B.Sc. 1st Semester (Honours) Examination, 2018 (CBCS)

Subject : Chemistry

Paper : CC-II

(Physical Chemistry-I)

Time: 2 Hours   **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words
as far as practicable.

1. Answer *any five* questions from the following: 2×5=10

   (a) 'Volume' parameter in ideal gas equation is either 'extensive' or 'intensive.'– Justify or criticize the statement.

   (b) Two van der Waals gases have the same 'b' but of different 'a'. Which one would occupy greater volume under same conditions of temperature and pressure and why?

   (c) Given that $\eta = \frac{1}{3}\rho c_a \lambda$, argue whether η should be proportional to ρ for a particular gas at a given temperature (symbols have their usual meanings).

   (d) An ideal gas undergoes free expansion into an evacuated vessel, state with reason whether this is a reversible or an irreversible process.

   (e) How much heat is necessary to convert 100g of ice at 0°C to water vapour (steam) at 100°C? Given $\Delta H_{fus} = 80$kcal kg^{-1}, $\Delta H_{vap} = 540$kcal kg^{-1} and heat capacity = 1.00 kcal kg^{-1} K^{-1}.

   (f) How much heat is released to dissolve 1 mol. of HCl(g) in a large amount of water? Given ΔH_f^0 for $H_3 \overset{+}{O}$, Cl^{-1} and HCl are 0.00, –40.00 and –22.06 kcal mol^{-1} respectively.

   (g) A first order reaction is never theoretically complete.— Explain mathematically.

   (h) The rate of a reaction is given by $\log k = A - \left(\frac{B}{T}\right) + C\log T$, where T is temperature. Find the value of Activation energy.

2. Answer *any two* questions from the following: 5×2=10

   (a) Define average speed and root-mean-square speed for gas molecules. Show which one is greater for molecules having a given mass. Why does the root-mean-square speed, rather than the average speed, have greater physical significance?   2+2+1=5

   (b)   (i) For a gas following the equation P (V–b) = RT, derive the expression for the Joule-Thompson co-efficient, i.e. μ_{JT}.

       (ii) It is possible for heat to flow from a body at a lower temperature to one at a higher temperature. Explain under what conditions such a process might occur. Give an example.

       (iii) Find the dimension of 'pressure multiplied by volume.'   2+2+1=5

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(c) (i) A gas decomposes at a rate of 8 units when 10% has already decomposed. If the process follows a 2nd order Kinetics, find the reaction when 55% of the gas has decomposed.

(ii) For a reaction the reactants A and B react to produce C and D. The rate law is:
Rate $= k_1$ [A] [B] $- k_2$ [C] [D]. What can be said about the nature of this reaction?— Explain. 4+1=5

(d) Define the Boyle temperature and arrive at an expression of it for a gas obeying van der Waals equation of state. 1+4=5

3. Answer *any two* questions from the following: 10×2=20

(a) (i) Find out the equation of state for a liquid for which the co-efficient of cubic expansion "α" and isothermal compressibility "k" are constants.

(ii) In corresponding state, gases have the same reduced temperatures and pressures. Under what conditions, hydrogen, carbon-dioxide and water have same reduced temperature and pressure, corresponding to nitrogen at 400K and 1 bar?

(iii) The distribution of molecular speeds is supposed to be given by the expression $dn_c = Ac^2 e^{-c^2/kt} dc$, A is a constant and other symbols have their usual meaning. (I) Evaluate A, (II) Calculate the average speed and (III) demonstrate a plot of $\left(1/c^2\right)\frac{dn_c}{dc}$ vs. c. 2+3+5=10

(b) (i) For the reaction, $X_2O_4(l) \to 2\,XO_2$ (g), at 25°C, the internal energy and entorpy changes are given as $\Delta E = 2 \cdot 1$ kcal and $\Delta S = 20$ calK^{-1} respectively. Calculate ΔG for the reaction and hence show whether the reaction written above is spontaneous.

(ii) State Carnot's theorem. Using this theorem, arrive at the Clausius theorem and hence show that ds $\geq$ đq/T (symbols have their usual meaning).

(iii) Assuming Helmholtz free energy A (T, V), derive $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V$. 3+5+2=10

(c) (i) Show that for an isothermal reversible change at constant pressure, the decrease in Gibbs free energy is a measure of the useful work available.

(ii) Joule-Thomson expansion is isoenthalpic,— Comment.

(iii) A heat engine operates between 900K and 300K. Find the maximum work available for every 1 kJ of heat supplied from the source. What will be the minimum heat discharged to the sink, when 9 kJ of heat is supplied by the source?

(iv) An ideal gas is heated from 300 to 1000 K and the pressure is allowed to rise from 1 to 2 bar. What is the change is molar entropy? 2+2+4+2=10

(d) (i) The first order gaseous decomposition of N_2O_4 into NO_2 has a rate constant (k) value of $4 \cdot 5 \times 10^3 s^{-1}$ at 1°C and an activation energy of 58 kJmol^{-1}. At what temperature k would be $1 \cdot 00 \times 10^4 s^{-1}$?

(ii) Write down the Michaelis-Menten mechanism for enzyme catalyzed reactions. Derive the steady state rate equation for such a mechanism and how the order of the reaction changes with substrate concentration in its high and low values. 3+7=10