COOCH BEHAR PANCHANAN BARMA UNIVERSITY

B.Sc. Honours 6th Semester Examinations, 2022

CHEMISTRY

INORGANIC CHEMISTRY-IV

CORE-13

Time Allotted: 2 Hours | Full Marks: 25

The figures in the margin indicate full marks.
All symbols are of usual significance.

GROUP-A

1. Answer any ***ten*** questions from the following: 1×10 = 10

(a) Calculate the value of '*x*' in $Co_2(CO)_x$ using 18 electron rule.

(b) Write down the formula of Collman's reagents.

(c) How many bridging carbonyls are present in $Mn_2(CO)_{10}$?

(d) Which *d* orbitals of Cr participate in π bonding with the ligands in $Cr(CO)_6$?

(e) What is the heptacity of cyclo-pentadienyl ring present in ferrocene?

(f) Draw the most stable structure of the oxidative addition product of Vaskas's complex with O_2 molecule.

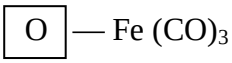
(g) What is the possible chemical composition of Ziegler-Natta catalyst?

(h) What are the alkylation products of ferrocene?

(i) What is oxidative addition reaction?

(j) Give one example of reductive carbonylation reaction.

(k) What is the oxidation state of Fe in the following complex?



(l) What is the hybridisation of Fe in $Fe_2(CO)_9$?

GROUP-B

Answer any *one* question from the following

2. (a) The carbonyl stretching frequencies of $[Mn(CO)_6]^+, [Cr(CO)_6]$ and $[V(CO)_6]^-$ occurs at 2090, 2000 and 1860 cm^{-1} respectively. Give reasons for such variation. 3

(b) Why Ethylene can not be hydrogenated by Wilkinson's catalyst? 2

3. (a) How terminal CO group can be distinguished from a bridging CO group — Explain briefly on basis of IR spectrum. 2

   (b) Why do ferrocene not undergo nitration reaction under similar condition to that of benzene? How can nitroferrocene be prepared? 3

4. (a) To a dry THF solution of $Fe(CO)_5$, metallic sodium is added and refluxed. CH_3Br is added to the reaction mixture. Predict the product with Chemical equation. 3

   (b) Classify the following reactions— (as oxidative addition, reductive elimination, insertion etc.) 2

   (i) $Ti\,Cl_4 + 2Et_3N \rightarrow TiCl_4\,(NEt_3)_2$

   (ii) $Co_2(CO)_8 + H_2 \rightarrow 2HCo\,(CO)_4$

GROUP-C

Answer any *one* question $10\times1 = 10$

5. (a) Discuss the mechanistic steps for the hydrogenation of olefins by Wilkinson's catalyst. 5

   (b) What is 'trans-effect'? Ni(II) does not show 'trans-effect' —Explain. 2+1

   (c) Predict the product of the following reactions. 2

   (i) $V(CO)_6 + NO \rightarrow$

   (ii) $H_3C - Mn(CO)_5 + SO_2 \rightarrow$

6. (a) Discuss briefly the differences of bridging efficiency of $Al_2(CH_3)_6$ and Al_2Cl_6. 3

   (b) What is Wacker process? Explain the role of $[PdCl_4]^{2-}$ in this reaction. 2+3

   (c) Show that cyclopentadienyl ligand is a flexidentate ligand. 2

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B.Sc. Honours 6th Semester Examinations, 2022

CHEMISTRY (PRACTICAL)

CORE-13

Time Allotted: 5 Hours | Full Marks: 15

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Qualitative Analysis of Inorganic Sample (Semi-Micro Method)

1. Students are advised to detect four radicals from the supplied Inorganic Samples marked as $I_n (n = 1, 2, 3, \cdots)$

   Perform Inorganic qualitative analysis as (Question No. 1) per the following points.

   A. Solubility Test:

Solvent	Cold	Warm
(i) H_2O		
(ii) Conc. HCl		
(iii) Conc. HNO_3		
(iv) Aquaregia		
(v) Insoluble in the above mentioned solvents if present.		

   B. Dry Test for basic radicals

Sl. No.	Experiment	Observation	Inference
1.	Ignition Test		
2.	Flame Test		
3.	Borax-bead Test		
4.	Oxidative fusion Test		
5.	Fluorescence Test		

   (Students are advised to write only positive observations in the above tabular form)

   C. Dry Test for acid radicals

Sl. No.	Experiment	Observation	Inference
1.	Sample + a few cc. Dil. H_2SO_4 and warm		
2.	Sample + a few cc. Conc^n H_2SO_4 and warms		
3.	Chromyl Chloride Test		
4.	Sample + Conc^n H_2SO_4 + Cu – turning and warm		
5.	Sample + MnO_2 + Conc^n H_2SO_4 + warm		

(Students are advised to write both positive and negative observations in the above mentioned tabular form)

D. Test for interfering acid radicals–

Sl. No.	Experiment	Observation	Inference
1.	A few cc. HNO_3 extract and ammonium molybdate in excess boil if required		
2.	Sample in dry test tube + a few cc. methanol / ethanol, the evolved gas is ignited on the mouth of the test tube		
3.	Repeat the experiment No. 2 with a few cc. of Conc^n H_2SO_4		

