

## West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2013

## Part - I

## CHEMISTRY — HONOURS

## Paper - II

Duration : 2 Hours

[ Maximum Marks : 50

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

The figures in the margin indicate full marks.

## CEMAT - 12-PA

Answer any two questions, taking one from each Unit.

## UNIT - I

1. a) Write down the Maxwell expression for the distribution of molecular speed in a plane and obtain the expression of average speed of the gas molecule from it.

$$\left[ \text{Given : } \int_0^{\infty} x^{1/2} e^{-x} dx = \frac{\sqrt{\pi}}{2} \right] \quad 4$$

- b) Calculate the number of binary collisions per  $\text{cm}^3$  in a nitrogen gas per sec at 2 atm pressure and  $30^\circ\text{C}$ . The diameter of the gas molecule is  $1.87 \text{ \AA}$ . 3

- c) Using equipartition energy principle calculate  $\gamma = \left( \frac{C_p}{C_v} \right)$  for an ideal gas. The gas molecule is non-linear triatomic. What is the limiting value of  $\gamma$  when the atomicity of the molecule becomes very large? 2 + 2
- d) Consider an ideal gas at 25°C. If the pressure is doubled, what effect does it have on the mean free path of a gas molecule? 2
2. a) i) Depict Maxwell speed distribution curves at two different temperatures  $T_1$  and  $T_2$  ( $T_2 > T_1$ ).
- ii) Explain their natures with the help of Maxwell equation.
- iii) How is it affected if the gas is changed from Helium to Argon?
- iv) What is the significance of the area under the curve between any two different speeds at constant temperature. 1 + 2 + 1 + 1
- b) At what temperature  $C_{rms}$  of He will be same with  $\langle C \rangle$  of  $O_2$  at 900 K? 2
- c) Derive an expression of the rate of effusion from wall collisions frequency of an ideal gas. 2
- d) For the movement of molecules in two dimension find out the fraction of molecules moving within the energy range  $9 k_B T$  to  $10 k_B T$ . 2
- e) Explain why the  $C_v$  value for nitrogen is always found to be less than that of chlorine molecule at ordinary temperature. 2

### UNIT - II

3. a) Justify that a gas obeying the equation of state —  

$$\left( P + \frac{a}{V_m^2} \right) V_m = RT$$
 does not possess the Boyle temperature. 2

- b) In the absolute method of determination of viscosity coefficient ( $\eta$ ) by Poiseuille formula, what should be the error in radius of viscometer if error in  $\eta$  is to be kept within  $\pm 4\%$ ? 2
- c) With the help of Andrew curves, show how far van der Waals equation explains the behaviour of real gas. 3
- d) What will happen for the height of liquid in capillary tube due to capillary rise of liquid if (i) radius of the capillary tube becomes double, (ii) capillary tube is broken at a level much below the height of liquid in capillary tube and (iii) inclined the capillary tube at an angle  $45^\circ$ ? 3
- e) "Surface tension of a liquid is zero at critical temperature." Justify or criticize. 2
4. a) Define vapour pressure of liquid. At  $100^\circ\text{C}$ , vapour pressure of water is 760 mm of Hg. Calculate the vapour pressure at  $25^\circ\text{C}$  assuming that  $\Delta H_{\text{vap}} = 9720 \text{ cal mol}^{-1}$  is almost constant in this range of temperature. 2 + 2
- b) Find the change in surface energy when two identical mercury droplets of diameter 1.5 mm merge isothermally to form one drop.  
[ Surface tension of Hg =  $490 \text{ dyne cm}^{-1}$  ] 3
- c) Gases NO and  $\text{CCl}_4$  obeying van der Waals equation have  $T_c$  and  $P_c$  values as given below :
- |                      | NO  | $\text{CCl}_4$ |
|----------------------|-----|----------------|
| $T_c / \text{K}$ :   | 177 | 550            |
| $P_c / \text{atm}$ : | 64  | 45             |
- Find which gas (i) has smaller value of  $a$ , (ii) has smaller value of  $b$  and (iii) behaves nearly ideal at 300 K and 10 atm. 3
- d) Identify the nature of attractive forces in each of the gases helium, argon and ammonia. How do such forces depend on the temperature and size of the species? 2

## CEMAT - 12-PB

Answer any two questions, taking one from each Unit.

