4.50 Match order of the reaction (in List – I) with the corresponding rate constant (in List – II) :

	List I (order)		List II (rate constant)
(A)	Zero	(p)	$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$
(B)	First	(q)	$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$
(C)	Second	(r)	$k = \frac{x}{t}$
(D)	Third	(s)	$k = \frac{1}{t}\log_e\left(\frac{a}{(a-x)}\right)$

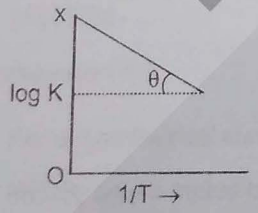
4.51 **Match the following :**

Column I	Column II
(A) If the activation energy is 65 kJ then how much time faster a reaction proceed at 25°C than at 0°C.	(p) 0
(B) Rate constant of a first - order reaction is 0.0693 min^{-1}. If we start with 20 mol L^{-1}, it is reduced to 2.5 mol L^{-1} in how many minutes.	(q) 11
(C) Half - lives of first - order and zeroth order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693 ? (If initial concentration are same for both zero and first order reactions.)	(r) 30
(D) The half-life periods are given , $[A]_0$ (M) 0.0677 0.136 0.272; $t_{1/2}$ (sec) 240 480 960; order of the reaction is	(s) 1/4
	(t) 2

SECTION - VI : INTEGER TYPE

4.52 A certain reactant XO_3^- is getting converted to X_2O_7 in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing agent which reacts only with XO_3^- and X_2O_7. In this process of reduction both the compounds converted to X^-. At t = 0, the volume of the reagent consumed is 30mL and at t = 9.212 min. the volume used up is 36 mL. Find the rate constant(in hr^{-1}) of the conversion of XO_3^- to X_2O_7 ? Asuming reaction is of Ist order. (Given that $\ell n\ 10 = 2.303$, $\log 2 = 0.30$).

4.53 The graph between log k and $\frac{1}{T}$ [K is rate constant (sec^{-1}) and T the temperature. (K)] is a straight line with OX = 5 and $\theta = \tan^{-1}\left(-\frac{1}{2.303}\right)$. Calculate the value of E_a is cal. ?



4.54 For the reaction A ⟶ products, the following data is given for a particular run.

time (min.) :	0	5	15	35
$\frac{1}{[A]}$ (M^{-1}) :	1	2	4	8

Determine the order of the reaction.

4.55 If $\frac{dx}{dt} = k\,[H^+]^n$ and rate becomes 100 times when pH changes from 2 to 1. Find the order of reaction.

4.56 The gas phase decomposition of dimethyl ether follows first order kinetics,

$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minute. Initially only dimethyl ether is present at a pressure of 0.40 atmosphre. What is the total pressure of the system after 12 minute ? Assume ideal gas behaviour. (Give your answer by multiplying 100)

4.57 In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 18 kcal/mol while it decreases to 6 kcal/mol when the decomposition was carried out in the presence of a catalyst at 300 K. How many times is the catalysed reaction faster than uncatalysed one ?

(Give your answer by multiplying 10^7)

4.58 Decomposition of H_2O_2 (Ist order)

$$H_2O_2(aq) \longrightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$$

Can be monitored by titration method by pressure measurement. If

Time (min)	t = 0	30	∞
Pressure (mm of Hg)	200	375	400

While when progress of same reaction was monitored by titration method or the volume of titrant consumed after 10 min was found to be 20 ml. Then complete the following table.

Time (min)	t = 0	10	30
Pressure (mm of Hg)	200	(b)	(c)
Volume of $KMnO_4$ consumed (ml)	(a)	20	(d)

TOPIC 5

STOICHIOMETRY

SECTION - I : STRAIGHT OBJECTIVE TYPE

5.1 15 gm $Ba(MnO_4)_2$ sample containing inert impurity is completely reacting with 100 ml of '11.2 V' H_2O_2, then what will be the % purity of Ba $(MnO_4)_2$ in the sample ?
(Atomic mass Ba = 137, Mn = 55)
(A) 5% (B) 10% (C) 50% (D) none

5.2 In what ratio should a 15% solution of acetic acid be mixed with a 3% solution of the acid to prepare a 10% solution (all percentages are mass/mass percentages) :
(A) 7 : 3 (B) 5 : 7 (C) 7 : 5 (D) 7 : 10

5.3 105 ml of pure water at 4°C saturated with NH_3 gas, yielded a solution of density 0.9 g/ml and containing 30% NH_3 by mass. Find the volume of resulting NH_3 solution.
(A) 66.67 ml (B) 166.67 ml (C) 133.33 ml (D) 266.67 ml

5.4 X gram of pure As_2S_3 is completely oxidised to respective highest oxidation states by 50 ml of 0.1 M hot acidified $KMnO_4$ then X, mass of As_2S_3 taken is : (Molar mass of As_2S_3 = 246)
(A) 22.4 g (B) 0.22 g (C) 64.23 g (D) None

5.5 Volume V_1 mL of 0.1M $K_2Cr_2O_7$ is needed for complete oxidation of 0.678 g N_2H_4 in acidic medium. The volume of 0.3 M $KMnO_4$ needed for same oxidation in acidic medium will be:
(A) $\frac{2}{5}V_1$ (B) $\frac{5}{2}V_1$
(C) 113 V_1 (D) can not be determined

5.6 100 ml of 0.1M $NaAl(OH)_2CO_3$ is neutralised by 0.25 N HCl to form NaCl, $AlCl_3$ and CO_2. Volume of HCl required is
(A) 10 mL (B) 40 mL (C) 100mL (D) 160 mL

5.7 100 mL of 0.1N I_2 oxidizes $Na_2S_2O_3$ in 50 ml solution to $Na_2S_4O_6$. The normality of this hypo solution against $KMnO_4$ (which oxidizes it to Na_2SO_4) would be
(A) 0.1 (B) 0.2 (C) 1.0 (D) 1.6.

