

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

First Semester 2022-2023, Mid Semester Examination (**Open Book**)

Subject: Physical Chemistry -I (PC-1)

Course Code: CHEM F211

Duration: 90 minutes

Date: November 4, 2022

Max. Marks: 60

Note: Please check that the question paper is printed on both sides. Attempt all the questions. **Start answering each question on a fresh page and answer all parts of the question together.** Pencil should not be used. Symbols have usual meaning.

Do not scribble on the question paper.

Q1. (i) At 573 K temperature and 0.60 atm. pressure the Joule-Thomson coefficient of N_2 is given by $\mu = 0.0142 - 2.60 \times 10^{-4}P$. Assuming the equation to be independent of temperature near 300°C determine the temperature drop which may be expected on Joule-Thompson expansion of the gas from 60 atm. to 20 atm. **[3 M]**

(ii) For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$, from this information show that $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$. Here, U and C_V are the internal energy and specific heat at constant volume respectively. **[2 M]**

(iii) Establish the relation $C_p - C_V = \frac{\alpha^2 VT}{\beta}$, where α and β is the thermal expansivity and isothermal compressibility respectively. C_p and C_V is the specific heat at constant pressure and constant volume respectively. T is the temperature and V is the volume. **[5 M]**

(iv) Define Helmholtz free energy (A) and explain its physical significance in just one sentence. Calculate ΔA for the vaporization of 0.1 mole H_2O at 1.0 atm. pressure and 100°C . [Given, molar volume of $H_2O(l)$ at 100°C is 18.8 ml mol^{-1} and that of $H_2O(g)$ is 30.6 L mol^{-1} .] **[3 M]**

(v) One mole of an ideal monoatomic gas undergoes a reversible isothermal change at 25°C temperature and 1 atm pressure. The final volume of the gas after the change is twice its initial volume. Calculate heat (q), work done (w) and enthalpy change (ΔH) for this process. **[2 M]**

Q2. (i) Compare the thermodynamic efficiency of the following engines. (a) An engine operates between 1000 K and 300 K, and (b) a combination of two engines where the first engine operates between 1000 K and 600 K and waste heat is passed to the second engine working between 600 K and 300 K. **[4 M]**

(ii) A given mass of an ideal gas ($C_p = 5 \text{ Cal K}^{-1} \text{ mole}^{-1}$) at 27°C is compressed adiabatically and reversibly to one quarter of its volume. Calculate the temperature after compression. Here C_p is the specific heat at constant pressure. **[3 M]**

(iii) The coefficient of compressibility (β) of water at 298 K is $4.9 \times 10^{-6} \text{ atm}^{-1}$, over the pressure range 1 to 25 atm. Calculate the amount of work required to compress a 1 mole liquid water from 1 atm. to 25 atm. at 298 K temperature. Compare this work with work involved in the compression of 1 mole ideal gas from 1 atm. to 25 atm. at 298 K temperature. In both cases consider the process as reversible. Please provide the unit in Joules. (**Density of water is 1 gm/ml at 298 K**) **[3 M]**

(iv) One mole of an ideal gas with $C_V = 3.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ initially at 273 K temperature, 1 atm. pressure and 22.4 litre volume is put through the following reversible cycle:

(a) State 1 to state 2, heated at constant volume to twice the initial temperature.

(b) State 2 to state 3 expanded adiabatically until it is back to initial temperature.

(c) State 3 to state 1 compressed isothermally back to state 1.

Depict the cycle in V vs T diagram and calculate the amount of heat transfer (q), work (w) and change in internal energy (ΔU) for this cycle. Write in just one sentence what conclusion you can derive from the results. [5 M]

Q3. (i) Calculate the enthalpy change (ΔH) at 1500 K for the reaction $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$, given that, $\Delta H_{300K} = 115.0$ Kcal and the values of C_p ($\text{cal mol}^{-1} \text{K}^{-1}$) are for $H_2(g) = 6.95 - 0.0002 T$, $O_2(g) = 6.10 + 0.0032 T$ and $H_2O(g) = 7.19 + 0.0024 T$. Here C_p is the specific heat at constant pressure. [5 M]

(ii) Calculate the change in entropy, ΔS , when 10 gm of ice at 0°C is added to 50 gm of water at 40°C in an isolated system. The latent heat of fusion of ice is 79.7 cal gm^{-1} , the specific heat of water is $1 \text{ cal gm}^{-1} \text{K}^{-1}$. [4 M]

(iii) What is the boiling point of water at a place where the atmospheric pressure is 600 mm Hg? The latent heat of vaporization is 540 cal/gm . [3 M]

(iv) Calculate the change in Gibbs free energy (ΔG) when 36 gm of water initially at 100°C and 10 atm. pressure are converted to vapor at 100°C and 0.01 atm. pressure. Given density of water is 1 gm/ml and the vapor obeys ideal gas law. [3 M]

Q4. (i) Calculate the number of phases (P), components (C) and degrees of freedom (F) of the following systems at equilibrium.

(a) An aqueous solution of H_2SO_4 and CH_3COOH

(b) Water at its freezing point.

(c) A saturated solution of Na_3PO_4 which is completely dissociates into its component ions, contains an excess of salt. [5 M]

(ii) At 140°C , the vapor pressure of pure C_6H_5Cl is 939.4 mm of Hg and that of pure C_6H_5Br is 495.8 mm of Hg. If a liquid mixture of C_6H_5Cl and C_6H_5Br forms an ideal solution, what will be the composition of the mixture in the liquid phase, which boils at 140°C under 1 atm. pressure? What will be composition in the vapor phase at this temperature? [3 M]

(iii) The following standard enthalpies of formation (ΔH_f^0) and entropies (S^0) of the substances at 25°C are given

Substance	ΔH_f^0 (Kcal)	S^0 (Cal K^{-1})
Methane (CH_4 , g)	-17.89	44.5
Formaldehyde (HCHO, g)	-27.7	52.3
Ethyl alcohol (C_2H_5OH , l)	-66.4	38.4

Calculate the standard free energy change and equilibrium constant at 25°C and 1 atm. pressure for the reaction $CH_4(g) + HCHO(g) \rightleftharpoons C_2H_5OH(l)$. [4 M]

(iv) Calculate activity coefficient of Ba^{2+} and Cl^- in a 0.05 M aqueous solution of $BaCl_2$ at 25°C . Also determine the mean activity coefficient of $BaCl_2$ in this solution at 25°C . The Debye-Huckel constant, $A = 0.509$ for an aqueous solution at 25°C . [3 M]

***** The End *****