

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 : 1×10

- (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  $\left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial S}{\partial T}\right)_V = \gamma$  (where  $\gamma$  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 ‘ $f$ ’ :

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

(h) Which of the terms,  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta S$  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  $\lambda$  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  $(\Delta G^0)_T$  is negative, then the reaction would always be spontaneous – Comment.

2. (a) The value of  $\Delta \bar{G}$  for the decomposition of one mole of  $H_2O(l)$  to  $H_2(g)$  and  $O_2(g)$  at 1 atm. and 298K is  $+237 \text{ KJmol}^{-1}$ . Calculate the minimum voltage required to decompose one mole of  $H_2O(l)$  to  $H_2(g)$  and  $O_2(g)$  at 1 atm. and 298K by electrolysis.

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- (b) Evaluate  $\left(\frac{\partial \bar{H}}{\partial P}\right)_T$  for a gas whose equation of state is  $P\bar{V} = RT + B(T)P$ , 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 :

$$w = \bar{C}_v T_1 \left[ \left( \frac{P_2}{P_1} \right)^{\frac{R}{\bar{C}_p}} - 1 \right]$$

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  $0.10 \text{ mol kg}^{-1}$   $\text{CaCl}_2$  (aq) solution is  $0.524$  at  $298\text{K}$ . 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  $298\text{K}$ ]
- (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  $\Delta G$  and  $\Delta S$  for mixing of 1 mole of helium, 2 mole of argon, and 3 moles of krypton at  $298\text{K}$  and  $1 \text{ atm}$ . Assume ideal behaviour of the gases.
- (b) State the chemical potential difference (qualitatively), if any, for the following pairs of the substances :
- (i)  $\text{H}_2\text{O} (l)$  at  $298.15\text{K}$  and  $1 \text{ atm}$  vs.  $\text{H}_2\text{O} (g)$  at  $298.15\text{K}$  and  $1 \text{ atm}$ .
- (ii)  $\text{H}_2\text{O} (s)$  at  $273.15\text{K}$  and  $1 \text{ atm}$ . vs.  $\text{H}_2\text{O} (l)$  at  $273.15\text{K}$  and  $1 \text{ atm}$ . 3+2
6. (a) For ozone at  $298\text{K}$ ,  $\Delta G_f^\circ = 163.43 \text{ KJ mol}^{-1}$ . Compute the equilibrium  $K_p$  for the reaction :



Assuming that the advancement at equilibrium,  $\xi_e$ , is very much less than unity. Show that

$$\xi_e = \frac{3}{2} \sqrt{P \cdot K_p} \quad (\text{let the original number of moles of } \text{O}_2 \text{ be } 3, \text{ and that of } \text{O}_3 \text{ be zero}).$$

- (b) All adiabatic process are iso-entropic — Comment. 3+2

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

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

Estimate the fugacity for the gas at 10 atm and 298 K. [Given 'b' =  $3.707 \times 10^{-2}$  L mol<sup>-1</sup>;

$$\ln \phi = \int_0^P \left( \frac{Z-1}{P} dP \right)]. \text{ All terms have got usual significance.}$$

- (b) For a certain reaction,  $\Delta G$  (in J mol<sup>-1</sup>) =  $14.0 + 7.0 \ln T - 72.0T$ .

Compute  $\Delta S$  of the reaction at 27°C.

3+2

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<sub>2</sub> 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  $\Delta H$  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,  $\Delta S_{\text{Total}} > 0$ . 3+2

10. (a) The molar enthalpy of vaporization of benzene at its normal boiling (80.09°C) is 30.72 KJ mol<sup>-1</sup>. Assuming that  $\Delta_{\text{vap}} \bar{H}$  and  $\Delta_{\text{vap}} \bar{S}$  being constant at their values at 80.09°C, calculate the value of  $\Delta_{\text{vap}} \bar{G}$  at 75°C, 80.09°C and 85°C. Interpret the result physically.

- (b) Discuss briefly the differential heat of solution. 3+2

11. (a) Will the conductometric titration curve for titration of H<sub>2</sub>SO<sub>4</sub> 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 ( $K_a = 1.8 \times 10^{-5}$ ) and strong base if concentration of salt is 0.01M in aqueous solution, after deducing the necessary expressions using exact calculations. 3+2

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12. (a) Determine the solubility product of AgCl at 298K using the following cell :



[Given :  $E_{\text{Ag}^+/\text{Ag}}^\circ = +.799\text{V}$ ,  $E_{\text{Ag}/\text{AgCl}/\text{Cl}^-}^\circ = +.2223\text{ v}$  at 298K]

- (b) The standard potential of  $\text{Cu} \mid \text{Cu}^{2+}$  and  $\text{Cu} / \text{Cu}^+$  are 0.337V and 0.530V respectively. Find out the equilibrium constant for the reaction  $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}$ . 2+3

13. (a) Can you use quinhydrone electrode above pH = 8? Explain.

- (b) Write down the cell reaction and calculate the potential of the cell :

$\text{Cl}_2$  (P = 1 atm)/NaCl (Soln)/ $\text{Cl}_2$  (P = 0.1 atm). Will the cell reaction be spontaneous? 2+3

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