5.8 25 mL of 2N HCl, 50 mL of 4N HNO_3 and x mL of 2M H_2SO_4 are mixture together and the total volume is made up to 1 L after dilution. 50 mL of this acid mixture completely reacted with 25 mL of a 1N Na_2CO_3 solution. The value of x is :
(A) 250 mL (B) 62.5 mL (C) 100 mL (D) None of these

5.9 An excess of NaOH was added to 100 mL of a ferric chloride solution. This caused the precipitation of 1.425 g of $Fe(OH)_3$. Calculate the normality of the ferric chloride solution
(A) 0.20 N (B) 0.50 N (C) 0.25 N (D) 0.40 N

5.10 0.4g of a polybasic acid H_nA (all the hydrogens are acidic) requires 0.5g of NaOH for complete neutralization. The number of replaceable hydrogen atoms in the acid and the molecular weight of 'A' would be : (Molecular weight of the acid is 96 gms/mole.)
(A) 1, 95 (B) 2, 94 (C) 3, 93 (D) 4, 92

5.11 A solution of $Na_2S_2O_3$ is standardized iodimetrically against 0.1262 g of $KBrO_3$. This process requires 45 mL of the $Na_2S_2O_3$ solution. What is the molarity of the $Na_2S_2O_3$?
(A) 0.2 M (B) 0.1 M (C) 0.05 M (D) 0.1 N

5.12 25.0 g of $FeSO_4 . 7H_2O$ was dissolved in water containing dilute H_2SO_4, and the volume was made up to 1.0 L. 25.0 mL of this solution required 20 mL of an N/10 $KMnO_4$ solution for complete oxidation. The percentage of $FeSO_4 \cdot 7H_2O$ in the acidic solution is
(A) 78% (B) 98% (C) 89% (D) 79%

5.13 25 mL of a solution containing HCl and H_2SO_4 required 10 mL of a 1 N NaOH solution for neutralization. 20 mL of the same acid mixture on being treated with an excess of $AgNO_3$ gives 0.1435 g of AgCl. The normality of the HCl and the normality of the H_2SO_4 are respectively
(A) 0.40 N and 0.05 N (B) 0.05 N and 0.35 N
(C) 0.50 N and 0.25 N (D) 0.40 N and 0.5 N

5.14 An queous solution containing 2.14 g KIO_3 was treated with 100 ml of 0.4 M KI solution, the weight of I_2 produced is -
(A) 6.096 (g) (B) 7.62 g (C) 30.48 g (D) 18.288 g

5.15 0.70 g of mixture $(NH_4)_2SO_4$ was boiled with 100 mL of 0.2 N NaOH solution till all the NH_3(g) evolved and get dissolved in solution itself. The remaining solution was diluted to 250 mL. 25 mL of this solution was neutralized using 10 mL of a 0.1 N H_2SO_4 solution. The percentage purity of the $(NH_4)_2SO_4$ sample is
(A) 94.3 (B) 50.8 (C) 47.4 (D) 79.8

5.16 A mixed solution of potassium hydroxide and sodium carbonate required 15 mL of an N/20 HCl solution when titrated with phenolphthalein as an indicator. But the same amount of the solution when titrated with methyl orange as an indicator required 25 mL of the same acid. The amount of KOH present in the solution is
(A) 0.014 g (B) 0.14 g (C) 0.028 g (D) 1.4 g

5.17 In an iodometric estimation, the following reaction occur

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 \; ; \qquad I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

0.12 mole of $CuSO_4$ was added to excess of KI solution and the liberated iodine required 120 mL of hypo. The molarity of hypo solution was :
(A) 2 (B) 0.20 (C) 0.1 (D) 1.0

5.18 **Consider the following statements and arrange in the order of true/false as given in the codes.**
S_1 : The reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$ is not an example of a redox reaction.
S_2 : The equivalent mass of $K_2Cr_2O_7$ in acidic medium is molar mass divided by two.
S_3 : The equivalent mass of a substance can be calculated without considering the reaction it undergoes.
(A) TFT (B) FTF (C) FFF (D) TTT

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

5.19 Choose the correct statement :
(A) 1 mole of MnO_4^- ion can oxidised 5 moles of Fe^{2+} ion in acidic medium
(B) 1 mole of $Cr_2O_7^{2-}$ ion can oxidised 6 moles of Fe^{2+} ion in acidic medium
(C) 1 mole of Cu_2S can be oxidised by 1.6 moles of MnO_4^- ion in acidic medium
(D) 1 mole of Cu_2S can be oxidised by 1.33 moles of $Cr_2O_7^{2-}$ ion in acidic medium

5.20 Which of the following statements is/are correct :

(A) Equivalent mass of Br_3O_8 in the given reaction is 23.
$Br_3O_8 + I^- + H^+ \longrightarrow Br_2 + I_2 + H_2O$

(B) In case of oxalic acid ($H_2C_2O_4$), the average oxidation number and individual oxidation number of Carbon have the same value.

