equilibrium |
| (C) For the equilibrium $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ inert gas is added at constant pressure at equilibrium | (r) Backward shift |
| (D) For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $Cl_2$ is removed at equilibrium. | (s) Final pressure is more than initial pressure |

**8.36**

| **Column-I** | **Column-II** |
|---|---|
| (A) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ On increase in volume at constant temperature | (p) Density of reacting mixture remains constant. |
| (B) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ On addition of inert gas at constant P & T | (q) Density of reacting mixture decreases |
| (C) $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$ On decrease in pressure at constant temperature | (r) Average molar mass of reacting mixture increases |
| (D) $2ICl_3(g) \rightleftharpoons I_2(g) + 3Cl_2(g)$, $\Delta H > 0$ On increase in pressure at constant temperature | (s) Average molar mass of reacting mixture decreases |
| | (t) Reaction moves in forward direction |

**8.37**

| **Column – I** | **Column – II** |
|---|---|
| (A) $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$; $\Delta H < 0$ | (p) High pressure and low temperature will favour formation of products. |
| (B) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $\Delta H > 0$ | (q) Increase in the amount of any of the product will definitely favour backward reaction. |
| (C) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; $\Delta H > 0$ | (r) Increase in temperature and doubling the volume of reaction vessel will cause the equilibrium to shift in similar direction. |
| (D) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H < 0$ | (s) A decrease in temperature will cause decrease in the value of equilibrium constant. |
| | (t) Increase in concentration of reactant the equilibrium is achieved will make the equilibrium shift towards product side. |

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**8.38** Match the following.

| **Reaction (Homogeneous gaseous phase)** | | **Degree of dissociation in terms of equilibrium constant** | |
|---|---|---|---|
| (A) | $A(g) + B(g) \rightleftharpoons 2\,C(g)$ | (p) | $(\sqrt{k})/(1+\sqrt{k})$ |
| (B) | $2\,A(g) \rightleftharpoons B(g) + C(g)$ | (q) | $(\sqrt{k})/(2+\sqrt{k})$ |
| (C) | $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ | (r) | $2\,k/(1+2k)$ |
| (D) | $AB(g) \rightleftharpoons \frac{A}{2}(g) + \frac{B}{2}(g)$ | (s) | $\frac{2\sqrt{k}}{1+2\sqrt{k}}$ |
| | | (t) | k |

## SECTION - VI : INTEGER TYPE

**8.39** $NH_3$ is heated initially at 15 atm from 27°C to 127°C at constant volume. At 127°C equilibrium is established. The new pressue at equilibrium at 127°C becomes 30 atm for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$. Then find the % of moles of $NH_3$ actually decomposed.

**8.40** The equilibrium constant for the reaction $Br_2(\ell) + C\ell_2(g) \rightleftharpoons 2BrC\ell(g)$ at 27°C is $k_p = 1$ atm. In a closed container of volume 164 L initially 10 moles of $C\ell_2$ are present at 27°C. What minimum mole of $Br_2(\ell)$ must be introduced into this container so that above equilibrium is maintained at total pressure of 2.25 atm. Vapour pressure of $Br_2(\ell)$ at 27°C is 0.25 atm. Assume that volume occupied by liquid is negligible. [R = 0.082 L atm $mole^{-1}$ $K^{-1}$, Atomic mass of bromine = 80].

**8.41** Following two equilibria are established on mixing two gases $A_2$ and C.

(i) $3A_2(g) \rightleftharpoons A_6(g)$ $K_P = 1.6\ atm^{-2}$

(ii) $A_2(g) + C(g) \rightleftharpoons A_2C(g)$

If $A_2$ and C are mixed in 2 : 1 molar ratio, calculate the equilibrium partial pressure of $A_2$, C, $A_2C$ and $K_P$ for the reaction (ii). Given that the total pressure to be 1.4 atm and partial pressure of $A_6$ to be 0.2 atm at equilibrium.

Give your answer multiply by 10.

**8.42** Two solids AB and $CB_2$ are simultaneously heated in a closed vessel to attain equilibrium.

$AB(s) \rightleftharpoons A(g) + B(g)$ ... (1)

$CB_2(s) \rightleftharpoons C(s) + 2B(g)$ ... (2)

$K_P$ for (1) and (2) reaction are $4.8 \times 10^{-6}$ and $5.76 \times 10^{-6}$. If partial pressure of A at equilibrium is $2 \times 10^{-x}$, find x.

**8.43** For given simultaneous reaction :

$X(s) \rightleftharpoons A(g) + B(s) + C(g)$ $K_{P_1} = 500$ atm

$Y(s) \rightleftharpoons D(g) + A(g) + E(s)$ $K_{P_2} = 2000$ atm

If total pressure = x, then write your answer after dividing by 25.

