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CHEMISTRY

Contents

SECTION-I (TOPIC WISE PROBLEMS)

Contents

SECTION-II (PRACTICE TEST PAPERS)

Answers & Solutions

SECTION-I (TOPIC WISE PROBLEMS)

Answers & Solutions

SECTION-II (PRACTICE TEST PAPERS)

SECTION-I
TOPIC WISE PROBLEMS

PHYSICAL CHEMISTRY

SECTION-I (TOPIC WISE PROBLEMS)

TOPIC 1

ELECTROCHEMISTRY

SECTION - I : STRAIGHT OBJECTIVE TYPE

1.1 The reduction potential of hydrogen half cell will be negative if (T = 298 K) :

(A) P_{H_2} = 1 atm and $[H^+]$ = 1.0 M (B) P_{H_2} = 2 atm and $[H^+]$ = 2.0 M

(C) P_{H_2} = 2 atm and $[H^+]$ = 1.0 M (D) P_{H_2} = 1 atm and $[H^+]$ = 2.0 M

1.2 A very thin copper plate is electro-plated with gold using gold chloride in HCl. The current was passed for 20 minutes and the increase in the weight of the plate was found to be 2 gram [Au = 197]. The current passed was:

(A) 0.816 amp. (B) 1.632 amp. (C) 2.448 amp. (D) 3.264 amp.

1.3 Given :

(i) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ $E^0 = x_1 V$

(ii) $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$ $E^0 = x_2 V$

Find E^0 for the following reaction :

$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

(A) $x_2 - x_1$ (B) $x_1 - x_2$ (C) $\frac{5x_1 - 2x_2}{3}$ (D) $\frac{2x_1 - 5x_2}{3}$

1.4 The solubility of $[Co(NH_3)_4Cl_2]\,ClO_4$ _____, if the $\lambda_{Co(NH_3)_4Cl_2^+} = 50$, $\lambda_{ClO_4^-} = 70$ and the measured resistance was 33.5 Ω in a cell with cell constant of 0.20 is _____

(A) 59.75 mmol/L (B) 49.75 mmol/L (C) 39.75 mmol/L (D) 29.75 mmol/L

1.5 We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution then the conductivity of this solution in terms of 10^{-7} Sm^{-1} units will be

[Given $\lambda^\circ_{(Ag^+)} = 4 \times 10^{-3}$ $Sm^2\,mol^{-1}$ $\lambda^\circ_{(Br^-)} = 6 \times 10^{-3}$ S $m^2\,mol^{-1}$, $\lambda^\circ_{(NO_3^-)} = 5 \times 10^{-3}$ $Sm^2\,mol^{-1}$]

(A) 39 (B) 55 (C) 15 (D) 41

1.6 The specific conductivity of an aqueous solution of a weak monoprotic acid is 0.00033 $ohm^{-1}cm^{-1}$ at a concentration 0.02 M. If at this concentration the degree of dissociation is 0.043, then calculate the value of Λ_0 (in $ohm^{-1}\,cm^2$ /eqt) :

(A) 483 (B) 438 (C) 348 (D) 384

1.7 At what $\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$ does the following cell have its reaction at equilibrium?

$Ag(s) \mid Ag_2CO_3(s) \mid Na_2CO_3(aq) \mid\mid KBr(aq) \mid AgBr(s) \mid Ag(s)$

$K_{SP} = 8 \times 10^{-12}$ for Ag_2CO_3 and $K_{SP} = 4 \times 10^{-13}$ for AgBr

(A) $\sqrt{1} \times 10^{-7}$ (B) $\sqrt{2} \times 10^{-7}$ (C) $\sqrt{3} \times 10^{-7}$ (D) $\sqrt{4} \times 10^{-7}$

1.8 For the cell prepared from electrode A and B, electrode A : $\frac{Cr_2O_7^{2-}}{Cr^{3+}}$, $E^0_{red.}$ = + 1.33 V and electrode B : $\frac{Fe^{3+}}{Fe^{2+}}$, $E^0_{red.}$ = 0.77 V, which of the following statement is **not correct?**

(A) The electrons will flow from B to A (in the outer circuit) when connections are made.
(B) The standard e.m.f. of the cell will be 0.56 V.
(C) A will be positive electrode.
(D) None of the above.

1.9 Acetic acid has $K_a = 1.8 \times 10^{-5}$ while formic acid has $K_a = 2.1 \times 10^{-4}$. What would be the magnitude of the emf of the cell

$$Pt(H_2)\left|\begin{matrix}0.1\text{ M acetic acid} + \\ 0.1\text{ M sodium acetate}\end{matrix}\right|\left|\begin{matrix}0.1\text{ M formic acid} + \\ 0.1\text{ M sodium formate}\end{matrix}\right|Pt(H_2)\text{ at } 25^\circ C\ ?$$

(A) 0.032 volt (B) 0.063 volt (C) 0.0456 volt (D) 0.055 volt

1.10 Consider the cell Ag(s)|AgBr(s)|Br^-(aq)|| Cl^-(aq) | AgCl(s) | Ag(s) at 25° C . The solubility product constants of AgBr & AgCl are 5×10^{-13} & 1×10^{-10} respectively. For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?

(A) 1 : 200 (B) 1 : 100 (C) 1 : 500 (D) 200 : 1

1.11 For a saturated solution of AgCl at 25°C, k = 3.4×10^{-6} ohm^{-1} cm^{-1} and that of H_2O (ℓ) used is 2.02×10^{-6} ohm^{-1} cm^{-1} . λ°_m for AgCl is 138 ohm^{-1} cm^2 mol^{-1} , then the solubility of AgCl in moles per liter will be :

(A) 10^{-5} (B) 10^{-10} (C) 10^{-14} (D) 10^{-16}

1.12 A current of 0.1A was passed for 4hr through a solution of cuprocyanide and 0.3745 g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition. (Cu GAM 63.5 or Cu– 63.5)

(A) 79% (B) 39.5 % (C) 63.25% (D) 63.5%

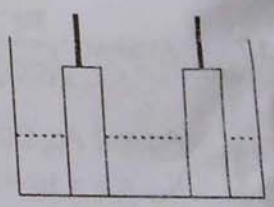
1.13 With t taken in seconds and I taken in Amp, the variation of I follows the equation $t^2 + I^2 = 25$
what amount of Ag will be electrodeposited with this current flowing in the interval 0–5 second ? (Ag GAM or Ag = 108)

(A) 22 mg (B) 66 mg (C) 77 mg (D) 88 mg

1.14 You are given the following cell at 298 K, $Zn\left|Zn^{++}_{(aq.)}\right|_{0.01M}\left|HCl_{(aq.)}\right|_{1.0\text{ lit.}}\left|H_2(g)\right|_{1.0\text{ atm.}}Pt$ with E_{cell} = 0.701V and $E^0_{Zn^{2+}/Zn} = -0.76$ V. Which of the following amounts of NaOH (equivalent weight = 40) will just make the pH of cathodic compartment to be equal to 7.0 :

(A) 0.4 grams (B) 4 grams (C) 10 grams (D) 2 grams

1.15 A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be



(A) 50 Ω (B) 100 Ω (C) 25 Ω (D) 200 Ω

1.16 The standard reduction potential of a AgCl/Ag electrode is 0.2 V and that of a silver electrode (Ag^+/Ag) is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M $AgNO_3$ solution is

(A) 0.5 mmol (B) 1.0 mmol (C) 2.0 mmol (D) 2.5 mmol

1.17 Calculate the cell EMF in mV for

$Pt \mid H_2(1atm) \mid HCl\ (0.01\ M) \mid AgCl(s) \mid Ag(s)$ at 298 K

if ΔG_f° values are at 25°C

$-109.56\ \frac{kJ}{mol}$ for AgCl(s) and

$-130.79\ \frac{kJ}{mol}$ for $(H^+ + Cl^-)$ (aq)

(A) 456 mV (B) 654 mV (C) 546 mV (D) None of these

1.18 Value of Λ_m^∞ for $SrCl_2$ in water at 25°C from the following data :

Conc. (mol/lt)	0.5	1
Λ_m (Ω^{-1} cm^2 mol^{-1})	260	250

(A) 270 (B) 260 (C) 250 (D) 255

1.19 Calculate the useful work of the reaction $Ag(s) + 1/2Cl_2(g) \longrightarrow AgCl(s)$

Given $E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{Ag|AgCl|Cl^-} = 0.22$ V

if $P_{Cl_2} = 1$ atm and $T = 298$ K

(A) 110 kJ/mol (B) 220 kJ/mol (C) 55 kJ/mol (D) 1000 kJ/mol

1.20 Select the correct statement if -

$E^\circ_{Mg^{2+}/Mg} = -2.4V$, $E^\circ_{Sn^{4+}/Sn^{2+}} = 0.1\ V$, $E^\circ_{MnO_4^-, H^+/Mn^{2+}} = 1.5\ V$, $E^\circ_{I_2/I^-} = 0.5\ V$

Here,

(A) MnO_4^- is the strongest oxidizing agent and Mg is the strongest reducing agent.

(B) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$ is a spontaneous reaction.

(C) $Mg^{2+} + Sn^{2+} \longrightarrow Mg + Sn^{4+}$ is a spontaneous reaction.

(D) Here, weakest oxidizing agent is Sn^{4+} and weakest reducing agent is Mn^{2+}

1.21 A cell $Ag \mid Ag^+ \| Cu^{++} \mid Cu$ initially contains 2M Ag^+ and 2M Cu^{++} ions. The change in cell potential after the passage of 10 amp current for 4825 sec is :

(A) – 0.0074 V (B) – 1.00738 V (C) – 0.0038 V (D) none

1.22 For the cell (at 298 K)

$Ag(s) \mid AgCl(s) \mid Cl^-(aq) \| AgNO_3(aq) \mid Ag(s)$

Which of following is correct -

(A) The cell emf will be zero when ($[Ag^+]$ in anodic compartment = $[Ag^+]$ in cathodic compartment)

(B) The amount of AgCl(s) precipitate in anodic compartment will decrease with the working of the cell.

(C) The concentration of $[Ag^+]$ = constant, in anodic compartment during working of cell.

(D) $E_{cell} = E^0_{Ag^+|Ag} - E^0_{Cl^-|AgCl|Ag} - \frac{0.059}{1}\log\frac{1}{[Cl^-]_a}$

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

1.23 A concentration cell Pt | $H_2(g)$ | HCl (aq) || $H_2SO_4(aq)$ | $H_2(g)$ | Pt is constructed using equal concentration of acids and equal number of moles of H_2 gas in both the compartments at the same temperature. If volume of H_2 gas at the anodic compartment is $\frac{1}{9}$ times the volume of H_2 gas at cathodic compartment.

Which of the following is/are correct for the given cell (log 2 = 0.3, log 3 = 0.48) $\frac{2.303\,RT}{F} = 0.06$ V

(A) Pressure of H_2 gas in both the cell compartments are equal

(B) Concentration of H^+ ion in both the cell compartments are unequal

(C) $E^\circ_{cell} = 0$ for the above cell

(D) $E_{cell} \neq 0$ for the above cell

1.24 Peroxodisulphate salts ($Na_2S_2O_8$) are strong oxidizing agents used as bleaching agents for fats, oil etc.

Given

$O_2(g) + 4H^\oplus(aq) + 4e^- \longrightarrow 2H_2O(\ell)$ $\quad E^\circ = 1.23$ V

$S_2O_8^{-2} + 2e^- \longrightarrow 2SO_4^{-2}$ (aq) $\quad E^\circ = 2.01$ V

Which of the following statements is (are) correct ?

(A) Oxygen gas can oxidize sulphate ion to per-oxo disulphate ion ($S_2O_8^{-2}$) in acidic solution.

(B) $O_2(g)$ is reduced to water

(C) Water is oxidised to O_2

(D) $S_2O_8^{-2}$ ions are reduced to SO_4^{-2} ions.

1.25 In which of the following cell (s) : $E_{cell} = E_{cell}^0$?

(A) $Cu(s) \,|\, Cu^{2+}(0.01M) \,||\, Ag^+(0.1M) \,|\, Ag(s)$

(B) $Pt, \underset{1atm}{H_2}(g) \,|\, pH = 1 \,||\, Zn^{2+}(0.01M) \,|\, Zn(s)$

(C) $Pt, \underset{1atm}{H_2}(g) \,|\, pH = 1 \,||\, Zn^{2+}(1M) \,|\, Zn(s)$

(D) $Pt, \underset{1atm}{H_2}(g) \,|\, H^{+} = 00.1M \,||\, Zn^{2+}(0.01M) \,|\, Zn(s)$

1.26 Indicate the ***correct*** statements :

(A) Conductivity cells have cell constant values independent of the solution filled into the cell

(B) DC (direct current) is not used for measuring the resistance of a solution.

(C) Kohlrausch law is valid both for strong and weak electrolytes.

