

**B.Sc. 1st Semester (Honours) Examination, 2017 (CBCS)****Subject : Chemistry****(Physical Chemistry-I)****Paper : CC-II (Theory)****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:  $2 \times 5 = 10$ 
  - (a) What is the 'equation of state'? If  $V$  is the volume of a gas and  $V_{id}$  is the volume in ideal condition, then what does  $V/V_{id}$  mean?
  - (b) What happens to the peak of the distribution curve of molecular speeds of given temperature if the gas is changed from He to Ar? —Explain.
  - (c) For any system  $\oint dH$  is zero. —Justify or Criticize.
  - (d) Heat of neutralization of HCN by NaOH is  $-12.13 \text{ kJ mol}^{-1}$ . Calculate the molar heat of ionization of HCN.
  - (e) Show that Joule-Thomson experiment is an irreversible process.
  - (f) Write down the integral form of  $\Gamma(n)$ . If the rate constant of a reaction has the unit of  $\text{mol. dm}^{-3} \cdot \text{s}^{-1}$ , what would be its order?
  - (g)  $F$  is a function of two variables  $x$  and  $y$ . Write down the condition for  $dF$  to be an exact differential.
  - (h) What are the basic differences between Collision theory and transition state theory?
  
2. Answer *any two* questions from the following:  $5 \times 2 = 10$ 
  - (a) (i) If an ideal gas at temperature  $T$  and pressure  $P$  has an average speed ( $C_a$ ), by how many times would  $C_a$  change if  $T$  is doubled at constant  $P$ ? 1+4=5  
(ii) Assuming that  $\text{CO}_2$  obeys van der Waals equation, estimate the diameter of  $\text{CO}_2$  molecules if the critical temperature and pressure of  $\text{CO}_2$  are  $31^\circ\text{C}$  and  $73 \text{ atm}$ , respectively. 1+4=5
  - (b) Show that  $C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$  and hence prove that  $C_P = C_V$  for water at  $4^\circ\text{C}$  when its density is maximum. 3+2=5
  - (c) A first order reaction is 20% complete in 10 minutes at  $25^\circ\text{C}$  and 40% complete in 12 minutes at  $40^\circ\text{C}$ . Calculate the energy of activation of the reaction. Find also the values of  $k$  at very high temperature. 4+1=5
  - (d) The hydrolysis of a substrate is simultaneously catalysed by  $\text{H}^+$  and  $\text{OH}^-$  ion and also occurs simultaneously. The reaction is of 1st order with respect to all species. Write down the expression for the rate constant. Hence show that rate is minimum when  $[\text{H}^+] = \left[ \frac{k_{\text{OH}^-}}{k_{\text{H}^+}} \cdot K_w \right]^{1/2}$  1+4=5

**Please Turn Over**

3. Answer any two questions from the following: 10×2=20
- (a) (i) Express van der Waals equation of state in the form of Virial equation of state and hence derive the expression for the second Virial coefficient.  
(ii) Calculate the frequency of collisions for N<sub>2</sub> at 21°C and 101325 Pa using ideal gas law. The effective diameter of N<sub>2</sub> is estimated from viscosity measurements to be 370 pm.  
(iii) What is turnover number? What is its critical value? 5+3+(1+1)=10
- (b) (i) State equipartition principle and comment on its validity.  
(ii) Assuming U as a function of S and V, write down the expression for dU. Using this expression arrive at the Maxwell relation,  $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$ .  
(iii) Calculate the change in molar entropy of helium (ideal gas) in the following process:  
1 He (298K, 1 bar) → 1 He (100K, 10 bar).  
(iv) Adiabatic P-V curve is more steeper than the isothermal one. —Explain. 3+3+2+2=10
- (c) (i) Draw the P-V Carnot cycle with an ideal gas as working substance with explanations and show that the enclosed area is equal to the work done. What will be the effect on efficiency if the ideal gas is replaced by a van der Waals gas, the source and sink temperatures remaining the same?  
(ii) Mention the sign of Joule-Thompson coefficient for helium gas and state the reason behind it.  
(iii) Calculate the molar entropy change for the freezing of water at 0°C. The latent heat of fusion is 333.5 J g<sup>-1</sup>. 5+3+2=10
- (d) (i) Show that for a first order reaction R → P, the concentration of the product can be represented as a function of time by [P] = a + bt + ct<sup>2</sup> + ... Express a, b, and c in terms of [R]<sub>0</sub> and k (the rate constant for the reaction).  
(ii) The reaction in aqueous solution involves the following two elementary steps:  
Step I → Hg<sub>2</sub><sup>2+</sup>  $\xrightleftharpoons[k_{-1}]{k_1}$  Hg<sup>2+</sup> + Hg (rapid equilibrium)  
Step II → Hg + Tl<sup>3+</sup>  $\xrightarrow{k_2}$  Hg<sup>2+</sup> + Tl<sup>-1</sup> (slow)  
Apply the steady state approximation to show that the reaction is negative order with respect to Hg<sup>2+</sup>.  
(iii) Arrive at the conditions under which the equality holds between the frequency factor and the rate constant in Arrhenius equation. 5+3+2=10