(C) In case of iodimetric titration, KI is made to react with an oxidising agent and the liberated I_2 gas is made to titrate with hypo solution.

(D) Equivalent mass of Cu_3P in the given reaction is M/11 (where M = mol. mass)
$Cu_3P + KMnO_4 + H^+ \longrightarrow Cu^{2+} + H_2PO_4^- + K^+ + Mn^{2+}$

5.21 A 5g sample containing Fe_3O_4 ($FeO + Fe_2O_3$) and an inert impurity is treated with excess of KI solution in the presence of dilute H_2SO_4. The entire iron converted to Ferrous ion along with liberation of Iodine. The resulting solution is diluted to 100 ml. 20 ml of the diluted solution requires 10 ml of 0.5M $Na_2S_2O_3$ solution to reduce the iodine present. Amongs the following select correct statements.

(A) % of Fe_2O_3 in sample is 40%
(B) % of FeO in sample is 28%
(C) % of inert impurity in sample is 42%
(D) % of inert impurity in sample is 32%

5.22 Calcium and magnesium ion from a 10^5 litre of sample of hard water was quantitatively precipitated as carbonates and weight of ppt obtained was found to be 568 g. Precipitate lost 264 g of weight on strong heating.

(A) Degree of hardness of water is 4 ppm
(B) Molarity of Ca^{2+} ions in hard water was 4×10^{-5} M
(C) Molarity of Mg^{2+} ions in hard water was 4×10^{-5} M
(D) Sum of molarity of Ca^{2+} & Mg^{2+} ions in hard water was 6×10^{-5} M

5.23 There are two sample of HCl having molarity 1M and 0.25 M. Find volume of these sample taken in order to prepare 0.75 M HCl solution. (Assume no water is used)

(A) 20 ml, 10 ml (B) 100 ml, 50 ml (C) 40 ml, 20 ml (D) 50 ml, 25 ml

5.24 Which of the following samples of reducing agents is /are chemically equivalent to 25 ml of 0.2 N $KMnO_4$ to be reduced to Mn^{2+} and water.

(A) 25 ml of 0.2 M $FeSO_4$ to be oxidized to Fe^{3+}
(B) 50 ml of 0.1 M H_3AsO_3 to be oxidized to H_3AsO_4
(C) 25 ml of 0.1 M H_2O_2 to be oxidized to H^+ and O_2
(D) 25 ml of 0.1 M $SnCl_2$ to be oxidized to Sn^{4+}

5.25* Fuming H_2SO_4 (oleum) is a homogenous mixture of H_2SO_4 and SO_3. Then which of the following statement(s) are correct :

(A) If H_2SO_4 and SO_3 are equimolar in an oleum sample, then strength of oleum is 110.11%

(B) If H_2SO_4 and SO_3 are having equal masses in an oleum sample, then strength of oleum is 111.25%

(C) Strength of an oleum sample may be less than 100%.

(D) If strength of oleum is (100 + x) %, then x g of water is to be added to 100 g oleum sample to convert whole of SO_3 to H_2SO_4.

5.26 If 100 ml of 1M H_2SO_4 solution is mixed with 100 ml of 98%(w/w) H_2SO_4 solution (d = 0.1 gm/ml) then :

(A) concentration of solution remains same
(B) volume of solution become 200 ml
(C) mass of H_2SO_4 in the solution is 98 gm
(D) mass of H_2SO_4 in the solution is 19.6 gm

5.27 An oleum smaple labelled as 104.5%, in 10 g of this sample 90 mg water is added then which is/are correct for resulting solution.

(A) Solution contain 10.09 g H_2SO_4
(B) Solution contain 15.86% free SO_3
(C) Solution contain 8.49 g H_2SO_4
(D) Solution contain 20% free SO_3

5.28 Which of the following contains the same number of molecules?
(A) 1g of O_2, 2g of SO_2
(B) 1g of CO_2, 1g of N_2O
(C) 112 ml of O_2 at STP, 224 ml of He at 0.5 atm and 273 K
(D) 1g of oxygen, 1g of ozone

5.29 0.1 M solution of KI reacts with excess of H_2SO_4 and KIO_3 solutions, according to equation
$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$; which of the following statement is correct
(A) 400 ml of the KI soluition react with 0.004 mole KIO_3
(B) 100 ml of the KI solution reacts with 0.006 mole of H_2SO_4
(C) 0.5 litre of the KI solution produced 0.005 mole of I_2
(D) Equivalent weight of KIO_3 is equal to $\left(\frac{\text{Molecular Weight}}{5}\right)$

SECTION - III : ASSERTION AND REASON TYPE

5.30 **STATEMENT-1 :** In the redox reaction $8\,H^+(aq) + 4\,NO_3^- + 6\,Cl^- + Sn(s) \longrightarrow SnCl_6^{2-} + 4\,NO_2 + 4\,H_2O$, the reducing agent is Sn(s).
STATEMENT-2 : In balancing half reaction, $S_2O_3^{2-} \longrightarrow S(s)$, the number of electrons added on the left is 4.
(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