(D) The k decreases but λ_M and λ_E increase on dilution.

1.27 A current of 2.68 A is passed for one hour through an aqueous solution of $CuSO_4$ using copper electrodes. Select the correct statement(s) from the following :

(A) increase in mass of cathode = 3.174 g

(B) decrease in mass of anode = 3.174 g

(C) no change in masses of electrodes

(D) the ratio between the change of masses of cathode and anode is 1 : 2 .

1.28 Which is/are correct among the followings?

Given, the half cell emf's $E^0_{Cu^{+2}|Cu} = 0.337$, $E^0_{Cu^{+1}|Cu} = 0.521$

(A) Cu^{+1} disproportionates.

(B) Cu and Cu^{2+} comproportionates (reverse of disproportionation into Cu^+).

(C) $E^0_{Cu|\,Cu^{+2}} + E^0_{Cu^{+1}|\,Cu}$ is positive.

(D) All of these.

1.29 The standard reduction potentials of some half cell reactions are given below :

$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$ $\quad E^0 = 1.455$ V

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad E^0 = 1.51$ V

$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$ $\quad E^0 = 1.61$ V

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $\quad E^0 = 1.71$ V

Pick out the correct statement :

(A) Ce^{+4} will oxidise Pb^{2+} to PbO_2

(B) MnO_4^- will oxidise Pb^{2+} to PbO_2

(C) H_2O_2 will oxidise Mn^{+2} to MnO_4^-

(D) PbO_2 will oxidise Mn^{+2} to MnO_4^-

1.30 Mark out the correct statement(s) regarding electrolytic molar conductivity.

(A) It increase as temperature increases.

(B) It experiences resistance due to vibration of ion at the mean position.

(C) Increase in concentration decreases the electrolytic molar conductivity of both the strong as well as the weak electrolyte.

(D) Greater the polarity of solvent, greater is the electrolytic molar conduction.

SECTION - III : ASSERTION AND REASON TYPE

1.31 **STATEMENT-1 :** Specific conductance decreases with dilution whereas equivalent conductance increases.
STATEMENT-2 : On dilution number of ions per millilitre decreases but total number of ions increases considerably.

(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.

1.32 **STATEMENT-1 :** Zinc protect the iron better than tin even after it cracks.

STATEMENT-2 : $E^0_{OP_{Zn}} < E^0_{OP_{Fe}}$ But $E^0_{OP_{Sn}} > E^0_{OP_{Fe}}$

(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.

1.33 **STATEMENT-1 :** On increasing dilution, the specific conductance keep on increasing.
STATEMENT-2 : On increasing dilution, degree of ionization of weak electrolyte increases and mobility of ions also increases.

(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.

1.34 **STATEMENT-1 :** $sE^0_{Fe^{++}|Fe} < E^0_{Ni^{++}|Ni}$ Fe electrode act as cathode and Ni electrode act as anode.

STATEMENT-2 : Because $\Delta G^\circ < 0$ and $E^\circ_{Cell} > 0$, so cell is possible.

(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

A fuel cell is a cell that is continuously supplied with an oxidant and a reductant so that it can deliver a current indefinitely.

Fuel cells offer the possibility of achieving high thermodynamic efficiency in the conversion of Gibbs energy into mechanical work. Internal combustion engines at best convert only the fraction $(T_2 - T_1)/T_2$ of the heat of combustion into mechanical work.

While the thermodynamic efficiency of the fuel cell is given by, $\eta = \frac{\Delta G}{\Delta H}$, where ΔG is the Gibbs energy change for the cell reaction and ΔH is the enthalpy change of the cell reaction.

A hydrogen-oxygen fuel cell may have an acidic or alkaline electrolyte.

$Pt \mid H_2(g) \mid H^+(aq.) \parallel H_2O(\ell) \mid O_2(g) \mid Pt$; $\frac{2.303RT}{F} = 0.06$

The above fuel cell is used to produce constant current supply under constant temperature & 30 atm constant total pressure conditions in a cylinder. If 10 moles H_2 and 5 moles of O_2 were taken initially. Rate of consumption of O_2 is 10 milli moles per minute.

The half-cell reactions are

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O(\ell)$ $\quad E^\circ = 1.246$ V

$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $\quad E^\circ = 0$

To maximize the power per unit mass of an electrochemical cell, the electronic and electrolytic resistances of the cell must be minimized. Since fused salts have lower electrolytic resistances than aqueous solutions, high-temperature electrochemical cells are of special interest for practical applications.

1.35 Calculate e.m.f. of the given cell at t = 0. (log 2 = 0.3).
(A) 1.255 V (B) 1.35 V (C) 1.3 V (D) 1.246 V

1.36 The above fuel cell is used completely as an electrolytic cell with Cu voltameter of resistance 26.94 Ω using Pt electrodes. Initially Cu voltameter contains 1 litre solution of 0.05 M $CuSO_4$. $[H^+]$ in solution after electrolysis (Assuming no change in volume of solution).
(A) 0.015 M (B) 0.03 M (C) 0.025 M (D) 0.01 M

1.37 If $\lambda_m^\infty(Cu^{2+}) = 0.01$ S m² mole⁻¹, $\lambda_m^\infty(H^+) = 0.035$ S m² mole⁻¹ and $\lambda_m^\infty(SO_4^{2-}) = 0.016$ S m² mole⁻¹, specific conductivity of resulting solution left in copper voltameter after above electrolysis is
(A) 2.57S m⁻¹ (B) 1.75 S m⁻¹ (C) 1.525 S m⁻¹ (D) 2.25 S m⁻¹

Comprehension # 2

The molar conductance of NaCl varies with the concentration as shown in the following table . and all values follows the equation

$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$

Where λ_m^C = molar specific conductance

λ_m^∞ = molar specific conductance at infinite dilution

C = molar concentration

Molar Concentration of NaCl	Molar Conductance in $ohm^{-1}\ cm^2\ mole^{-1}$
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At Infinite dilution, conductance of Cl^- and SO_4^{-2} are 80 $ohm^{-1}\ cm^2\ mole^{-1}$ and 160 $ohm^{-1}\ cm^2\ mole^{-1}$ respectively.

1.38 What is the molar conductance of NaCl at infinite dilution ?
(A) 147 $ohm^{-1}\ cm^2\ mole^{-1}$ (B) 107 $ohm^{-1}\ cm^2 s\ mole^{-1}$
(C) 127 $ohm^{-1}\ cm^2\ mole^{-1}$ (D) 157 $ohm^{-1}\ cm^2\ mole^{-1}$

1.39 What is the cell constant of the conductivity cell (C)
(A) 0.385 cm^{-1} (B) 3.85 cm^{-1} (C) 38.5 cm^{-1} (D) 0.1925 cm^{-1}

1.40 If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4 the obserbed resistance was 400 ohm. What is the molar conductance of Na_2SO_4.
(A) 19.25 $ohm^{-1}\ cm^2\ mole^{-1}$ (B) 96.25 $ohm^{-1}\ cm^2\ mole^{-1}$
(C) 385 $ohm^{-1}\ cm^2\ mole^{-1}$ (D) 192.5 $ohm^{-1}\ cm^2 s\ mole^{-1}$

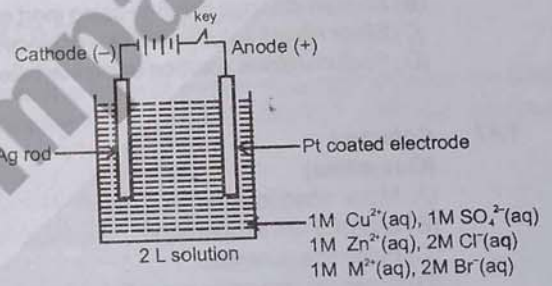
Comprehension # 4

The process of using an electric current to bring about chemical change is called electrolysis. Electrolysis is a process of oxidation and reduction at the respective electrodes due to external current passed in the electrolyte.

The product obtained during electrolysis depends on following factors.

- The nature of the electrolyte
- The concentration of electrolyte
- The nature of the electrode.

Consider the electrolysis of following cell containing aq. solution of $CuSO_4$, $ZnCl_2$ and MBr_2 by using pure silver rod as a cathode and Pt electrode as anode. Assume that M^{2+} does not further oxidise and can not form complex with NH_3. Assume no hydrolysis of any ion.



$E^0_{Cu^{2+}/Cu} = 0.34$ V; $E^0_{M^{2+}/M} = -0.10$ V; $E^0_{Zn^{2+}/Zn} = -0.76$ V; $E^0_{H_2O/H_2} = -0.828$ V; $E^0_{Ag^+/Ag} = 0.80$ V, $\frac{2.303\,RT}{F} = 0.06$

1.41_ After passing 20 amp current from battery for 28950 sec. the remaining conc. of ions in solution given in passage would be : (Assume current efficiency to be 100%).
(A) $[Cu^{2+}] = 0.5M$, $[M^{2+}] = 0.5M$, $[Zn^{2+}] = 0.1M$ (B) $[Cu^{2+}] \approx 0$ M, $[M^{2+}] = 0.5M$, $[Zn^{2+}] = 0.5M$
(C) $[Cu^{2+}] = 0.5M$, $[M^{2+}] = 0.5M$, $[Zn^{2+}] = 0.5M$ (D) $[Cu^{2+}] \approx 0$ M, $[M^{2+}] = 0.5M$, $[Zn^{2+}] = 1M$

1.42_ What will be the volume of gases formed at anode at STP by electrolysis of above solution after passing 20 amp current for 28950 sec. (Assume current efficiency to be 100% and one mole of gas occupies 22.4 L volume at STP).
(A) 44.8 L Br_2 (B) 22.4 L Br_2 (C) 22.4 L Cl_2 (D) 44.8 L Cl_2

1.43_ If 36 mol of NH_3(g) is passed in electrolytic solution given in comprehension (assume no volume change by addition of NH_3), then what would be decreasing order of reduction potential of following :
{ $K_f [Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$ and $K_f [Zn(NH_3)_4]^{2+} = 1 \times 10^9$ }
(A) $M^{2+} > Cu^{2+} > Zn^{2+}$ (B) $Cu^{2+} > M^{2+} > Zn^{2+}$ (C) $M^{2+} > Zn^{2+} > Cu^{2+}$ (D) $Cu^{2+} > M^{2+} > Zn^{2+}$

SECTION - V : MATRIX - MATCH TYPE

1.44 Given $E^0_{Cu^{+2}/Cu}$ = 0.34 V

$E^0_{Cl_2/Cl^-}$ = 1.36 V

$E^0_{Br_2/Br^-}$ = 1.08 V

$E^0_{I_2/I^-}$ = 0.54 V

Column- I

(A) $Cu^{+2} + 2Cl \rightarrow Cu + Cl_2$

(B) $Cl_2 + Cu \rightarrow Cu^{+2} + 2Cl^-$

(C) $2I^-$ + starch solution + chlorine water

(D) $2Br^-$ + CCl_4 + chlorine water

Column- II

(p) Can produce electricity in the galvanic cell

(q) Can be made to occur in electrolysis cell

(r) Appearance of brown colour

(s) Appearance of violet colour

1.45 **Match the following :**

Column I

(A) Working concentration cell

(B) Spontaneous cell reaction

(C) Non - working Daniel cell

(D) Working fuel cell

Column II

(p) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ + electrical energy

(q) $E^\circ_{cell} = 0$

(r) $E_{cell} > 0$

(s) Galvanic cell

(t) For working of concentration cell, concentration of cation in anodic compartment should be less then the cathodic compartment

1.46 Match the column :

Column-I

(A) Molten $PbCl_2$ using inert electrode

(B) Sodium chloride solution using inert electrode

(C) Silver nitrate solution with silver electrode

(D) Sodium nitrate solution using inert electrode

Column-II

(p) Metal of salt will reduced

(q) $H_2O + 2e \rightarrow H_2(g) + 2OH^-$

(r) Solution become basic after electrolysis

(s) Solution become neutral after electrolysis

(t) Solution become acidic after electrolysis

1.47 **Column-I**

(Quantities)

(A) Molar conductance

(B) emf of a cell in operation

(C) Electrode potential

(D) Standard reduction potential

Column-II

(Factors on which dependency exist)

(p) Temperature

(q) Concentration of species involved

(r) Nature of substance involved

(s) No. of electrons lost or gained in the reaction

(t) is on additive property.

SECTION - VI : INTEGER TYPE

1.48 A sparingly soluble salt MX is dissolved in water to prepare 1 L saturated solution. Now 10^{-6} mole NaX (assume 100% dissociation) is added into this. Conductivity of this solution is 29×10^{-6} S/m. If K_{sp} of MX is $a \times 10^{-b}$, then find value of (a + b). a is a natural number & $1 \le a \le 9$.

