Birla Institute of Technology and Science Pilani –333031, Rajasthan
1st semester 2017-2018, Mid-Semester Test (Closed Book)
Course Title: Physical Chemistry I, Course No. CHEM F211
Max Marks: 60, Time: 1hr 30 mins, Date: 11.10.17

Answer all questions with proper units. Rough work can be done alongside your answer.

Useful Data: R = 8.314 J K^{-1} mol^{-1}, R = 82.06 cm^3 atm mol^{-1} K^{-1}, R = 1.987 cal mol^{-1} K^{-1}, latent heat of vaporization of water at normal boiling point = 539.4 cal g^{-1}, Density of water at 100 °C and 1 atm = 0.958 g cm^{-3}.

Important instruction to be followed: In case of derivation write all steps clearly one after another. Anything written alongside your answer will not be considered.

Q1. **(i)** Briefly explain with a schematic diagram of the system how to carry out a reversible adiabatic compression of a gas (answer with bullet points). **(ii)** What could be the effect of this process on the gas? Explain with the help of first of law thermodynamics. **5M+1.5M**

Q2. Mention True or False for the following statements giving a brief reason for your answer (**Marks will be awarded only if reason is given**): **1M×3=3M**

(i) A process in which the final temperature equals the initial temperature must be an isothermal process.

(ii) If a closed system at rest in the absence of external fields undergoes an adiabatic process that has $w = 0$, then the systems temperature must remain constant.

(iii) If $\Delta S_{sur} = -\Delta S_{sys}$, the process is at equilibrium.

Q3. 50 gm of water vaporizes at 100 °C and 1 atm pressure. Calculate q, w, ΔU, ΔH, ΔS, ΔG and ΔA for this process in calorie unit. Assume that water vapor behaves like an ideal gas.

0.5M+3M+1M+0.5M+1M+1M+2M

Q4. **(i)** An irreversible process is taking place in a one phase closed system which is in mechanical and thermal equilibrium and doing only P-V work. Show that, $dU = TdS - PdV + \Sigma \mu_i dn_i$. **5M**

(ii) If a chemical reaction is taking place in a closed system which is in mechanical and thermal equilibrium doing only P-V work and the reacting species are held at constant temperature and pressure, then starting with a suitable Gibbs equation show that the reaction Gibbs energy = $\Sigma \nu_i \mu_i$.

2M

Q5. **(i)** For the following isothermal process at temperature T:

$$\text{Real gas at P} \underset{\Delta H_m(a)}{\overset{a}{\rightarrow}} \text{Real gas at 0 bar} \underset{\Delta H_m(b)}{\overset{b}{\rightarrow}} \text{Ideal gas at 0 bar} \underset{\Delta H_m(c)}{\overset{c}{\rightarrow}} \text{Ideal gas at P}$$

Show that the total molar enthalpy change, $\Delta H_m = \int [T(\partial V_m/\partial T)_P - V_m]dP$ clearly deriving expressions for ΔH_m(a), ΔH_m(b) and ΔH_m(c). **4.5M+2.5M+1M**

(ii) Starting with a virial equation expressed as a power series in P, derive an expression for ΔH_m in terms of van der Waals constants a and b for the above mentioned isothermal process in part (i) neglecting the higher terms in the power series. Given that, $B = B^+RT$. **8M**

(iii) Calculate ΔH_m (in J mol^{-1}) for the process in part (i) for C_3H_8 gas at 298 K and 1 bar assuming that C_3H_8 gas follows van der Waals equation of state. Given that, for C_3H_8, T_c = 369.8 K, P_c = 41.9 atm; 1 bar = 0.987 atm. (Note that at 1 bar pressure the higher terms in a virial equation of state can be neglected). **3.5M**

Q6. One mole of a gas obeys equation of state, $PV_m = RT\,(1 + B^+P)$ undergoes a change of state from 200 atm and 373 K to 20 atm and 345 K.

(i) Calculate ΔS_m for this process assuming that B^+ and $C_{p,m}$ remain constant in this temperature range with values of -1.5×10^{-3} atm^{-1} and 20.79 J K^{-1}mol^{-1}, respectively. **6M**

(ii) What would be the final temperature in a Joule-Thomson expansion from the same initial state to a state with a pressure of 50 atm of the same gas. Assume that Joule-Thomson coefficient remains constant in the temperature range 340 K to 380 K. **2M**

Q7. (i) At 25 ºC, the density of an ethanol-water solution with 40% of ethanol by mass is 0.912 g cm^{-3}. What is the partial molar volume of the ethanol in the solution? Given that, the partial molar volume of water in the solution is 17.3 cm^3 mol^{-1}; molecular weights of water and ethanol are 18 and 46 g mol^{-1}, respectively. **4M**

(ii) Show that $S_i = -(\partial\mu_i/\partial T)_{P,\,n_j}$ **3M**

END