(Students are advised to write both positive and negative observations in the above mentioned tabular form)

E. Confirmatory Test for acid radicals (Na_2CO_3 extract is not mandatory for water soluble sample)

Sl. No.	Radical(s) Present	Confirmatory Test

F. Confirmatory Test for basic radicals–

Sl. No.	Radicals Present	Name the Gr.	Solvent	Confirmatory Test

Students are advised to report insoluble part if present in the above mentioned section. viz. E and F

G. Probable composition

Marks distribution pattern— (for Q. No. 1 only)

Section	Marks
A	0.5
B	2
C	1
D	1.5
E and F	1.5 × 4 = 6
G	1

2. Laboratory Note Book 1

3. Viva-voce 2

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B.Sc. Honours 6th Semester Examinations, 2022

CHEMISTRY

PHYSICAL CHEMISTRY-V

CORE-14

Time Allotted: 2 Hours | Full Marks: 25

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.
All symbols are of usual significance.

GROUP-A

1. Answer any ***ten*** questions from the following: 1×10 = 10

(a) When are two eigen functions mutually orthogonal?

(b) Write down the operator corresponding to linear momentum in y-direction.

(c) $f(x) = xe^{-x^2}$ is an odd function. Justify.

(d) Which of the following molecules give pure rotational spectra:

HCl, CO, CH_3Cl, N_2.

(e) For a normalised wave function ψ, what will be the value of $\int(\psi^*\psi\, d\tau)_{\text{all space}}$?

(f) Write down the SI unit of molar extinction coefficient.

(g) What is the Einstein's photoelectric equation?

(h) What are anti-Stokes lines in Raman spectroscopy?

(i) The intensities of hot band are usually very weak and become intense on increasing temperature, –Why?

(j) Write down the expression for zero point energy of a particle in one-dimensional box.

(k) State Frank-Condon principle.

(l) Give one example of Photosensitizer.

GROUP-B

Answer any *one* question from the following 5×1 = 5

2. (a) Distinguish between photochemical reactions and thermal reactions. 2+3

(b) Derive the Lambert-Beer's law in photochemistry.

3. (a) Starting from the Schrodinger equation, derive the equation of wave function $\left(\psi_n = A\sin\frac{n\pi x}{l}\right)$ for particle in a one-dimensional box. 4+1

(b) Explain why a value of quantum number $n = 0$ is not permitted.

4. (a) Write down the full Schrodinger equation (including all attraction and repulsion terms) for $\mathrm{Li}(n=3)$ atom. 2+3

   (b) The average solar energy incident per hour on Cooch Behar is $10^7\ \mathrm{J/m^2}$. Calculate the number of photons falling on unit square centimetre in one second. Take the average wavelength of light 550 nm.

GROUP-C

Answer any *one* question from the following 10×1 = 10

5. (a) With the help of Jablonski diagram briefly explain the phenomenon of fluorescence, phosphorescence, intersystem crossing, internal conversion and vibrational relaxation. 5+3+2

   (b) Why pure vibrational transition without affecting rotation is not permitted?

   (c) What are the P, Q and R branches in vibrational-rotational spectroscopy?

6. (a) From uncertainty principle show that electron cannot exist in the nucleus. Given that, radii of nucleus is of the order $10^{-14}\ \mathrm{m}$. 3+3+2+2

   (b) A particle of mass "m" is in a 3D cube with sides "L". It is in the third exited state. Corresponding to $n^2 = 11$, calculate the possible combinations of n_1, n_2 and n_3.

   (c) The gap between two successive rotational lines of a diatomic molecule AB is $10\ \mathrm{cm^{-1}}$. Find the frequency of $\mathrm{J}=1$ to $\mathrm{J}=2$ transition.

   (d) How would you explain very high and very low quantum yields of some photochemical reactions?

7. (a) Explain Born-Oppenheimer approximation used in molecular spectroscopy. 2+3+3+2

   (b) How do HCl and DCl differ in respect of vibrational spectra? Explain each case separately.

   (c) Show that the function $h(x) = \sin(nx)$ is an eigen function of the operator $\frac{d^2}{dx^2}$ but not $\frac{d}{dx}$. What is the eigen value of the former?

   (d) Sketch the vibrational modes of CO_2. Explain which of them will be IR active and Raman active.

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CHEMISTRY (PRACTICAL)

CORE-14

Time Allotted: 3 Hours | Full Marks: 15

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1. Verify Lambert-Beer's law and find out the unknown concentration from Colorimetric / Spectrophotometric analysis:

   (a) Derivation of working formula. 3

   (b) Prepare $\left(\frac{M}{1000}\right)$ order standand $K_2Cr_2O_7$ solution as stock solution and prepare at least 05 sets of solution of different concentration from the stock solution by dilution method. 2+2

   (c) Find the absorbance of the solutions using 430 nm wavelength of light in a spectrophotometer. Plot an absorbance versus concentration graph from the above results and find out the concentration of given unknown solution. 3+2

   (d) Viva-voce 2

   (e) Submit Signed LNB 1

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