INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
Department of Chemistry
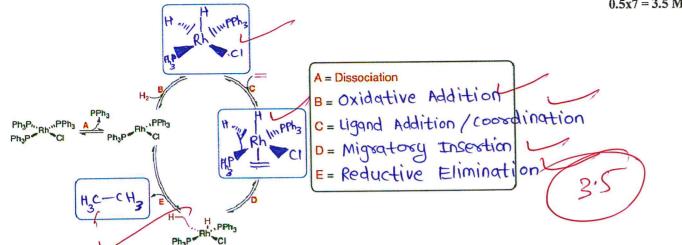**CH-101 (B.Tech. 1st Semester), End-Semester Examination-2019**

Name: Pradnesh P. kalkar   Roll No: 190123046   Tutorial Gr: T-18   [Sw]

Duration: 2.00 - 5.00 PM   Full marks: 60   Date: 27/11/2019   Signature of Invigilator

Answer all the questions. Write the answers inside the box. Only fully correct answers will be considered and there will be no partial marks unless specified. Tick inside appropriate box for the applicable questions. Increasing/decreasing order must be strictly considered wherever asked for. Answers in this sheet will be considered final and not in supplementary sheets.

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1. Based on the relationship between Einstein A and B coefficients, the ratio of A/B at 300 nm to that at 900 nm would be:
(A) 1/27 ☐ ; (B) 27 ✓ ; (C) 9 ☐ ; (D) 1/9 ☐   **2.0 Marks**

2. If the angle between the two hybridized orbitals $\Psi_1 = 0.45\Psi_{2s} + b\Psi_{2p_y} + 0.55\Psi_{2p_z}$ and $\Psi_2 = 0.45\Psi_{2s} - b\Psi_{2p_y} + 0.55\Psi_{2p_z}$ is 104.5° then the value of b is about:
(A) 0.00 ☐ ; (B) 0.55 ☐ ; (C) 0.45 ☐ ; (D) 0.70 ✓   **2.0 Marks**

3. The C-H bond (harmonic oscillator) vibrational frequency is 1.44 x 10^13 Hz. The force required to stretch the C-H bond (harmonic oscillator) by 0.2 Å is:
(A) 250 pN ✓ ; (B) 500 pN ☐ ; (C) 250 nN ☐ ; (D) 500 nN ☐   **2.0 Marks**

4. Butadiene is a conjugated molecule and can be considered (for particle-in-a-box model) to be linear with length of 578 pm. With the mass of electron, 9.109 x 10^-31 kg and Planck's constant being 6.626 x 10^-34 J, the absorbance band due to energy difference of 9.02 x 10^-19 J would be due to transitions between quantum states:
(A) 1 and 2 ☐ ; (B) 2 and 3 ✓ ; (C) 3 and 4 ☐ ; (D) 4 and 5 ☐   **2.0 Marks**

5. For nitrogen molecule at room temperature (T = 300 K), the typical rotational transition frequency is 30 GHz and $\delta v / v = 2.3 \times 10^{-6}$; where $\delta v = \frac{2v}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2}$. The line width would be about:
(A) 70 GHz ☐ ; (B) 70 Hz ☐ ; (C) 70 MHz ☐ ; (D) 70 kHz ✓   **2.0 Marks**

6. For a solution with absorbance of 2.0 at 600 nm, the %transmittance is:
(A) 100.0 ☐ ; (B) 1.0 ☐ ; (C) 10.0 ☐ ; (D) 0.1 ☐   **2.0 Marks**

7. In a region of space, a particle with mass m and with zero total energy has a time-independent wave function as is written in the right; where A and L are constants. The expression for the potential energy V(x) of the particle is, $\psi(x) = Axe^{-x^2/L^2}$
(A) $\frac{2h^2}{mL^4}\left(x^2 - \frac{3L^2}{2}\right)$ ✓ ; (B) $\frac{2h^2}{mL^4}\left(\frac{3L^2}{2} - x^2\right)$ ☐ ; (C) $\frac{\hbar^2}{mL^4}\left(x^2 - \frac{3L^2}{2}\right)$ ☐ ; (D) $\frac{h^2}{mL^4}\left(\frac{3L^2}{2} - x^2\right)$ ☐   **2.0 Marks**