Given : $\lambda^0_{x^-} = 4 \times 10^{-3}$ S m^2 mol$^-$

$\lambda^0_{Na^+} = 5 \times 10^{-3}$ S m^2 mol$^-$

$\lambda^0_{M^+} = 6 \times 10^{-3}$ S m^2 mol$^-$

1.49 100 ml, 0.05M $CuSO_4$ solution is electrolysed by using current of 0.965 A for 100 min. Find the pH of solution at the end of electrolysis.

1.50 Small spherical ball of silver metal used in jewellery having diameter 0.1 cm, which is obtained by the electrolytic deposition. It total number of balls in jewellery is 10, 000, then calculate the applied amount of electricity in coulombs, which is used on the deposition on electrodes having entire surface 0.12 m^2. [Density of Ag = 10.5]
It is assumed that 3.5% electricity consumed as wastage during electrolysis and 60% of electrode body immersed in electrolyte. [Give your answer in multiple of 10^4]

1.51 The E°_{Cell} = 1.18 V for
$Zn(s) \mid Zn^{+2}$ (1M) || Cu^{+2} (1M) |Cu(s).
Determine the value of x if when excess granulated zinc is added to 1 M Cu^{+2} solution the $[Cu^{+2}]_{aq}$ becomes 10^{-x} M. (T = 298 K, $\frac{2.303RT}{F} = 0.059$)

1.52 In the acid base titration [H_3PO_4 (0.1M) + NaOH (0.1M)] e.m.f of the solution is measured by coupling this electrodes with suitable reference electrode. When alkali is added pH of solution is in acoordance with equation

$$E_{cell} = E^\circ_{cell} + 0.059\ pH$$

For H_3PO_4 $Ka_1 = 10^{-3}$; $Ka_2 = 10^{-8}$; $Ka_3 = 10^{-13}$
What is the cell e.m.f. at the IInd end point of the titration if E°_{cell} at this stage is 1.3805 V.

1.53 The e.m.f. of a cell corresponding to the reaction

$Zn + 2H^+ (aq) \longrightarrow Zn^{2+} (0.1M) + H_2(g)$ (1 atm)

is 0.26 volt at 25°C. Calculate the pH of the solution at the hydrogen electrode.

1.54 A fuel cell uses $CH_4(g)$ and forms CO_3^{2-} at the anode. It is used to power a car with 80 Amp. for 0.96 hr. How many litres of $CH_4(g)$ (at STP.) would be required ? (V_m = 22.4 L/mol) (F = 96500). Assume 100% efficiency.

1.55 For the cells in opposition,
$Zn(s) \mid ZnCl_2(sol.) \mid AgCl(s) \mid Ag \mid AgCl(s) \mid ZnCl_2(sol.) \mid Zn(s)$
C_1 = 0.02 M $\qquad$ C_2 = 0.5 M
Find out the emf (in millivolt) of the resultant cell ? (Take log 2 = 0.3, $\frac{RT}{F}$ at 298 K = 0.060)

1.56 The conductivity of a solution may be taken to be directly proportional to the total concentration of the charge carries (ions) present in it in many cases. Using the above fact find the percent decrease in conductivity (k) of a solution of a weak monoacidic base BOH when its 0.1 M solution is diluted to double its original volume. ($K_b = 10^{-5}$ for BOH)(take $\sqrt{50} = 7.07$) (Mark the answer to nearest integer)

1.57 At 0.04 M concentration the molar conductivity of a solution of a electrolyte is 5000 Ω^{-1} cm^2 mol^{-1} while at 0.01 M concentration the value is 5100 Ω^{-1} cm^2 mol^{-1} . Making necessary assumption (Taking it as strong electrolyte) find the molar conductivity at infinite dilution and also determine the degree of dissociation of strong electrolyte at 0.04 M.

TOPIC 2

IONIC EQUILIBRIUM

SECTION - I : STRAIGHT OBJECTIVE TYPE

2.1 Calculate $[H^+]$, $[HCOO^-]$ and $[OCN^-]$ in a solution that contains 0.1M HCOOH ($K_a = 2.4 \times 10^{-4}$) and 0.1 M HOCN ($K_a = 4 \times 10^{-4}$).
(A) $[H^+] = 8 \times 10^{-3}$ M (B) $[HCOO^-] = 3 \times 10^{-3}$ M (C) $[OCN^-] = 5 \times 10^{-3}$ M (D) All of these

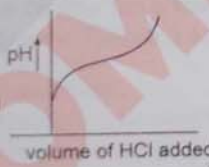
2.2 To prepare a buffer solution of pH = 4.04, amount of Barium acetate to be added to 100 mL of 0.1 M acetic acid solution [$pK_b(CH_3COO^-) = 9.26$] is :
(A) 0.05 mole (B) 0.025 mole (C) 0.1 mole (D) 0.005 mole

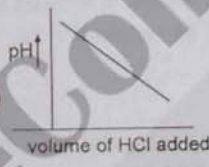
2.3 A 1.458 g of Mg reacts with 80.0 ml of a HCl solution whose pH is –0.477. The change in pH when all Mg has reacted. (Assume constant volume. Mg = 24.3 g/mol.) (log 3 = 0.47, log 2 = 0.301)
(A) –0.176 (B) +0.477 (C) –0.2385 (D) 0.3

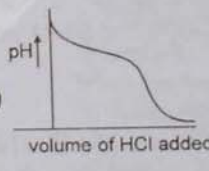
2.4 Find the ΔpH(initial pH – final pH) when 100 ml 0.01 M HCl is added in a solution containing 0.1 mmoles of $NaHCO_3$ solution of negligible volume ($Ka_1 = 10^{-7}$, $Ka_2 = 10^{-11}$ for H_2CO_3) :
(A) 6 + 2 log3 (B) 6 – log3 (C) 6 + 2log2 (D) 6 – 2log3

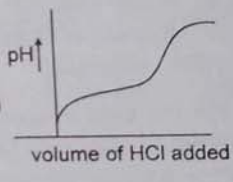
2.5 The ionization constant of benzoic acid is 6.46×10^{-5} and K_{SP} for silver benzoate is 2.5×10^{-13}. How many times silver benzoate more soluble in a buffer of pH = 3.19 as compared to its solubility in pure water ?
(A) 3.317 (B) 9.5 (C) 1000 (D) 7.5

2.6 When 100 ml of 0.1 M NaCN solution is titrated with 0.1 M HCl solution the variation of pH of solution with volume of HCl added will be :

(A) 

(B) 

(C) 

(D) 

2.7 The indicator constant for an acidic indicator, HIn is 5×10^{-6} M. This indicator appears only in the colour of acidic form when $\frac{[In^-]}{[HIn]} \le \frac{1}{20}$ and it appears only in the colour of basic form when $\frac{[HIn]}{[In^-]} \le \frac{1}{40}$.
The pH range of indicator is :
(A) 3.7 – 6.9 (B) 4.0 – 6.6 (C) 4.0 – 6.9 (D) 3.7 – 6.6

2.8 Ionisation constant of each HA (weak acid) and BOH (weak base) are 3.0×10^{-7} each at 298K. The percentage degree of hydrolysis of BA at the dilution of 10L is :
(A) 25 (B) 50 (C) 75 (D) 40

2.9 Which of the following concentrations of NH_4^+ will be sufficient to prevent the precipitation of $Mg(OH)_2$ from a solution which is 0.01 M $MgCl_2$ and 0.1 M NH_3 (aq). Given that : K_{SP} of Mg $(OH)_2 = 2.5 \times 10^{-11}$ and K_b for NH_3(aq) $= 2 \times 10^{-5}$.
(A) 0.01 M (B) 0.02 M (C) 0.001 M (D) 0.04 M

2.10 $pOH = 7 - 0.5\ pK_a + 0.5\ pK_b$ is true for aqueous solution containing which pair of cation and anion :
(A) $C_6H_5NH_3^+$, CH_3COO^- (B) NH_4^+, F^-
(C) Both (A) and (B) (D) None of these

2.11 An acid-base indicator which is a weak acid has a pK_a value = 5.35. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms? pK_a of acetic acid = 4.75. [log 2 = 0.3]

(A) 4 : 1 (B) 7 : 1 (C) 5 : 1 (D) 2 : 1

2.12 The indicator constant of phenolphthalein is approximately 10^{-8}. A solution is prepared by adding 100.01 c.c. of 0.01 N sodium hydroxide to 100.00 c.c. of 0.01N hydrochloric acid. If a few drops of phenolphthalein are now added, what fraction of the indicator is converted to its coloured form?

(A) $\frac{1}{3}$ (B) $\frac{3}{4}$ (C) $\frac{1}{2}$ (D) $\frac{9}{11}$

2.13 A certain mixture of HCl and CH_3–COOH is 0.1 M in each of the acids. 20 ml of this solution is titrated against 0.1M NaOH. By how many units does the pH change from the start to the stage when the HCl is almost completely neutralised? K_a for acetic acid = 1.8×10^{-5}.

(A) 2.03 (B) 0.775 (C) 2.325 (D) 3.172

2.14 A buffer solution is made by mixing a weak acid HA ($K_a = 10^{-6}$) with its salt NaA in equal amounts. What should be the amount of acid or salt that should be added to make 90 ml of buffer solution of buffer capacity 0.1 ?

(A) 10 mmoles (B) 22 mmoles (C) 9 mmoles (D) 11 mmoles

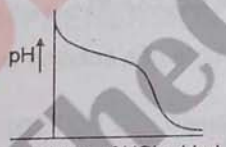
2.15 A sample of water has a hardness expressed as 80 ppm of Ca^{2+}. This sample is passed through an ion exchange column and the Ca^{2+} is replaced by H^+. What is the pH of the water after it has been so treated? [Atomic mass of Ca = 40]

(A) 3 (B) 2.7 (C) 5.4 (D) 2.4

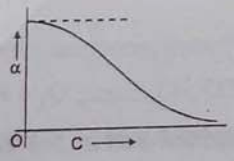
2.16 To a 100 mL of 0.1 M weak acid HA solution, 22.5 mL of 0.2 M solution of NaOH are added. Now, what volume of 0.1 M NaOH solution be added into above solution, so that pH of resulting solution be 4.7 :
[Given : $(K_b(A^-) = 5 \times 10^{-10}]$

(A) 5 mL (B) 20 mL (C) 10 mL (D) 15 mL

2.17 (a) When 100 ml of 0.1 M NaCN solution is titrated with 0.1 M HCl solution the variation of pH of solution with volume of HCl added will be :



(b) Variation of degree of dissociation α with concentration for a weak electrolyte at a particular temperature is best represented by :



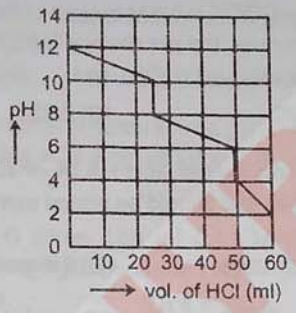
(c) 0.1 M acetic acid solution is titrated against 0.1 M NaOH solution. The difference in pH between 1/4 and 3/4 stages of neutralization of acid will be 2 log 3.

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

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

2.18 The variation of pH during the titration of 0.5 N Na_2CO_3 with 0.5 N HCl is shown in the given graph. The following table indicates the colour and pH ranges of different indicators :

Indicator	Range of colour change	Colour in acid	Colour in base
Thymol blue	1.2 to 2.8	Red	Yellow
Bromocresol red	4.2 to 6.3	Red	Yellow
Bromothymol blue	6.0 to 7.6	Yellow	Blue
Cresolphethalein	8.2 to 9.8	Colourless	Red



Based on the graph and the table, which of the following statements are true ?

(A) The first equivalence point can be detected by cresolphthalein.

(B) The complete neutralisation can be detected by bromothymol blue.

(C) The second equivalence point can be detected by bromocresol red.

(D) The volume of HCl required for the first equivalence point is half the volume of HCl required for the second equivalence point.

2.19 Which of the following solutions when added to 1L of a 0.1 M CH_3COOH solution will cause no change either in the degree of dissociation of CH_3COOH or in the pH of the solution. $K_a = 1.8 \times 10^{-5}$ for CH_3COOH?

(A) 3 mM HCOOH ($K_a = 6 \times 10^{-4}$) (B) 0.1 M CH_3COONa

(C) 1.34 mM HCl (D) 0.1 M CH_3COOH

2.20 A 1 litre solution of pH = 1 diluted upto 10 times. What volume of a solution with pH = 2 is to be added in diluted solution so that final pH remains '2'.

(A) 1 litre (B) 10 litre (C) 100 litre (D) 25 litre

2.21 Select the correct statements :

(A) pH of $NaHCO_3$ solution can be given by $\frac{pK_{H_2CO_3} + pK_{HCO_3^-}}{2}$

(B) Al^{3+} ion is amphoteric

(C) K_{SP} values of metal nitrates are very-very high

(D) Na^+ (aq). is conjugate acid of NaOH (aq).