5.31 **STATEMENT-1 :** Among Br^-, O_2^{2-}, H^- and NO_3^-, the ions that cannot act as oxidising agents are Br^- and H^-.
STATEMENT-2 : Br^- and H^- cannot be reduced.
(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

5.32 **STATEMENT-1 :** In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume required at the equivalence point is twice that of the acid required using phenolphthalein indicator.
STATEMENT-2 : Two mole of HCl are required for the complete neutralization of one mole of Na_2CO_3.
(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

632 g of sodium thiosulphate ($Na_2S_2O_3$) reacts with copper sulphate to form cupric thiosulphate which is reduced by sodium thiosulphate to give cuprous compound which is dissolved in excess of sodium thiosulphate to form a complex compound sodium cuprothiosulphate ($Na_4[Cu_6(S_2O_3)_5]$).

$$CuSO_4 + Na_2S_2O_3 \longrightarrow CuS_2O_3 + Na_2SO_4$$

$$2CuS_2O_3 + Na_2S_2O_3 \longrightarrow Cu_2S_2O_3 + Na_2S_4O_6$$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \longrightarrow Na_4[Cu_6(S_2O_3)_5]$$

Sodium cuprothiosulphate

In this process, 0.2 mole of sodium cuprothiosulphate is formed. (O = 16, Na = 23, S = 32)

5.33 The average oxidation states of sulphur in $Na_2S_2O_3$ and $Na_2S_4O_6$ are respectively.
(A) + 5 & + 2 (B) + 2 & + 2.5 (C) + 5 & 2.5 (D) + 2 & + 4

5.34 Moles of sodium thiosulphate reacted and unreacted after the reaction are respecticvely.
(A) 3 & 2 (B) 2 & 3 (C) 2.2 & 1.8 (D) 1.8 & 2.2

5.35 If instead of given amount of sodium thiosulphate, 2 moles of sodium thiosulphate along with 3 moles of $CuSO_4$ were taken initially. Then moles of sodium cuprothiosulphate formed is
(A) 0 (B) 1 (C) 1.5 (D) 2

Comprehension # 2

We know that balancing of a chemical equation is entirely based on law of conservation of mass. However the concept of Principle of Atom Conservation (POAC) can also be related to law of conservation of mass in a chemical reaction. So, POAC can also act as a technique for balancing a chemical equation. For example, for a reaction :

$$ABC_3 \longrightarrow AB + C_2$$

On applying POAC for A, B & C and relating the 3 equations, we get : $\frac{n_{ABC_3}}{2} = \frac{n_{AB}}{2} = \frac{n_{C_2}}{3}$ (n_x : number of moles of X)

Thus, the coefficients of ABC_3 , AB & C_2 in the balanced chemical equation will be 2,2 & 3 respectively and the balanced chemical equation can be represented as :

$$2ABC_3 \longrightarrow 2AB + 3C_2$$

Now answer the following questions :

5.36 Which of the following relation is correct regarding the numerical coefficients p,q,r in the balanced chemical equation :

$$pA + qB_2 \longrightarrow rA_2B_5$$

(A) 2p = r (B) q = 1.25 p (C) r = 2q (D) q = 0.8p

5.37 If the weight ratio of C and O_2 present is 1 : 2 and both of reactants completely consume and form CO and CO_2 and we will obtain a gasous mixture of CO and CO_2. What would be the weight ratio of CO and CO_2 in mixture.
(A) 11 : 7 (B) 7 : 11 (C) 1 : 1 (D) 1 : 2

5.38 If the atomic masses of X and Y are 10 & 30 respectivetly, then the mass of XY_3 formed when 120 g of Y_2 reacts completely with X is :

Reaction $X + Y_2 \longrightarrow XY_3$

(A) 133.3 g (B) 200 g (C) 266.6 g (D) 400 g

Comprehension # 3

Oleum is considered as a solution of SO_3 in H_2SO_4 , which is obtained by passing SO_3 in solution of H_2SO_4. When 100 g sample of oleum is diluted with desired weight of H_2O then the total mass of H_2SO_4 obtained after dilution is known as % labelling of oleum.

For example, a oleum bottle labelled as '109% H_2SO_4' means the 109 g total mass of pure H_2SO_4 will be formed when 100 g of oleum is diluted by 9 g of H_2O which combines with all the free SO_3 to form H_2SO_4 as

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

5.39 What is the % of free SO_3 in an oleum that is labelled as '104.5% H_2SO_4' ?
(A) 10 (B) 20 (C) 40 (D) None of these

5.40 If excess water is added into a 100 g bottle sample labelled as "112% H_2SO_4" and is reacted with 5.3 g Na_2CO_3, then find the volume of CO_2 evolved at 1 atm pressure and 300 K temperature after the completion of the reaction : [R = 0.0821 L atm mol^{-1} K^{-1}]

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

(A) 2.46 L (B) 24.6 L (C) 1.23 L (D) 12.3

5.41 1 g of oleum sample is diluted with water. The solution required 54 ml of 0.4 N NaOH for complete neutralization. The % of free SO_3 in the sample is :
(A) 74 (B) 26 (C) 20 (D) None of these