8. Consider an electron traveling towards a stepped potential barrier (see figure on right) with energy of the particle (E) more than the barrier (V_0). The wave functions at the left side of the barrier and that at the barrier are $\psi_1(x) = A\exp(ik_1 x) + B\exp(-ik_1 x)$ and $\psi_2(x) = C\exp(ik_2 x)$, respectively. The expression for the reflection coefficient, $R = |B|^2/|A|^2$ would be:
(A) $(k_1+k_2)^2/(k_1-k_2)^2$ ☐ ; (B) $(k_1-k_2)/(k_1+k_2)$ ☐ ; (C) $(k_1-k_2)^2/(k_1+k_2)^2$ ✓ ; (D) $(k_1-k_2)/(k_1+k_2)$ ☐   **2.0 Marks**

9. Two copper nanowires are insulated by a copper oxide nano-layer that provides a 10.0-eV potential barrier. The tunneling probability between the nanowires by electron, with energy 9.00-eV, through a 1.00-nm thick oxide layer would be,
Use $T = 16\varepsilon(1-\varepsilon)e^{-2\kappa L}$ Also, $\varepsilon = E/V$ and $\kappa = \{2m(V-E)\}^{1/2}/\eta$
(A) 0.0051% ✓ ; (B) 0.068% ☐ ; (C) 0.0043% ☐ ; (D) 0.034% ☐   **2.0 Marks**

10. When the lower energy state of the molecule is a singlet state, the phosphorescence in a molecule occurs due to transition between the following states: **2.0 Marks**
(A) Triplet to Singlet ✓ ; (B) Triplet to Triplet ☐ ; (C) Singlet to Triplet ☐ ; (D) Singlet to Singlet ☐

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11. Each of the given complexes shows one IR band for CO stretching. Write the correct CO stretching frequency (v_{co} : 2046 cm⁻¹, 1788 cm⁻¹ and 1883 cm⁻¹) inside the box beside the given complexes.
(A) $Co(CO)_4^-$ | 1883 cm⁻¹ | ; (B) $Ni(CO)_4$ | 2046 cm⁻¹ | ; (C) $Fe(CO)_4^{2-}$ | 1788 cm⁻¹ | 0.5 x3 =1.5 Marks

12. Indicate whether the following exhibit Strong (S), Weak (W) or No (N) Jahn-Teller distortions.
(A) $[Cr(CN)_6]^{3-}$ | N | ; (B) $[Co(NH_3)_6]^{2+}$ | S | ; (C) $[Cu(H_2O)_6]^{2+}$ | S | **1.0 Mark**

13. The ground state terms of $[Ni(H_2O)_6]^{2+}$ and $[NiCl_4]^{2-}$ are, respectively (Please Tick)
(A) $^3T_{2g}$ and $^3A_2$ ☐ ; (B) $^1T_{1g}(F)$ and $^4A_2$ ☐ ; (C) $^3A_{2g}$ and $^3T_1(F)$ ✓ ; (D) $^3T_{1g}(F)$ and $^4A_2$ ☐   **2.0 Marks**

14. Consider Orgel diagram of *high-spin* octahedral Co(II) complex. Arrange the transitions in increasing order of their wavelength of absorption.   **2.0 Marks**

$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) < {}^4T_{1g}(F) \rightarrow {}^4A_{2g} < {}^4T_{1g}(F) \rightarrow {}^4T_{2g}$

15. For given set of elements or complexes, arrange them in the increasing order of the indicated property.   **2.0 Marks**

