

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2019

FIRST YEAR (BATCH 2019-22)

INDUSTRIAL CHEMISTRY (Honours)

Paper : II [CC2]

Date : 13/12/2019

Time : 11 am – 1 pm

Full Marks : 50

Answer any five questions of the following:

[5×10]

1. a) Isothermal reversible work of expansion for an ideal gas is greater than that for an irreversible process between the same initial and final state – Explain. [4]
b) K_{eq} for the reaction $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$ is 0.531 at 298K. Calculate $E_{Ag^+/Ag}^0$. (Given $E_{Fe^{3+}/Fe^{2+}} = 0.77V$) [2]
c) Sketch the plot of conductometric titration of HCl with NaOH and explain it. [2]
d) Ionic conductivity at infinite dilution of Al^{3+} and SO_4^{2-} ions are $189 \text{ S cm}^2 \text{ eq}^{-1}$ and $160 \text{ S cm}^2 \text{ eq}^{-1}$ respectively. Calculate the equivalent conductance of $Al_2(SO_4)_3$ at infinite dilution. [2]
2. a) The mobility of NH_4^+ ion is $7.623 \times 10^{-8} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$. Calculate:
(i) The ionic conductivity of the NH_4^+ ion.
(ii) The velocity of the ion if 15.0 V is applied across electrodes 25 cm apart. [2+2]
b) 3 mol $H_2(g)$ and 1 mol $N_2(g)$ are in two compartments of equal volume respectively at same temperature. What is the value of ΔS_{mix} when partition between the compartments is removed. (Assume perfect gas behavior). [3]
c) Show that $\mu_{JT} = V / C_p (\alpha T - 1)$ where α is the temperature co-efficient of volume expansion. [3]
3. a) Efficiency of a carnot engine working between 127°C and $t^\circ\text{C}$ (where $t > 127^\circ\text{C}$) is 0.5. Calculate t and heat rejected to the surrounding when work done by the engine per cycle is 100J. [2]
b) Point out the characteristics of a first and second order phase transition and give their corresponding plots. [3]
c) A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 ml to 375 ml at a constant temperature of 37.0°C . What is the value of q , w and ΔU for this process? [3]
d) Heat capacity at constant pressure is greater than heat capacity at constant volume. Why? [2]
4. a) Define "ionic mobility". Derive a relation between ionic mobility and ionic conductance (λ) at infinite dilution. [4]
b) Categorize the following properties of a thermodynamic system extensive or intensive?
Specific heat capacity, internal energy, molar volume & chemical potential. [2]
c) Proof that $(\partial S / \partial V)_T = (\partial P / \partial T)_V$. [2]
d) Prove that for an ideal gas adiabatic slope is steeper than isothermal for P vs. V diagram. [2]

5. a) Calculate the change in entropy for the process: Benzene (268 K, liq) to Benzene (268 K, Solid) Given: Normal freezing point of benzene 278 K; $\Delta H(\text{fusion}) = 9956 \text{ J/mole}$; $C_p(\text{liq}) = 127.3 \text{ Jmol}^{-1}\text{K}^{-1}$; $C_p(\text{solid}) = 123.6 \text{ Jmol}^{-1}\text{K}^{-1}$. [4]
- b) Why the equivalent conductance of weak electrolytes at infinite dilution values cannot be obtained by plotting equivalent conductance vs. $\sqrt{C}$ where for strong electrolyte it obtained from the plot – Explain with proper justification. [3]
- c) Calculate the E^0 for the cell $\text{Pt}|H_2|H^+(aq)||Fe^{3+}(aq)|Fe$
- Given at 298K, $E^0_{Fe^{2+}/Fe} = -0.44V$ and $E^0_{Fe^{3+}/Fe^{2+}} = 0.77V$. [3]
6. a) The decomposition of acetaldehyde was studied in the gas phase at 791 K. The results of two measurements are:

Initial Conc. (mol/L)	9.72 (10^{-3})	4.56 (10^{-3})
Half-life(s)	328	572

- i) What is the Order of the reaction?
- ii) Calculate the rate constant for the reaction with proper unit. [3]
- b) A drug product is known to be ineffective after it is decomposed 25%. After 20 months, the original concentration was dropped from 5.0 mg/ml to 4.2 mg/ml. Assuming the decomposition is first order, what should be the expiration time on the label? [3]
- c) Draw the Jablonski diagram showing each state and processes. State Franck-Condon principle and explain its role in Jablonski diagram. [4]
7. a) Show that $t_{1/2} = \frac{1}{[A]^{n-1}}$ for a reaction that is n th order in A ($n \neq 1$). [3]
- b) State Stark-Einstein Law of Photochemical equivalence. [2]
- c) Explain Steady state principle. Derive the overall rate equation for a parallel reaction where reactant A is simultaneously converted to B and C and the rate constants are k_1 and k_2 respectively. [2+3]
8. a) Consider a photochemical reaction $A \xrightarrow{h\nu} B + C$. when irradiated with light of wavelength 2537 Å during a certain period, the light energy absorbed = $3.436 \times 10^8 \text{ erg}$ and the number of moles of B formed = $3.64 \times 10^{-6} \text{ mole}$. Calculate the quantum yield. [3]
- b) The quantum yield for the decomposition of HI is 2 but after sometime it comes down from 2. Explain with proper mechanism. [3]
- c) Why chain inhibition step is occurred in HBr chain reaction? [2]
- d) Explain: HCl and HBr chain reactions are occurred but HI not. [2]

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