This question paper contains 3 printed pages.]

Your Roll No. .....

4323 **A**

M. Tech./Sem. III

CHEMICAL SYNTHESIS AND PROCESS TECHNOLOGIES

Paper—Module–9 : Solution Chemistry

Time : 3 *Hours* *Maximum Marks* : 38

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

Answer ***three*** *questions in all including.*

Question No. 1 *which is compulsory.*

1. (a) What are the various ways of achieving selectivity in complexometric titration of a mixture of metal ions ? Give examples for each of these. 5

(b) For stepwise complexation reaction between metal and ligand derive the relationship

$\frac{d \log \alpha_C}{d \log [A]} = C - \bar{n}$ where $\bar{n}$ and α_C are the formation functions and [A] is free ligand concentration. 5

[P.T.O.

(c) For a spectrometric titration 4

$$S + T \rightarrow P$$

draw the titration curves under the following conditions

(i) $\epsilon_S = \epsilon_P$

(ii) $\epsilon_S = \epsilon_P = 0, \epsilon_T > 0$

(iii) $\epsilon_P = \epsilon_T = 0, \epsilon_S > 0$

2. (a) Define mean molar extinction coefficient $\bar{n}$. How this has been used by Yatsimirskii for calculation of $\beta_1, \beta_2 \ldots \beta_n$ values for a complexation reaction between metal M and ligand L. 4

(b) Using $\bar{n}$ – [L] data describe elimination method for finding β_1 and β_2 values for 1 : 1 and 1 : 2 complexation reactions between M and L. 4

(c) Suggest two methods for simultaneous complexometric estimations of a mixture of Cu + Zn in a solution. 4

3. (a) For a back titration of M_I and M_{II} in presence of excess EDTA, derive the following relation 6

$$pM_{II} = pM_{II}' + [\log K_{M_I Y} - \log K_{M_{II} Y} + \log [M_{II} L] - \log [M_I L_1]]$$

(b) Estimate the accuracy in estimation of 10^{-3} M Zn in presence of 10^{-2} M Mg. Given $K_{ZnY} = 16.5$, $\log K_{MgY} = 8.7$, $pZn_{trans} = 5.6$. 6

4. (a) For a cation exchange reaction of the type 4

$$Na^{+}(R) + M^{n+} \rightarrow M^{n+}(R) + n(Na^{+})$$

Show that $\frac{\lambda_0}{\lambda} = \phi$

and this ratio varies as a function of added ligand. λ_0 and λ are the distribution ratio (of metal M^{n+} between resin and solution) in the absence and presence of ligand respectively.

(b) For complexometric titration derive the following titration error formula

$$\text{Error} = \frac{4\,6\,\Delta\ PM}{(C_M\ K_{ML})^{1/2}}$$ 4

(c) In the pH-metric method for the determination of stability constants, show that 4

$$\frac{T_L - [L]}{T_M} = \frac{\sum_{n=1}^{n=N} n\beta n[L]^n}{\sum_{n=0}^{N} \beta_n [L]^n}$$

Where the terms have usual meanings.