

2022

CHEMISTRY — HONOURS

Paper : CC-5

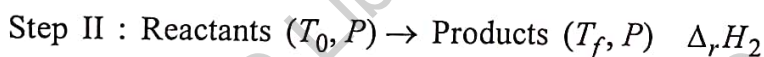
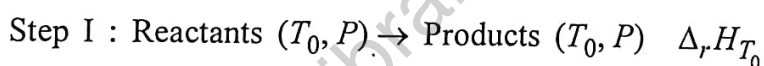
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Full Marks : 50

*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 γ_{\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 $\text{p}K_a$.
— 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.

(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 : $\text{Pb(s)} + 2\text{AgCl(s)} + 2\text{I}^-(\text{aq}) \rightleftharpoons 2\text{Ag(s)} + \text{PbI}_2(\text{s}) + 2\text{Cl}^-(\text{aq})$.

3+2

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X(3rd Sm.)-Chemistry-II/CC-5/CBCS

(2)

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

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

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

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

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 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. $\text{deg}^{-1}\text{g}^{-1}$ 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 :

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

(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 $b = 0.05 \text{ Lmol}^{-1}$, 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 $W(\text{i}) < W(\text{ideal}) < W(\text{ii})$. 5

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



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

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

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 ΔU 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

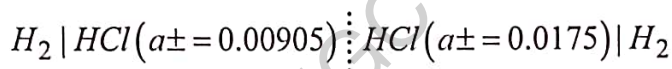
8. (a) 'The standard state of a real gas is a hypothetical state in which the gas is at a pressure p° and behaving perfectly'— how do you justify the validity of this assumption?

(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.

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

γ_A and γ_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 Fe^{+2} and 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 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 $C - D > 0$.