Birla Institute of Technology and Science Pilani –333031, Rajasthan
1st semester 2016-2017, Mid-Semester Test
Course Title: Physical Chemistry I, Course No. CHEM F211
Max Marks: 60, Time: 1hr 30 mins, Date: 06.10.16

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 = 0.0821 L atm K^{-1} mol^{-1}, R = 82.06 cm^3atm mol^{-1} K^{-1}, 1 cal = 4.2 Joule

Q1. Briefly explain how to carry out each of the following processes: **2M×3 = 6M**

(i) Reversible isothermal compression of a gas
(ii) Reversible constant pressure cooling of a gas
(iii) Reversible change of state of a gas from (P_1, V_1, T_1) to (P_2, V_2, T_2)

Q2. 1.00 mol of an ideal gas is the working substance of an engine. The engine operates in a cycle consisting of three steps: (Step 1) an adiabatic expansion from an initial volume of 10.0 L to a pressure of 1.00 atm and a volume of 20.0 L, (Step 2) a compression at constant pressure to its original volume of 10.0 L, and (Step 3) heating at constant volume to its original pressure. All the steps are reversible. (i) Show this cycle on a P-V diagram, (ii) For each step of the cycle, find the heat exchange, q (in Joule), and (iii) Find the efficiency of this cycle. Given that, C_p = (7/2)R and C_v = (5/2)R. Assume C_p and C_v are independent of temperature. **2M+6M+2M =10M**

Q3. Using $\Delta S = C_v \ln(T_2/T_1) + nR \ln(V_2/V_1)$ for the entropy change of an ideal gas, show explicitly that the entropy change is zero for a reversible adiabatic expansion from state (V_1, T_1) to state (V_2, T_2). **5M**

Q4. Suppose that a closed system consisting of two phases α and β is in thermal and mechanical equilibrium and is capable of P-V work only has not yet reached phase equilibrium. If substance j flows spontaneously from α phase to β phase then show that $\mu_j^{\alpha} > \mu_j^{\beta}$. **5M**

Q5. Two moles of a van der Waals gas of volume 10 L at 25 °C is changed to 20 L at 60 °C. Estimate ΔU (in Joule) for the process. Given that, $a = 1.35 \times 10^6$ cm^6atm mol^{-2} and $C_{V,m}$ = 30.5 J K^{-1} mol^{-1}. Assume that $C_{V,m}$ remains constant in this temperature range. **8M**

Q6. Berthelot equation of state for real gases is $[P + (a/TV_m^2)](V_m - b) = RT$.

(i) Expand the Berthelot equation into the form of virial equation expressed as a power series in $1/V_m$. **4M**
(ii) Give the Berthelot's prediction for the second (B) and third virial (C) coefficients. **1M+1M**
(iii) Starting with the virial equation expressed as a power series in P show that the Berthelot equation gives at T and P: **9M**

$$H_m^{id} - H_m^{re} = [(3a/RT^2) - b]P + \ldots\ldots$$

P.T.O.

Q7. Two components A and B form an ideal solution at all compositions. When the values of $\Delta_{mix}G/n$ (n = total number of moles of A and B) at 25 °C and 1 bar are plotted from $x_B = 0$ to $x_B = 1$, a symmetric curve with a minimum at $x_B = 0.5$ is obtained. The tangent of the curve at $x_B = 0.5$ intersects the $x_B = 0$ axis at – 0.414 kcal mol^{-1}. Estimate $\mu_A - \mu_A^*$ and $\mu_B - \mu_B^*$ at $x_B = 0.5$. Compare these results with those calculated from the definition of ideal solution in terms of chemical potential of each component in the mixture at same conditions. **3M+2M**

Q8. Benzene and toluene form ideal solutions at all compositions. The vapor pressures of pure benzene and pure toluene at 20 °C are 74.7 Torr and 22.3 Torr, respectively. A certain solution of these two components has a vapor pressure of 50.6 Torr at 20 °C. Estimate the mole fractions of benzene and toluene in the liquid mixture and in the vapor phase. **4M+2M**

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