M.Sc. 4th Semester Examination, 2021

CHEMISTRY

(Inorganic Chemistry Special)

Paper : CHEM 401E

Course ID: 41451

Time: 2 Hours **Full Marks: 40**

The figures in the right-hand side margin indicate full 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) Give any two essential characteristics which a nuclide has for exhibiting the Mössbauer effect.

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

(c) Give one example of molecular rectifiers.

(d) What causes white rust?

(e) How do you remove the tosyl group from N-protected Azathiacrowns?

(f) "Choice of the base is crucial to the successful synthesis of crown ethers"- Explain.

(g) What is atmospheric corrosion?

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

(a) (i) Arrange the isomer shift value of the following ions in increasing order: Sn, Sn^{2+} and Sn^{4+}. Give suitable explanation.

(ii) How many numbers of allowed transitions are possible in the Mössbauer spectrum of an iron containing sample, recorded in the presence of a static magnetic field.

3+2=5

(b) (i) In the ^{57}Fe Mossbauer experiment source of 25.5 keV is moved towards the absorber at a velocity of 5.5 mms^{-1}. Calculate the shift in frequency of the source for this sample in MHz.

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

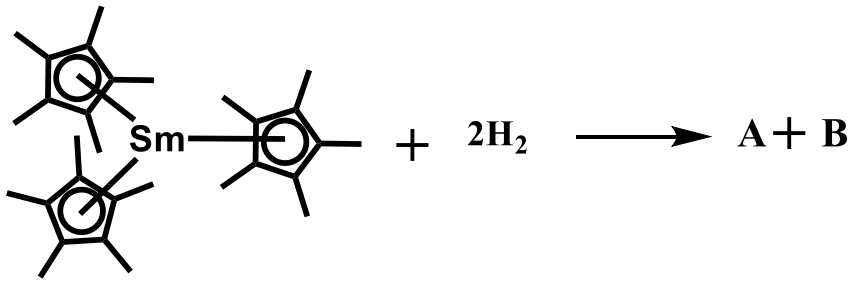
(c) (i) Why caesium carbonate is preferred over caesium compounds in macrocyclization reactions as basic reagents?

(ii) What is the difference between Carcerands and Hemicarcerands? Give one application of hemicarceplexes. 2+(1+2)=5

(d) (i) Give one example of water-soluble cryptophanes along with its applications.

(ii) What is the role of macrocycles in Phase-transfer catalysis (PTC)? 3+2=5

(e) (i) Write down the structure of A and B.



(ii) Comment on the formulae of the alkyls formed by the lanthanides with the CH_3, CH_2SiMe_3, CMe_3 and $CH(SiH_3)_2$ ligands.

(iii) Predict the geometry of $[Ln(CH_2SiMe_3)_3(THF)_2]$. 2+2+1=5

(f) Give one example of each of the NAND and OR logic gates. 2.5+2.5=5

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

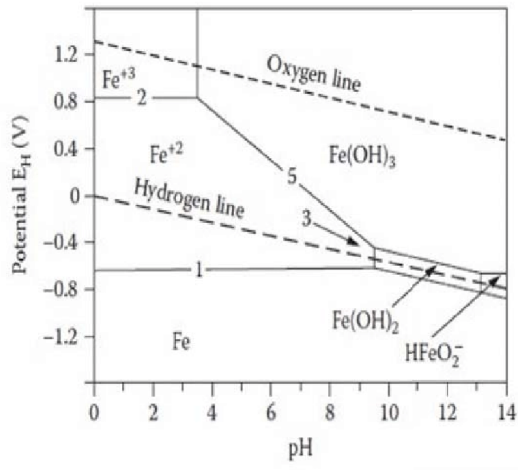
(a) (i) The compound $K_4[Fe(CN)_6]\cdot 3H_2O$ gives single line Mössbauer spectrum with no quadrupole splitting-Explain

(ii) Calculate the recoil velocity and energy of a Mossbaur nucleus having at.wt. 60 if the emitted gamma-ray has a frequency 1.84 × 1014Hz. (N = 6.023 × 1023, h = 6.626 × 10−34 Js, c = 3.0 × 108 $m.s$ −1)

(iii) Explain the following terms in the instrumentation of Mossbauer spectroscopy: vibrator and absorber.

(iv) What do you mean by “template effect”? 2+4+2+2=10

(b) Pourbaix diagram for the iron-water system 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) How can old iron objects survive a few hundred years under water? 3+3+2+2=5