2.22 Buffer solution A of a weak monoprotic acid and its sodium salt in the concentration ratio x : y has pH = $(pH)_1$. Buffer solution B of the same acid and its sodium salt in the concentration ratio y : x has pH = $(pH)_2$. If $(pH)_2 - (pH)_1 = 1$ unit and $(pH)_1 + (pH)_2 = 9.5$ units, then

(A) $pK_a = 4.75$ (B) $\frac{x}{y} = 2.36$ (C) $\frac{x}{y} = 3.162$ (D) $pK_a = 5.25$

SECTION - III : ASSERTION AND REASON TYPE

2.23 **STATEMENT-1 :** Phenolphthalein can be used as an indicator in the titration of weak acid with NaOH.
STATEMENT-2: Near the end point in the titration of weak acid with NaOH, the pH of the solution is alkaline due to hydrolysis of anion.
(A) Statement-1 is true, Statement-2 is true; Statement-2 is the correct explanation of Statement-1.
(B) Statement-1 is true, Statement-2 is true; Statement-2 is not the correct explanation of Statement-1
(C) Statement-1 is false, Statement-2 is true.
(D) Statement-1 is true, Statement-2 is false.

2.24 **STATEMENT-1 :** It is difficult to distinguish the strengths of the strong acids such as HCl, H_2SO_4, HNO_3, HBr, HI or $HClO_4$ in dilute aqueous solutions.
STATEMENT-2 : In dilute aqueous solution all strong acids donate a proton to water and are essentially 100% ionised to produce a solution containing H_3O^+ ions plus the anions of strong acid.
(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

2.25 **STATEMENT-1 :** 0.20 M solution of NaCN is more basic than 0.20 M solution of NaF.
STATEMENT-2 : 0.20 M solution of NaCN is more basic than 0.20 M solution of CH_3COONa.
(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

2.26 **STATEMENT-1 :** A substance that can either act as an acid or a base is called ampholyte.
STATEMENT-2 : Bisulphide ion (HS^-) and bicarbonate ion (HCO_3^-) are ampholytes.
(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

Consider a solution of CH_3COONH_4 which is a salt of weak acid & weak base.
The equilibrium involved in the solutions are :

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ .....(1)

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$ .....(2)

$H^+ + OH^- \rightleftharpoons H_2O$ .....(3)

If we add these three reactions, then the net reaction is

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$ .....(4)

Both CH_3COO^- and NH_4^+ get hydrolysed independently and their hydrolysis depends on
(i) their initial concentration
(ii) the value of K_h which is $\frac{K_w}{K_a}$ for CH_3COO^- and $\frac{K_w}{K_b}$ for NH_4^+.

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore unless & until the value of $\frac{K_w}{K_a}$ and $\frac{K_w}{K_b}$ or K_a and K_b is same, the degree of hydrolysis of ion can't be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need now to look at the third reaction i.e., combination of H^+ and OH^- ions. It is obvious that this reaction happens only because one reaction produced H^+ ion and the other produced OH^- ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the comsumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore we conclude that firstly the hydrolysis of both the ions occurs more in the presence of each other (due to consumption of the product ions) than in each other is absence. Secondly the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of K_h) is affected more than the one whose K_h is greater. Hence we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

2.27 In the hydrolysis of salt of weak acid & weak base :

(A) degree of hydrolysis of cation and anion is different

(B) degree of hydrolysis of cation and anion is same

(C) degree of hydrolysis of cation and anion is different and they can never be assumed same.

(D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.

2.28 For 0.1 M CH_3COONH_4 salt solution given, $K_{a_{CH_3COOH}} = K_{b_{NH_4OH}} = 2 \times 10^{-5}$.

In this case : degree of hydrolysis of cation and anion is

(A) exactly same (B) slightly different

(C) can't say (D) different but can be take approximatly same

2.29 In a solution of $NaHCO_3$, the amphiprotic anion can undergo ionization to form H^+ ion and hydrolysis to form OH^- ion.

$$HCO_3^- + H_2O \overset{\text{ionization}}{\rightleftharpoons} CO_3^{2-} + H_3O^+$$

$$HCO_3^- + H_2O \overset{\text{hydrolysis}}{\rightleftharpoons} H_2CO_3 + OH^-$$

To calculate pH, suitable approximation is :

(A) $[CO_3^{2-}] = [H_2CO_3]$ (B) degree of ionization = degree of hydrolysis

(C) both (A) and (B) (D) neither 'A' nore 'B'

Comprehension # 2

When aluminium salts are added to water, $A\ell^{3+}$ ions are immediately attracted to the negative end of polar water molecules. They form hexaaquaaluminum(III) ions, $[Al(H_2O)_6]^{3+}$. This is often written simply as $Al^{+3}(aq)$. However the electric field associated with small, highly charged Al^{+3} ion is so intense that it draws electrons in the O – H bonds of water towards itself. This enables the water molecules to become donors. In aqueous solution, free water molecules act as bases and the following equilibrium is established ;

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H_3O^+$$

Thus, solutions of Al^{+3} salts are acidic, in fact as acidic as vinegar. When a base stronger than H_2O, e.g. S^{2-} is added to aqueous aluminium salts further H^+ ions are removed from $[Al(H_2O)_6]^{3+}$ and insoluble aluminium hydroxide precipitates.

$$2[Al(H_2O)_6]^{3+}(aq) + 3S^{2-}(aq) \longrightarrow 2[Al(OH)_3(H_2O)_3](s) + 3H_2S(g)$$

More stronger base can remove $4H^+$ ions as follows :

$$[Al(H_2O)_6]^{3+} + 4OH^- \rightleftharpoons [Al(OH)_4(H_2O)]^-(aq) + 4H_2O(l)$$

2.30 Which of $[Al(H_2O)_6]^{3+}$, H_2S or H_2O is the strongest acid ?
(A) $[Al(H_2O)_6]^{3+}$ (B) H_2S (C) H_2O (D) all are same

2.31 A base which will behave just like S^{2-} :
(A) CO_3^{2-} (B) CH_3OH (C) NH_4^+ (D) NH_2^-

2.32 Another ion that would behave similar to Al^{+3} (aq) in forming an acidic solution is :
(A) $Be^{2+}_{(aq)}$ (B) $Ba^{2+}_{(aq)}$ (C) Na^+ (D) Tl^+

2.33 $[Al(OH)_3(H_2O)_3]$ (s) more simply written as $Al(OH)_3$(s) is :
(A) acidic (B) basic (C) neutral (D) amphoteric

2.34 Which gas would get absorbed when passed into a solution of Al^{+3} (aq) ?
(A) NH_3 (B) NO (C) CO (D) O_2

SECTION - V : MATRIX - MATCH TYPE

2.35 Match the effect of addition of 0.1 M KOH to 0.1 M, 50 ml H_3PO_4. Ka_1, Ka_2, Ka_3 are the I, II, III ionisation constant of H_3PO_4 :

Column-I	Column-II
(A) 75 ml of KOH	(p) $pH = P^{Ka_1}$
(B) 25 ml of KOH	(q) $pH = P^{Ka_2}$
(C) 150 ml of KOH	(r) $pH = \frac{P^{Ka_2} + P^{Ka_3}}{2}$
(D) 100 ml of KOH	(s) $pH = 7 + \frac{1}{2}[P^{Ka_3} + \log C]$
	(t) $pOH = 7 - \frac{1}{2}[P^{Ka_3} + \log C]$

2.36 We mix equal volume of two aqueous solution. Match the following :

Column I	Column II (pH at 25°C)
(A) 0.2 M KOH + 0.5 M HCOOH	(p) 0.7
(B) 0.1 M NaCl + 0.1 M $NaNO_3$	(q) between 1 to 7
(C) 0.1 M NH_4Cl + 0.1 M NaOH	(r) 7
(D) 0.5 M HCl + 0.1 M NH_4OH	(s) greater than 7
$[\log_{10} 2 = 0.3]$	(t) less than 7

2.37 Match the following :
If k_a of HCN $= 5 \times 10^{-10}$, k_a of HOCN $= 3.2 \times 10^{-4}$, k_b of $NH_3 = 1.8 \times 10^{-5}$, k_a of $CH_3COOH = 1.8 \times 10^{-5}$
(All data at 25°C)

Column-I	Column-II (pH at 25°C)
(A) 10^{-2} M NaCN	(p) pH > 7
(B) 100 ml of 10^{-1} M NaCl + 100 ml of 10^{-1} M HCl + 300 ml of 10^{-1} M NaOH	(q) pH ≠ 7
(C) 10^{-1} M HCl + 10^{-1} M HCN	(r) pH < 7
(D) 10^{-1} M NH_4OCN	(s) pH = 7
	(t) pOH < 7

2.38 **Column-I** **Column-II**

Given : $K_{a1} = 5 \times 10^{-7}$, $K_{a2} = 5 \times 10^{-11}$ for H_2CO_3

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$; $K_b(NH_4OH) = 1.8 \times 10^{-5}$

(A) $NaHCO_3$ (aq.)	(p) Significant cationic hydrolysis
(B) CH_3COONH_4 (aq.)	(q) Significant anionic hydrolysis
(C) $K_2SO_4.Al_2(SO_4)_3.24H_2O$ (aq.)	(r) Acidic (pH < 7)
(D) NaCN (aq)	(s) Basic (pH > 7)
	(t) pH is independent of concentration

2.39

Column- I	**Column- II**
(A) NH_4Cl in water	(p) Neutral solution which does not undergo hydrolysis
(B) CH_3COONa in water	(q) Cationic hydrolysis
(C) NH_4CN in water	(r) Anionic hydrolysis
(D) NaCl in water	(s) Both Cationic and Anionic hydrolysis

SECTION - VI : INTEGER TYPE

2.40 $[H^+]$ concentration in 0.01 M H_2O_2 solution ($K_{a_1} = 3 \times 10^{-12}$ and $K_{a_2} \approx 0$) is x M. Fill first two digits of 10^8 x as answer.

2.41 Solid BaF_2 is added to a solution containing 0.1 mole of sodium oxalate solution (1 litre) until equilibrium is reached. If the Ksp of BaF_2 and $BaC_2O_4(s)$ is 10^{-6} & 10^{-7} respectively. Assume addition of BaF_2 does not cause any change in volume and no hydrolysis of any of the cations or anions. (Given : $\sqrt{116} = 10.77$)

If concentration of Ba^{2+} ions in resulting solution at equilibrium is represented as 2.7×10^{-x}, then x is :

2.42 What is the ratio of moles of $Mg(OH)_2$ and $Al(OH)_3$ present in 1 lit saturated aqueous solution of $Mg(OH)_2$ & $Al(OH)_3$ (K_{SP} of $Mg(OH)_2 = 4 \times 10^{-12}$ and K_{SP} of $Al(OH)_3 = 1 \times 10^{-33}$). Give answer by multiplying by 10^{-16}.

2.43 When NaOH solution is gradually added to the solution of a weak acid (HA), the pH of the solution is found to be 5.0 at the addition of 10.0 mL of NaOH and 6.0 at the further addition of 10.0 mL of same NaOH. (Total volume of NaOH = 20 mL) calculate pK_a for HA [log 2 = 0.3]

[Fill your answer in the form of multiple of 10^{-1} for example if your answer is 2.1 then fill 21 as your answer]

2.44 Calculate the hydrogen ion concentration (in mol/dm^3) in a solution containing 0.04 mole of acetic acid and 0.05 mole of sodium acetate in 500 mL of solution. Dissociation constant for acetic acid is 1.75×10^{-5}. Report your answer after multiplying by 2×10^6.

TOPIC 3 SOLUTIONS AND COLLIGATIVE PROPERTIES

SECTION - I : STRAIGHT OBJECTIVE TYPE

3.1 The vapour pressure of the solution of two liquids A(p° = 80 mm) and B(p° = 120 mm) is found to be 100 mm when $x_A = 0.4$. The result shows that :
(A) Solution exhibits ideal behaviour.
(B) Solution shows positive deviation.
(C) Solution shows negative deviation.
(D) Solution will show positive deviation for lower concentration and negative deviation for higher concentrations.

