EASTERN UNIVERSITY, SRI LANKA
THIRD EXAMINATION IN SCIENCE (EXTERNAL DEGREE)
EXCH 303 ORGANOMETALLIC CHEMISTRY, NON-AQUEOUS SOLVENTS AND SURFACE CHEMISTRY
(REPEAT-2004)

Time : 03 Hours

Answer six questions only, selecting at least one question from each parts A, B and C.

PART A

1) a) State whether each of the following would act as an acid or a base in liquid HF.

BF_3, SbF_5, H_2O, CH_3COOH

In each case, write equation(s) to show the basis for your answer.

b) Acetic acid act as a differentiating solvent for strong acids whereas water act as a leveling solvent for strong acids. Explain this statement.

c) Why are non-polar compounds usually insoluble in strongly polar solvents?

2) a) Write balanced chemical equations for the auto-ionization of,

i) Liquid H_2S.
ii) Liquid HF.
iii) Glacial acetic acid.

b) Discuss the following statements.

i) Potassium uride ($H_2NCONHK$) cannot be prepared in aqueous solutions; however, it could be readily prepared in liquid NH_3.
ii) Even though the salts as a whole are less soluble in liquid sulphur dioxide than in water, iodide salts are more soluble in liquid sulphur dioxide.

c) Explain the powerful reducing action of a solution of alkali metals in liquid ammonia.

3) a) What are the chemical reactions that can take place in liquid ammonia? Briefly describe them with one example for each.

b) Give balanced chemical equations for the following reactions:

i) Sulphamic acid ($SO_2\begin{matrix}NH_2\\OH\end{matrix}$) in NH_3

ii) CH_3COOH in H_2SO_4
iii) BCl_3 in H_2SO_4
iv) PCl_5 in HF.

c) Acetamide behaves as a weak base in aqueous solution but shows acidic property in liquid NH_3.

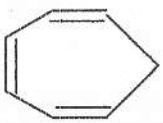
PART B

4) a) Manganese carbonyl **D** having empirical formula $Mn(CO)_5$, is diamagnetic and shows strong absorption only at 2500 cm^{-1} in the region where CO stretching frequencies are observed. Deduce the structure of manganese carbonyl **D**.

b) Give the products (**A-F**) of the following reactions.

i) $Mo(CO)_6 + C_5H_5Na \longrightarrow \underline{A} \xrightarrow{CH_3I} \underline{B}$

ii) $C_5H_6 + Fe(CO)_5 \longrightarrow \underline{C} \xrightarrow{\Delta} \underline{D}$

iii) $Mo(CO)_6 +$  $\longrightarrow \underline{E} \xrightarrow{PhC^+BF_4^-} \underline{F}^+ + PhH$

c) Indicate whether the following organometallic compounds obey the EAN rule or not.

i) $(\eta^6\text{-}C_6H_6)_2Fe$

ii) $[HFe(CO)_4]^-$

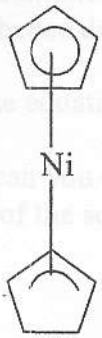
iii) $[Fe(CO)_2(NO)_2]$

iv) $[V(CO)_6]$

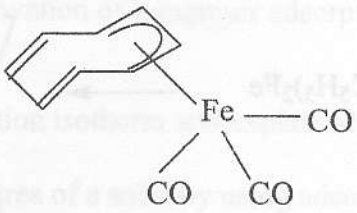
v) $[Mn(h^3\text{-}C_3H_5)(CO)_4]$

5) a) Indicate the monohapto, dihapto, trihapto, tetrahapto, pentahapto and bridging ligands present in the following compounds

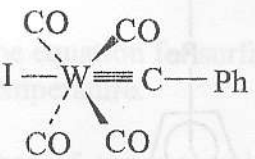
i)



ii)



iii)



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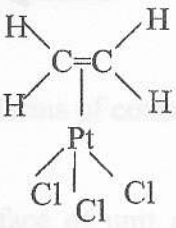
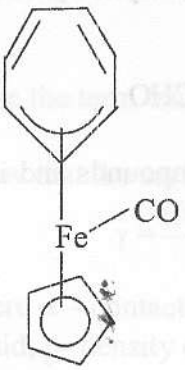


b) Give the systematic names of the following organometallic compounds.

i)

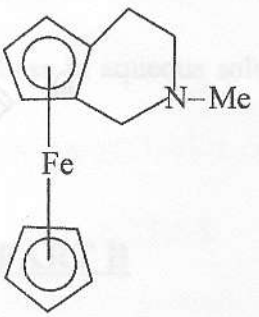


ii) $[Fe\ (\eta^5\text{-}C_5H_5)]$

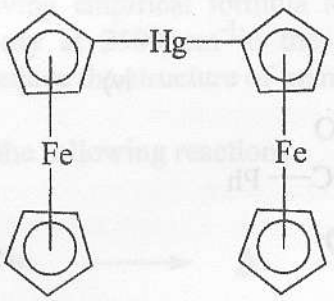
iii) $\left[Fe(CO)_2(NO)_3\right]$

c) Show by means of equations, how the following transformations may be effected via organometallic intermediates. Give, wherever possible, the experimental conditions.

i) $(C_5H_5)_2Fe$ ⟶



ii) $Fe(CO)_5$ ⟶



d) The frequencies of CO stretching in $Co(CO)_6$ and $Cr(CO)_6$ are found at 2143 cm^{-1} and 2000 cm^{-1} respectively. Give reasons for this difference.

6) a) Explain the bonding in π- allyl complexes.

b) Give the mechanism for the reactions involved in the catalytic cycle of ,

$$CH_2{=}CH_2 \xrightarrow[HCo(CO)_4]{H_2/CO} CH_3CH_3CHO$$

c) Discuss the molecular structures of the following compounds and indicate the IR spectral evidence of these structures.

i) $Fe_2(CO)_9$ ii) $Mn_2(CO)_{10}$

PART C

7). (a) Define the term 'adsorption' and give four differences between physical and chemical adsorption.

(b) Outline the assumptions made during the derivation of Langmuir adsorption isotherm and hence derive the equation.

(c) Write down the equation for the BET adsorption isotherm and explain all the terms in it.

(b) Explain how can you determine the surface area of a solid by using adsorption measurement of the solid

8). (a) Define the term 'surface excess'.

(b)Write down the equation for surface excess (Γ) in terms of concentration, surface tension and temperature.

(c) J_N, the number of gas molecules striking a surface of unit area (1 cm^2) in one second is given by the following equation:

$J_N = PN_A / (2\pi MRT)^{1/2}$ where N_A is the Avogadro number, P is the pressure of the gas, M is the molecular mass of the gas molecule and T is the temperature. How many molecules will strike a $1cm^2$ surface in one second at 298.15 K and a gas pressure of 1.05×10^{-6} Pa?

9). (a) (i) Define the term 'surface tension'.

(ii) Show that the surface tension γ is given by

$$\gamma = \frac{(b + a/3)\rho g a}{2\cos\alpha}$$

Where α contact angle, a – radius of the capillary tube, b – height of the liquid, ρ- density of the liquid and g-standard acceleration of free fall.

(b) The contact angle of a liquid is assumed to be zero. The height of the liquid level is 5.00 cm at 20^0 C in a clean glass capillary tube of radius 0.20 mm. Calculate the surface tension of the liquid at 20^0 C.
(The density of the liquid at 20^0 C is 998.2 $kgcm^{-3}$)

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