This question paper contains 3 printed pages.

4341

Your Roll No.....

M.Tech. / II Sem. **A**

CHEMICAL SYNTHESIS AND PROCESS TECHNOLOGIES
Paper - 202
(Solution Chemistry & Catalysis in Chemical Synthesis)

Time : 3 hours *Maximum Marks : 70*

(Write your Roll No. on the top immediately on receipt of this question paper.)

Use a separate answer book for each section.

SECTION - A

Attempt all questions
Use of Non-programmable calculator is allowed.

1. a) The metal ion M^{2+} reacts with the ligand ion L^-, forming a coloured complex. a series of solutions was prepared in which the analytical concentration of M^{2+} was 1.00×10^{-4}M, while the conc. of L^- varied. The following data was obtained by measuring the absorbance at 510nm, where only the complex absorbs. in a 1.00cm cell :

$C_L \times 10^{-4}$M	Absorbance at 510nm
0.250	0.148
0.500	0.294
0.750	0.434
1.00	0.543
1.25	0.580
1.50	0.589
1.75	0.592
2.00	0.594
2.50	0.597
3.00	0.599

(i) Determine the formula of the complex.
(ii) Calculate the molar absorptivity of the complex at 510nm.
(iii) Calculate the stability constant of the complex. *06*

OR

The absrobance of a series of solutions containing 3×10^{-4} M ligand L and varying concentration of the metal M are given below.

$T_M \times 10^{-3}$	1.0	2.0	3.0	5.0	8.0
Absorbance	0.162	0.285	0.390	0.553	0.716

Find the dissociation constant of the complexation reaction and the molar asborptivity of the complex from the above data. 06

b) In the pH - metric method for the determination of stability constants show that

$$\frac{L_t - [A]}{L_t} = \frac{\sum_{n=1} n\beta_n [A]^n}{\sum_{n=0} \beta_n [A]^n}$$

where the terms have usual meanings. 06

2 a) Show the value of conditional formation constant of a metal M_1 with ligand L in presence of metal N_2 is given by :

$$\log K'M_1 = \log K - pM_{(1)}$$ 05

b) Calculate theoretical titration error if 1×10^{-3}M Mg^{2+} solution is titrated with 5×10^{-3}M EDTA solution at pH 10.0 using In^{3-} indicator. Assume that at transition point, the following percentage of indicator has been converted from MgIn to In^{3-}

(i) 50%

(ii) 90%

Given : $\log K_{MgIn} = 5.44$, $\log K_{Mg-EDTA} = 8.7$ and at pH 10, $\alpha_{EDTA(H)} = 0.45$ 06

OR

Estimate the accuracy attained in the complexometric titration of 10^{-3}M Zn^{2+} ions in the presence of 0.1 Mg^{2+} ions

Given : $\log K_{ZnY} = 16.5$,

$\log K_{MgY} = 8.7$

$pZn_{(eq.)} = 5.6$ 06

3 a) Explain the following (any three)

(i) Conditional constants are more important then stoichiometric constants in complexometric titrations.

(ii) Thermodynamic and stoichiometric equilibrium constants

(iii) Relationships between different functions, n, ϕ and α

(iv) The log k values for Zn - EDTA and Ca - EDTA complexes are 16.5 and 10.7 respectively. But EDTA reacts with calcium instead of zinc which has higher log k value when titration is performed using NH_4 NH Cl buffer. 06

b) What do you understand by equivalence point and end point in titration ? Derive an expression for calculating the titration error if the free metal ion concentration at the end point, the total concentration of the metal ion and the stability constant of the complex which is $> 10^7$ are given. 06

OR

Explain the method for finding the equilibrium constant using solvent extraction technique, when only the complex MA_2 is extractable into organic phase. 06

SECTION - B

Note : Attempt all questions.

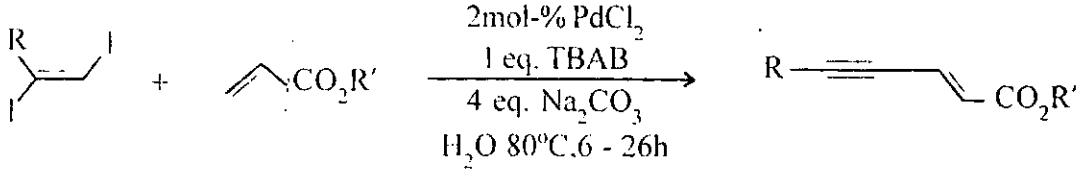
1. Give a mechanistic explanation for Zeigler - Natta polymerisation *04*

2. Write short notes on (any three)
   (a) Alkene metathesis
   (b) Water gas shift reaction
   (c) Green chemistry and catalysis
   (d) 18 electron rule. *09*

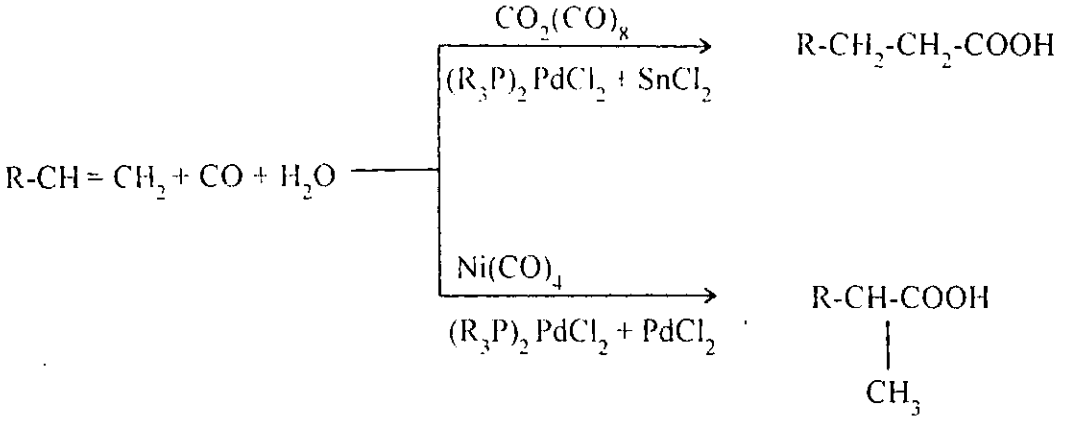
3. Show the catalytic cycle for the formation of ethanoic acid with rhodium based catalyst ? *05*

4. Write down the mechanism of the following reactions. *12*

a)



b)



5. Write down the product and the mechanism of the following reaction ? *05*