3.2 Barium ions, CN^- and Co^{2+} form an ionic complex. If this complex is 75% ionised in aqueous solution with Vant Hoff factor (i) equal to four and paramagnetic moment is found to be 1.73 BM (due to spin only) then the hybridisation state of Co (II) in the complex will be :
(A) sp^3d (B) d^2sp^3 (C) sp^3d^2 (D) dsp^3

3.3 Osmotic pressure [in atm] of a 0.1 M solution of $K_4[Fe(CN)_6]$, which undergoes 50% dissociation, will be _____ at 27°C :
(A) 7.38 (B) 3.69 (C) 405.9 (D) none of these

3.4 In an ideal mixture of liquids A and B the mole fraction of A is 0.25. If the ratio of P_A^0 to P_B^0 is 7/3, how many repeated distillations would be required as a "minimum" to obtain a small quantity of distillate which has a mole fractionof A, better than 0.80?
(A) 4 (B) 2 (C) 3 (D) 5

3.5 How many m.moles of sucrose should be dissolved in 500 grams of water so as to get a solution which has a difference of 103.57°C between boiling point and freezing point ?
(K_f = 1.86 K Kg mol^{-1}, K_b = 0.52 K Kg mol^{-1})
(A) 500 m.moles (B) 900 m.moles (C) 750 m.moles (D) 650 m.moles

3.6 Which of the following has been arranged in order of decreasing freezing point?
(A) 0.05 M KNO_3 > 0.04 M $CaCl_2$ > 0.140 M sugar > 0.075 M $CuSO_4$
(B) 0.04 M $BaCl_2$ > 0.140 M sucrose > 0.075 M $CuSO_4$ > 0.05 M KNO_3
(C) 0.075 M $CuSO_4$ > 0.140 M sucrose > 0.04 M $BaCl_2$ > 0.05 M KNO_3
(D) 0.075 M $CuSO_4$ > 0.05 M $NaNO_3$ > 0.140 M sucrose > 0.04 M $BaCl_2$

3.7 A solution of x moles of sucrose in 100 grams of water freezes at –0.2°C. As ice separates the freezing point goes down to 0.25°C. How many grams of ice would have separated?
(A) 18 grams (B) 20 grams (C) 25 grams (D) 23 grams

3.8 A sample of air is saturated with benzene (vapour pressure = 100 mm Hg at 298 K) at 298K, 750mm Hg pressure. If it is isothermally compressed to one third of its initial volume, the final pressure of the system is
(A) 2250 torr (B) 2150 torr (C) 2050 torr (D) 1950 torr

3.9 Available solutions are 1L of 0.1 M NaCl and 2L of 0.2 M $CaCl_2$. Using **only these two solutions** what maximum volume of a solution can be prepared having $[Cl^-]$ = 0.34 M exactly. Both electrolytes are strong
(A) 2.5 L (B) 2.4 L (C) 2.3 L (D) None of these

3.10 Consider equimolal aqueous solutions of $NaHSO_4$ and NaCl with ΔT_b and $\Delta T'_b$ as their respective boiling point elevations. The value of $\lim_{m \to 0} \frac{\Delta T_b}{\Delta T'_b}$ will be :

(A) 1 (B) 1.5 (C) 3.5 (D) $\frac{2}{3}$

3.11 A solute 'S' undergoes a reversible trimerization when dissolved in a certain solvent. The boiling point elevation of its 0.1 molal solution was found to be identical to the boiling point elevation in case of a 0.08 molal solution of a solute which neither undergoes association nor dissociation. To what percent had the solute 'S' undergone trimerization?

(A) 30% (B) 40% (C) 50% (D) 60%

3.12 For a solution of 0.849 g of mercurous chloride in 50 g of $HgCl_2(\ell)$ the freezing point depression is 1.24°C. K_f for $HgCl_2$ is 34.3. What is the state of mercurous chloride in $HgCl_2$? (Hg GAM 200, Cl 200 or Hg = 200, Cu GAM 35.5 or Cu = 35.5)

(A) as Hg_2Cl_2 molecules (B) as HgCl molecules

(C) as Hg^+ and Cl^- ions (D) as Hg_2^{2+} and Cl^- ions

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

S_1 : Vapour pressure is a colligative property.

S_2 : Freezing point of a solution is always lower than that of the pure solvent.

S_3 : Acetic acid undergoes association in benzene. The molar mass of acetic acid, determined by elevation of boiling point is always higher than its normal molar mass.

S_4 : Osmotic pressure measurements can be used for determination of molar mass of polymers.

(A) FFFF (B) FTTT (C) TTTT (D) TFTF

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

3.14 The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask, 2 moles of A are mixed with 6 moles of B. Further to the mixture, 32 g of an ionic non-volatile solute MCl (partially ionised, mol. mass = 70 u) were also added. Thus, the final vapour pressure of solution was found to be 420 mm of Hg. Then, identify the correct statement(s) : (Assume the liquid mixture of A and B to behave ideally).

(A) The numerical value of relative lowering in vapour pressure upon addition of solute MCl is 1/15.

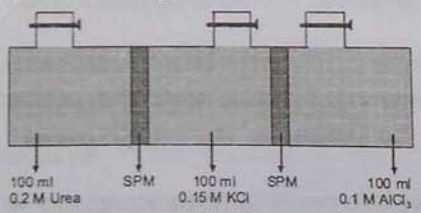
(B) The solute MCl is 25% ionised in the above question.

(C) The solute MCl is 23.33% ionised in the above question.

(D) Upon addition of excess $Pb(NO_3)_2$, the number of moles of $PbCl_2$ precipitated is 2/35.

3.15 Consider the following system.

Three different aqueous solution each having volume 100 ml are taken and kept in contact as shown.



After sufficient time (Consider temp constant & 100% dissociation of strong electrolyte)

(A) Volume of urea solution will be $\frac{100}{3}$ ml.

(B) Volume of $AlCl_3$ solution will be $\frac{400}{3}$ ml.

(C) There will be no change in volume of KCl solution.

(D) Volume of both KCl and $AlCl_3$ solutions will increase.

3.16 2.25 g of a Non volatile substance dissolved in 250 g of C_6H_6 . This solution shows depression in F.P. by 0.256 K. Which of the following is /are correct :
Given that : (K_b and K_f for C_6H_6 is 2.53 $Kmolal^{-1}$ and 5.12 $Kmolal^{-1}$, BP of C_6H_6 = 353.3 K)
(A) Molar mass of substance is = 180
(B) B.P. of solution is = 353.42 K
(C) Relative lowering in vapour pressure of solvent = 0.0038
(D) All are not correct

3.17 Which of following statements are incorrect about Henry's law ?
(A) It is applicable at all P as well as concentration
(B) It is applicable at all temperature
(C) Solubility of N_2, NH_3, O_2, HCl in water can be explained by Henry's law.
(D) Raoult's law is special case of Henry's law.

3.18 In which of the following pairs of solutions will the values of the vant Hoff factor be the same?
(A) 0.05 M K_4 [$Fe(CN)_6$] and 0.10 M $FeSO_4$
(B) 0.10 M K_4[$Fe(CN)_6$] and 0.05 M $FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$
(C) 0.20 M NaCl and 0.10 M $BaCl_2$
(D) 0.05 M $FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$ and 0.02 M KCl . $MgCl_2$. $6H_2O$

3.19 Vapour pressure of solution containing 6g of a non-volatile solute in 180 g of water is 20.0 torr. If 1 mole water is further added vapour pressure increases by 0.02 torr. Which of the following is true ?
(A) The molecular weight of solute is 54g mol^{-1}
(B) The vapour pressure of pure water is 20.22 torr
(C) Addition of more water in the solution will further raise the vapour pressure of solution.
(D) The vapour pressure of pure water is 22.22 torr

3.20 Two liquids A and B form an ideal solution. The solution has a vapor pressure of 700 torr at 80°C. It is distilled till 2/3rd of the solution is collected as condensate. The composition of the condensate is $x'_A = 0.75$ and that of the residue is $x''_A = 0.30$. If the vapor pressure of the residue at 80°C is 600 Torr, which of the following is/ are true?
(A) The composition of the original liquid was $x_A = 0.6$.
(B) The composition of the original liquid was $x_A = 0.4$.
(C) $P_A^0 = \frac{2500}{3}$ Torr.
(D) $P_B^0 = 500$ Torr.

SECTION - III : ASSERTION AND REASON TYPE

3.21 **STATEMENT-1** : Perfectly ideal solution is not possible with respect to binary solution of two liquids.
STATEMENT-2 : No two substances can have exactly the same nature of intermolecular forces & also of the same magnitude.
(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

3.22 **STATEMENT-1** : When a cell is placed in hypertonic solution, it shrinks.
STATEMENT-2 : Reverse osmosis is used for desalination of water.
(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

3.23 **STATEMENT-1 :** The difference in the boiling points of equimolar solution of HCl and HF decreases as their molarity is decreased.
STATEMENT-2 : The extent of dissociation decreases steadily with increasing dilution.
(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

3.24 **STATEMENT-1 :** When 'a' mL of a 0.1 molal urea solution is mixed with another 'b' mL of 0.1 molal glucose solution, the boiling point of the solution is no different from the boiling points of the samples prior to mixing but if 'a' mL of 0.1 molal urea is mixed with 'b' mL of 0.1 molal HF, the boiling point of the mixture is different from the boiling points of the separate samples .
STATEMENT-2 : HF is an electrolyte (weak) whereas glucose is a non 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

SECTION - IV : COMPREHENSION TYPE

Comprehension # 1

IDEAL SOLUTION AT FIXED TEMPERATURE

Consider two liquids 'B' and 'C' that form an ideal solution. We hold the temperature fixed at some value T that is above the freezing points of 'B' and 'C'. We shall plot the system's pressure P against x_B, the **overall mole fraction** of B in the system : 3.25

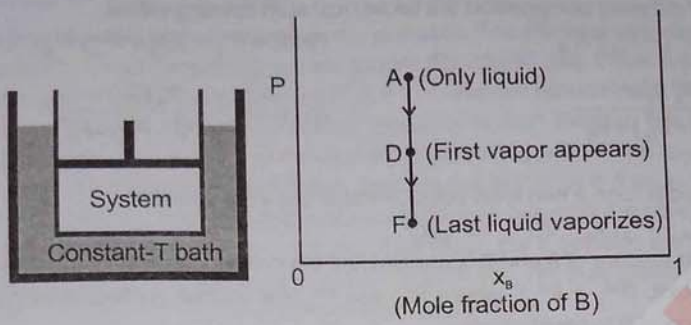
$$x_B = \frac{n_{B,total}}{n_{total}} = \frac{n_B^{\ell} + n_B^{v}}{n_B^{v} + n_C^{\ell} + n_C^{v} + n_B^{\ell}}$$

Where n_B^{ℓ} and n_B^{v} are the number of moles of B in the liquid and vapor phases, respectively. For a closed system x_B is fixed, although n_B^{ℓ} and n_B^{v} may vary.

Let the system be enclosed in a cylinder fitted with a piston and immersed in a constant-temperature bath. To see what the P-versus–x_B phase diagram looks like, let us initially set the external pressure on the piston high enough for the system to be entirely liquid (point A in figure) As the pressure is lowered below that at A, the system eventually reaches a pressure where the liquid just begins to vaporizes (point D). At point D, the liquid has composition x_B^{ℓ} where x_B^{ℓ} at D is equal to the overall mole fraction x_B since only an infinitesimal amount of liquid has vapourized. What is the composition of the first vapour that comes off ? Raoult's law, $P_B \equiv x_B^{v} P_B^0$ relates the vapour-phase mole fractions to the liquid composition as follows :

$$x_B^{v} = \frac{x_B^{\ell} P_B^0}{P} \text{ and } x_C^{v} = \frac{x_C^{\ell} P_C^0}{P} \qquad \ldots\ldots\ldots\ldots (1)$$

Where P_B^0 and P_C^0 are the vapour pressures of pure 'B' and pure 'C' at T, where the system's pressure P equals the sum $P_B + P_C$ of the partial pressures, where $x_B^{\ell} = \frac{n_B^{\ell}}{(n_B^{\ell} + n_C^{\ell})}$, and the vapor is assumed ideal.



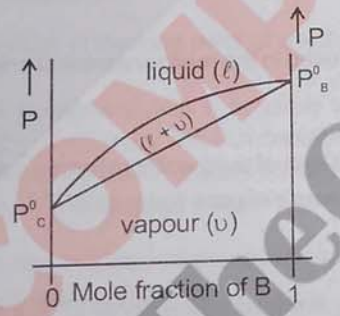
$$\frac{x_B^v}{x_C^v} = \frac{x_B^\ell P_B^*}{x_C^\ell P_C^*}$$ ideal solution ..... (2)

Let B be the more volatile component, meaning that $P_B^0 > P_C^0$. Above equation then shows that $x_B^v / x_C^v > x_B^\ell / x_C^\ell$. The vapor above an ideal solution is richer than the liquid in the more volatile component.

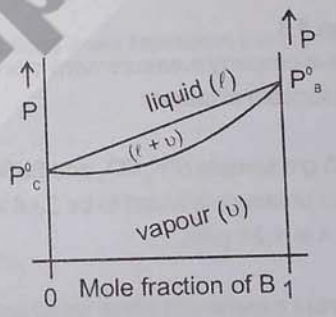
Equations (1) and (2) apply at any pressure where liquid –vapor equilibrium exists, not just at point D. Now let us isothermally lower the pressure below point D, causing more liquid to vaporize. Eventually, we reach point F in figure, where the last drop of liquid vaporizes. Below F, we have only vapor. For any point on the line between D and F liquid and vapor phases coexist in equilibrium.

