2022

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*** from the rest.

1. Answer ***any ten*** questions from the following : 1×10

(a) Show that the volume $V = f(P, T)$ for a fixed amount of ideal gas is a state function.

(b) Justify that absolute zero temperature cannot be attained since efficiency of a reversible Carnot engine must be less than 1.

(c) State whether the derivatives are extensive or, intensive $\left(\frac{\partial V}{\partial T}\right)_P, \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$.

(d) State with reason what will happen (in terms of cooling or, heating) if H_2 gas is expanded adiabatically in a closed system.

(e) Is Hess's law a corollary of the 1st law of thermodynamic?

(f) What is meant by an 'electrode reversible with respect to an ion'?

(g) The entropy of a closed system can never decrease— justify or, criticize.

(h) Show that the mean ionic activity ($a\pm$) of ions with respect to a solution of an electrolyte K_3PO_4 in water, is 2.28 C$\gamma\pm$ (C = Concentration), where $\gamma\pm$ is the mean ionic activity coefficient.

(i) Explain why the amide ion in liquid ammonia has abnormally high transport number.

(j) The glass electrode functions only in aqueous solutions— justify or, criticize.

(k) If 5 mol dm^{-3} of NaOAc and 5 mol dm^{-3} of AcOH are mixed, pH should be equal to Pk_a. — Comment if you disagree.

2. (a) The reaction, Reactants $(T_0, P) \rightarrow$ Products (T_f, P) is carried out under adiabatic condition and occurs in following two steps.

Step I : Reactants $(T_0, P) \rightarrow$ Products (T_0, P) $\Delta_r H_{T_0}$

Step II : Reactants $(T_0, P) \rightarrow$ Products (T_f, P) $\Delta_r H_2$

(i) Show that $T_f = -\frac{\Delta_r H_{T_0}}{C_P(\text{products})} + T_0$

Assume that C_P (reactants) and C_P (products) are independent of temperature.

(ii) Justify T_f is adiabatic flame temperature.

(b) Construct a cell for the overall cell reaction : $Pb(s) + 2AgCl(s) + 2I^-(aq) \rightleftharpoons 2Ag(s) + PbI_2(s) + 2Cl^-(aq)$. 3+2

3. Ideal gas (1 mol, 298*K*, V) $\xrightarrow{\text{Free expansion}}$ Ideal gas (1 mol, 298*K*, 2V)

$$\begin{tikzcd}\text{Ideal gas (1 mol, 298}K\text{, V)} \arrow[r, "\text{Free expansion}"] & \text{Ideal gas (1 mol, 298}K\text{, 2V)} \arrow[l, bend left, "\text{Reversible}"]\end{tikzcd}$$

(i) Calculate $\oint \frac{dQ}{T}$ for the cycle.

(ii) Calculate ΔS_{cycle}, $\Delta S_{forward}$ and $\Delta S_{backward}$

(iii) Show that $\Delta S_{forward} \neq \frac{Q_{forward}}{T}$. 5

4. (a) 0.5 mole water at 1 atm pressure undergoes the process : $H_2O(l, -10°C) \rightarrow H_2O(s, -10°C)$. Compute ΔS for the process from the following data : Specific heat capacity of water and ice over the temperature range is 1.0 and 0.5 cal. $deg^{-1}g^{-1}$ respectively; latent heat of fusion of ice is 80.0 $cal.g^{-1}$ at 0°C. Comment on the ΔS of surrounding and universe.

(b) Graphically show that equivalent conductance at infinite dilution values can be obtained by plotting equivalent conductance vs. $\sqrt{C}$ for strong electrolytes but not for weak electrolytes. 3+2

5. (a) Using Le Chatelier principle, establish the following relation :

$\left(\frac{\partial \xi_{eq}}{\partial T}\right)_P = \frac{\Delta H}{TG''_{eq}}$ & $\left(\frac{\partial \xi_{eq}}{\partial P}\right)_T = \frac{-(\Delta vg)RT}{P\,G''eq}$ (for an ideal gas, Δvg is the difference between number of moles of gaseous products and reactants.)

