RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

SECOND YEAR B.A./B.SC. THIRD SEMESTER (July – December) 2014 Mid-Semester Examination, September 2014

Date : 15/09/2014 Time : 2 pm - 4 pm

CHEMISTRY (Honours) Paper : III

Full Marks : 50

[Use a separate answer book for each group]

<u>Group – A</u>

(Answer <u>Question No. 1 or 2</u> and <u>Questions No. 3 or 4</u>)

1. a) The rate law for the reaction is $A + B \rightarrow \text{products}$ is $dP_A / dt = -kP_A P_B$ and the half life at 25°C is 30 min, when $P_A^\circ = P_B^\circ = 0.01 \text{ atm}$. Calculate—

(i) the rate constant, k, (ii) $t_{\frac{1}{2}}$, the time for P_A to drop to $1/4^{\text{th}}$ of its original value. [3]

- b) For the opposing reaction $A \xrightarrow[k_B]{k_B} B$, show that $[A] = [A]_0 \frac{k_B + k_A \exp[-(k_A + k_B)t]}{k_A + k_B}$. [3]
- c) From the Maxwellian distribution of speed of gas molecules how does one conclude about the variation of rate of gaseous chemical reaction with change in temperature? [2]
- 2. a) For consecutive reaction of type



A, B, C are reactants and P, Q are products. If X is a reactive intermediate, then establish the condition for steady state of X. [3]

- b) The reaction $A+B \rightarrow P$ obeys rate law d[A]/dt = -k[A][B]. In experiment 1, the initial concentrations of A and B are 0.01 (M) and 2(M), respectively. In experiment 2, at same temperature, the initial concentrations are both equal to a value C₀. Derive the value of C₀, such that the time for half reaction will be same for two experiments. [2]
- c) If the initial concentration of the reactant for $(A \rightarrow P)$ is made double, the $t_{\frac{1}{2}}$ becomes half. What

is the order of reaction?

- d) Draw a qualitative plot of concentrations of reactant and product against time for a consecutive 1st order reaction. [1]
- 3. a) Discuss the effect of introduction of an inert gas on the equilibrium of the reaction

$$2\mathrm{CO}(\mathrm{g}) + \mathrm{O}_2(\mathrm{g}) = 2\mathrm{CO}_2(\mathrm{g})$$

at constant temperature and pressure.

- 600K dissociation of $PCl_5(g)$ b) At the degree of according to the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 0.920 under 5 atm pressures. What is the degree of dissociation under 1 atm pressure? [2]
- c) Consider the equilibrium : $NH_2COONH_4(S) \rightleftharpoons 2NH_3(g) + CO_2(g)$

at a temperature T and total pressure P. Express K_P for this reaction as a function of P. [2]

d) Find out the mean ionic activity of $0.01M \text{ K}_2\text{SO}_4$ solution at 25°C. (Given A = 0.51 for water at 25°C) [2]

[2]

[2]

- 4. a) Derive suitable expression to show how a change in temperature affects the equilibrium of a reaction. [3]
 - b) Consider the equilibrium : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ Find out the expression of degree of dissociation of $N_2O_4(g)$ as function of total pressure. [2]
 - c) A solute B is soluble in water as well as water-immiscible organic solvent X. In the organic solvent, B polymerises as $nB \rightleftharpoons B_n$. Discuss a method by which the value of 'n' can be determined. [3]

<u>Group – B</u>

(Answer <u>any one</u> of the following)

5. a) Rank the isomers within each set in order of increasing heat of formation (lowest first). [2]



- b) Show how to synthesize 3-decyne from acetylene and any necessary alkyl halides. [2]
- c) What two constitutional isomers could be formed in the following reaction? Which one is major product? [2]

$$\underbrace{\qquad \qquad }_{+} \underbrace{MeO_2C}_{+} \underbrace{CO_2Me}_{heat} \underbrace{}_{+} \underbrace{}_{+} \underbrace{Keat}_{+} \underbrace{Kea$$