3.25 If the above process is repeated for all other compositions of mixture of C and B. If all the points where vapours start converting into liquid are connected and all the points where vapours get completely converted into liquid are connected then obtained graph will look like.

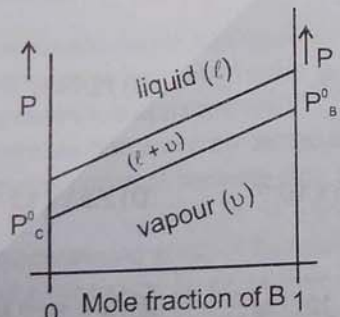
(A)



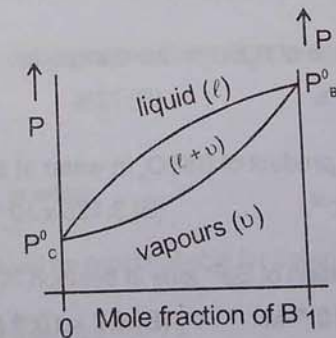
(B)



(C)



(D)



3.26 The equation of the curve obtained by connecting all those points where the vapors of above mixture (all mixtures of different composition are taken) just start forming will be

(A) $P = P^0_C + (P^0_B - P^0_C)\, X'_B$ (B) $P = P^0_B + (P^0_B - P^0_C)\, X'_B$

(C) $P = \dfrac{P^0_B P^0_C}{X^0_B(P^0_C - P^0_B) + P^0_B}$ (D) $P = \dfrac{P^0_B P^0_C}{X'_B(P^0_C - P^0_B) + P^0_B}$

3.27 Two liquids A and B form a non ideal solution which obey the equation $P_T = P^\circ_A + 3(P^\circ_B - P^\circ_A)\, x_B + 2(P^\circ_A - P^\circ_B)x_B^2$.
When equimolar mixture of A and B is distilled find the composition (by mole) when this mixture will have a single boiling point. ($P^\circ_B > P^\circ_A$) where P°_A and P°_B are vapour pressures of pure A and B respectively
X_B = mole fraction of B in liquid phase :

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

Comperhension # 2

The pressure of two pure liquid A and B which form an ideal solutions are 400 mm Hg and 800 mm Hg respectively at temperature T. A liquid containing 3 : 1 molar composition pressure can be varied. The solutions is slowly vaporized at temperature T by decreasing the applied pressure starting with a pressure of 760 mm Hg. A pressure gauge (in mm) Hg is connected which given the reading of pressure applied.

3.28 The reading of pressure Gauge at which only liquid phase exists.

(A) 499 (B) 399 (C) 299 (D) None

3.29 The reading of pressure Gauge at bubble point is

(A) 500 (B) 600 (C) 700 (D) None

3.30 The reading of pressure Gauge at which only vapour phase exists is

(A) 501 (B) 457.14 (C) 425 (D) 525

Comprehension # 3

Colligative property measurement is one of the techniques used in the measurement of chemical quantities with reasonable accuracy.

If a 40.65 gm sample of K_2SO_4 and $BaSO_4$ is dissolved in 900 gm of pure water to form a solution 'A' at 57°C its vapour pressure is found to be 39.6 torr while vapour pressure of pure water at 57°C is 40 torr. Density of solution A is 1.24 g/ml.

In a different experiment when small amount of pure $BaSO_4$ is mixed with water at 57°C it gives the osmotic rise of 4.05×10^{-5} atm.

(R = 0.082 Lt.-atm/mol-K ; K = 39, Ba = 137, S = 32, O = 16)

3.31 Percentage of K_2SO_4 in the sample is :

(A) 65.75% (B) 72% (C) 60.35% (D) 78.74%

3.32 Solubility product of $BaSO_4$ in water at 57°C is :

(A) 5×10^{-19} (B) 3.125×10^{-13} (C) 5.625×10^{-13} (D) 2.25×10^{-12}

3.33 Concentration of Ba^{2+} ions in solution 'A' is :

(A) 3.5×10^{-18} M (B) 4.7×10^{-15} M (C) 2.5×10^{-12} M (D) 4×10^{-13} M

3.34 Elevation in boiling point of solution A is (K_b water = 0.54 K-kg/mol) :

(A) 0.3 K (B) 0.1 K (C) 0.04 K (D) 0.05 K

Comprehension # 4

A system of greater disorder of molecules is more probable. The disorder of molecules is reflected by the entropy of the system. A liquid vaporises to form a more disordered gas. When a solute is present, there is additional contribution to the entropy of the liquid due to increased randomness. As the entropy of solution is higher than that of pure liquid, there is weaker tendency to form the gas. Thus, a solute (non volatile) lowers the vapour pressure of a liquid, and hence a higher boiling point of the solution.
Similarly, the greater randomness of the solution opposes the tendency to freeze. In consequence, a lower the temperature must be reached for achieving the equilibrium between the solid (frozen solvent) and the solution. Elevation of B.Pt. (ΔT_b) and depression of F.Pt. (ΔT_f) of a solution are the colligative properties which depend only on the concentration of particles of the solute, not their identity. For dilute solutions, ΔT_b and ΔT_f are proportional to the molality of the solute in the solution.

$\Delta T_b = K_b m$ $\quad K_b$ = Ebullioscopic constant = $\dfrac{RT_b^{\circ 2} M}{1000\ \Delta H_{vap}}$

And $\Delta T_f = K_f m$ $\quad K_f$ = Cryoscopic constant = $\dfrac{RT_f^{\circ 2} M}{1000\ \Delta H_{fus}}$ (M = molecular mass of the solvent)

The values of K_b and K_f do depend on the properties of the solvent. For liquids, $\dfrac{\Delta H_{vap}}{T_b^{\circ}}$ is almost constant.

[**Troutan's Rule**, this constant for most of the **unassociated liquids** (not having any strong bonding like Hydrogen bonding in the liquid state) is equal to 90 J/mol.]
For solutes undergoing change of molecular state is solution (ionization or association), the observed ΔT values differ from the calculated ones using the above relations. In such situations, the relationships are modified as $\Delta T_b = i K_b m$; $\Delta T_f = i K_f m$
where i = Van't-Hoff factor, greater than unity for ionization and smaller than unity for association of the solute molecules.

3.35 Depression of freezing point of which of the following solutions does represent the cryoscopic constant of water?
(A) 6% by mass of urea in aqueous solution
(B) 100g of aqueous solution containing 18 g of glucose
(C) 59 g of aqueous solution containing 9 g of glucose
(D) 1 M KCl solution in water.

3.36 Dissolution of a non-volatile solute into a liquid leads to the -
(A) decrease of entropy
(B) increase in tendency of the liquid to freeze
(C) increases in tendency to pass into the vapour phase.
(D) decrease in tendency of the liquid to freeze

3.37 To aqueous solution of NaI, increasing amounts of solid HgI_2 is added. The vapor pressure of the solution
(A) decreases to a constant value
(B) increases to a constant value
(C) increases first and then decreases
(D) remains constant because HgI_2 is sparingly soluble in water.

3.38 A liquid possessing which of the following characteristics will be most suitable for determining the molecular mass of a compound by cryoscopic measurements?
(A) That having low freezing point and small enthalpy of freezing
(B) That having high freezing point and small enthalpy of freezing
(C) That having high freezing point and small enthalpy of vaporisation
(D) That having large surface tension

3.39 A mixture of two immiscible liquids at a constant pressure of 1 atm boils at a temperature
(A) equal to the normal boiling point of more volatile liquid.
(B) equal to the mean of the normal boiling points of the two liquids.
(C) greater than the normal boiling point of either of the liquid.
(D) smaller than the normal boiling point of either of the liquid.

SECTION - V : MATRIX - MATCH TYPE

3.40

Column- I electrolyte	Column- II i (van't off factor)
(A) Urea, Glucose, Fructose	(p) 1 : 0.8 : 1
(B) NaCl, $MgCl_2$, K_2SO_4	(q) 1 : 2 : 3
(C) $Al_2(SO_4)_3$, Na_3PO_4, $K_4[Fe(CN)_6]$	(r) 1 : 1 : 1
(D) Glucose, NaCl, $CaCl_2$	(s) 2 : 3 : 3

3.41

Column I	Column II
(A) Acetone + $CHCl_3$	(p) $\Delta S_{mix.} > 0$
(B) Ethanol + Water	(q) $\Delta V_{mix.} > 0$
(C) $C_2H_5Br + C_2H_5I$	(r) $\Delta H_{mix.} < 0$
(D) Acetone + Benzene	(s) Maximum boiling azeotropes
	(t) Minimum boiling azeotropes

3.42 **Match the Column**

Column-I	Column-II
(A) 0.1 M $Al_2(SO_4)_3$	(p) Solution with highest boiling point.
(B) 0.1 M $AlPO_4$	(q) Van't Hoff factor is greater than 1.
(C) 0.1 M urea.	(r) Solution with lowest osmotic pressure.
(D) 0.1 M $MgCl_2$	(s) Solution with lowest freezing point.

SECTION - VI : INTEGER TYPE

3.43 Two liquids 'A' (molecular mass = 40) and 'B' (Molecular mass = 20) are partially miscible. When 1 mol of A and 3 mol of B are shaken together and allowed to settle, two layer L_1 and L_2 are formed as shown in diagram. **(Mol)(P)[T]**

Layer 'L_1' contains 0.1 mole fraction of 'A' and layer 'L_2' contains 0.4 mole fraction of A calculate simple ratio of masses of layer L_1 to layer L_2. If your answer is $\frac{x}{y}$ then report as (x + y).

3.44 A solution of A (ℓ) and B (ℓ) with 30 mole percent of A is in equilibrium with its vapour which contains 60 mole percent of A. Assuming ideality of the solution and its vapour calculate the ratio of vapour pressure of pure A to that of pure B. (Report your answer as ratio × 2)

3.45 An ideal solution was prepared by dissolving some amount of can sugar (non-volatile) in 0.9 moles of water. The solution was then cooled just below its freezing temperature (271 K) where some ice get separated out. The remaining aqueous solution registered a vapour pressure of 700 torr at 373 K. Calculate the mass of ice separated out, if the the molar heat of fusion of water is 6 kJ.

3.46 If osmotic pressure of 1 M aqueous solution of H_2SO_4 at 500 K is 90.2 atm. Calculate Ka_2 of H_2SO_4. Give your answer after multiplying 10 with Ka_2. (Assuming ideal solution).
(Given : Ka_1 of H_2SO_4 is ∞, R = 0.082 lt-atm/mol-K).

3.47 2.56g of sulfur in 100g of CS_2 has depression in freezing point of 0.01^oC. $K_f = 0.1^o molal^{-1}$. Hence, the atomicity of sulfur in CS_2 is

3.48 0.0125 mol of sucrose is dissolved in 100 gm of water and it undergo partial inversion according to following equation

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

If elevation in boiling point of solution is 0.104°C calculate $\frac{1}{10}$ mol percentage of sugar inverted

($K_{b,\,H_2O} = 0.52$).

3.49 25 ml of FeC_2O_4 dissolved in 186 gm of water calculate depression in freezing point. If 10 ml of same FeC_2O_4 titrated with 30 ml of 0.4 M $KMnO_4$ in acidic medium (k_f for H_2O = 1.86, Assume 100% ionisation of FeC_2O_4).

3.50 In 10^3 Litre sample of hard water $CaSO_4$ and $MgSO_4$ is present. If elevation in Boiling point is 0.000052°C. Calculate the degree of Hardness of hard water. (K_b for H_2O = 0.52)

3.51 The vapour pressure of fluorobenzene at t°C is given by the equation

$$\log p\ (\text{mm Hg}) = 7.0 - \frac{1250}{t+220}$$

Calculate the boiling point of the liquid in °C if the external (applied) pressure is 5.26% more than required for normal boiling point. (log 2 = 0.3)

3.52 1g of arsenic dissolved in 86 g of benzene brings down the freezing point to 5.31 °C from 5.50 °C. If K_f of benzene is 4.9 $\frac{^oC}{m}$, the atomicity of the molecule is : (As = 75 or As GAM 75)

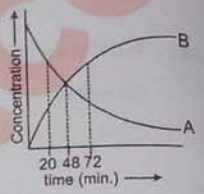
3.53 Assume liquefied petroleum gas (LPG) is a 50-50 (by mole) mixture of n-pentane and n-butane. Calculate the calorific value (in kJ/mol) of gas available from a newly filled cylinder.
Give your answer divide by 100.

	n-butane, C_4H_{10}	n-pentane, C_5H_{12}
Vapour pressure	1800 Torr	600 Torr
Calorific value	2800 kJ/mol	3600 kJ/mol

TOPIC 4 CHEMICAL KINETICS & RADIOACTIVITY

SECTION - I : STRAIGHT OBJECTIVE TYPE

4.1 For a first order reaction, $nA \rightarrow B$ whose concentration vs time curve is as shown in the figure. If half-life for this reaction is 24 minutes. Find out the value of n.



