

2007

CHEMISTRY

PAPER-III

Full Marks :75

Time : 3 hours

Answer **five questions** taking at least
two from each Group

*The figures in the right-hand margin indicate marks
Candidates are required to give their answers in their
own words as far as practicable*

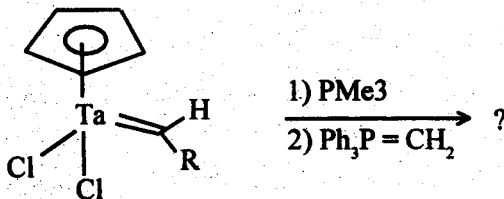
Illustrate the answers wherever necessary

GROUP-A

1 (a) Discuss the bonding in transition metal alkene
(ethylene) complexes. 5

(b) Complete the following reaction:

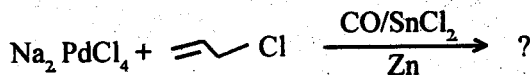
(1)



(Turn Over

(2)

(ii)



(c)

How will you synthesise



from NiCl_2

2

(d) What do you mean by 'fluxionality'? Explain with suitable example. 4

2. (a) Discuss the structure and magnetic properties of iron-sulphur clusters in different kind of Fe - S proteins. 6

(b) Explain the formation of hematin and discuss how this can be prevented. 4

(c) Discuss (any two): 5

(i) Bohr effect

(ii) Trigger mechanism

(iii) Difference between Fischer and Schrock carbene.

3 (a) How could you estimate a copper solution using EDTA by Spectrophotometric titration? 2

- (b) Elucidate the basic principle of flame photometry.
- (c) What do you mean by quenching of fluorescence ? 2
- (d) Explain schematically the instrumental setup of Atomic Absorption Spectrophotometer mentioning the function of each component. 3
- (e) What are the two types of coulometric methods used in analysis 2
- (f) What is the role of the supporting electrolyte in voltammetry and Coulometry ?
4. (a) Write note on one dimensional solid.
- (b) Comment on the anion ,of alkali metal.
- (c) Comment on the it bond of phosphonitrilic compounds. 2
- (d) Why boranes are getting greater attention in recent time ? 2
- e) Write note on Structure determination of cluster. compounds. 3

V3 Elucidate the structure of

BSH9 and Os5 (CO) 152 _

- S. (a) Using symmetry principle, obtain the hybrid orbitals for the sigma bond in CH₄. (Character table for the appropriate point group will be supplied). 6
- (b) a_1 , e_2 and e_3 are the three unit vectors along X, Y and Z axes respectively of a Cartesian co-ordinate system.., Find the matrix for a rotation of 30° about the e_2 vector (Consider counter clockwise passive mode of rotation). 4
- (c) Using symmetry principle, sketch a qualitative MO energy level diagram of NH₃. (Character table for the appropriate point group will be supplied). 5

GROUP -B

6. (a) [Ni (H₂O)]²⁺ gives absorption bands at 8500, 15,200 and 26,000 cm⁻¹ . Explain. 3
- (b) Explain why [V (H₂O)]³⁺ shows two instead of three absorption peaks in its spectrum. 3

- (c) How will you determine the composition of a complex by, 'slope-ratio' method. or 'Jobs method'. 4
- (d) Discuss (any two): 21 x 2
2
-) 'A'-mechanism
- (ii) Macrocyclic effect
- (iii) Stability constant of complex.
- (a)' What do you mean by isopoly and heteropoly acids? 3
- (b) How will you synthesize (i) Wilkinson's catalyst (ii) *cis*-[Pt (Cl)₂ NH₃ NO₂] from [Pt Cl₄]²⁻.
- (c) What do you mean by 'Creutz Taube Complex'?
- (d) Why NMR technique is used for detection of fluxionality? 3
- (e) Discuss N₂ fixation.

8. (a) Briefly describe 'Stokes shift'. 2
- (b) Describe the characteristics of molecules that fluoresce. 2
- (c) **Establish a relationship between percent transmittance and absorbance in spectrophotometry.** 2
- (d) Pd (II) and Au (III) present in a mixture is determined spectrophotometrically by reaction with **methiomeprazine**. The absorption **num** for the Pd-complex **occurs at 480 nm** while that for Au-complex is at 635 nm. Molar absorptivity (E) data at these **wavelengths are as follows :**

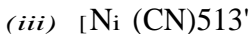
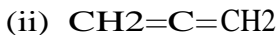
	480 nm	635 nm
Pd-complex	3.55 x 10 ³	5.64 x 10 ²
Au-complex	2.96 x 10 ³	1.45 x 10 ⁴

A 25 ml sample was treated with an excess of **methiomeprazine** and subsequently **diluted to 50 ml**, calculate the **molar concentration of Pd (II), Cpd and Au (III), CA., in the sample if the diluted solution had an absorbance of 0.533 at 480 nm and 0.590 at 635 nm when measured in a 1.00 cm cell.** 3

- (e) How can you measure **manganese** in steel by atomic absorption method? 3
- (f) **Distinguish between Voltammetry and Polarography.** 3
- (a) **Differentiate polynuclear classical complex to that of metal cluster.** 2
- (b) **Why elements of 2nd and 3rd transition series only form cluster in higher oxidation states though cluster in lower oxidation state is common to all transition elements.**
- (c) **How Re₂C₁₈2 is being synthesized? Discuss its structure.** 4
- (d) From the M. O. diagram compare
 (i) **colour of Mo₂Cl₉⁴⁻ and Re₂C₁₈2-**
 (ii) **structure of OS₂C₁₉²⁻ and Re₂C₁₈^{2'}.**
-) **Though 'Mo' can form both Mo₂C₁₈⁴⁻ and [Mo₆C₁₈]⁴⁺ Y^{e+}, 'Re' is different in this respect. Justify.** 3

10. (a) Determine the symmetry point group of the following molecules (any three): 2 x 3

(i) CHCl₃



(b) For C_{2v} the reflection operations belong to different classes while for C_3 , all the reflection operations belong to the same class. Explain. 3-

(c) 'No molecule can have only two orthogonal C_2 -axes of symmetry.' Explain. 3

(d) 'Construct matrix presentation of rotation symmetry by an angle θ , where three Cartesian axes serve as base vector. 3

Relevant Character Tables

g_d	E	$8C_3$	$3C_2$	$6S_4$	bad
A1	1	1	1	1	$x^2+y^2+z^2$
A2	1	1	1	-1	
E	2	-1	2	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T1, F, 3		0	-1	.1	(R_i, R_j, R_s)
T2, F2 3		0			$(x, y, z) \quad (xy, xz, yz)$

(9)

	<i>E</i>	<i>2C3</i>	<i>3av</i>			
A1	1	1	1	z		+ y ² ; z ²
A2	1	1	-1	Rz		
<i>E</i>	<i>L</i>	- <i>I</i>	p	(x, y); (^R	Ry)	(x ² - y ² , xy), 1As, yz)