(b) Comment on the sign of G''_{eq}. (where terms have their usual meaning) 5

6. Develop equations for the reversible isothermal *P-V* work of a gas that obeys (i) van der Waals equation with $a = 0$ and (ii) van der Waals equation with $b = 0$. Calculate the work done by the gas for doubling the volume for case (i) where $b = 0.05$ $Lmol^{-1}$, for case (ii) where $a = 4.2L^2$ atm mol^{-2} and also for ideal gas. Take $V_i = 1L$, $n = 1$ mol, $T = 298$ K.

Explain the reason of the order W(i) < W(ideal) < W(ii). 5

7. (a) When 1 mol glucose is oxidized at 298 K the following reaction is observed :

$C_6H_{12}O_6(S) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

Given $\Delta U_r = -2808$ kJ mol^{-1}

$\Delta_r S = +182.4$ K^{-1} mol^{-1}

for the above reaction at 298 K. How much of this energy change can be extracted as :

(i) heat at constant pressure

(ii) work

(iii) compare the values of ΔU and maximum work available from the reaction and comment on the data.

(b) Show that $\left[\dfrac{\partial(\Delta \mathrm{G/T})}{\partial(1/\mathrm{T})}\right]_{\mathrm{P}} = \Delta \mathrm{H}\_$. 3+2

8. (a) 'The standard state of a real gas is a hypothetical state in which the gas is at a pressure p^{o} and behaving perfectly'— how do you justify the validity of this assumption?

(b) The Helmholtz energy of one mole of a gas is expressed as

$$A = -\left(a/V\right) - RT\ln\left(V-b\right) + f(T)$$

where 'a' and 'b' are constants. Set up an expression for the pressure of the gas. 3+2

9. The emf of the cell with transference :

$$H_2 \mid HCl\left(a\pm = 0.00905\right) \vdots HCl\left(a\pm = 0.0175\right) \mid H_2$$

at 298 K is 0.028 V. The corresponding cell without transference has an emf of 0.01696 V. Calculate the transference number of H^+ ion and the value of the junction potential. 5

10. (a) For a given aqueous solution of sucrose — using the integrated Gibbs-Duhem equation — show that.

$d\ln\gamma_B = -\left(\dfrac{x_A}{x_B}\right) d\ln\gamma_A$, at constant T & P.

γ_A and γ_B being the activity coefficients of water and sucrose, respectively.

(b) Using the expression of coefficient of performance $[(\mathrm{COP})_{\mathrm{max}}]$ of refrigerator, justify that attaining absolute zero leads to the violation of perpetual motion of first kind. 2+3

11. (a) The pk values of H_3PO_4 are : $pk_1 = 2.1$, $pk_2 = 7.2$ and $pk_3 = 12.0$. Calculate the pH of 0.1M aqueous solution of Na_2HPO_4.

(b) The solubility product increases with ionic strength. Explain why. 3+2

12. (a) An ideal operating Carnot engine operates between two heat reservoirs at 1000°C and 300°C. Another heat engine operates within the same temperature limit. In the later engine, 2/5th of the heat absorbed at the higher temperature is wasted as heat discharged at the lower temperature. State Carnot's theorem-1 and analyze whether it is possible to construct such an engine in reality or not?

(b) A solute is dissolved in a mixture of two immiscible liquid solvents A and B. If in B, the solute gets dimerised, then from thermodynamic consideration, show that the ratio $\dfrac{C_A}{\sqrt{C_B}}$ will be constant at a particular temperature. [C_A & C_B denotes concentrations of solute in respective solvent.] 2½+2½

13. (a) Set up the cell and calculate the equilibrium constant of the reaction between Fe^{+2} and MnO_4^- in 1M acetic acid medium.

Given : $E^{\circ}_{Fe^{+3}/Fe^{+2}} = 0.77$ volt

$E^{\circ}_{MnO_4^-/Mn^{+2}/H^+} = 1.51$ volt, at 298 K

(b) 10 ml of 0.1M NaOH is added to solution (i) and (ii).

Solutions (i) and (ii) are taken in conductivity cells of cell-constant 1.00 cm^{-1}.

		Observations
(i)	10 ml of 0.1(M) CH_3COOH + 10 ml of 0.1(M) NaOH	Conductance of the solution changed from A Siemens to B Siemens
(ii)	10 ml of 0.1(M) HCl+10 ml of 0.1(M) NaOH	Conductance of the solution changed from C Siemens to D Siemens

Justify that $A - B < 0$ and $C - D > 0$.

3+2