## UNIT - I

5. a) From first law of thermodynamics, we have  $\oint dq = \oint d\omega$ . Does it contradict the second law of thermodynamics? Explain. 2
- b) Show that  $\left(\frac{\partial S}{\partial V}\right)_{P, n} = \frac{C_p}{TV\alpha}$   
 where,  $dS = \left(\frac{C_p}{T}\right)dT - V\alpha dP$  and  $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ . 2
- c) From Carnot cycle, arrive at Clausius inequality. 2
- d) 1 mol of an ideal gas is kept in a cylinder covered by a movable, weightless and frictionless piston at  $P_1, V_1, T$ . The pressure is suddenly changed to  $P$  and the system is allowed to expand isothermally until the volume is  $V$ . The pressure is again lowered to  $P_2$  and the expansion is continued isothermally until the volume is  $V_2$ . Show that work done will be maximum for this two-stage expansion process if  $P = \sqrt{P_1 P_2}$ . Also find the expression of  $W_{max}$  in terms of  $P_1$  and  $P_2$ . 3
- e) Calculate the change in entropy when 1 kg ice at  $0^\circ\text{C}$  and 1 atm is heated to  $273^\circ\text{C}$  and 2 atm pressure.  
 Given :  $\Delta H_{fus(273)} = 1440 \text{ cal mol}^{-1}$ ,  $\Delta H_{vap(373)} = 9720 \text{ cal mol}^{-1}$ ,  
 $C_p(l) = 18 \text{ cal K}^{-1} \text{ mol}^{-1}$  and  $C_p(v) = 8.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ . 4
6. a) Classify the following into extensive and intensive properties : 2
- i) Molar volume
  - ii) Surface tension
  - iii) Heat capacity
  - iv) Osmotic pressure.

b) Since,  $C_v = \left( \frac{\partial U}{\partial T} \right)_{v, n}$  by definition, one writes without any restriction,  
 $\Delta u = C_v \Delta T$ . Explain why it is not correct generally. 2

c) The standard enthalpy of combustion of  $C_2H_5OH(l)$  at  $25^\circ C$  is  $-327 \text{ kcal.mol}^{-1}$ . The standard enthalpy of formation of  $CO_2(g)$  and  $H_2O(l)$  at  $25^\circ C$  are  $-94.0 \text{ kcal mol}^{-1}$  and  $-68.3 \text{ kcal.mol}^{-1}$  respectively. Find out the standard enthalpy of formation of  $C_2H_5OH(l)$  at  $25^\circ C$ . 3

d) Show that :

i)  $\left( \frac{\partial S}{\partial V} \right)_{T, n} - \left( \frac{\partial P}{\partial T} \right)_{v, n} = 0$

ii)  $C_p - C_v = \left[ V - \left( \frac{\partial H}{\partial P} \right)_{T, n} \right] \left( \frac{\partial P}{\partial T} \right)_{v, n}$  2 + 2

e) Prove that the gas obeying the equation —

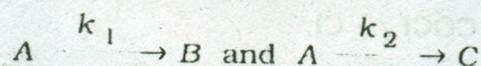
$$P(V_m - b) = RT$$

does not have any inversion temperature. 2

### UNIT - II

7. a) Comment on the statement "First order reaction never goes to completion". 2

b) Consider the following first order two competing reactions :



Show that

i)  $\frac{[B]}{[C]} = \frac{k_1}{k_2}$  at any time during the reaction

ii) Set initial condition :

$$[B]_0 = [C]_0 = 0 \text{ and } \frac{k_1}{k_2} = 2, \text{ give a schematic plot of } [A], [B] \text{ and}$$

$[C]$  as function of time on the same graph. 1 + 2

- c) A first order reaction is 20% complete in 10 min at 25°C and 40% complete in 12 min at 40°C. Calculate the energy of activation for the reaction. 3
- d) Show that the ratio of  $t_{1/2} : t_{1/4}$  of any  $n^{\text{th}}$  order reaction ( $n \neq 1$ ) with same initial concentration of the reactants, can be written as a function of  $n$  alone. 2
- e) Explain the effect of ionic strength on the rate constant of the following reactions : 2
- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2 + \text{OH}^- \rightarrow \text{Products}$
  - $\text{Fe}^{2+} + \text{Co}(\text{C}_2\text{O}_4)_3^{3-} \rightarrow \text{Products}$
8. a) Explain that zero order reaction cannot be a single step reaction. Does such a reaction go to completion ? 2 + 1
- b) Formation of phosgene,  $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$  is a chain reaction. The steps are
- $$\text{Cl}_2 \xrightarrow{k_1} 2 \text{Cl}$$
- $$\text{Cl} + \text{CO} \xrightarrow{k_2} \text{COCl}$$
- $$\text{COCl} + \text{Cl}_2 \xrightarrow{k_3} \text{COCl}_2 + \text{Cl}$$
- $$\text{Cl} + \text{Cl} \xrightarrow{k_4} \text{Cl}_2$$
- Applying steady state approximation for Cl and COCl, derive the rate law. 3
- c)  $\text{H}_3\text{O}^+$  acts as a homogeneous catalyst in the reaction of inversion of sucrose. At pH = 3 the reaction in aqueous solution proceeds with constant half-life of 50 minutes. What value of half-life would you expect at pH = 4 ? 3

- d) The rate constant of a second order gas reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$  is  $0.0234 \text{ L mol}^{-1} \text{ s}^{-1}$  at  $400^\circ\text{C}$  and the activation energy is  $150 \text{ kJ mol}^{-1}$ . Calculate  $\Delta^\ddagger H^0$  ( standard enthalpy of activation ) and  $\Delta^\ddagger S^0$  ( standard entropy of activation ) for this reaction.

$$\left[ h = 6.626 \times 10^{-27} \text{ ergs} ; R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \right] . \quad 3$$