This question paper contains 6 printed pages.

7646 *Your Roll No .....*

M.Tech / II SEM.

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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 separate answer scripts for Section A & Section B.

SECTION A

Attempt three questions in all, including Q No 1 which is a compulsory question Q No 1 carry 11 marks and rest of the questions carry 12 marks each
Use of Scientific Calculator is allowed

1 a) Define ϕ, α_c & $\bar{n}$ for the following reaction

$Cu^{2+} + 4NH_3 \rightleftharpoons [(Cu(NH_3)_4]^{2+}$

which takes place in various steps Derive a relation between these functions. *03*

b) (i) Define masking

(ii) Why conditional stability constants are more important than stoichiometric stability constants in complexometric titrations *03*

c) Small amounts of Magnesium are to be determined complexometrically in the presence of large amounts of

PTO

Zinc The titration is performed with EDTA at pH = 10 with Eriochrome black T as indicator after the Zinc has been masked by means of "tetren" (tetraethylene pentamin = T) added in approx 0 1M excess

Estimate the accuracy of visual titration in

(a) 10^{-2} M Mg in the presence of 0 1M Zn

(b) 10^{-3} M Mg in the presence of 0 1 M Zn

Given $\log \alpha_{y(H)} = 0\ 5$, $\log \alpha_{Zn(T)} = 14\ 0$

$\log K_{Zn\,y} = 16\ 5$, $\log K_{Mg\,y} = 8\ 7$.

$pMg_{trans} = 5\ 4$ *05*

2 a) What do you understand by back titrations When it is necessary. *04*

Show that

$$TE = \frac{[M_{II}\,L]}{[M_I L]\,[M_{II}]\,K_{M_{II}L}} - \frac{[M_{II}]\,K_{M_{II}L}}{[M_{II}L]\;K_{M_IL}} - \frac{[M_{II}]}{[M_IL]}$$

b) What is the most suitable conc.of added Mg y when titrating calcium in 10^{-3} M conc with EDTA at pH=10 using EBT as an indicator Given that

$\log K_{Ca\,y} = 10\ 2$, $\log K_{Mg\,y'} = 8\ 2$,

$pM_{trans} = 5\ 4$, $pCa_{eq} = 6\ 6$ *04*

c) What do you understand by metallochromic indicators ? Prove that

$pM'_{trans} = \log K_{M'I'}$ *04*

3 a) Calculate the conditional stability constant of calcium complex with EDTA at pH = 10 Given that $\log K_{Ca\ EDTA} = 10\ 7$ The protonation constants of EDTA are

$\log K_1(H) = 10\ 34,\ \log K_2(H) = 6\ 24,$
$\log K_3(H) = 2\ 75,\ \log K_4(H) = 2\ 07$ *04*

b) A metal ion M^{n+} has been estimated spectrophotometrically using legend L according to the following reaction

$mM + nL \rightleftharpoons MmLn$

Using Job's method of continuous variation, show that, in a plot of absorbance (A) of the complex Vs mole fraction of legend (x), the maximum into the plot corresponds to $\frac{x_{max}}{1 - x_{max}} = \frac{n}{m}$ *04*

c) The formation of the 1, 10 - phenanthroline complex of cadmium is investigated by the polasographic method. The total conc. of cadmium and the concentration of supporting electrolyte, KNO_3, are constant, whereas the concentration of 1, 10 - phenanthroline is varied. All the solution contain 40% ethanol and the pH is 6 6.

$T_{cal} = 2 \times 10^{-4}M$ & $T_{KNO_3} = 10^{-1}M$.

Protonation constant of 1, 10 - phenanthroline

$\log k = 4\ 95$

The half wave potentials measured against SCE and determined from the polarograms, the wave heights in mm, are as follows.