Comprehension # 5

Molality : It is defined as the number of moles of the solute present in 1kg of the solvent. It is denoted by 'm'.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Number of kilo-grams of the solvent}}$$

Let w_A grams of the solute of molecular mass m_A be present in w_B grams of the solvent, then

$$\text{Molality (m)} = \frac{w_A}{m_A \times w_B} \times 1000$$

Relation between mole fraction and Molality :

$$X_A = \frac{n}{N+n} \quad \text{and} \quad X_B = \frac{N}{N+n}$$

$$\frac{X_A}{X_B} = \frac{n}{N} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_A \times m_B}{w_B \times m_A}$$

$$\frac{X_A \times 1000}{X_B \times m_B} = \frac{w_A \times 1000}{w_B \times m_A} = m \quad \text{or} \quad \frac{X_A \times 1000}{(1-X_A)m_B} = m$$

5.42 If the ratio of the mole fraction of a solute is changed from $\frac{1}{3}$ to $\frac{1}{2}$ in the 800 g of solvent then the ratio of molality will be :

(A) 1 : 3 (B) 3 : 1 (C) 4 : 3 (D) 1 : 2

5.43 The mole fraction of the solute in the 12 molal solution of Na_2CO_3 is :

(A) 0.822 (B) 0.177 (C) 1.77 (D) 0.0177

5.44 What is the quantity of water that should be added to 16 gm, methanol to make the mole fraction of methanol as 0.25 –

(A) 27 gm. (B) 12 gm. (C) 18 gm. (D) 36 gm.

5.45 A 300 gm, 30% (w/w) NaOH solution is mixed with 500 gm 40% (w/w) NaOH solution. What is % (w/v) NaOH. if density of final solution is 2 gm/ml.

(A) 72.5 (B) 65 (C) 62.5 (D) None

5.46 What is the molality of final solution obtained in the above problem

(A) 1.422 (B) 14.22 (C) 15.22 (D) None

SECTION - V : MATRIX - MATCH TYPE

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

List-I	List-II
(A) $FeS_2 \rightarrow Fe^{+3} + SO_2$	(p) M/20
(B) $Fe_2S_3 \rightarrow 2FeSO_4 + SO_2$	(q) M/5
(C) $KMnO_4$ in acidic medium	(r) M/8
(D) $Cu_2S \rightarrow Cu^{2+} + SO_2$	(s) M/11

5.48

Column I	Column II
(A) Sn^{+2} + MnO_4^- (acidic) 3.5 mole 1.2 mole	(p) Amount of oxidant available decides the number of electrons transfer
(B) $H_2C_2O_4$ + MnO_4^- (acidic) 8.4 mole 3.6 mole	(q) Amount of reductant available decides the number of electrons transfer
(C) $S_2O_3^{-2}$ + I_2 7.2 mole 3.6 mole	(r) Number of electrons involved per mole of oxidant > Number of electrons involved per mole of reductant
(D) Fe^{+2} + $Cr_2O_7^{-2}$ (acidic) 9.2 mole 1.6 mole	(s) Number of electrons involved per mole of oxidant < Number of electrons involved per mole of reductant.

5.49 Match the reacting mixture in column– I with the reagent in column – II

Column – I	Column – II
(A) $H_2C_2O_4 + NaHC_2O_4$	(p) NaOH
(B) $NaHPO_4 + NaNO_2$	(q) HCl
(C) $Fe_2(SO_4)_3 + FeC_2O_4$	(r) $KMnO_4$
(D) $FeO + Fe_2O_3$	(s) Zinc dust

5.50 Match the following :

Column I	Column II
(A) 4.5 m solution of $CaCO_3$ density 1.45 gm/ml	(p) Mole fraction of solute is 0.2
(B) 3 M 100 ml H_2SO_4 mixed with 1 M 300 ml H_2SO_4 solution	(q) Mass of the solute is 360 gm
(C) 14.5 m solution of Ca	(r) Molarity = 4.5
(D) in 2 litre solution of 4 M NaOH, 40 gm NaOH is added.	(s) Molarity 1.5
(E) 5m (molal) NaOH solution	(t) 16.66 % (w/w) of NaOH in solution.

SECTION - VI : INTEGER TYPE

5.51 Polychlorinated biphenyls, PCBs, known to be dangerous enviromental pollutants, are a group of compounds with the general empirical formula $C_{12}H_mCl_{10-m}$, where m is an integer. What is the value of m, if percentage of carbon atom in the compound is 40 ?

5.52 50 ml of water sample, containing temporary hardness only, required 0.1 ml of M/50 HCl for complete neutralisation. Calculate the temporary hardness of water in ppm.

5.53 Calcium phosphide (Ca_3P_2) formed by reacting calcium orthophosphate ($Ca_3(PO_4)_2$) with magnesium was hydrolysed by water. The evolved phosphine (PH_3) was burnt in air to yield phosphorus pentoxide (P_2O_5). How many grams of magnesium metaphosphate would be obtained, if 19.2 g of magnesium were used for reducing calcium phosphide. (At. wt. Mg = 24, P = 31)

$$Ca_3(PO_4)_2 + Mg \longrightarrow Ca_3P_2 + MgO$$

$$Ca_3P_2 + H_2O \longrightarrow Ca(OH)_2 + PH_3$$

$$PH_3 + O_2 \longrightarrow P_2O_5 + H_2O$$

$$MgO + P_2O_5 \longrightarrow Mg(PO_3)_2$$

magnesium metaphosphate

5.54 0.2828 g of iron wire was dissolved in excess dilute H_2SO_4 and the solution was made upto 100 mL. 20 mL of this solution required 30 mL of N/30 $K_2Cr_2O_7$ solution for exact oxidation. Calculate percent purity of Fe in wire.