**8.44** If a mixture 0.4 mole $H_2$ and 0.2 mole $Br_2$ is heated at 700 K at equilibrium, the value of equilibrium constant is $0.25 \times 10^{10}$ then find out the ratio of concentrations of $(Br_2)$ and (HBr) (Report your answer as $\frac{Br_2}{HBr} \times 10^{11}$)

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## TOPIC 9

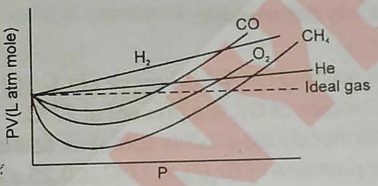
# GASEOUS STATE

## SECTION - I : STRAIGHT OBJECTIVE TYPE

**9.1** The density of steam at 27°C and $8.314 \times 10^4$ pascal is 0.8 Kg $m^{-3}$. The compressibility factor would be
(A) 0.75 (B) 1 (C) 0.88 (D) 1.1

**9.2** A 4 : 1 molar mixture of He and $CH_4$ gases is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. The ratio of number of moles of He to $CH_4$ in the mixture effusing out initially will be :
(A) 8 : 1 (B) 1 : 8 (C) 1 : 4 (D) 4 : 1

**9.3** The curve of pressure volume (PV) against pressure (P) of the gas at a particular temperature is as shown, according to the graph which of the following is / are incorrect (in the low pressure region):



(A) $H_2$ and He show positive deviation from ideal gas equation.
(B) CO, $CH_4$ and $O_2$ show negative deviation from ideal gas equation.
(C) $H_2$ and He show negative deviation while $CO_2$, $CH_4$ and $O_2$ show positive deviation.
(D) $H_2$ and He are less compressible than that of an ideal gas while $CO_2$, $CH_4$ and $O_2$ more compressible than that of ideal gas.

**9.4** For 10 minute each, at 0°C, from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 4 litre capacity. The resulting pressure is 2.8 atm and the mixture contains 0.4 mole of nitrogen. What is the molar mass of unknown gas?
(A) 448 g $mol^{-1}$ (B) 224 g $mol^{-1}$ (C) 226 g $mol^{-1}$ (D) None of these

**9.5** Three gases A, B and C are at same temperature if their r.m.s speed are in the ratio $1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$ then their molar masses will be in the ratio :
(A) 1 : 2 : 3 (B) 3 : 2 : 1 (C) $1 : \sqrt{2} : \sqrt{3}$ (D) $\sqrt{3} : \sqrt{2} : 1$

**9.6** $SO_2$ and $CH_4$ are introduced in a vessel in the molar ratio 1 : 2. The ratio of molecules of two gases present in the container when their rate of effusion becomes equal is :
(A) 1 : 2 (B) 2 : 1 (C) 4 : 1 (D) 1 : 4

**9.7** The volume occupied by 2.0 mole of $N_2$ at 200 K and 8.21 atm pressure, if $\frac{P_C V_C}{RT_C} = \frac{3}{8}$ and $\frac{P_r V_r}{T_r} = 2.4$, is
(A) 1.8 L (B) $\left(\frac{5}{8}\right)$ L (C) 12.8 L (D) 3.6 L

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**9.8** At a certain temperature for which RT = 25 lit. atm. $mol^{-1}$, the density of a gas, in gm $lit^{-1}$, is $d = 2.00\,P + 0.020\,P^2$, where P is the pressure in atmosphere. The molecular weight of the gas in gm $mol^{-1}$ is

(A) 25 (B) 50 (C) 75 (D) 100

**9.9** A mixture of carbon monoxide and carbon dioxide is found to have a density of 1.7 g/lit at S.T.P. The mole fraction of carbon monoxide is

(A) 0.37 (B) 0.40 (C) 0.30 (D) 0.50

**9.10** If equal masses of oxygen and nitrogen are placed in separate containers of equal volume at the same temperature, which one of the following statements is true? (Mol wt. $N_2 = 28$, $O_2 = 32$)

(A) Both flasks contain the same number of molecules.

(B) The pressure in the nitrogen flask is greater than in the oxygen flask.

(C) More molecules are present in the oxygen flask.

(D) Molecules in the oxygen flask are moving faster on the average than the ones in the nitrogen flask.

