Mid-Semester Examination (CYL100) 2024-25-M Semester

Full Marks: 60 Time: 2 h

Comment on the observation with a schematic diagram that the addition of hydrogen gas to the complex trans-[W(CO)₃(PCy₃)₂] (Cy = cyclohexyl) results in the formation of two complexes that are in equilibrium with one another. One complex has the tungsten center in a formal W(0) oxidation state while the other is in a formal W(2+) oxidation state. Removal of the H₂ atmosphere regenerates the starting material.

5 Marks

2. Suppose the crystallinity (X) of a polymer can be written as X = %Crystallinity/100. Then show that the density of the totally amorphous polymer (ρ_a) can be written as follows:

$$\rho_{\rm a} = \frac{\text{X-1}}{\text{X}/\rho_{\rm c} - 1/\rho_{\rm s}}$$

Where ρ_s is the density of a specimen for which the percent crystallinity is to be determined and ρ_c is the density of the perfectly crystalline polymer.

5 Marks

3. Draw the structure of the products A-C in the following scheme: 2 + 2 + 1 = 5 marks

(i)
$$CI_{M_{1}}$$
 $Pt_{M_{1}}$ $Pt_{M_{1}}$ $Pt_{M_{2}}$ $Pt_{M_{3}}$ $Pt_{M_{1}}$ $Pt_{M_{1}}$ $Pt_{M_{2}}$ $Pt_{M_{3}}$ $Pt_{M_{1}}$ $Pt_{M_{2}}$ $Pt_{M_{3}}$ $Pt_{M_{3}}$

- Which among the following compounds are hypervalent? Indicate the N-X-L notation for them: PhICl₂, Ph₅Te, XeO₂F₂, ClF₃, and SF₄.
 5 Marks
- 5. The enthalpy of hydration of Fe⁺² is 48 kJ/mol higher than the expected value assuming no CFSE. Estimate the $10Dq_0$ value of $[Fe(OH_2)_6]^{+2}$.

 5 Marks
- 6. (a) Explain whether Fe_3O_4 will adopt a normal or inverse spinel structure. (b) Considering the normal spinel structure of $MgAl_2O_4$, predict whether Mg^{+2} will occupy the tetrahedral hole or octahedral hole.

 4 + 1 = 5 Marks
- 7. Comment on the molar extinction coefficients (in L mol⁻¹ cm⁻¹) of the strongest visible absorption bands of the following complexes are [Mn(H₂O)₆]²⁺: 0.035; [MnBr₄]²⁻: 4.0; [Co(H₂O)₆]²⁺: 10; and [CoCl₄]²⁻: 600. 5 Marks

8. (a) Explain which of the following polymers (P1 or P2) will have the higher glass transition temperature (Tg) value.

- (b) With the increase of water or moisture content of the polymer the Tg value increase or decrease and why?
 3+2=5 Marks
- 9. (a) Write down three characteristic features of Wilkinson's catalyst. (b) Explain why ethylene cannot be hydrogenated by using Wilkinson's catalyst?

 2.5 + 2.5 = 5 Marks
- 10. The following data were obtained for the catalytic hydrogenation of cyclopropyl substrate with a series of hydrogenation catalysts. Determine individually which among them gives the best TON and TOF value.
 5 Marks

Entry	Catalyst	% Product
1	Pd(PPh ₃) ₄	37
2	(PPh ₃) ₃ RhCl	35
3	[(COE) ₂ IrCl] ₂	38
4	[(COD)RhCl] ₂	50
5	[(COD)IrCl] ₂	25

^a2.75 mM catalyst and 0.138 M substrate were used

11. The given cationic/anionic complexes obey the 18-electron rule. Identify the charge on the complexes).5 Marks

12. Among [Ni(CO)₄], [Co(CO)₄], and [Fe(CO)₄]² complexes, which one should have (a) a longer M-C bond and (b) a shorter CO stretching frequency?

5 Marks