5.55 One litre of a sample of hard water contain 4.44 mg $CaCl_2$ and 1.9 mg of $MgCl_2$. What is the total hardness in terms of ppm of $CaCO_3$?

5.56 An oxide of a metal contains 40% oxygen, by weight. What is the equivalent weight of the metal?

5.57 A sample consisting of chocolate-brown powder of PbO_2 is allowed to react with excess of KI and iodine liberated is reacted with N_2H_4 in another container The volume of gas liberated from this second container at STP was measured out to be 1.12 litre. Find out volume of decimolar NaOH required to dissolve PbO_2 compietely.(Assume all reactions are 100% compiete).
Give your answer divide by 100.

5.58 Based on the following informaion, determine value of x and y :

$$(CH_3)_x AlCl_y\ (0.643\ g) \longrightarrow xCH_4\ (g)\ (0.22\ g) + y\ Cl^- + Al^{3+} \xrightarrow{AgNO_3} AgCl\ (s)\ (0.996\ g).$$

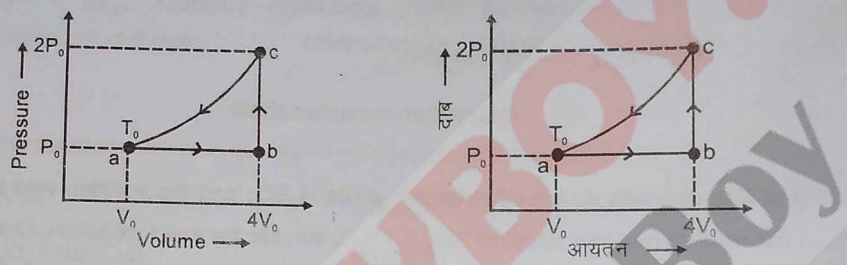
5.59 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. Find the Volume(V) (mL) of stock solution required to prepare a 500 mL solution of 0.4 M HCl.
Report your answer as V/5

TOPIC 6

THERMODYNAMICS

SECTION - I : STRAIGHT OBJECTIVE TYPE

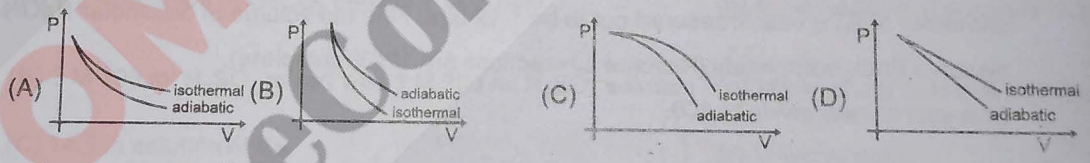
6.1 One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then the change in the internal energy of gas from a to b and b to c is respectively :



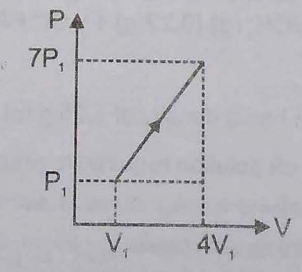
(A) $\frac{9P_oV_o}{2}$, 6 RT_o (B) $\frac{9P_oV_o}{2}$, 10 RT_o (C) $\frac{15P_oV_o}{2}$, 6 RT_o (D) $\frac{15P_oV_o}{2}$, 10 RT_o

6.2 Consider the following data : $\Delta_f H°$ (N_2H_4, ℓ) = 50 kJ/mol, $\Delta_f H°$ (NH_3, g) = –46 kJ/mol, B.E. (N–H) = 393 kJ/mol and B.E. (H–H) = 436 kJ/mol,
Δ_{vap} H (N_2H_4, ℓ) = 18 kJ/mol
Calculate the N – N bond energy in kJ/mol for N_2H_4.
(A) 190 kJ/mol (B) – 190 kJ/mol (C) 95 kJ/mol (D) – 95 kJ/mol

6.3 The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is :



6.4 In the process shown in the figure on an ideal diatomic gas, the value of q and ΔH respectively is :



(A) 79.5 P_1V_1 and 94.5 P_1V_1 (B) 55.5 P_1V_1 and 94.5 P_1V_1
(C) 12 P_1V_1 and 0 (D) 79.5 P_1V_1 and defined ($\because$ P varies)

6.5 For an ideal gas having molar mass M, specific heat at constant pressure can be given as :

(A) $\frac{\gamma RM}{\gamma - 1}$ (B) $\frac{R}{M(\gamma - 1)}$ (C) $\frac{RM}{\gamma - 1}$ (D) $\frac{\gamma R}{M(\gamma - 1)}$

6.6 At 1000 K water vapour at 1atm. has been found to be dissociated into H_2 and O_2 to the extent of 3×10^{-5} %. Calculate the free energy decrease of the system, assuming ideal behaviour.

