2021

CHEMISTRY — HONOURS

Paper : CC-5

Full Marks : 50

The figures in the margin indicate full marks. Candidates are required to give their answers in their own words as far as practicable.

Answer question no. 1 and any eight questions from the rest. (Q. 2 to Q. 13)

- 1. Answer any ten questions from the following :
 - (a) What is Debye–Falkenhagen effect?
 - (b) What do you mean by the standard state of a real gas?
 - (c) Despite the fact that alternate current (A.C.) is applied to determine the conductance of a solution, why the platinum electrodes are platinized?
 - (d) Show that $\left(\frac{\partial S}{\partial T}\right)_P / \left(\frac{\partial S}{\partial T}\right)_V = \gamma$ (where γ is heat capacity ratio).
 - (e) 'The work needed to change an adiabatic system from one specified state to another specified state is the same however the work is done'- justify or criticize.
 - (f) Give a plausible mechanism of very high conductance of H⁺ in aqueous medium.
 - (g) Though fugacity has got unit (atm or bar) we write the following equation which contains logarithm of 'f':

$$\mu_i = \mu_i^0 + RT \ln f - \text{Justify.}$$

- (h) Which of the terms, ΔG , ΔH , ΔS , ΔS universe must be zero when ice melts at 273.15K and 1 atm?
- (i) In the light of entropy change, justify Planck-Kelvin statement.
- (j) What amongst L (conductance), K, and λ of an electrolytic cell is changed if the cell constant is changed?
- (k) Set up a cell where the following reaction takes place : $3Fe^{+2} = 2Fe^{+3} + Fe$.
- (l) If $(\Delta G^{o})_{T}$ is negative, then the reaction would always be spontaneous Comment.
- 2. (a) The value of $\Delta \overline{G}$ for the decomposition of one mole of H₂O (*l*) to H₂ (*g*) and O₂ (*g*) at 1 atm. and 298K is +237 KJmol⁻¹. Calculate the minimum voltage required to decompose one mole of H₂O (*l*) to H₂ (*g*) and O₂ (*g*) at 1 atm. and 298K by electrolysis.

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 1×10

- (b) Evaluate $\left(\frac{\partial \overline{H}}{\partial P}\right)_T$ for a gas whose equation of state is $P\overline{V} = RT + B(T)P$, where the parameter 'B' is only function of T. 3+2
- 3. (a) Show that the work involved in a reversible, adiabatic process using one mole of an ideal gas is given by :

$$\omega = \overline{C_{\nu}} T_1 \left[\left(\frac{P_2}{P_1} \right)^{R/C_p} - 1 \right]$$

where T_1 being the initial temperature, and P_1 and P_2 being the initial pressure and final pressure respectively.

- (b) Distinguish between 'bond energy' and 'bond dissociation energy'. 3+2
- 4. (a) The mean activity coefficient of a 0.10 mol kg⁻¹ CaCl₂ (aq) solution is 0.524 at 298K. What is the percentage error in the value predicted by the Debye-Hückel limiting law? Why this law is called limiting? [Given, A = 0.51 at 298K]
 - (b) Efficiency of a Carnot engine can be increased either by increasing the temperature of the higher-temperature reservoir or by decreasing the temperature of the lower-temperature reservoir. Show which case is more efficient. 3+2
- 5. (a) Calculate ΔG and ΔS for mixing of 1 mole of helium, 2 mole of argon, and 3 moles of krypton at 298K and 1 atm. Assume ideal behaviour of the gases.
 - (b) State the chemical potential difference (qualitatively), if any, for the following pairs of the substances :
 - (i) $H_2O(l)$ at 298.15K and 1 atm vs. $H_2O(g)$ at 298.15K and 1 atm.
 - (ii) $H_2O(s)$ at 273.15K and 1 atm. vs. $H_2O(l)$ at 273.15K and 1 atm. 3+2
- 6. (a) For ozone at 298K, $\Delta G_{f}^{o} = 163.43 \text{ KJ mol}^{-1}$. Compute the equilibrium K_p for the reaction :

$$3O_2$$
 (g) $\Longrightarrow 2O_3$ (g) at 298K

Assuming that the advancement at equilibrium, ξe , is very much less than unity. Show that

$$\xi e = \frac{3}{2} \sqrt{P.K_P}$$
 (let the original number of moles of O₂ be 3, and that of O₃ be zero).