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

4.2 $^{24}_{11}Na$ (half-life = 15 hrs.) is known to contain some radioactive impurity (half-life = 3 hrs.) in a sample. This sample has an initial activity of 1000 counts per minute, and after 30 hrs it shows an activity of 200 counts per minute. What percent of the initial activity was due to the impurity ?

(A) 10 (B) 40 (C) 5 (D) 20

4.3 In a hypothetical reaction

$A(aq) \rightleftharpoons 2B(aq) + C(aq)$ (1^{st} order decomposition)

'A' is optically active (dextro-rototory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence the progress of reaction can be monitored by measuring rotation of plane of polarised light or by measuring volume of H_2O_2 consumed in titration.
In an experiment, the optical rotation was found to be $\theta = 30°$ at t = 20 min. and $\theta = 15°$ at t = 50 min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_2O_2 consumed at t = 30 min. (from start) is 30 ml then volume of H_2O_2 consumed at t = 90 min. will be:

(A) 60 ml (B) 45 ml (C) 52.5 ml (D) 90 ml

4.4 At a certain temperature, the first order rate constant k_1 is found to be smaller than the second order rate constant k_2. If the energy of activation E_1 of the first order reaction is greater than energy of activation E_2 of the second order reaction, then with increase in temperature.

(A) k_1 will increase faster than k_2, but always will remain less than k_2
(B) k_2 will increase faster than k_1
(C) k_1 will increase faster than k_2 and becomes equal to k_2
(D) k_1 will increase faster k_2 and becomes greater than k_2

4.5 In the formation of HBr from H_2 & Br_2, following mechanism is observed.

(A) $Br_2 \rightleftharpoons 2Br\bullet$ Equilibrium step

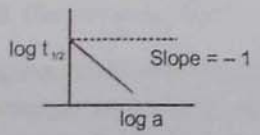
(B) $H_2 + Br\bullet \longrightarrow HBr + H\bullet$ Slow step

(C) $H\bullet + Br_2 \longrightarrow HBr + Br\bullet$ Fast step

Calculate the rate of reaction, if concentration of hydrogen is twice that of bromine and the rate constant is equal to one rutherford. Concentration of bromine is 1 M.

(A) 2×10^6 dps (B) 10×10^9 dps (C) $20 . 2 \times 10^{10}$ dps (D) 4×10^2 dps

4.6 A graph between log $t_{1/2}$ and log a (abscissa), a being the initial concentration of A in the reaction is given For reaction A → Product, the rate law is :



(A) $\frac{-d[A]}{dt} = K$ (B) $\frac{-d[A]}{dt} = K[A]$ (C) $\frac{-d[A]}{dt} = K[A]^2$ (D) $\frac{-d[A]}{dt} = K[A]^3$

4.7 In a gaseous phase reaction, $A_2(g) \longrightarrow B(g) + \frac{1}{2}C(g)$. The increase in pressure from 100 mm to 110 mm is observed in 5 minute. The rate of disappearance of A_2 in mm min^{-1} is :
(A) 4 (B) 8 (C) 16 (D) 2

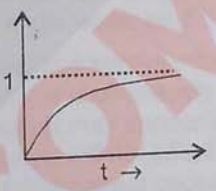
4.8 For a 1st order reaction (gaseous) (constant V, T) :
$a\,A \longrightarrow (b-1)\,B + 1\,C$ (with b > a) the pressure of the system rose by $50\left(\frac{b}{a}-1\right)$ % in a time of 10 min. The half life of the reaction is therefore.
(A) 10 min (B) 20 min (C) 30 min (D) 40 min.

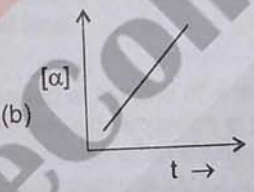
4.9 For a certain reaction the variation of the rate constant with temperature is given by the equation
$\ln k_t = \ln k_0 + \frac{(\ln 3)t}{10}$ $(t \geq 0°C)$
The value of the temperature coefficient of the reaction is :
(A) 0.1 (B) 1.0 (C) 10 (D) 3

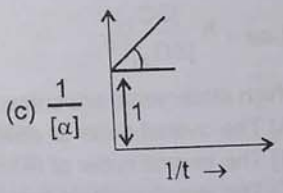
4.10 A reaction takes place in three steps ; the respective rate constants are k_1, k_2 and k_3. The overall rate constant $k = \frac{k_1 k_3}{k_2}$. If energies of activation are 40 , 30 and 20 kJ, the overall energy of activation is (assumming 'A' to be constant for all) :
(A) 10 (B) 15 (C) 30 (D) 60

4.11 In a certain reaction, 10% of the reactant decomposes in one hour, 20 % in two hours, 30% in three hours and so on. The dimensions of the rate constant is :
(A) $hour^{-1}$ (B) mole $litre^{-1}$ sec^{-1} (C) litre $mole^{-1}$ sec^{-1} (D) mole sec^{-1}

4.12 Some graph are sketched for the reaction A → B (assuming different orders). Where 'α' represent the degree of dissociation.

(a) 

(b) 

(c) 

The order of reaction are respectively.
(A) 0, 1, 2 (B) 1, 0, 2 (C) 2, 0, 1 (D) 1, 2, 0

4.13 Compounds A and B react with a common reagent with first order kinetics in both cases. If 99% of A must react before 1% of B has reacted, what is the minimum ratio for their respective rate constants?
(A) 916 (B) 229 (C) 500 (D) 458

4.14 The activity per ml of a solution of radioactive substance is x. How much water be added to 200 ml of this solution so that the acitivity falls to x/20 per ml after 4 half-lives ?
(A) 100 ml (B) 150 ml (C) 80 ml (D) 50 ml.

4.15 A reaction with respect to X is zero order till the concentration is reduced to half of initial concentration. Then the reaction become first order with respect to it. if the value of rate constants for the zero order and first order are equal to k (in magnitude), then find the time taken to reduce the concentration of X to $\frac{1}{16}$ th of its original concentration X_0.
(A) $\frac{1}{2k}+\frac{3\ell n2}{k}$ (B) $\frac{x_0}{2k}+\frac{3\ell n2}{k}$ (C) $\frac{x_0}{2k}+\frac{4\ell n2}{k}$ (D) $\frac{1}{2k}+\frac{4\ell n2}{k}$

4.16 For the decomposition of $H_2O_2(aq)$ it was found that V_{O_2} (t = 15 min.) was 100 mL (at 0°C and 1 atm) while V_{O_2} (maximum) was 200 mL (at 0°C and 2 atm). If the same reaction had been followed by the titration method and if $V^{(cM)}_{KMnO_4}$ (t = 0) had been 40 mL, what would $V^{(cM)}_{KMnO_4}$ (t = 15 min) have been ?

(A) 30 mL (B) 25 mL (C) 20 mL (D) 15 mL

4.17 A reaction can take place by two paths. k_1 and k_2 are rate constants for the two paths & E_1 and E_2 are their respective activation energies.
At temperature T_a : $k_1 > k_2$, $E_1 < E_2$.
if temperature is raised to T_b, the rate constants change to k_1' & k_2'. Which relation is correct between k_1, k_2, k_1' & k_2' (considering activation energy does not change with temperature).

(A) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$ (B) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ (C) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$ (D) $\frac{k_1'}{k_2'} > \frac{k_1}{k_2}$

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

S_1 : The rate of the reaction A → B having the rate law $-\frac{d[A]}{dt} = k[A][B]$ when plotted against time will exhibit a maximum at some time.
S_2 : A catalyst in a chemical reaction increases the forward E_a and decreases the backward E_a
S_3 : A catalyst in a chemical reaction decreases both forward and backward E_a
S_4 : For a first–order reaction, the time required to reduce successively the concentration of reactant by a constant fraction is always same.
(A) TTTT (B) FFFF (C) FTFT (D) TFTT

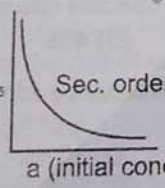
SECTION - II : MULTIPLE CORRECT ANSWER TYPE

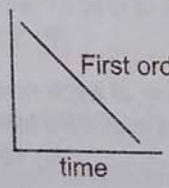
4.19 If the rate of reaction, $2SO_2(g) + O_2(g) \xrightarrow{Pt} 2SO_3(g)$ is given by :

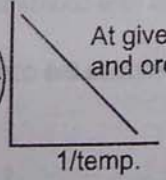
$$\text{Rate} = K\frac{[SO_2]}{[SO_3]^{1/2}}$$

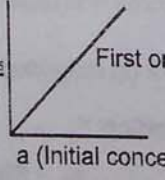
which statements are correct :
(A) The overall order of reaction is –1/2
(B) The overall order of reaction is +1/2
(C) The reaction slows down as the product SO_3 is build up
(D) The rate of reaction does not depend upon concentration of SO_3 formed

4.20 Which is **correct** graph :

(A) 

(B) 

(C) 

(D) 

4.21 For a certain reaction A $\longrightarrow$ products, the $t_{1/2}$ as a function of $[A]_0$ is given as below :

$[A]_0$ (M) :	0.1	0.025
$t_{1/2}$ (min.) :	100	50

Which of the following is true :

(A) The order is $\frac{1}{2}$

(B) $t_{1/2}$ would be $100\sqrt{10}$ min for $[A]_0 = 1$ M

(C) The order is 1

(D) $t_{1/2}$ would be 100 min for $[A]_0 = 1$ M

4.22* For the reaction $2A + B \longrightarrow C$ with the rate law $\frac{d[C]}{dt} = k[A]^1[B]^{-1}$ and started with A and B in stoichiometric proportion. Which is/are true?

(A) unit of k is Ms^{-1}

(B) [A], [B] and [C] all will be linear functions of time

(C) [C] = 2kt

(D) [C] = kt

4.23 The reaction $2NO + Br_2 \longrightarrow 2NOBr$ follows the mechanism :

(1) $NO + Br_2 \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} NOBr_2$

(2) $NOBr_2 + NO \xrightarrow{\text{Slow}} 2NOBr$

Which of the following is/are true regarding this :

(A) The order of the reaction with respect to NO is two.

(B) The molecularity of the steps (1) and (2) are two each.

(C) The molecularity of the overall reaction is three.

(D) The overall order of the reaction is three.

4.24 The polarimeter readings in an experiment to measure the rate of inversion of cane suger (1st order reaction) were as follows

time (min) :	0	30	∞
angle (degree) :	30	20	-15

Identify the **true** statement (s) ? [log 2 = 0.3, log 3 = 0.48, log 7 = 0.84 , $\log_e 10 = 2.3$]

(A) The half life of the reaction is 75 min

(B) The solution is optically inactive at 120 min.

(C) The equimolar mixture of the products is dextrorotatory

(D) The angle would be 7.5° at half time

4.25 Identify the true statement(s)

(A) A catalyst is chemically unchanged at the end of a reaction

(B) A catalyst may appear in the kinetic rate equation of the reaction

(C) A catalyst will not affect the composition of an equilibrium mixture

(D) A catalyst cannot cause a non-spontaneous ($\Delta G > 0$) reaction to proceed

4.26 The half–period T for the decomposition of ammonia on tungsten wire, was measured for different initial pressures P of ammonia at 25°C. Then

P (mm Hg)	11	21	48	73	120
T (sec)	48	92	210	320	525

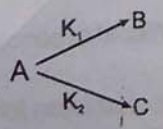
(A) Zero order reaction

(B) First order reaction

(C) Rate constant for reaction is 0.114 mol lit.$^{-1}$ sec^{-1}.

(D) Rate constant for reaction is 1.14 seconds.

4.27 The substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :



$K_1 = 10^{-2}$ sec^{-1} and $K_2 = 4 \times 10^{-2}$ sec^{-1}

If the corresponding activation energies of parallel reaction are 100 and 120 kJ mol^{-1} then the net activation energy of A is / are :

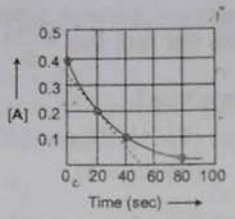
(A) 120 KJ mol^{-1} (B) 116 KJ mol^{-1} (C) 100 KJ mol^{-1} (D) 150 KJ mol^{-1}

4.28 A certain reaction obeys the rate equation (in the integrated form) $[C^{(1-n)} - C_0^{(1-n)}] = (n-1)kt$ where C_0 is the initial concentration and C is the concentration after time, t. Then :

(A) The unit of k for n = 1 is sec^{-1} (B) The unit of k for n = 2 is litre mol^{-1} sec^{-1}

(C) The unit of k for n = 3 is mol $litre^{-1}$ sec^{-1} (D) The unit of k for n = 3 is $litre^2$ mol^{-2} sec^{-1}

4.29* A certain reaction **A → B** follows the given concentration (Molarity)–time graph. Which of the following statement(s) is/are true ?



