

2022

## CHEMISTRY — HONOURS

Paper : CC-5

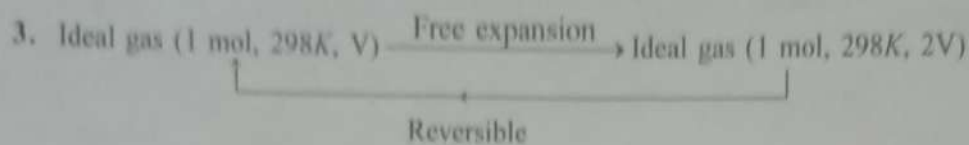
Full Marks : 50

*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
- Show that the volume  $V=f(P, T)$  for a fixed amount of ideal gas is a state function.
  - Justify that absolute zero temperature cannot be attained since efficiency of a reversible Carnot engine must be less than 1.
  - State whether the derivatives are extensive or, intensive  $\left(\frac{\partial V}{\partial T}\right)_P, \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ .
  - State with reason what will happen (in terms of cooling or, heating) if  $H_2$  gas is expanded adiabatically in a closed system.
  - Is Hess's law a corollary of the 1st law of thermodynamic?
  - What is meant by an 'electrode reversible with respect to an ion'?
  - The entropy of a closed system can never decrease— justify or, criticize.
  - 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.
  - Explain why the amide ion in liquid ammonia has abnormally high transport number.
  - The glass electrode functions only in aqueous solutions— justify or, criticize.
  - If  $5 \text{ mol dm}^{-3}$  of NaOAc and  $5 \text{ mol dm}^{-3}$  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 ( $T_f, P$ )  $\Delta_r H_2$
- Show that  $T_f = -\frac{\Delta_r H_{T_0}}{C_p(\text{products})} + T_0$   
Assume that  $G_p$  (reactants) and  $C_p$  (products) are independent of temperature.
  - 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

Please Turn Over



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

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

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

5

4. (a) 0.5 mole water at 1 atm pressure undergoes the process :  $\text{H}_2\text{O}(l, -10^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -10^\circ\text{C})$ . Compute  $\Delta S$  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.  $\text{deg}^{-1}\text{g}^{-1}$  respectively; latent heat of fusion of ice is 80.0 cal. $\text{g}^{-1}$  at  $0^\circ\text{C}$ . Comment on the  $\Delta S$  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 :

$$\left(\frac{\partial \xi_{eq}}{\partial T}\right)_P = \frac{\Delta H}{T G''_{eq}} \quad \& \quad \left(\frac{\partial \xi_{eq}}{\partial P}\right)_T = \frac{-(\Delta v_g)RT}{P G''_{eq}}$$

(for an ideal gas,  $\Delta v_g$  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)

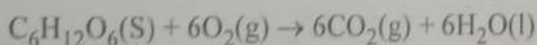
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6. Develop equations for the reversible isothermal  $P$ - $V$  work of a gas that obeys (i) van der Waals equation with  $a = 0$  and (ii) van der Waals equation with  $b = 0$ . Calculate the work done by the gas for doubling the volume for case (i)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

Explain the reason of the order  $W(i) < W(\text{ideal}) < W(\text{ii})$ .

5

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



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

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

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  $\Delta U$  and maximum work available from the reaction and comment on the data.

(b) Show that  $\left[ \frac{\partial(\Delta G/T)}{\partial(1/T)} \right]_p = \Delta H_-$ . 3+2

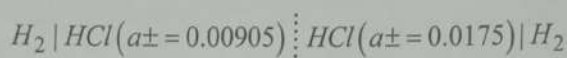
8. (a) 'The standard state of a real gas is a hypothetical state in which the gas is at a pressure  $p^\circ$  and behaving perfectly'— how do you justify the validity of this assumption?

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

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

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 :



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.

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

$\gamma_A$  and  $\gamma_B$  being the activity coefficients of water and sucrose, respectively.

(b) Using the expression of coefficient of performance  $[(COP)_{\max}]$  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  $1000^\circ C$  and  $300^\circ C$ . Another heat engine operates within the same temperature limit. In the later engine,  $2/5$ th 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  $\frac{C_A}{\sqrt{C_B}}$  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  $\text{Fe}^{+2}$  and  $\text{MnO}_4^-$  in 1M acetic acid medium.

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

$E_{\text{MnO}_4^-/\text{Mn}^{+2}/\text{H}^+}^\circ = 1.51$  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  $1.00 \text{ cm}^{-1}$ .

		Observations
(i)	10 ml of 0.1(M) $\text{CH}_3\text{COOH}$ + 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