VIT

Vellore Institute of Technology

2

SCHOOL OF ADVANCED SCIENCES

Department of Chemistry

Fall Semester 2023-24

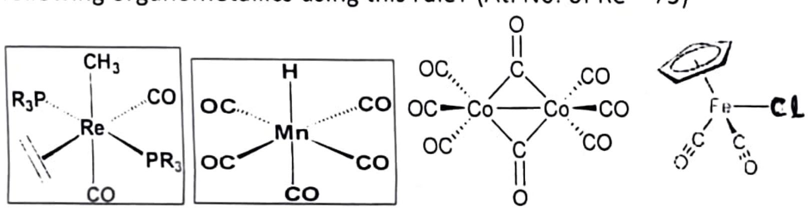
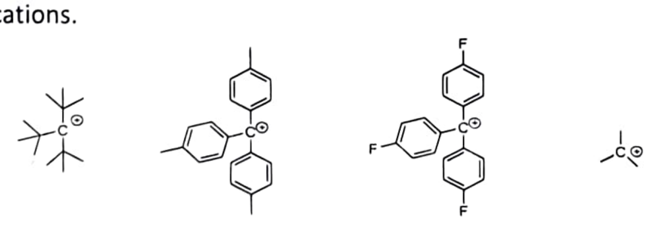
Continuous Assessment Test – I

Course Code: BCHY101L **Duration** : 90 Minutes **Slot** : D1+TD1

Course Name: Engineering Chemistry **Max. Marks** : 50

Class Numbers: VL2023240106278/6212/ 6214/6216/6218/ 6237/6242/6246/ 6250/6254/6262/ 6274/ 6282/6286/6290

Faculty Names: Dr. Priyankar Paira/Dr. Sriraghavan K/Dr. Buvaneswari G/Dr. Loganathan Rangasamy/Dr. Satish Kumar G/Dr. Manish Kumar Mishra/Dr. Abir Sarbajna/Dr. Tapas Ghatak/Dr. Ganesh Babu S/Dr. Tamas Kumar Panda/Dr. Badal Kumar Mandal/Dr.Sasikumar S/Dr. Madhumitha G/Dr. Asharani I.V/Dr. Mausumi Goswami

QN	Answer **ALL** the questions (5 x 10 = 50 Marks)	Marks	CO	BL
1	Elucidate the d-orbital energy levels and the distribution of d electrons among them, state the geometry and hybridization, label whether they are paramagnetic or diamagnetic, and state whether this is low or high spin complex. (At. No. of Ir = 77) $[Fe(CN)_6]^{3-}$, $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{2+}$, $[Ir(NH_3)_6]^{3+}$	10	CO1	BL3
2	What is 18-electron Rule? How do you explain the stability of the following organometallics using this rule? (At. No. of Re = 75) 	10	CO1	BL4
3	**(a)** Comment on the significance of Mg in Chlorophyll. **(b)** Find out the spin-only magnetic moment, Δ_0 and geometry of following metal complexes: $[Ni(CN)_4]^{2-}$ and $[Ni(Cl)_4]^{2-}$	(5 + 5)	CO1	BL1
4	**(a)** Write down the structure, oxidation state, hybridization and magnetic moment of the sandwich organometallic compound which is used as an anti-knocking agent in the fuel. **(b)** How do the 's' character and resonance influence the stability of carbanions? Explain with suitable examples.	(5 + 5)	CO1	BL2
5	**(a)** Describe the stability order of methyl radical, ethyl radical, isopropyl radical and tert-butyl radical. **(b)** Predict the decreasing order of stability of the following carbocations.  (a) (b) (c) (d)	(5 + 5)	CO1	BL3

b>a>d>c.

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$[Fe(CN)_6]^{3-}$, $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{2+}$, $[Ir(NH_3)_6]^{3+}$
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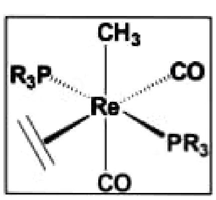
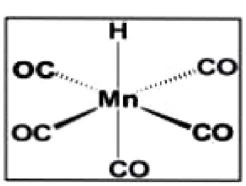
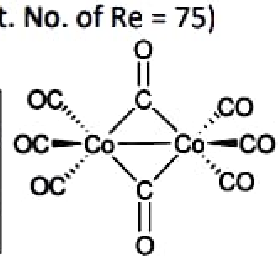
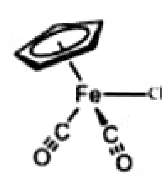
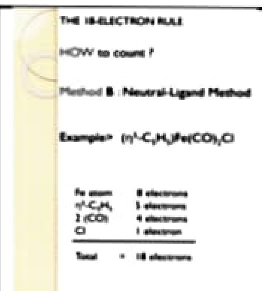
<tr><td></td><td>$[Fe(CN)_6]^{3-}$</td><td>$[CrF_6]^{3-}$</td><td>$[Co(NH_3)_6]^{2+}$,</td><td>$[Ir(NH_3)_6]^{3+}$</td></tr>
<tr><td>Oxidation state</td><td>III</td><td>III</td><td>II</td><td>III</td></tr>
<tr><td>Nature of ligand hybridization</td><td>d^2sp^3</td><td>$sp^3 d^2$</td><td>sp^3d^2</td><td>d^2sp^3</td></tr>
<tr><td>Geometry</td><td>Inner orbital Octahedral</td><td>Inner orbital Octahedral</td><td>Outer orbital Octahedral</td><td>Inner orbital Octahedral</td></tr>
<tr><td>Magnetic property</td><td>Paramagnetic Low spin</td><td>Paramagnetic High spin</td><td>Paramagnetic Low spin</td><td>diamagnetic</td></tr>
</table>
Strong and week field ligand
2.5 X 4 = 10</td><td>10</td><td>CO1</td><td>BL3</td></tr>
<tr><td>2</td><td>What is 18-electron Rule? How do you explain the stability of the following organometallics using this rule? (At. No. of Re = 75)








