

CHEMISTRY-I

Full Marks - 70

Time - 3 Hours

The figures in the right hand margin indicate full marks for the questions.

Questions No. 1 is compulsory and any five from the rest.

Answer to all parts of a question must be written at one place only.

($h=6.626 \times 10^{-34}$ Js, $R=8.314 \text{ JK}^{-1}\text{mol}^{-1}$, $c=3 \times 10^8$ m/s, $m_u = 1.6605 \times 10^{-27}$ kg., $N = 6.023 \times 10^{23}$, $m_e = 9.1 \times 10^{-31}$ kg., $e=1.6 \times 10^{-19}$ C,

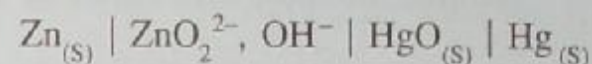
Atomic wt. : C = 12.00, O = 15.9994, H = 1.008, D = 2.016, F = 18.994)

P.T.O.

1. Answers in brief : 2×10

- (a) Give an example of oblate symmetric top molecule. Give the relationship between moment of inertia of this molecule.
- (b) Calculate the energy of the photon for a light of wavelength 400 nm.
- (c) Find the degree of dissociation of 0.01 M CH_3COOH solution. ($K_a = 7.2 \times 10^{-4}$)
- (d) At the triple of water, which of the following curve has a larger slope and why :
Solid \rightarrow vapour, Liquid \rightarrow vapour.
- (e) The plot of $\ln K$ vs $1/T$ gave a straight line and the slope was found to be -1.2×10^4 K. Calculate the activation energy.
- (f) The unit cell of gold has a FCC structure. Calculate the mass of a gold unit cell ($M_{\text{Au}} = 197$ gm/mol).
- (g) Heat of neutralization of NH_4OH and CH_3COOH is -51.46 kJ/mol. Calculate $\Delta H_{\text{ion}}^\circ$ of NH_4OH (for strong acid and strong base $\Delta H_{\text{neut}} = -57.1$ kJ/mol)

(h) Write down the net cell reaction for :



- (i) Calculate the number of vibrational degree of freedom for CO_2 molecule.
- (j) Write down the reactions involved in a dry cell.
2. (a) Write the molecular orbital configuration of N_2 and NO molecule. Compare their stability and magnetic properties. 3
- (b) Calculate the voltage required to accelerate and electron to have a velocity of 1.87×10^9 m/s. What will be the deBroglie wavelength ? 3
- (c) Calculate the uncertainty in velocity for a colloidal particle with mass 6×10^{-16} kg., If the uncertainty in position is 1 nm. 2
- (d) Discuss the physical significance of ψ and ψ^2 . 2
3. (a) The force constants of HF and DF molecules are same i.e. 9.7×10^2 Nm^{-1} . Calculate the

zero point energy of DF molecule and compare the value with that of HF molecule.

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(b) The separation of lines in the microwave spectra of CO molecule was found to be 298 m^{-1} . Calculate the bond length of CO molecule.

3

(c) A compound with molecular formula XY_2 shows two IR active bands at 667 cm^{-1} (degenerate) and 2349 cm^{-1} . Speculate the structure of the molecule and assign the bands to its modes of vibrations.

3

4. (a) For the reaction $\text{I}_{2(g)} \rightleftharpoons 2\text{I}_{(g)}$, the equilibrium constant is 3.76×10^{-5} at 727°C . If one mole of I_2 is taken in a two litre flask, calculate the equilibrium concentrations of I_2 and I.

4

(b) Show that : $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

3

(c) Show that $W_{\text{rev.}} > W_{\text{irr}}$ for an ideal gas.

3

5. (a) If $V = f(P, T)$, then show that dV is an exact differential for an ideal gas.

2

(b) Two moles of an ideal gas at one atm. Pressure and 27°C undergoes the following processes ; (i) heat is absorbed at constant volume till the pressure is doubled. (ii) Isothermal and reversible expansion till the pressure is reduced to 0.8 atm. (iii) adiabatic compression till initial stage is achieved. Calculate ΔE , Q , W for the total cycle. ($C_v = 40 \text{ JK}^{-1} \text{ mol}^{-1}$.)

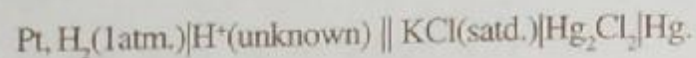
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(c) Calculate (i) ΔG^0 and (ii) minimum temperature at which the reaction is reversible for the reaction $\text{H}_2\text{S}_{(g)} + \text{O}_{2(g)} = \text{H}_2\text{O}_{(l)} + \text{SO}_{2(g)}$ from the following data :

$\Delta H_f^0(\text{H}_2\text{S}_{(g)}) = -20.15 \text{ KJ/mol}$, $\Delta H_f^0(\text{H}_2\text{O}_{(l)}) = -285.84 \text{ KJ/mol}$, $\Delta H_f^0(\text{SO}_{2(g)}) = -296.9 \text{ KJ/mol}$, $S_o(\text{O}_2) = 205.03 \text{ J/mol}$, $S_o(\text{H}_2\text{S}) = 248.53 \text{ J/mol}$, $S_o(\text{H}_2\text{O}) = 69.92 \text{ J/mol}$, $S_o(\text{SO}_2) = 248.53 \text{ J/mol}$.

4

6. (a) The emf of the following cell is 0.445V :



Calculate the pH of the solution.

$$E^0_{\text{KCl}(\text{satd.})} = 0.2415\text{V.} \quad 3$$

- (b) The voltages of a cell at 25°C and 20°C are 0.35252 V and 0.35333 V respectively. If the number of electrons involved in the overall reaction is two, calculate ΔG^0 , ΔH^0 , ΔS^0 at 25°C. 4

- (c) The equilibrium constant for the reaction :
 $\text{Ag}(\text{s}) + \text{Fe}^{3+}(\text{aq}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Fe}^{2+}(\text{aq})$ is 0.335. Find out the standard electrode potential of $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$, if standard reduction potential of $\text{Ag}^+ | \text{Ag}$ is 0.799 V. 3

7. (a) Find out the order of the reaction

$\text{A} + 2\text{B} \rightarrow \text{C} + \text{D}$ from the following data :

Rate ($\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$)	[A] ($\text{mol} \cdot \text{dm}^{-3}$)	[B] ($\text{mol} \cdot \text{dm}^{-3}$)
0.0032	0.1	0.1
0.0096	0.3	0.1
0.0064	0.1	0.2

Which of the following mechanism agree with the rate law ?

- (i) $2\text{A} \rightarrow \text{A}_2, \text{A}_2 + \text{B} \rightarrow \text{C} + \text{D}$
 (ii) $\text{A} + \text{B} \rightarrow \text{E}, \text{E} + \text{B} \rightarrow \text{C} + \text{D}$ 4
- (b) The values of rate constants for a reaction at 356°C and 443°C are $3 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $2.5 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively. Calculate E_a for forward and backward reaction if H is 16.32 kJ/mol. 4

- (c) Differentiate between catalytic poisoning and negative catalyst with example. 2
8. (a) Find out the pH of a buffer solution containing 0.2 M formic acid and 0.1 M sodium formate solution. ($K_a = 1.8 \times 10^{-4}$). 3
- (b) Draw a neat sketch and discuss the equilibrium phase diagram of water system. 3
- (c) Predict the kind of transition taking place in (i) Cl_2 molecule and (ii) carbonyl group in electronic spectroscopy. 2
- (d) What are the coordination numbers of each ion present in rutile TiO_2 molecule at ordinary temperature and pressure ? 2