

**5 SEM TDC CHM M 1 (N/O)**

**2 0 1 8**

( November )

**CHEMISTRY**

( Major )

Course : 501

**( Physical Chemistry—II )**

( New Course )

Full Marks : 48

Pass Marks : 14

Time : 2 hours

*The figures in the margin indicate full marks  
for the questions*

1. Select the correct answer of the following :  $1 \times 5 = 5$

(a) For the reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ ;  
 $\frac{d[\text{NH}_3]}{dt} = 4 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The rate

of decomposition of  $\text{N}_2$  is

(i)  $6 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

(ii)  $8 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

(iii)  $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

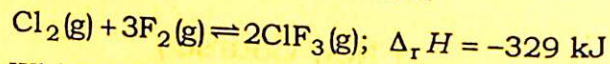
(iv)  $10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

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(b) Which of the following 0.01 m aqueous solutions will have the lowest freezing point?

- (i)  $\text{KNO}_3$
- (ii)  $\text{Al}(\text{NO}_3)_3$
- (iii)  $\text{C}_6\text{H}_{12}\text{O}_6$
- (iv)  $\text{Ba}(\text{NO}_3)_2$

(c) The exothermic formation of  $\text{ClF}_3$  is represented by the reaction



Which of the following will increase the quantity of  $\text{ClF}_3$  in an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{F}_2$  and  $\text{ClF}_3$ ?

- (i) Increasing the temperature
- (ii) Removing  $\text{Cl}_2$
- (iii) Increasing volume of the container
- (iv) Adding  $\text{F}_2$

(d) Adsorption is accompanied by

- (i) decrease in enthalpy and increase in entropy
- (ii) increase in enthalpy and increase in entropy
- (iii) decrease in enthalpy and decrease in entropy
- (iv) increase in enthalpy and decrease in entropy

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(e) The gold numbers of A, B, C and D are 0.04, 0.002, 10 and 25 respectively. The protecting powers of A, B, C and D are in the order

- (i)  $A > B > C > D$
- (ii)  $B > A > C > D$
- (iii)  $D > C > B > A$
- (iv)  $C > A > B > D$

2. Answer any *five* questions of the following :

2×5=10

(a) Show that a first-order reaction can be studied even when the initial concentration of the reactant is unknown.

(b) A solution contains 6 g urea and 18 g glucose in 1000 cc of water at 27 °C. Calculate the osmotic pressure of the solution.

(c) Show that

$$\left( \frac{\partial \mu_i}{\partial p} \right)_{T, n_1, n_2, \dots} = \bar{V}_i$$

(d) Heat of adsorption is greater for chemisorption than physisorption. Why?

(e) State and explain Hardy-Schulze rule.



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- (f) Describe how the activation energy of a reaction may be determined.
- (g) What is fugacity? Write its physical significance.

UNIT—I

3. Answer any *two* questions of the following :  
6×2=12

- (a) Using a suitable mechanism for the reaction  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ ; and assuming steady-state approximation for H and Br, derive the following rate expression for the formation of HBr

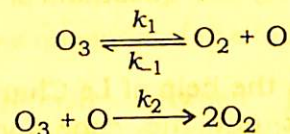
$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

where  $k$  and  $k'$  are constants.

- (b) (i) Show that for a first-order reaction, the time required for 99.9% completion of the reaction is 10 times that required for 50% completion.
- (ii) Discuss the limitations of the bimolecular collision theory of gaseous reaction.
- (iii) Give one example of pseudo-unimolecular reaction.
- (iv) What is steady-state approximation?

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- (c) The following mechanism has been suggested for the decomposition of  $\text{O}_3$  :



Assuming  $k_{-1}[\text{O}_2] > k_2[\text{O}_3]$ , show that the rate of the overall reaction is

$$-\frac{d[\text{O}_3]}{dt} = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$$

What could be concluded from the appearance of  $\frac{1}{[\text{O}_2]}$  in the rate equation?  
5+1=6

UNIT—II

4. Answer any *one* question of the following : 5

- (a) (i) State Nernst distribution law. How is the law modified when the solute undergoes association in one of the solvents?  
1+3=4
- (ii) State Henry's law. 1
- (b) Explain the term 'molal elevation constant'. Derive the relation between the boiling point elevation of a solution and the mole fraction of the dissolved solute. How is the expression utilized for determining molar mass of non-volatile solute?  
1+3+1=5

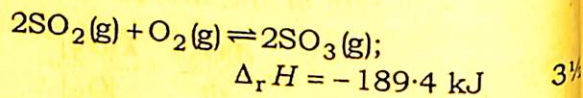


## UNIT—III

5. Answer any *two* questions of the following :

$3\frac{1}{2} \times 2 =$

- (a) With the help of Le Chatelier's principle, work out the condition which would favour the formation of  $\text{SO}_3(\text{g})$  in the reaction



- (b) Explain the term 'chemical potential'. Derive Gibbs-Duhem equation for two-component system.  $1 + 2\frac{1}{2} = 3\frac{1}{2}$

- (c) Deduce the relationship between  $\Delta G^\circ$  and  $K_c$  of a reversible reaction.  $3\frac{1}{2}$

## UNIT—IV

6. Answer any *one* question of the following :

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- (a) Derive Langmuir adsorption isotherm and show that Freundlich isotherm is a special case of this isotherm.  $3 + 1 = 4$

- (b) (i) Write four differences between physical adsorption and chemical adsorption. 2

- (ii) Give reason why a finely divided substance is more effective as an adsorbent. 2

( Continued )

## UNIT—V

7. Answer any *one* question of the following : 5

- (a) (i) Distinguish between peptization and coagulation of colloids. 2

- (ii) Explain why lyophilic sols are more stable than lyophobic sols. 2

- (iii) Define zeta potential. 1

- (b) Write short notes on the following :  $2\frac{1}{2} \times 2 = 5$

- (i) Protective action of lyophilic colloid

- (ii) Donnan membrane equilibria