(b) All adiabatic process are iso-entropic — Comment.

3+2

(2)

7. (a) Find an expression for the fugacity of a gas obeying the equation $P = \frac{RT}{V_m - b}$ and

hence
$$Z = 1 + \frac{bP}{RT}$$
.

Estimate the fugacity for the gas at 10 atm and 298 K. [Given 'b' = 3.707×10^{-2} L mol⁻¹;

$$\ln\phi = \int_{0}^{P} \left(\frac{Z-1}{P} dP\right)$$
]. All terms have got usual significance.

- (b) For a certain reaction, ΔG (in J mol⁻¹) = $14.0 + 7.0 \ln T 72.0T$. Compute ΔS of the reaction at 27°C.
- **8.** (a) Prove the following relation :

$$\left(\frac{\partial H}{\partial V}\right)_T = -V^2 \left(\frac{\partial P}{\partial T}\right)_V \left[\frac{\partial \left(\frac{T}{V}\right)}{\partial V}\right]_P$$

(b) The Joule-Thomson coefficient of a van der Waals gas is given by the expression :

$$\mu_{J,T} = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right]$$

- (i) State if H_2 gas can be liquefied at all.
- (ii) Pre-cooled van der Waals gases are more effective to be used for Joule-Thomson cooling - explain. 3+2
- 9. (a) Show that the value of ΔH for the adiabatic expansion of a perfect gas may be calculated by integration of dH = VdP, and evaluate the integral for reversible adiabatic expansion.
 - (b) Show that for a real gas undergoing the Joule–Thomson expansion, $\Delta S_{Total} > 0$. 3+2
- 10. (a) The molar enthalpy of vaporization of benzene at its normal boiling (80.09°C) is 30.72 KJ mol⁻¹. Assuming that $\Delta_{vap} \overline{H}$ and $\Delta_{vap} \overline{S}$ being constant at their values at 80.09°C, calculate the value of $\Delta_{vap} \overline{G}$ at 75°C, 80.09°C and 85°C. Interpret the result physically.
 - (b) Discuss briefly the differential heat of solution.
- (a) Will the conductometric titration curve for titration of H₂SO₄ and oxalic acid separately with NaOH be same? Explain with diagram.
 - (b) Find the pH and degree of hydrolysis of a salt of a weak acid (Ka = 1.8×10^{-5}) and strong base if concentration of salt is 0.01M in aqueous solution, after deducing the necessary expressions using exact calculations. 2+3

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3+2

(3)

3+2

- 12. (a) Determine the solubility product of AgCl at 298K using the following cell : Ag(s) | AgCl(s) | Cl⁻ || Ag⁺ | Ag(s)[Given : $E^{o}_{Ag^{+}/Ag} = +.799V$, $E^{o}_{Ag/AgCl/Cl^{-}} = +.2223 v$ at 298K]
 - (b) The standard potential of Cu | Cu²⁺ and Cu / Cu⁺ are 0.337V and 0.530V respectively. Find out the equilibrium constant for the reaction $2Cu^+ \rightleftharpoons Cu^{2+} + Cu$. 2+3

(4)

- 13. (a) Can you use quinhydrone electrode above pH = 8? Explain.
 - (b) Write down the cell reaction and calculate the potential of the cell : $Cl_2 (P = 1 \text{ atm})/NaCl (Soln)/Cl_2 (P = 0.1 \text{ atm})$. Will the cell reaction be spontaneous? 2+3