Birla Institute of Technology & Science, Pilani, Rajasthan – 333031

First Semester 2023-2024, Mid Semester Examination (**Open Book**)

Subject: Physical Chemistry -I (PC-1) **Course Code**: CHEM F211

Time: 90 minutes **Date:** 13/10/2023 **Max. Marks**: 60

Instructions to the students:

1. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. **In a derivation write all the intermediate steps. In case of missing steps, marks will be deducted.**
4. Write brief answers to the point with proper justifications.
5. Do not exchange your calculator.

Useful Data: C_P-C_V = R, R = 8.314 J mole^{-1} K^{-1} (2 cal mol^{-1} K^{-1}, 0.082 Lit atm mol^{-1} K^{-1}), 1 cal = 4.18 J, 1 litre = 1 dm^3, 1 atm = 760 torr = 1.01325×10^5 Pa, Latent heat of freezing of water is -80 cal/gm

Q1. (a) One mole of water vapor undergoing a cyclic process from an initial state at T = 250 K and P = 2 bar. The work required for this process is 450 J. Determine the amount of heat for this process. Also find out whether this heat will be absorbed or released by the system. [**3M**]

(b) Imagine a system which is surrounded by an adiabatic wall. The system consists of two parts 1 and 2. These two parts are separated by a movable, thermally conducting and impermeable wall. Both the parts are held at constant P and capable of performing P-V work only. Apply $\Delta H = q_P$ to the entire system and to each part to prove $q_1 + q_2 = 0$. Here q_1 and q_2 are the heat flow for part 1 and 2 respectively. **[3M]**

(c) For the temperature range 300-500 K and low to moderate pressure range, the molar heat capacity of oxygen is found to follow the equation $C_{P,m} = a + bT$ where $a = 6.15\ cal\ mol^{-1}K^{-1}$ and $b = 0.00310\ cal\ mol^{-1}K^{-2}$. A 2 mol of O_2 gas is heated reversible from 30^{0}C to 130^{0}C at a constant pressure P = 1 atm. Determine $q, w, \Delta U\ and\ \Delta H$ for this process. Assume ideal gas behavior for oxygen. Provide proper sign to q and w. **[6M]**

(d) A 2 mol of a perfect monoatomic gas undergoing the following processes

(i) $(2\ atm, 400K) \rightarrow (4\ atm, 600K)$ and (ii) $(30\ L, 500K) \rightarrow (50L, 500K)$. Determine the entropy change ΔS for each of these processes. The monoatomic gas has $C_{V,m} = 1.5R$ for all temperatures. **[5M]**

(e) For the vaporization of water establish the condition under which water will vaporize spontaneously. The enthalpy of vaporization is $\Delta H = 9590\ cal\ mol^{-1}$ and entropy of vaporization is $\Delta S = 26\ cal\ mol^{-1}K^{-1}$. **[3M]**

Q2. (a) For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2\ (g)$ at 40^{0}C and 1 atm, N_2O_4 is found to be 30% dissociated. Determine the K_P for this reaction. Determine the degree of dissociation of N_2O_4 if the reaction is performed at 10 atm and 40^{0}C. Show that the results agree with Le-Chatelier's principle. **[5M]**

(b) Find out for the following processes, which of ΔU, ΔH, ΔG, ΔA, ΔS, and ΔS_{univ} must be zero.

I. A hydrogen gas is burned in an adiabatic calorimeter of fixed volume.
II. A non-ideal gas is undergoing a Carnot cycle.
III. Ice is melted at 0^0C and 1 atm
IV. A non-ideal gas undergoes a Joule-Thomson expansion.

Provide a brief justification for your answer. **[4M]**

(c) The standard enthalpy of formation ΔH_f^0 and standard entropies (S^0) of the substances for the reaction $CuBr_2(s) \rightleftharpoons CuBr(s) + \frac{1}{2}Br_2(g)$ is given in the following table

Substance	$\Delta \boldsymbol{H_f^0}$ $(\boldsymbol{Kcal\ mol^{-1}})$	$\boldsymbol{S^0}$ $(\boldsymbol{cal\ mol^{-1}K^{-1}})$
$CuBr_2(s)$	-33.2	30
$CuBr(s)$	-25.0	22
$Br_2(g, 1\ atm)$	7.4	58.6

Find out the feasibility of this reaction at 200^0C and 300^0C. **[5M]**

(d) Suppose you climb a mountain where the atmospheric pressure is found to be 600 mm Hg. What would be the boiling point of water in that mountain? The latent heat of vaporization of water is 540 cal/gm. **[3M]**

(e) For each of the following conditions find out which phase of water has the lowest chemical potential (i) 25^0C and 1 atm, (ii) 25^0C and 0.1 torr and (iii) 0^0C and 500 atm. Justify your answer with proper argument. **[3M]**

Q3. (a) For ethane (C_2H_6) the second virial coefficient $B = -186\ cm^3\ mol^{-1}$ and third virial coefficient $C = 1.06 \times 10^4\ cm^6\ mol^{-2}$. A 28.8 gm of ethane is kept in 999 cm^3 cylinder at 25^0C. Use the virial equation to determine the pressure of ethane in that container. Neglect the higher order terms of the virial equation after C. Compare the result with ethane where we assume ideal gas behavior of ethane. Explain any difference in the result with proper justification. Molecular weight of ethane is 30.07 gm/mol. **[5M]**

(b) The vapor pressure of hexane and octane in their pure state are 1836 and 354 torr, respectively at 100^0C. The liquid mixture of these two compounds at a certain composition has a vapor pressure of 666 torr at 100^0C. Find the mole fractions of these compounds in the liquid mixture and in the vapor phase. Assume that the liquid mixture behaves like an ideal solution. **[5M]**

(c) A liquid mixture of hexane and heptane has a vapor pressure 95 torr at 30^0C. The mole fraction of hexane in the liquid and vapor phase is 0.31 and 0.56 respectively. Find the vapor pressure of pure heptane and hexane at 30^0C. State any approximation made. **[5M]**

(d) A 100 gm of toluene is mixed with 100 gm of benzene at 20^0C and 1 atm. Determine $\Delta_{mix}H, \Delta_{mix}V, \Delta_{mix}S, and\ \Delta_{mix}G$ for this mixing. Assume this as an ideal solution. **Provide the results in SI unit.** Molecular weight of benzene and toluene is 78.11 gm/mol and 92.14 gm/mol respectively. **[5M]**