P.G. Semester-IV Examination, 2023

CHEMISTRY

Course ID : 41451 **Course Code : CHEM-401E**

Course Title : Inorganic Chemistry Special

Time : 2 Hours Full Marks : 40

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer any **five** of the following questions: 2×5=10

   a) What case will result in Mössbauer spectrum for a delta shift of 0.00 mm/s?

   b) Give one example of AND logic gate.

   c) Comment on the metal ion affinity of podands and crown ethers.

   d) Why the Doppler effect is important in Mössbauer spectroscopy?

   e) Write down the product of the reaction between $CeCl_2$ and $K_2C_8H_8$ in diglyme.

   f) Define preorganization.

   g) Name two lanthanides which are well known to exhibit +2 oxidation.

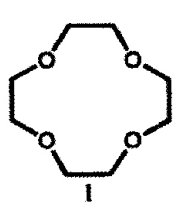
2. Answer any **four** of the following questions: 5×4=20

   a) Give one example of each of the NAND and OR logic gates. $2\frac{1}{2}+2\frac{1}{2}=5$

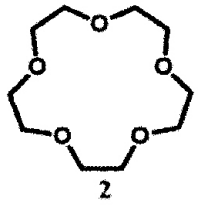
   b) i) Write one application of hemicarceplexes.

      ii) Explain the role of macrocycles in Phase-transfer catalysis (PTC) giving suitable example. 2+(1+2)=5

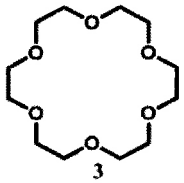
   c) Binding data in methanol given below for a series of interactions between crown ethers 1-4 and cations:



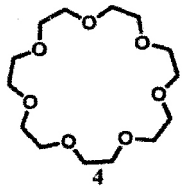
logK (Li^+) = 0.50
logK(Na^+) = 0.73
logK (K^+)= 0.86



logK (Li^+) = 1.42
logK(Na^+) = 3.42
logK (K^+) = 3.38



logK (Na^+) = 4.00
loaK (K^+) = 6.10
logK (Cs^+) = 4.62



logK (K^+) = 4.41
logK (Cs^+) = 5.02

i) Suggest an explanation for the selectivity observed for the binding of 18-crown-6 towards cations.

ii) The binding of cations to the different sized crown ethers might not follow the predicted trend. Justify the statement. $2\frac{1}{2}+2\frac{1}{2}=5$

d) i) In the ^{57}Fe Mossbauer experiment source of 25.5 keV is moved towards the absorber at a velocity of 5.5 mm/s. Calculate the shift in frequency of the source for this sample in MHz.

ii) Which one will be corroded at a higher rate in deaerated HC1 medium among iron and zinc and why? 3+2=5

e) i) Why cesium carbonate is preferred over other cesium compounds in macrocyclisation reactions as basic reagents?

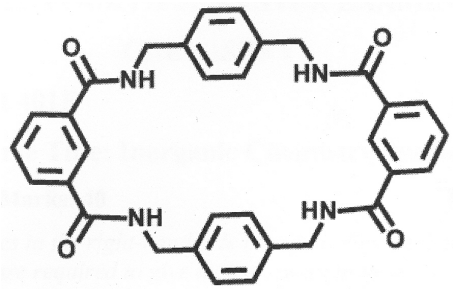
ii) Give one example of water-soluble cryptophanes along with its applications. 2+3=5

f) Design one fluorescent sensor for Hg^{2+} and one for Picric acid. $2\frac{1}{2}+2\frac{1}{2}=5$

3. Answer any **one** of the following: 10×1=10

a) i) How do you synthesize $Sm(cp^*)_2(thf)_2$ from $SmI_2(THF)_2$? Write down the product formed in the reaction between dinitrogen and $Sm(cp^*)_2(thf)_2$.

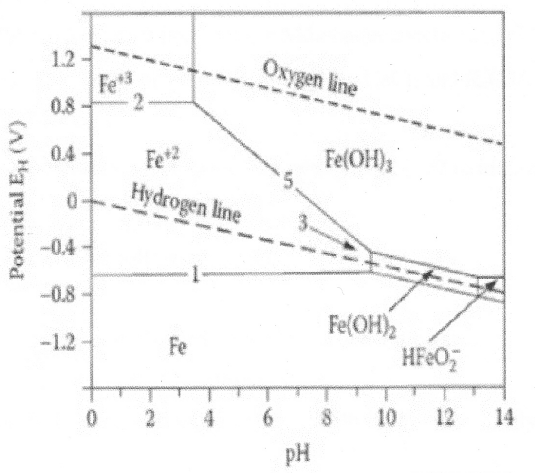
ii) The condensation reaction between isophthaloyl dichloride and para-xylenediamine was expected to give the macrocyclic product shown below. The mass of the product was double that expected. What was the actual product obtained from the reaction? Give an explanation for its formation.



Expected product

iii) Why do isopoly- and heteropoly-acid of molybdenum and tungsten prefer edge sharing over the corner connection? (2+2)+3+3=10

b) Pourbaix diagram for the iron-water system is shown below:



i) Using the Pourbaix diagram for Fe provided, write a balanced half-reaction for reduction of Fe(III) to Fe(II) at pH = 5.

ii) Calculate the potential at pH= 7, considering the Fe(III)/Fe(II) reduction potential +0.45 V at pH = 5.

iii) Why the line to the right of Fe^{3+} in the Pourbaix diagram is vertical?

iv) Why old iron objects survive for few hundred years under water? 3+3+2+2=10

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