T(phen)M	E½(V)	id(mm)
0	-0.591	170
10^{-3}	-0 745	135
2×10^{-3}	-0 790	122
4×10^{-3}	-0 822	120
10×10^{-3}	-0 862	113
20×10^{-3}	-0 895	113

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Determine the composition & stability constant of the complex formed *04*

4 a) The complexation reaction

$$M + nHL \longrightarrow ML_n + nH^+$$

which occurs in stepwise manner has been investigated by pH Metric method If T_L & T_M are total legand conc & total metal conc resp , show that

$$pL = \log\left[\frac{1 + B_i^H [H^+]}{T_L - \bar{n}\, T_M}\right] \qquad 04$$

b) In the solvent extraction technique for the determination of the stability constants of the complex Show that

$\log g = \log \alpha_c + \log \beta_c \beta_N^+ + (C - N) \log L$ in the presence of large excess of legand, where g the distribution ratio of metal in two phases, β_N & β_c are overall formation constants for ML_N & ML_C complexes respectively

Calculate the % of metal (M) present as free ion and as thiocyanato and hydroxo complexes in solution which is 0 1M potassium thiocyanate and contains a small concentration of M, at pH 7 as well as at pH 9 The overall stability constants are as follows -

For Thiocyanato complexes,

$\log \beta_1 = 1\,2$, $\log \beta_2 = 1\,6$ & $\log \beta_3 = 1\,8$

For Hydro complexes

$\log \beta_1 = 4\,6$ *04*

SECTION - B

Attempt all questions

1 Explain the following by taking suitable examples *3 x 3 = 9*

(i) Generation of coordinatively unsaturated metal centre is an important step in catalysis

(ii) σ- and π-bonding is essential for transition metal ions to act as good catalyst

(iii) Tolman parameters to measure the electronic and steric effects.

2 Attempt any two of the following: *2 x 5 = 10*

(i) Suggest a catalyst and explain the catalytic cycle involved in the conversion of allyl alcohol into propionaldehyde

(ii) Discuss the mechanism of catalytic conversion of ethylene to acetaldehyde using $PdCl_2$ as a catalyst

(iii) Discuss the mechanism of heterogeneously catalyzed Fischer- Tropsch reaction

3. Explain any two of the following: *2 x 5 = 10*

(i) Explain hydroformylation of alkene with mechanism and suitable example

(ii) What do you understand by the term stereo regular polymerization? Discuss the catalytic cycle of Zeigler-Natta stereo regular polymerization of propylene.

(iii) Explain the mechanism of hydrocyanation reaction of propene using Ni-catalyst.

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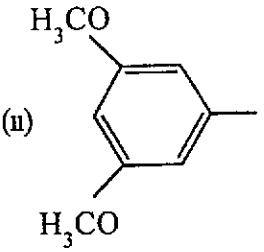
4 Write the product for the following reactions

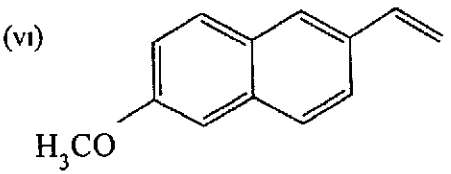
(i) $BuOCH = CH_2 + PhBr \xrightarrow[\text{Ionic Liquid}]{\substack{Pd(OAc)_2 \\ PPh_3 \\ NEt_3}}$

(ii)  $\xrightarrow[NEt_3]{Pd(OAc)_2,\ P(o\text{-tolyl})_3} CH_2 = CH_2$

(iii) $CH_3CH_2CH = CH_2 \xrightarrow[H_2O/\ O_2]{PdCl_2,\ CuCl_2}$

(iv) $CH_3C \equiv CH + CO + CH_3OH \xrightarrow[\text{2-pyridylphosphine}]{Pd^{2+}}$

(v) $CH_2 = CHCH_2Br + CO + CH_3CH_2OH \xrightarrow{\text{Pd (II) complex}}$

(vi)  $\xrightarrow[HCN, hexane]{Ni\text{- cat}}$