Ans. Definition 2
Calculate the 18 electron and stability 4 x 2 = 8</td><td>10</td><td>CO1</td><td>BL4</td></tr>
</table>

Re(+1) 6e- 2 PR_3 4e- 2 CO 4e- CH_3^- 2e- $CH_2=CH_2$ 2e- Total = 18e-	Mn(+1) d^6 6e- 5 CO 10e- H^- 2e-	Co = 9 3 terminal co = 6 2 bridge co = 2 Co-Co = 1 Total 18	

3

(a) Comment on the significance of Mg in Chlorophyll.

Any five points.

1. **Mg(II) prefers tetrahedral geometry rather than square planar geometry. But in Chlorophyll it is in square planar geometry**
2. **Mg(II)-N bonds in chlorophyll is strained – the electrons involved in bonding can be excited upon light absorption as strain is relived in excited state**
3. **The Mg2+ forms only weak spin-orbit coupling with excited state of the tetrapyrrole ring and thus it hinder the transfer of the energy of light in the forms of fluorescent or heat**
4. **In presence of Mg, rigidity of porphyrin ring will increase, excited state life time will increase-phosphorescence**
5. **Antenna chlorophylls – polymers of chlorophyll are formed due to the coordination of the carbonyl part of one chlorophyll with Mg(II) of other chlorophyll**
6. **The coordination of water in the axial position with Mg(II) favors splitting of water to form H atom that provides electron for photosynthetic process – active reaction center in photosynthesis**

(b) Find out the spin-only magnetic moment, Δ_0 and geometry of following metal complexes: $[Ni(CN)_4]^{2-}$ and $[Ni(Cl)_4]^{2-}$

Ans.

From VBT (4 marks)	CFT (1mark)
• Oxidation state of Ni = +2, • Geometry=, square planar, dsp • Diamagnetic, No. of unpaired electron=0,	Only describe the order of Δ_0 using the concept of strong and week field ligand
• Oxidation state of Ni=+2, • sp3. tetrahedral, • No. of upaired electron= 2, paramagnetic • μ=n(n+2)	

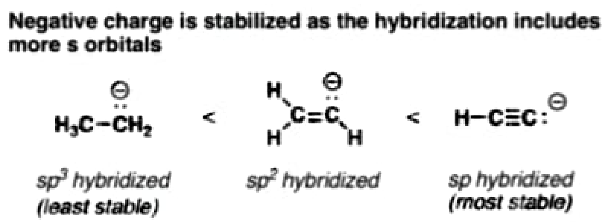
CN = strong field ligand; Cl = Weak field ligand

(5 Marks)

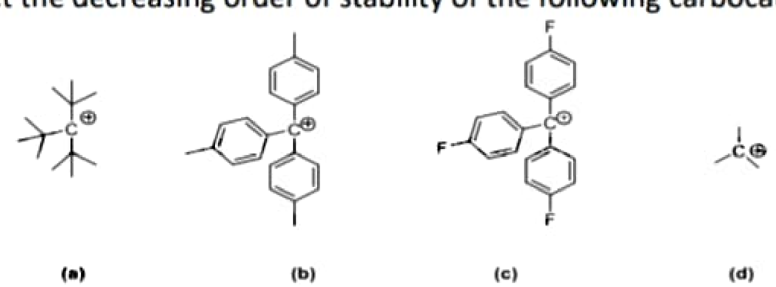
(5 + 5) CO1 BL1

<table>
<tr>
<td>4</td>
<td>(a) Write down the structure, oxidation state, hybridization and magnetic moment of the sandwich organometallic compound which is used as an anti-knocking agent in the fuel.
• Ferrocene structure (2marks)
• Oxidation state (1mark)
• d2sp2 hybridization (1mark)
• dimaganetic (1mark)

(b) How do the ‘s’ character and resonance influence the stability of carbanions? Explain with suitable examples.

Ans. Based on s character-greater the s character higher the stability
❖ An s orbital is closer to the nucleus than the p orbital in a given main quantum level and it possesses lower energy.
❖ An electron pair in an orbital having large s character is, therefore, more tightly held by the nucleus and hence of lower energy than an electron pair in an orbital having small s character.
❖ Hence, a carbanion at an sp hybridized (50% s character) carbon atom is more stable than a carbanion at a sp^2 hybridized (33.33% s character) carbon atom, which in turn is more stable than a carbanion at an sp^3 hybridized (25% s character) carbon atom.


</td>
<td>(5 + 5)</td>
<td>CO1</td>
<td>BL2</td>
</tr>
<tr>
<td>5</td>
<td>(a) Describe the stability order of methyl radical, ethyl radical, isopropyl radical and tert-butyl radical.
• Order of stability : tert-butyl radical> isopropyl radical>methyl radica (2marks)
• Presenting actual structure of each intermediate (1 mark)
• Explain based on Inductive effect and hyperconjugation trends (2 marks

(b) Predict the decreasing order of stability of the following carbocations.


• Order of increasing stability : b>a>d>c (1mark)
• Suitable explanation for each intermediate (1mark)
</td>
<td>(5 + 5)</td>
<td>CO1</td>
<td>BL3</td>
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</table>

a	b	c	d
Strong Inductive (+I) effect	Resonance effect (+R)	Resonance effect (-R) And –ve inductive effect	Less Inductive and less Hyper conjugation