- d) A mixture of 0·1 mole of (2E, 4E)–2, 4–hexadiene and 0·1 mole of (2E, 4Z) –2, 4–hexadiene was allowed to react with 0·1 mole of tetra cyanoethylene (TCNE). After the reaction, the unreacted diene was found to consist of only one of the starting 2,4–hexadiene isomers. Which isomer did not react? Explain.
- e) Predict the product in the fllowing reactions :

i)
$$\longrightarrow O \xrightarrow{Cl^{\wedge}CO_{2}Et}{K^{+}O^{-}Bu^{+}} (A) \xrightarrow{H_{3}O^{+}} (B) \xrightarrow{O}{O} (C)$$

Ph $\longrightarrow N \xrightarrow{O}{OH} (C)$

Give mechanism for the formation of (B) from (A).

ii)
$$ACOH \to P \xrightarrow{K^+O^-Bu^t} Q$$

 $ACOH \to P \xrightarrow{K^+O^-Bu^t} Q$
 $ACOH \to P \xrightarrow{K^+O^-Bu^t} Q$
 $ACOH \to Q$
 $CHO \xrightarrow{SH} , PTS \\ C_6H_6, \Delta \to R \xrightarrow{n-BuLi} -78^\circ C \to S$

Give mechanism for the formation of X for Q+S.

- 6. a) What six-carbon cnjugated diene would give the same single product from either 1, 2– or 1,4– addition of HBr? Show mechanism. [2]
 - b) Give the product for each of the following reactions.

i)
$$\underbrace{\overset{Me}{\overbrace{}}}_{Me_{2}CHOH} \xrightarrow{Na/liq_{NH_{3}}}$$

[3]

[2] [4+4]

ii)
$$\xrightarrow{\text{CO}_2\text{H}} \xrightarrow{\text{Na/liqNH}_3} \xrightarrow{\text{Na/liqNH}_3}$$

Which one of the above reactions is faster with respect to benzene.

Show the products of the following reactions : c)



Carry out the following conversion. Mechanism is not necessary. d)



<u>Group – C</u> (Answer <u>Question No. 7 or 8</u> and <u>Question No. 9 & 10</u>)

- a) Explain the Lewis acid and base character of SO₂ with examples. $[2\frac{1}{2}]$ b) Write the hard-hard (H–H) and soft-soft (S–S) interaction and stability by FMO. [3] Explain the analytical separation of copper (II) and Cadmium (II) by KCN with appropriate acidc) base concept. $[2\frac{1}{2}]$ $Fe_3O_3 + 3CO_2 \xrightarrow{\Delta} Fe_2(CO_3)_3$ Comment about the feasibility of the reaction and stability of the 8. a) product. Acidity parameter of Fe_2O_3 and CO_2 is -1.7 and 5.5. $[2\frac{1}{2}]$ For the reaction, $PH_3 + NaNH_2 \rightleftharpoons NaPH_2 + NH_3$ indicate the direction of the reaction with b) explanation. $[1\frac{1}{2}]$
 - c) Explain the stronger interaction between
 - $R_2O \cdot BF_3$ over $R_2S \cdot BF_3$ and i)
 - ii) $R_2S \cdot BH_3$ over $R_2O \cdot BH_3$

7.

- 9. a) Draw the MO energy diagram of CO and explain the π acid character of CO. [3]
 - Although CO and N₂ are isoelectronic species but CO is π acid ligand but N₂ is a poor ligand. b) Justify. [2]

[4]

[3]

 $[4 \times 2]$

Or,

	a) b)	State and explain Walsh's rule with diagram. BeH ₂ is linear but H ₂ O is angular : Explain.	[4] [1]		
10.	a)	What do you mean by Inner metallic complex? Give an example of a compound with cationic ir	nner		
		metallic complex and anionic inner metallic complex.	[1+1]		
	b)	Mention two experimental evidences in favour of Werner's theory on coordination compounds.	[11/2]		
	c)	Write down the I.U.P.A.C name of the following compounds (any two):	[11/2]		
		i) $[Co(NH_3)_6][Cr(CN)_6]$			
		ii) $[(CO)_4Co-Re(CO)_5]$			
		iii) $[Br_2Pt(SMe_2)PtBr_2]$			
Or,					

a) Distinguish between—

	i) Ambidentate Ligands and flexidentate Ligands.	
	ii) Inert Complex and Labile Complex	[1½×2]
b)	What do you mean by Fluxional Complex compound	[1]

c) The stability of $[Ni(en)_3]^{2+}$ is much greater than $[Ni(NH_3)_6]^{2+}$; explain. [1]

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