BW-(O)CH-II/17

2017

CHEMISTRY - II

Time Allowed : 3 Hours

Full Marks : 200

If the questions attempted are in excess of the prescribed number, only the question attempted first up to the prescribed number shall be valued and the remaining ones ignored. Answer may be written either in English or in Bengali but all answers must be in one and the same language.

SECTION - I

This section comprises 15 questions in three Groups. Answer **Any Ten** questions taking at least three questions from each Group.

GROUP - A

1. Why Cuprous ion readily disproportionates into Cupric ion and Copper (O) ?

2. Graphite is covalent but behaves as conductor - explain.

3. Antimonate has the formula of $\left[Sb(OH)_6\right]^{-1}$ while arsenate has AsO_4^{-3} - why ?

4. Why iodine is capable of forming most of the polyhalides ?

5. Dimagnetic $\left[Co(NH_3)\right]F_3$ on heating at $115^{\circ}C$ is converted to a paramagnetic complex. Name the complex and explain its paramagnetism.

4×5

GROUP - B

6. Mention the basic assumptions and two limitations of the Langmuir's adsorption isotherm.

7. The vapour pressure of A is 939.4 mm of mercury and that of B is 495.8 mm at $140^{\circ}C$. Assuming that they form an ideal solution what will be the composition of mixture, which boils at $1400^{\circ}C$ under 1 atm pressure. What will be the composition of the vapour at this temperature ?

8. The rate of decomposition of acetaldehyde can be studied by measuring the pressure in a system at constant volume and temperature. Express the rate of the reaction in terms of rate of change of pressure. The reaction is $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$.

9. A drug is known to be ineffective after it has decomposed 30%. The original concentration of one sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming the decomposition to be first order, what will be the expiration time of the sample. What is the half-life of the drug ?

10. Pure and dry nitrogen gas was bubbled through a solution of 2.25 gm of a non-volatile solute (A) in 150 gm benzene and then through pure benzene. The loss in weight of solution was 2.154 gm and that of benzene was 0.016 gm. Calculate the molecular weight of A. 4×5

P. T. O.

GROUP - C

11. What happens when α-chloro cycohexanone is treated with NaOEt ? Write possible reaction pathway.

12. Write the products formed on reaction between 4-tert-butylcyclo hexanone and $LiAlH_4$. Explain the product ratio what you achieved.

13. Schemetically represent the following reaction with mechanism.

$$NO_2-C_6H_4-CHO \xrightarrow[CH_3CH_2CO_2Na]{(CH_3CH_2CO)_2O}$$
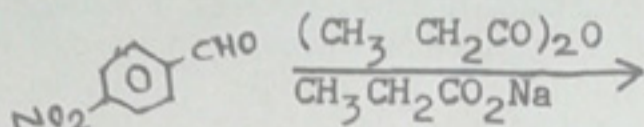
14. Carryout optical resolution of $(\pm)$-PhCHOHMe.

15. How many stereoisomers are possible for PhCHOH-CH=CH Ph ? Write their structure with proper stereochemistry.
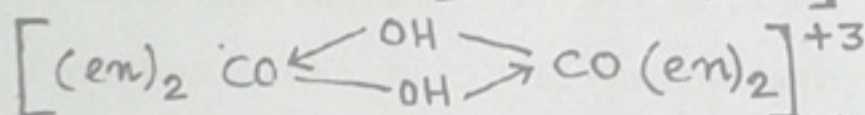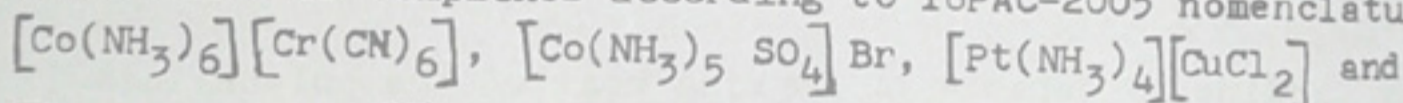
4×5

SECTION - II

This section comprises 6 questions in three groups. Answer **Any Four** questions taking at least one question from each group.

GROUP - A

16. (a) Classify ligands into different types giving examples. Write stereochemistry of Cr(III), Co(II), Co(III) and Cu(II) coordination complexes.