(A) $-\Delta G = 90{,}060$ cal (B) $-\Delta G = 20$ cal (C) $-\Delta G = 480$ cal (D) $-\Delta G = -45760$ cal

6.7 In the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ at 550°C, when the initial pressure of CO & Cl_2 are 250 and 280 mm of Hg respectively. The equilibrium pressure is found to be 380 mm of Hg. Calculate the degree of dissociation of $COCl_2$ at 1 atm. What will be the extent of dissociation, when N_2 at a pressure of 0.4 atm is present and the total pressure is 1 atm.

(A) 0.32 and no change (B) 0.32 and 0.4

(C) 0.4 and 0.3 (D) In presence of N_2 dissociation cannot take place

6.8 When 1 mole of an ideal gas at 20 atm pressure and 15 L volume expands such that the final pressure becomes 10 atm and the final volume becomes 60 L. Calculate entropy change for the process ($C_{p,m} = 30.96$ J mole^{-1} K^{-1})

(A) 80.2 J.k^{-1} mol^{-1} (B) 62.42 kJ.k^{-1} mol^{-1} (C) 120×10^2 Jk^{-1} mol^{-1} (D) 27.22 J.k^{-1} mol^{-1}

6.9 During winters, moisture condenses in the form of dew and can be seen on plant leaves and grass. The entropy of the system in such cases decreases as liquids possess lesser disorder as compared to gases. With reference to the second law, which statement is **correct**, for the above process ?

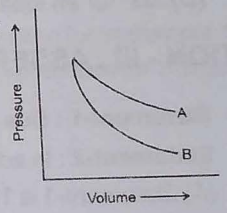
(A) The randomness of the universe decreases

(B) The randomness of the surroundings decreases

(C) Increase is randomness of surroundings equals the decrease in randomness of system

(D) The increase in randomness of the surroundings is greater as compared to the decrease in randomness of the system.

6.10 P–V plots for two gases during an adiabatic process are given in the figure : Plot A and plot B should correspond to : (Assume ideal behaviour)



(A) He and O_2

(B) SO_2 and Ar

(C) O_2 and He

(D) Both (B) and (C)

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

S_1 : Change in state function between two states is a definite quantity and does not depend on path.

S_2 : Intensive properties can't be algebraically added or subtracted.

S_3 : Ratio of two extensive properties result into a parameter that depends on amount of substance.

S_4 : Molar heat capacity is a path function.

The correct order of true / false of the above statements is

(A) F T F T (B) F F F T (C) T T F T (D) T T T F

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

6.12 10 moles of a liquid L are 50% converted into its vapour at its boiling point (273°C) and at a pressure of 1 atm. If the value of latent heat of vapourisation of liquid L is 273 L atm/mole, then which of the following statements is/are correct : Assume volume of liquid to be negligible and vapour of the liquid to behave ideally.

(A) Work done by the system in the above process is 224 L atm.

(B) The enthalpy change (ΔH) for the above process is 1365 L atm (with respect to magnitude only)

(C) The entropy of the system increases by 2.5 L atm in the above process.

(D) The value of ΔU for the above process is 1589 L atm.

6.13 One mole of an ideal diatomic gas (C_v = 5 cal) was transformed from initial 25°C and 1 L to the state when temperature is 100°C and volume 10 L. Then for this process(R = 2 calories/mol/K) (take calories as unit of energy and kelvin for temperature)

(A) $\Delta H = 525$ (B) $\Delta S = 5 \ln \frac{373}{298} + 2 \ln 10$

(C) $\Delta E = 525$

(D) ΔG of the process can not be calculated using given information.

6.14 From the following data, mark the option(s) where ΔH is correctly written for the given reaction.

Given : $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$; $\Delta H = -57.3$ kJ

$\Delta H_{solution}$ of HA(g) = –70.7 kJ/mol

$\Delta H_{solution}$ of BOH(g) = 20 kJ/mol

$\Delta H_{ionization}$ of HA = 15 kJ/mol and BOH is a strong base.

Reaction	ΔH_r (kJ/mol)
(A) $HA(aq) + BOH(aq) \longrightarrow BA(aq) + H_2O$	–42.3
(B) $HA(g) + BOH(g) \longrightarrow BA(aq) + H_2O$	–93
(C) $HA(g) \longrightarrow H^+(aq) + A^-(aq)$	–55.7
(D) $B^+(aq) + OH^-(aq) \longrightarrow BOH(aq)$	–20

6.15 Which of the following statement(s) is/are **false** ?

(A) $\Delta_r S$ for $\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ is positive

(B) $\Delta E < 0$ for combustion of $CH_4(g)$ in a sealed container with rigid adiabatic system.

(C) ΔG is always zero for a reversible process in a closed system

(D) ΔG° for an ideal gas reaction is a function of pressure

SECTION - III : ASSERTION AND REASON TYPE

6.16 **Statement-1 :** Due to adiabatic free expansion temperature of real gas may increase

Statement-2 : In adiabatic free expansion, temperature is always constant irrespective of real or ideal gas

(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

6.17 **Statement-1 :** When a gas at high pressure expands against vacuum, the magnitude of work done is maximum.

Statement-2 : Work is a path function

(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

6.18 **Statement-1 :** 'Diamonds are forever' is generally quoted for diamond as rate of conversion of diamond to graphite at room condition is nearly zero.

