

**B.Sc.(Honours)Examination, 2018****Semester-III****Chemistry (Honours)****Course: BCHC-33****( Physical Chemistry)****Time: Three Hours****Full Marks: 30**

Questions are of value as indicated in the margin.

Answer *any three* questions.

1. a) Find an expression to calculate change of free energy per mole ( $\mu$ ) of an ideal gas with pressure at constant temperature. Plot the result. Show that in this case, change of  $\mu$  is due to change of entropy. 1+1+1
- b) Calculate  $\mu$  in terms of T and P for the following equation of states  
 (i)  $\left(\frac{P\bar{V}}{RT}\right) = 1 + \left(b - \frac{a}{RT}\right) \frac{P}{RT}$  and (ii)  $P(\bar{V} - b) = RT$  (Symbols have usual meaning). 1+1
- c) State the Le Chatelier principle. Could you justify it based on thermodynamics? Comment on the following statements with proper reasons.  
 i) The compressibility of a reactive system is much greater than that of non-reactive one.  
 ii) The heat capacity of a reactive system is much larger than that of a non-reactive one. 0.5+2.5+1+1
2. a) Justify which of the following functions are acceptable as wave function:  
 (i)  $e^{-x}$  ( $0 \leq x \leq \infty$ ), (ii)  $e^{-x}$  ( $-\infty \leq x \leq \infty$ ), (iii)  $\cos x$  ( $-\infty \leq x \leq \infty$ ). 2+2+2
- b) Find out the following commutations  
 (i)  $[\hat{x}, \hat{p}_x]$ , (ii)  $[\hat{x}^n, \hat{p}_x]$ . (terms have usual meaning) 2+2
3. a) Define rate of a reaction, rate law and rate constant. What are the importance of rate law and rate constant? 2+2
- b) Zero order reaction can not be an elementary reaction. – Explain. 1
- c) First order reaction never comes to completion – explain. 1
- d) Find the rate law of the following 1st order reaction in terms of pressure.  

$$\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$$
 Where  $P_0$  be the initial pressure of  $\text{N}_2\text{O}_5$  and  $P_t$  be the total pressure at any time t. 2
- e) Derive the rate law for a firsts order opposing reaction. 2
4. a) What is steady state approximation? 1
- b) Applying steady state approximation find the rate law of the following reaction: 4  

$$\text{CH}_3\text{CHO} \xrightarrow{k_1} \cdot\text{CH}_3 + \cdot\text{CHO}$$

$$\cdot\text{CH}_3 + \text{CH}_3\text{CHO} \xrightarrow{k_2} \text{CH}_4 + \cdot\text{CH}_2\text{CHO}$$

$$\cdot\text{CH}_2\text{CHO} \xrightarrow{k_3} \cdot\text{CH}_3 + \text{CO}$$

$$\cdot\text{CH}_3 + \cdot\text{CH}_3 \xrightarrow{k_4} \text{CH}_3\text{CH}_3$$
- c) Prove the following relations:  
 (i)  $S = \sum_i n_i \bar{S}_i$ , (ii)  $V = \sum_i n_i \bar{V}_i$ , (iii)  $H = \sum_i n_i \bar{H}_i$ . 1+1+1
- d) The partial molar volume of all the gases in the mixture of ideal gases in same. Comment on the statement with proper justification. 2

**P.T.O.**

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5. a) Determine  $\langle x \rangle$  for a particle in a 1-d box. Is the value of  $\langle x \rangle$  is same for any quantum state?  
Explain your answer. 2+2+1
- b) Account for the temperature dependence of the equilibrium constant based on thermodynamics. 2
- c) Knowing that  $dS = \left( \frac{C_P}{T} \right) dT - V\alpha dp$ ,

Show that

i)  $\left( \frac{\partial S}{\partial P} \right)_V = k \frac{C_V}{\alpha T}$

ii)  $\left( \frac{\partial S}{\partial V} \right)_P = \frac{C_P}{\alpha VT}$

iii)  $-\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial P} \right)_S = \frac{k}{\gamma}$

where the symbols have usual meaning.

1+1+1

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