Elements/Complexes	Property	Increasing order
$Mo(CO)_3(PCl_3)_3$, $Mo(CO)_3(PF_3)_3$, $Mo(CO)_3(P(OMe)_3)_3$	CO Stretching Frequency	$Mo(CO)_3(P(OMe)_3)_3 < Mo(CO)_3(PCl_3)_3 < Mo(CO)_3(PF_3)_3$
B, F, Li, C, N, O and Be	First Ionization Potential	$Li < B < Be < C < O < N < F$
$[Fe(H_2O)_6]^{2+}$, $[Ru(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$	CFSE	$[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Ru(H_2O)_6]^{3+}$
$[Cr(NH_3)_6]^{3+}$, $[CrCl_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, $[Cr(CN)_6]^{3-}$	Wavelength of Absorption	$[Cr(CN)_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(H_2O)_6]^{3+} < [CrCl_6]^{3-}$

16. Indicate the number of valence electron on each metal complex.   0.5 x 4 = 2 Marks

Metal Complexes				
No of valence electrons	18	14	18	32

17. Which of the following are true when, one compares the highlighted bond angles and bond lengths? (Tick)   **2.0 Marks**

Complexes				
Bond angle		✓		
Complexes				
Bond length		✓		

18. Which of the following statements are true (T) and which are false (F).   0.5 x 8 = 4.0 Marks

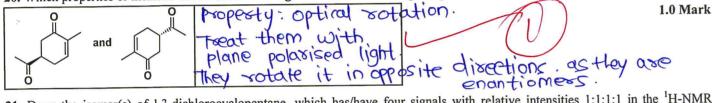| Sl	Statements	T / F
i)	The electronic absorption spectra of $[Mn(H_2O)_6]^{2+}$ shows a strong absorption due to the transition of electron from t_{2g} (non-bonding)→e_g (σ*)	F
ii)	According to CFT, the correct d–orbital splitting pattern for square–planar complex is $d_{xz} = d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$	T
iii)	In octahedral homoleptic complex with CO, the first d-electron is filled in t_{2g} bonding molecular orbital	T
iv)	The ground state term of $[Pt(Cl)_2(NH_3)_2]^{2+}$ is ^1F	F
v)	$[Rh(PPh_3)_3Cl]$ is less reactive than $[Ir(PPh_3)_3Cl]$ towards oxidative addition of H_2	T
vi)	The C–O bond in $H_3B(CO)$ is stronger than that in $Ni(CO)_4$	T
vii)	In the case of "non–electrophilic intact oxidative addition" two mono anionic ligands are generated starting from a neutral ligand	F
viii)	$[(dppe)Pt(CH_3)_2(I)]$ is more reactive than $[(dppe)Pt(CH_3)_3]^+$ towards reductive elimination of ethane	F

19. The scheme below depicts the hydrogenation of ethylene catalyzed by [RhCl(PPh₃)₃]. Fill in the **blank rounded rectangles** with appropriate molecular structures. If reaction **A** is dissociation of a neutral molecule, name the corresponding reactions **B, C, D** and **E**.
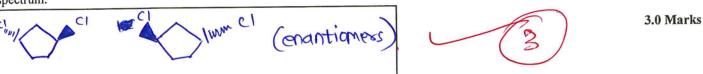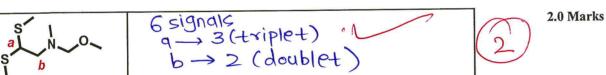
0.5x7 = 3.5 Marks

A = Dissociation
B = *Oxidative Addition*
C = *Ligand Addition / coordination*
D = *Migratory Insertion*
E = *Reductive Elimination*

3.5

20. Which properties or methods can be used to distinguish between following compounds?

1.0 Mark

Property: optical rotation.
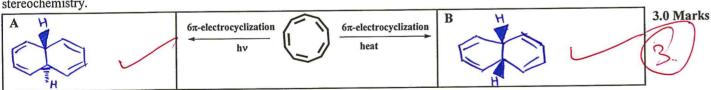*Treat them with plane polarised light. They rotate it in opposite directions. as they are enantiomers.*