Statement-2 : At room condition, conversion of diamond into graphite is spontaneons.

(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

6.19 **Statement-1 :** The magnitude of the work involved in an isothermal expansion is greater than that involved in an adiabatic expansion.
Statement-2 : P–V curve (P on y-axis and V on x-axis) decrease more rapidly for reversible adiabatic expansion compared to reversible isothermal expansion starting from same initial state.
(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

6.20 **Statement-1 :** The amount of work done in the isothermal expansion is greater than work done in the adiabatic system for same final volume.
Statement-2 : In the adiabatic expansion of a gas temperature and pressure both decrease due to decrease in internal energy of the system.
(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

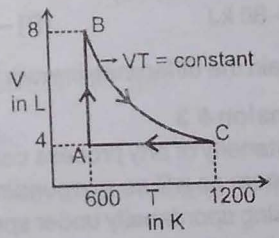
6.21 **Statement-1 :** Heat of neutralization of HCl and NaOH is same as that of H_2SO_4 with NaOH.
Statement-2 : HCl, H_2SO_4 and NaOH are all strong electrolyte.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 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

6.22 **Statement-1 :** In the following reaction : $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = \Delta U - RT$
Statement-2 : ΔH is related to ΔU by the equation, $\Delta H = \Delta U + \Delta n_g RT$
(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. 33 to 34

Two moles of an ideal monoatomic gas undergoes a cyclic process ABCA as shown in V–T diagram below :

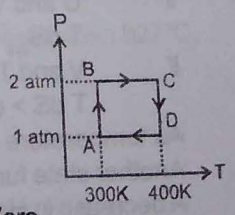


6.23 Heat supplied to the gas during the process AB is :
(A) 1200R ℓn2 (B) 1800R
(C) 1200R (D) Zero

6.24 Work done by the gas during the entire cycle is :
(A) 600R (1–ℓn2) (B) 1200R
(C) 1200R (1–ℓn2) (D) Zero

Comprehension

One mole of Helium gas undergoes a reversible cyclic process ABCDA as shown in the figure. Assuming gas to be ideal, answer the following questions :



6.25 What is the value of ΔH for the overall cyclic process :
(A) – 100 Rℓn2 (B) +100Rℓn2 (C) +200Rℓn2 (D) Zero

6.26 What is the value of 'q' for the overall cyclic process :
(A) $-100\ R\ell n2$ (B) $+100R\ell n2$ (C) $+200R\ell n2$ (D) $-200R\ell n2$

6.27 What is the net work involved in the process A to C :
(A) $-100\ R(1-\ell n8)$ (B) $300R\ell n2$ (C) $-100\ R(1+\ell n8)$ (D) 200 J

6.28 Polytropic process for ideal gas is given as PV^n = constant. For polytropic process for an ideal gas, the expression for work obtained is :

$$W = \frac{P_1V_1\left[\left(\frac{V_2}{V_1}\right)^x - 1\right]}{(y)}$$ Report your answer as (x + y).

(A) 0 (B) 1 (C) 2 (D) 3

Comprehension # 2

Internal Energy (E, also denoted by U) :

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy .

$E = E_{Translational} + E_{Rotational} + E_{Vibrational} + E_{bonding} + ...$

$\Delta E = E_{Final} - E_{Initial}$.

$\Delta E = q_v$, heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas .

It is an extensive property & a state function . It is exclusively a function of temperature.

If $\Delta T = 0$; $\Delta E = 0$ as well.

The internal energy of a certain substance is given by the following equation :

$$U = 3\ PV + 84$$

where U is given in kJ/kg, P is in kPa, and V is in m^3/kg

A system composed of 3 kg of this substance expands from an intial pressure of 400 kPa and a volume of 0.2 m^3 to a final pressure 100 kPa in a process in which pressure and volume are related by PV^2 = constant.

6.29 If the expansion is quasi-static, then the value of q is :
(A) 80 kJ (B) 60 kJ (C) 40 kJ (D) 120 kJ

6.30 In another process the same system expands according to the same pressure-volume relationship as in above question, but from the same initial state to the same final state as in above question, but the heat transfer in this case is +30 kJ. Then the work transfer for this process is :
(A) – 80 kJ (B) – 60 kJ (C) – 90 kJ (D) –150 kJ

6.31 Explain the difference in work transfer in question (6.25) and (6.26).

Comperehension # 3

Spontaneity of any process can be predicted with the help of ΔS_{total}. But this requires calculation of changes in system as will as surroundings. If some criteria (depending upon the system only) can be developed for checking spontaneity under specific conditions, then that would be a more useful parameter. The criteria can be derived from Clausius inequality.

$T\ dS \geq q$, (> sign for irreversible process = sign for rev. process)

or $T\ dS > dU - W$ for an irreversible. process

or $T\ dS_{sys} > dU_{sys.} + p\ dV$ [consider no non-PV work]

If U and V are constant,

$T\ dS_{sys} > 0$ or $(dS)_{U,V} > 0$ for spontaneous process

if V and T are constant

$T\ dS > dU$ or $dU - T\ dS < 0$

As temperature is constant, $dU - d(TS) < 0$ or $d(U - TS) < 0$

Another state function A(Helmholtz's function) $= U - TS$

A decrease in Helmholtz function (A) under constant volume and temperature is the criteria of spontaneity of a process.