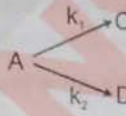
(A) The reaction is second order with respect to A

(B) The rate for this reaction at 20 second will be 7×10^{-3} M s^{-1}

(C) The rate for this reaction at 80 second will be 1.75×10^{-3} M s^{-1}

(D) The [B] will be 0.35 M at t = 60 second

4.30 Consider the following case of competing 1st order reactions.



After the start of the reaction at t = 0 with only A, the [C] is equal to the [D] at all times. The time in which all three concentrations will be equal is given by :

(A) $t = \frac{1}{2k_1} \ell n\, 3$ (B) $t = \frac{1}{2k_2} \ell n3$ (C) $t = \frac{1}{3k_1} \ell n2$ (D) $t = \frac{1}{3k_2} \ell n2$

4.31 Decomposition of $3\,A(g) \longrightarrow 2\,B(g) + 2C(g)$ follows first order kinetics. Initially only A is present in the container. Pressure developed after 20 min. and infinite time are 3.5 and 4 atm respectively. Which of the following is true.

(A) $t_{50\%} = 20$ min (B) $t_{75\%} = 40$ min (C) $t_{99\%} = 64/3$ min (D) $t_{87.5\%} = 60$ min

SECTION - III : ASSERTION AND REASON TYPE

4.32 **STATEMENT-1 :** If the activation energy of reaction is zero temperature, will have no effect on the rate constant.

STATEMENT-2 : Lower the activation energy faster is the reaction.

(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

4.33 **STATEMENT-1 :** For $A + 2B \longrightarrow C$ (rate= $K[A]^1[B]^0$), the half life time of reaction is only defined when concentration of A and B are in stoichometric ratio

STATEMENT-2 : For above reaction, half life of reaction is directly proportional to concentration of A and not to concentration of B due to its zero order.

(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

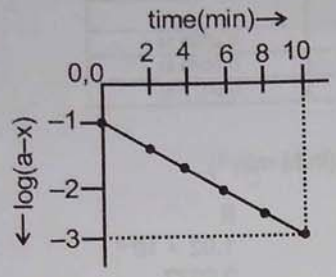
SECTION - IV : COMPREHENSION TYPE

Paragraph for Question Nos. 34 to 35

For I[st] order decomposition of $SO_2Cl_2(g)$,

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

a graph of log (a – x) v/s t is shown in figure



answer the following questions using above information.

4.34 What is the rate constant (in sec^{-1}) ?
(A) 0.2 (B) 4.6×10^{-1} (C) 7.7×10^{-3} (D) 1.15×10^{-2}

4.35 What is rate of reaction at t = 10 min [in mole/Lit./sec]
(A) 0.2×10^{-3} (B) 4.6×10^{-4} (C) 7.7×10^{-6} (D) 1.15×10^{-5}

Comperhension # 4

The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentration of the reactants raised to some powers for the general reaction

$aA + bB \longrightarrow cC + dD$

Rate law takes the form

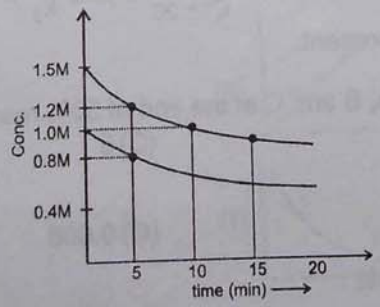
$r = k [A]^x [B]^y$

where x and y are number that must be determined experimentely k is the rate constant and [A] and [B] are concentration of A & B respectively.

4.36 Gaseous reaction $A \longrightarrow B + C$ follows first order kinetics concentration of A changes from 1M to 0.25 M in 138.6 min. Find the rate of reaction when conc. of A is 0.1 M.
(A) 10^{-2} M min^{-1} (B) 10^{-3} M min^{-1} (C) 10^{-4} M min^{-1} (D) 10^{-5} M min^{-1}

4.37 The initial rate of zero order reaction of the gaseous equation $A(g) \longrightarrow 2B(g)$ is 10^{-2} M min^{-1} if the initial concentration of A is 0.1 M what would be concentration of B after 60 seconds ?
(A) 0.09 M (B) 0.01 M (C) 0.02 M (D) 0.03 M

4.38 The variation of concentration of 'A' with time in two experiments starting with two different initial concentration of 'A' is given by the following graph. The reaction is represented by $A(aq) \longrightarrow B(aq)$ what is rate of reaction (M/min) when conc. of A in aqueous solution was 1.8 M :



(A) 0.072 M min^{-1} (B) 0.1296 M min^{-1}. (C) 0.036 M min^{-1} (D) 1 M min^{-1}

Comprehension

Study the following experiment and answer the questions at the end of it.
The following reactions was studied at 25°C in benzene solution containing 0.10 M pyridine

$$\underset{A}{CH_3OH} + \underset{B}{(C_6H_5)_3CCl} \longrightarrow \underset{C}{(C_6H_5)_3C.OCH_3} + HCl$$

The following sets of data were observed :

Set	Initial concentration		time difference	Final concentration [C]
	$[A]_0$	$[B]_0$		
I	0.10 M	0.05 M	25 min	0.0033 M
II	0.10 M	0.10 M	15 min	0.0039 M
III	0.20 M	0.10 M	7.5 min	0.0077 M

4.39 Rates $\frac{d[C]}{dt}$ in sets I , II and III are respectively (in M min^{-1}) :

	I	II	III
(A)	1.30×10^{-4}	2.6×10^{-4}	1.02×10^{-3}
(B)	0.033	0.0039	0.0077
(C)	0.02×10^{-4}	0.04×10^{-4}	0.017
(D)	None of above		

4.40 Rate law of the above experiment is :
(A) $r = k[A][B]$ (B) $r = k[A]^3[B]$ (C) $r = k[A][B]^2$ (D) $r = k[A]^2[B]^0$

4.41 Rate constant of the above experiment is :
(A) 1.3×10^{-1} (B) 2.6×10^{-2} (C) 2.6×10^{-1} (D) 1.3×10^{-2}

Comprehension # 4

From the following data answer the questions :

Reaction : $A + B \longrightarrow P$

[A] M	[B] M	Initial rate M sec^{-1}	
		300 K	400 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	

4.42 The order w.r.t A is :
(A) 1 (B) 2 (C) 3 (D) – 1.

4.43 The value of rate constant at 300 K is (M^{-2} sec^{-1}) :
(A) 2.667×10^8 (B) 2.667×10^5 (C) 2.667×10^6 (D) 2.667×10^9

4.44 The energy of activation for reaction (KJ/mol) is :
(A) 20.83 (B) 13.83 (C) 15.23 (D) 10.23

Comprehension # 5

For a hypotherical elementary reaction $A \xrightarrow{k_1} 2B$, $A \xrightarrow{k_2} 2C$ where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

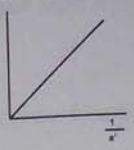
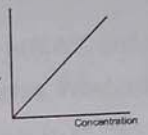
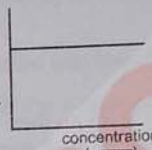
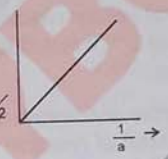
4.45 The total number of moles of A, B and C at the end of 50% reaction are :
(A) 2 (B) 3 (C) 5 (D) None

4.46 Number of moles of B are :
(A) 2 (B) 1 (C) 0.666 (D) 0.333

4.47 The sum of mole of (B) and (C) is :
(A) 2 (B) 3 (C) 1 (D) 4

SECTION - V : MATRIX - MATCH TYPE

4.48

Column- I		Column- II	
(A)	Zero	(p)	
(B)	First	(q)	
(C)	Second	(r)	
(D)	Third	(s)	

4.49 For A + B $\longrightarrow$ C in column - II the graphs given can be from any of these four types.

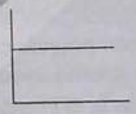
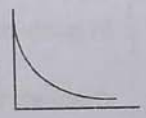
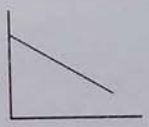
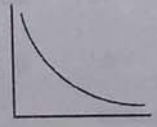
(a) $-\frac{dA}{dt}$ Vs time (x axis)

(b) $t_{1/2}$ Vs initial conc. (x axis)

(c) $\left(\frac{C_0 - C_t}{C_t}\right)$ Vs time (x axis)

(d) Conc. Vs time (x axis)

Match the graphs in Column–II for the given order of reactions in Column – I

Column – I		Column – II	
(A)	I[st] order	(p)	
(B)	Zero order	(q)	
(C)	Second order	(r)	
(D)	Pseudo first order	(s)	
		(t)	

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)	$k = \frac{1}{t}\log_e\left(\frac{a}{(a-x)}\right)$

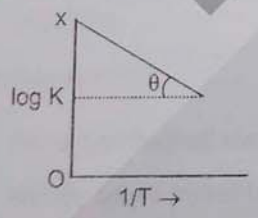
4.51 **Match the following :**

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 $FeSO_4.7H_2O$ 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 completely.(Assume all reactions are 100% complete).
Give your answer divide by 100.

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

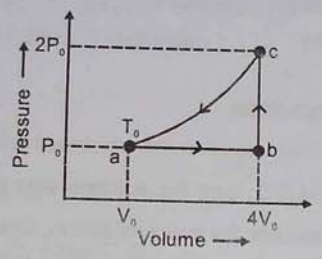
$$(CH_3)_x AlCl_y\ (0.643\ g) \longrightarrow xCH_4\ (g)\ (0.22\ g) + y\ Cl^- + Al^{3+} \xrightarrow{AgNO_3} AgCl\ (s)\ (0.996\ g).$$

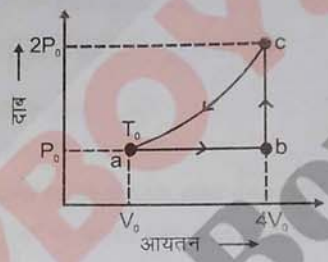
5.59 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. Find the Volume(V) (mL) of stock solution required to prepare a 500 mL solution of 0.4 M HCl.
Report your answer as V/5

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 :





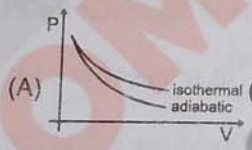
(A) $\frac{9P_oV_o}{2}$, $6RT_o$ (B) $\frac{9P_oV_o}{2}$, $10RT_o$ (C) $\frac{15P_oV_o}{2}$, $6RT_o$ (D) $\frac{15P_oV_o}{2}$, $10RT_o$

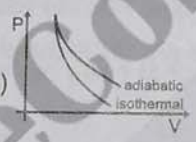
6.2 Consider the following data : $\Delta_f H°(N_2H_4, \ell) = 50$ kJ/mol, $\Delta_f H°(NH_3, g) = -46$ kJ/mol, B.E. (N–H) = 393 kJ/mol and B.E. (H–H) = 436 kJ/mol, $\Delta_{vap} H(N_2H_4, \ell) = 18$ kJ/mol

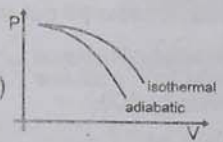
Calculate the N – N bond energy in kJ/mol for N_2H_4.

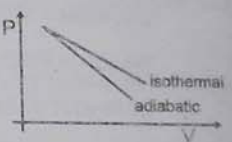
(A) 190 kJ/mol (B) – 190 kJ/mol (C) 95 kJ/mol (D) – 95 kJ/mol

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

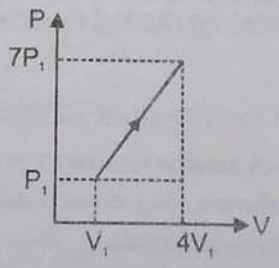
(A) 

(B) 

(C) 

(D) 

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 ?

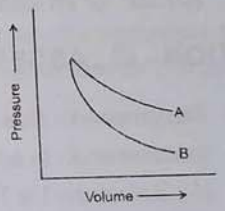
(A) The randomness of the universe decreases

(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) $\Delta G°$ 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

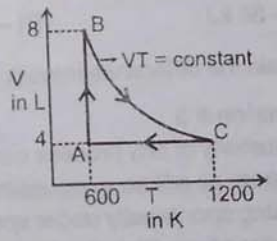
6.21 **Statement-1 :** Heat of neutralization of HCl and NaOH is same as that of H_2SO_4 with NaOH.
Statement-2 : HCl, H_2SO_4 and NaOH are all strong electrolyte.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2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

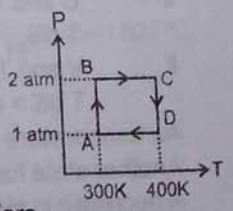


6.23 Heat supplied to the gas during the process AB is :
(A) 1200R ℓn2 (B) 1800R
(C) 1200R (D) Zero

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.