INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR
Mid-Autumn Semester Examination 2022-23
Department of Chemistry
Subject No. **CY11003** Subject Name: **Chemistry**
Date:__.12.2022 Session:____, Duration: 2 Hrs. Full Marks: 30

Write answers to the parts of each question together at one place.
Symbols carry their usual meaning. This question paper contains 6 questions, 2 pages.
No question will be entertained during the examination.

Gas constant (R) = 8.314 J K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1}; Faraday Constant (F) = 96500 C mol^{-1}

Question 1.

Choose the correct answer from the given options. **[1 x 5 = 5]**

(i) 3 moles of carbon dioxide gas absorb 1200 J of heat at constant volume to increase its temperature from 300 K to 400 K. The change in internal energy of the gas is
a. 400 J b. 3600 J c. 2400 J d. 1200 J

(ii) A Carnot heat engine operates with a source at temperature T_1 and a sink at temperature T_2. T_1 and T_2 can vary between 300 K and 1000 K, but $T_1 - T_2$ is always fixed at 100 K. The highest possible efficiency of such a Carnot engine is
a. 0.66 b. 0.33 c. 0.25 d. 0.10

(iii) The region inside the inversion curve has ____ Joule-Thomson coefficient and the region outside the inversion curve has ____ Joule-Thomson coefficient.
a. positive, positive c. negative, negative
b. negative, positive d. positive, negative

(iv) A process has reached equilibrium keeping T and V unaltered. The condition that is satisfied, is
a. $\Delta G = 0$ b. $\Delta G < 0$ c. $\Delta A = 0$ d. $\Delta A < 0$

(v) In the Nernst equation, $E = E^0 - \frac{RT}{nF} \ln Q$, the term Q can be replaced with the equilibrium constant K when
a. $E = E^0$ b. $\frac{RT}{nF} = 1$ c. $E = 0$ d. $E^0 = 1$

Question 2.

(a) Show that $U = G - P\left(\frac{\partial G}{\partial P}\right)_T - T\left(\frac{\partial G}{\partial T}\right)_P$ **[2]**

(b) 2 moles of an ideal gas at 45 °C are compressed adiabatically and reversibly from 75 litres to 20 litres. Calculate w, ΔU, and ΔH for the process. [Given: $C_{V,m} = 2.5\ R$ for the gas]. **[3]**

Question 3.

(a) Which of the quantities (ΔU, ΔH, ΔS, ΔG, and ΔA), is/are zero for

i. Joule-Thomson expansion of an ideal gas

ii. Carnot cycle

iii. the reaction between hydrogen and oxygen to form water at constant T and P [2]

(b) One mole of water vapor is compressed reversibly to liquid water at 373 K and 1 atm. Calculate ΔH, ΔS, ΔG, and ΔA for the process.

(Given: Consider water vapor as an ideal gas; the molar volume of water << molar volume of water vapor; The latent heat of vaporization of water is 540 cal g^{-1} and the latent heat of freezing of water is 80 cal g^{-1}). [3]

Question 4.

(a) Considering $S = f(T, P)$ and using an appropriate Maxwell relation, determine the variables that define X to complete the expression $TdS = C_p dT - XdP$. [2]

(b) (i) What is the entropy of mixing in J K^{-1} mol^{-1} of 112 g of oxygen and 56 g of nitrogen at 25 °C assuming they are ideal gases? (ii) Keeping the mass of oxygen constant, what is the mass of nitrogen required to achieve the maximum entropy of mixing? What is the value of the maximum ΔS_{mix} possible? (Molecular mass: Oxygen 32 g mol^{-1}; Nitrogen 28 g mol^{-1}). [3]

Question 5.

(a) The equilibrium constant of the reaction $2\ C_3H_6\,(g) \rightleftharpoons C_2H_4\,(g) + C_4H_8\,(g)$ fits the expression $\ln K = -1.04 - \frac{1088}{T} + \frac{1.51 \times 10^5}{T^2}$ in the range of 300 K to 600 K. Calculate the standard reaction enthalpy at 400 K. [2]

(b) For an isolated system with $S = S(V, U)$, show that two phases are in thermal equilibrium only if their temperatures are same, assuming the phases to be mechanically rigid. [3]

Question 6.

(a) Standard electrode potential of the couples $MnO_4^-|Mn^{2+}$ and $CO_2(g)|C_2O_4^{2-}$ at 25°C are 1.51 V and −0.49 V, respectively. (i) Design the cell and write the half-cell reactions and the net cell reaction. (ii) Calculate the ΔG^O and equilibrium constant (K_a) at 25°C and comment on whether the reaction can be used for quantitative estimation of oxalic acid by potassium permanganate. [2]

(b) Consider the cell $Zn(s)\,|\,ZnCl_2\,(aq, 0.005\ mol\ Kg^{-1})\,|\,Hg_2Cl_2(s)\,|\,Hg(l)\,|\,(Pt(s)$. Given $E^O\,(Zn^{2+}/Zn)$ = −0.7628 V and $E^0\,(Hg_2Cl_2\,|\,Hg)$ = +0.2676 V. The measured value of the cell potential is +1.2272 V at 25°C.

i) Write down the half cell and net cell reaction.

ii) Determine the reaction Gibbs free energy (in kJ mol^{-1}) $\Delta G_{reaction}$ and $\Delta G^O_{reaction}$.

iii) Given that $dE/dT = -4.52 \times 10^{-4}$ V K^{-1}, Calculate ΔS and ΔH of the reaction at 25°C. [3]

End of Question Paper