(1)

21. Draw the isomer(s) of 1,3-dichlorocyclopentane, which has/have four signals with relative intensities 1:1:1:1 in the ¹H-NMR spectrum.
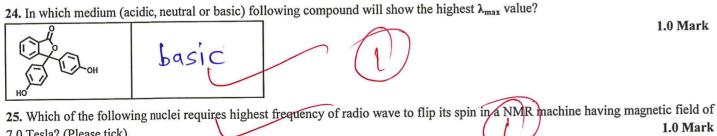
3.0 Marks

(enantiomers)

3

22. How many signals are expected in ¹H-NMR spectrum of the following compound? Provide the multiplicity of protons on carbon *a* and *b*.

2.0 Marks

6 signals
a → 3 (triplet)
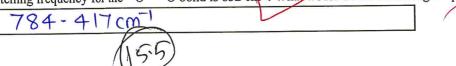*b → 2 (doublet)*

2

23. Provide the structures of the major products (**A** and **B**) formed in the following pericyclic reactions with proper relative stereochemistry.
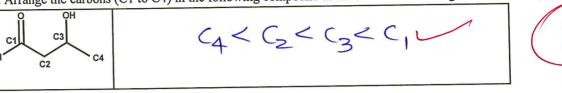
3.0 Marks

A — 6π-electrocyclization, hv — 6π-electrocyclization, heat — **B**

3

24. In which medium (acidic, neutral or basic) following compound will show the highest λ_{max} value?

1.0 Mark

basic

(1)

25. Which of the following nuclei requires highest frequency of radio wave to flip its spin in a NMR machine having magnetic field of 7.0 Tesla? (Please tick).

1.0 Mark

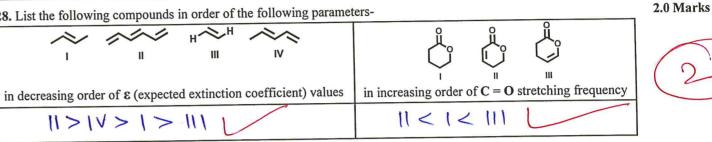(a) Unshielded ¹H nuclei ✓   (b) Unshielded ¹³C nuclei ☐   (c) Shielded ¹H nuclei ☐   (d) Shielded ¹³C nuclei ☐

26. Stretching frequency for the ¹⁶O – ¹⁶O bond is 832 cm⁻¹. What would be the stretching frequency for ¹⁸O – ¹⁸O bond?

1.0 Mark

784 - 417 cm⁻¹

15.5

27. Arrange the carbons (C1 to C4) in the following compound in the order of increasing chemical shift (δ) values.

1.0 Mark

$C_4 < C_2 < C_3 < C_1$
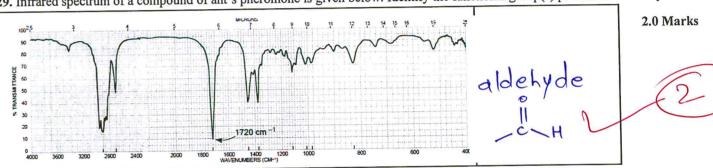
(1)

28. List the following compounds in order of the following parameters-

2.0 Marks

in decreasing order of ε (expected extinction coefficient) values	in increasing order of C = O stretching frequency
II > IV > I > III	II < I < III

(2)

29. Infrared spectrum of a compound of ant's pheromone is given below. Identify the functional group(s) present in the compound.

2.0 Marks

1720 cm⁻¹

aldehyde
$-\overset{O}{\overset{||}{C}}-H$

(2)

30. A compound with molecular formula of C_3H_4O has the following IR-spectrum and ¹H-NMR spectrum. Provide the exact molecular structure of the compound.

3.0 Marks

$HC \equiv C - CH_2 - OH$

(3)

8