$10 + 10$

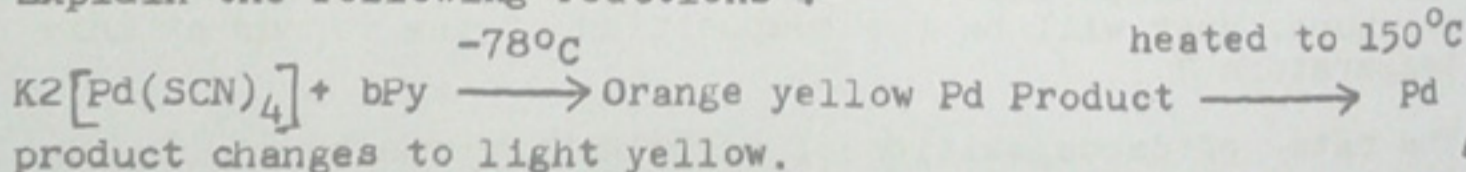(b) Write names of complexes according to IUPAC-2005 nomenclature.
$[Co(NH_3)_6][Cr(CN)_6]$, $[Co(NH_3)_5 SO_4]Br$, $[Pt(NH_3)_4][CuCl_2]$ and

$$\left[(en)_2 \, Co \underset{OH}{\overset{OH}{\rightleftarrows}} Co \, (en)_2 \right]^{+3} .$$

10

(c) What do you understand by inner metallic complexes of First and second orders ? Explain with examples.

10

17. (a) Why is the color of $[Cu(NH_3)_4]^{+2}$ different from that of $[Cu(H_2O)_6]^{+2}$?

4

(b) Explain the following reactions :-

$$K2[Pd(SCN)_4] + bPy \xrightarrow{-78^{\circ}C} \text{Orange yellow Pd Product} \xrightarrow{\text{heated to } 150^{\circ}C} Pd$$
product changes to light yellow.

4

(c) How myoglobin functions as oxygen transport proteins while ferrodoxine as electron transport proteins ?

8

(d) How would you distinguish between cis and trans isomers of a complex ? $(NH_4)_3[FeF_6]$ has magnetic moment of 5.92 BM, whereas $K_3[Fe(CN)_6]$ has 1.73 BM - Explain both on valence bond model and crystal field model.

$4 + 4$

(e) Represent the bonding in metal carbonyl with special reference to nickel tetra carbonyl. Show that same bonding scheme is extended in hexacyno complexes like $K_3[Mn(CN)_6]$.

8

(f) Show electron shell and structural feature in metal nitrosyl of dimeric Roussin's salt, $[Fe(NO)_2(SCH_3)]_2$.

8

Contd...P/3.

GROUP - B

18. (a) Derive Clapeyron equation and from it the Clausius-Clapeyron equation. What is the boiling point of water at a place where the atmospheric pressure is 600 mm. (latent heat of vaporization of water = 540 cal/gm). 12

(b) Derive expressions for $\Delta_{mix}G$, $\Delta_{mix}S$, $\Delta_{mix}H$ and $\Delta_{mix}V$ for the formation of an ideal solution from two liquids A and B. Show that the excess enthalpy and excess volume are both equal to the observed enthalpy and volume of mixing. 12

(c) Arrive at the Raoult's law from the kinetic or thermodynamic point of view. Show that in a binary liquid mixture if one constituent obeys Raoult's law then the other constituent will also follow Raoult's law. 8

(d) Show that the population of the rotational energy levels of a rigid rotor is a maximum for $J = \sqrt{\dfrac{kT}{2hcB}} - \dfrac{1}{2}$ where the terms have their usual significances, J = rotational quantum number. 8

19. (a) Derive the expression for the time-dependence of product (P) concentration for the following reaction scheme $A \rightarrow I \rightarrow P$, where the rate constants for the first order processes from $A \rightarrow I$ and from $I \rightarrow P$ are k_1 and k_2, respectively. When does the time dependence of the product concentration of the above mentioned reaction scheme becomes identical to the time dependence of product concentration for the reaction scheme, $A \rightarrow P$ for which the process is first order with a rate constant k_1. 12

(b) The microwave spectra of BrF shows several lines at a spacing of 0.722 cm^{-1}. If the mass of Br and F are 78.9 a.u and 19 a.u respectively, calculate the Br-F bond distance. [given 1 a.u = 1.661×10^{-27} Kg]. 8

(c) Show that for the opposing reaction $A \rightleftharpoons B$, $k_1 + k_{-1} = \dfrac{1}{t} \ln \dfrac{x_e}{x_e - x}$ when the initial concentration of A and B are a_o and zero, respectively. k_1 and k_{-1} are the rate constants for the first order forward and the backward processes, respectively and x_e is the equilibrium concentration of the product B. Find the value of $(k_1 + k_{-1})$ when the initial concentration of A and B are a_o and x_o, respectively. 10

