2020

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 should be the criteria for a thermodynamic process to qualify as a *reversible* one?

(b) Arrange the following electrolytes in increasing order of their Λ_0 (equivalent conductance at infinite dilution) values :

NaCl, NaOH, HCl, LiCl

(c) Which law of thermodynamics is related to the concept of temperature of a system? State the law.

(d) Concentration is a mass dependent thermodynamic property. Yet it is an intensive property. Explain.

(e) Why is $\overline{C}_p$ of a gas greater than its $\overline{C}_v$?

(f) For an acid-buffer (HA/A^-) the pH is equal to the pK_a of the weak acid only when $[HA] : [A^-] = 2:1$. Criticize the statement.

(g) For a reversible isobaric process *only* $\Delta H = q$. Comment.

(h) If the equivalent conductance at infinite dilution of an aqueous solution of $CaCl_2$ at a particular temperature be Λ^o_{eq}, then what will be the Λ^o_m (molar conductance) at the same temperature? – Justify.

(i) What will be the value of K_c / K_p for the reaction $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ in terms of RT? (Assume ideal gas behaviour).

(j) Under what condition(s) do the transport numbers $t_{\oplus}$ and $t_{\ominus}$ of a uni-univalent electrolyte approach equality?

(k) Why are glass electrodes kept immersed in a slightly acidic solution when not in use?

(l) What is the basic criterion of choosing a uni-univalent electrolyte in a salt-bridge in order to minimize the liquid junction potential?

2. (a) Show that the reversible work of expansion of an ideal gas is greater in magnitude than in the irreversible case.

(b) 1·00 moles of an ideal gas ($\overline{C}_p = 2{\cdot}5R$) at 1·0 atm and 300 K undergoes a reversible change so that the volume is doubled. The enthalpy change is 2078·5 $Jmol^{-1}$ and the heat absorbed is 1675 $Jmol^{-1}$. Calculate the final temperature, final pressure and the work done during the process. 2+3

3. The heat of combustion of methane is (–881·25) k J·mol^{-1} at 298 K. Calculate the *adiabatic* flame temperature when one mole of methane is completely burnt in air (4 : 1 mole ratio of $N_2 : O_2$), in the theoretical ratio.

Data : $H_2O(l) \rightarrow H_2O(g);\ \Delta H^\circ(298K) = 43{\cdot}60 kJ\cdot mol^{-1}$

$\overline{C}_p\,(CO_2) = 26{\cdot}00 + 43{\cdot}5 \times 10^{-3}T$

$\overline{C}_p\,(H_2O, g) = 30{\cdot}36 + 9{\cdot}61 \times 10^{-3}T$

$\overline{C}_p\,(N_2) = 27{\cdot}30 + 5{\cdot}23 \times 10^{-3}T$; in units of $J\cdot K^{-1}\cdot mol^{-1}$. 5

4. (a) For an expansion process involving a gas the quantity PV^{γ} = constant. Identify the nature of the gas and the characteristics of the process. [$\gamma = C_p/C_v$].

(b) Draw the P–V and T–S diagram of an ideal gas undergoing a Carnot cycle. What do the enclosed areas of the diagram signify in the two cases? Justify your answer. 2+3

5. (a) For an ideal gas, the absolute entropy (S) is expressed as $S = \frac{n}{2}\left(\alpha + 5R\ln\frac{U}{n} + 2R\ln\frac{V}{n}\right)$ where n is the number of moles, α is a constant and other symbols have their usual significance.

Calculate $\overline{C}_V$ and comment on the atomicity of the gas.

(b) Calculate the difference between ΔG and ΔA at 27ºC for the reaction (P = 1 atm)

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)\,.$$ 3+2

6. (a) Show that $(\partial u / \partial V)_T = 0$ for a gas obeying the equation-of-state $P(V - nb) = nRT$. (Assume the relevant Maxwell relation).

(b) One mole of supercooled water at (–8ºC) and 1 atm pressure turns into ice at (–8ºC). Calculate the entropy change of the system, surroundings and the net entropy change. Heat capacity of water and ice, at 1 atm, may be taken as 75·42 $JK^{-1}mol^{-1}$ and 37·20 $JK^{-1}mol^{-1}$ respectively.

ΔH (fusion) = 6008 $Jmol^{-1}$, at 273 K. 2+3

7. (a) Show that for the i-th component in a mixture $(\partial\mu_i / \partial P)_{T,n} = \overline{V_i}$

(b) Consider the reaction : $H_2(g) + I_2(g) \rightarrow 2HI(g)$. If there are 2 moles of H_2, 1 mole of I_2 and 0 moles of HI present at the time of start, express the free energy of a reaction in terms of the degree of advancement, ξ. If the standard free energy change of a reaction is positive, can the reaction proceed in the forward direction? Comment. 2+3

8. (a) Starting from the van't Hoff reaction isotherm show that the equilibrium for an exothermic reaction shifts to the right on lowering of temperature.

(b) Dinitrogen trioxide dissociates according to the equation $N_2O_3(g) \rightleftharpoons NO_2(g) + NO(g)$. At 25ºC, 1 atm pressure (total), the degree of dissociation is 0·30. Calculate $\Delta_r G^o$ for the reaction at 298 K. 2+3

9. A Hittorf cell fitted with silver-silver chloride electrodes, is filled with HCl solution that contains 0·3856mg HCl/gram of water. An electric current of 2 mA is passed through the solution for exactly 180 minutes. At the end of electrolysis the cathode solution weighs 51·7436 g and contains 0·0267 g HCl. The anode solution weighing 52·0461 g contains 0·0133 g HCl. What is the transport number of $H^{\oplus}$? 5

10. (a) For a strong electrolyte like KCl, depict graphically the variation of specific conductance and equivalent conductance with concentration. Explain the plots.

(b) Calculate the mean ionic activity coefficient at 25ºC of a 0·001 molar solution of $K_3\,Fe(CN)_6$ in water. [A = 0·51, at 25ºC] 3+2

11. (a) Derive the expression for the pH, in case of hydrolysis of a salt of weak acid and strong base, using an exact treatment.

(b) Find out the magnitude of K_w (the ionic product of water) at 25ºC.

[Given that $E^o(H_2 / OH^-) = -0{\cdot}83$ V] 3+2

12. (a) Set up the electrochemical cell where the following process takes place :

$$ZnCl_2(a_1) \rightarrow ZnCl_2(a_2)$$

(b) You are supplied with 0·1 (N) NH_4OH and 0·1 (N) HCl solutions. Show how you will use these solutions to prepare 100 ml of a buffer solution of pH = 9.0 (K_b for $NH_4OH = 2\times10^{-5}$). 3+2

13. (a) Explain the principle of determination of pH of a buffer solution using the quinhydrone electrode.

(b) The solubility product of a sparingly soluble salt AB_2 is $7{\cdot}47\times10^{-9}$ at 288 K and $1{\cdot}39\times10^{-8}$ at 298 K. Calculate the molar heat of solution of the salt. 3+2