**9.11** The critical volume of a gas is 0.072 lit. $mol^{-1}$. The radius of the molecule will be, in cm

(A) $\left(\frac{3}{4\pi}\times10^{-23}\right)^{\frac{1}{3}}$ (B) $\left(\frac{4\pi}{3}\times10^{-23}\right)^{\frac{1}{3}}$ (C) $\left(\frac{3\pi}{4}\times10^{-23}\right)^{\frac{1}{3}}$ (D) $\left(\frac{3}{4\pi}\times10^{-8}\right)^{\frac{1}{3}}$

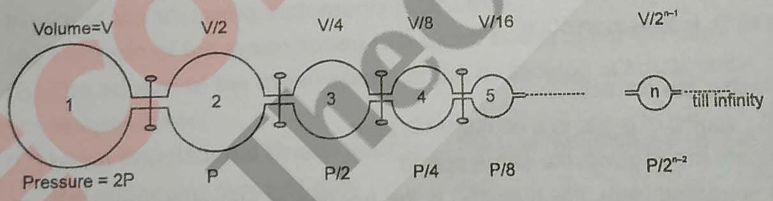
**9.12** The van der Waal's constant 'b' for $N_2$ and $H_2$ has the values 0.04 lit $mol^{-1}$ and 0.025 lit $mol^{-1}$. The density of solid $N_2$ is 1 g $cm^{-3}$. Assuming the molecules in the solids to be close packed with the same percentage void, the density of solid $H_2$ would be (in g $cm^{-3}$)

(A) 0.114 (B) 0.682 (C) 1.466 (D) 0.071

**9.13** If the number of molecules of $SO_2$ (molecular weight = 64) effusing through an orifice of unit area of cross-section in unit time at 0°C and 1 atm pressure is n. The number of He molecules (atomic weight = 4) effusing under similar conditions at 273°C and 0.25 atm is

(A) $\frac{n}{\sqrt{2}}$ (B) $n\sqrt{2}$ (C) 2n (D) $\frac{n}{2}$

**9.14**



Infinite number of flasks are connected to one another as shown above. The volume and pressure in each flask vary as shown. The stopcocks are initially closed. The common pressure, when all the stopcocks are opened, is : (Assume constant temperature)

(A) P (B) $\frac{1}{2}P$ (C) $\frac{P}{4}$ (D) $\frac{4}{3}P$

**9.15** A certain gas effuses out of two different vessels A and B. A has a circular orifice while B has a square orifice of length equal to the radius of the orifice of vessel A. The ratio of rate of diffusion of the gas from vessel A to that from vessel B is

(A) π : 1 (B) 1 : π (C) 1 : 1 (D) 3 : 2

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**9.16 Consider the following statements and arrange in the order of true/false as given in the codes.**
The correct order of True/False of the following statements is :
$S_1$ : Rate of diffusion and effusion of a gas increases by increasing the pressure and decreasing the temperature.
$S_2$ : An ideal gas has vander waal's constant a and b equal to zero.
$S_3$ : If an ideal gas is expanded adiabatically against a constant pressure then $TV^{\gamma-1}$ = constant
(A) T T F (B) F F T (C) T T T (D) F F F

**9.17 Consider the following statements and arrange in the order of true/false as given in the codes.**
$S_1$ : Speed possessed by maximum number of molecules of gas is called most probable speed.
$S_2$ : Molecular speeds are function of temperature for a particular gas.
$S_3$ : If amount of gas is increased then most probable speed also increases.
$S_4$ : The root mean square speed of an ideal gas is proportional to $\frac{1}{\sqrt{d}}$
(A) T T T F (B) F FT F (C) T T F T (D) T F T F

## SECTION - II : MULTIPLE CORRECT ANSWER TYPE

9.18 Choose the correct option(s)
(A) At low pressure (nearly 1 atm), compressibility factor for $H_2$ gas is greater than 1 at 273 K.
(B) Compressibility factor for a vander Waal's gas at its critical condition is less than 1.
(C) Boyle's temperature of a gas is lesser than its critical temperature.
(D) vander Waal's constant 'a' for $NH_3$ is greater than that of $CH_4$.

9.19 The densities of three gases $O_2$, $SO_2$ and $H_2$ are measured at 400K and 1 atm. They are 0.8 g/L, $\frac{32}{15}$ g/L and $\frac{1}{25}$ g/L respectively. Which of the following statements is/are correct for these gases? (Use R = $\frac{1}{12}$ L atm/mol–K).
(A) $SO_2$ is showing negative deviation from ideal behaviour.
(B) $O_2$ is more compressible than ideal gas under these conditions.
(C) $H_2$ is behaving ideally.
(D) Boyle's temperature of $O_2$ is less than 400K.

9.20 Which of following statements are correct
(A) Average velocity of molecules of a gas in a container is zero.
(B) All molecules in a gas are moving with the same speed.
(C) If an open container is heated from 300 K to 400 K the fraction of air which goes out with respect to originally present is $\frac{1}{4}$.
(D) If compressibility factor of a gas at STP is less than unity then its molar volume is less than 22.4 L at STP.

9.21 If the pressure of the gas contained in a closed vessel is increased by 20% when heated by 273°C then it's initial temperature must have been
(A) 1092°C (B) 1029 K (C) 1365°C (D) 1365 K