(d) When acetone vapour is irradiated with light of wavelength 3130 Å, it decomposes as shown below

$$(CH_3)_2CO(g) \xrightarrow{h\nu} C_2H_6(g) + CO(g)$$

Using a reaction cell of 60.3 ml capacity and a temperature of 56°C irradiated for 23000 seconds at a rate of 85,200 erg per sec produced a change in pressure from 760 mm to 790.4 mm. Calculate (i) the number of molecules of acetone decomposed and (ii) the quantum yield. 10

P. T. O.

GROUP – C

20. (a) Draw all possible stereoisomers of 2,3-Dibromobutane in Fischer projection formula. Determine R/S notation of the compounds. Comment on their optical activity property. 8

(b) Schemetically represent the major and minor product formed in the reaction between (R)-2-phenyl propanal and Ph MgBr. Explain their formation. 6

(c) Predict products of the following two reactions with mechanistic explanation.

6
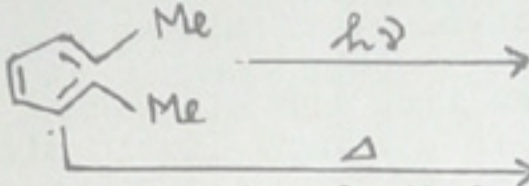
(d) Carry out synthesis of ethyl acetoacetate involved. Explain mechanism. 6

(e) Carry out following transformations with mechanism involved.

6
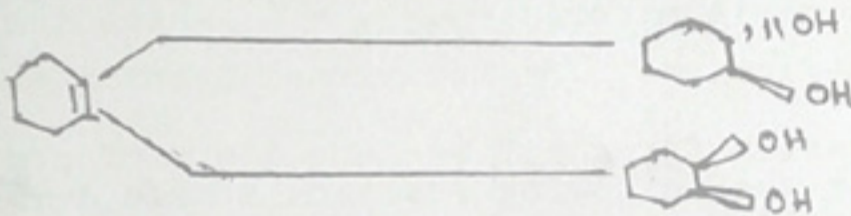
(f) Write the structure of Wilkinson's catalyst and use it for hydrogenation of an alkene. Explain mechanism. 4
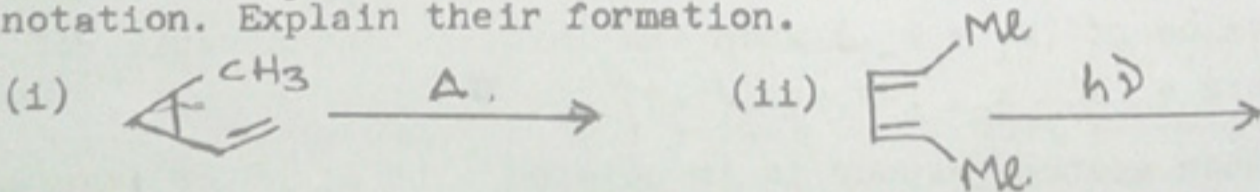
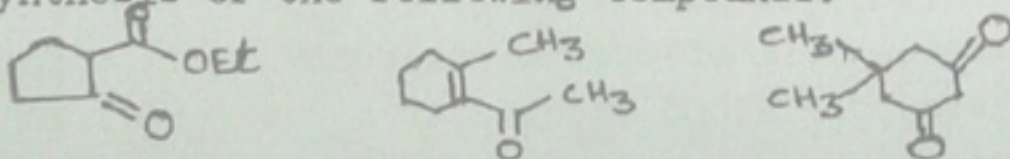(g) Carry out following reaction with mechanism of formation.

4
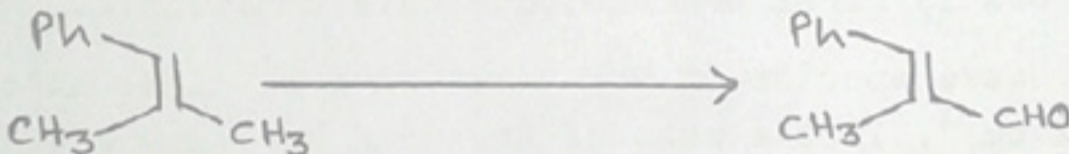
21. (a) Draw the energy profile diagram for conformational change of n-butane with respect to C_2-C_3 bond. Represent all conformers in Newman projection formula and comment on their population. 8

(b) Draw chair conformation of (R,S)-1,2-Dimethyl cyclohexane and comment on its chirality. 4

(c) Predict the product formed in the following reactions with R/S notation. Explain their formation.

8

(d) Using appropriate starting materials and reagents carry out synthesis of the following compounds.

12

(e) Write the product(s) of the following reaction with mechanism of formation.

8