Model Solutions

INChO 2005

Problem 1 16 marks

Rates of Chemical Reactions and Arrhenius Equation

1.1 $r = 2.0 \times 10^{-6} \times 0.1 = 2.0 \times 10^{-7}$ mol dm^{-3} s^{-1}

$= 1.2 \times 10^{-8}$ mol mL^{-1} min^{-1}

1.2 (iv) the concentration of **A** decreases with time ☒

1.3 Units of A = units of k = s^{-1} (those of frequency)

1.4 A= 3.14×10^{11} dm^3 mol^{-1}s^{-1}

E_a = 193.2 kJ/mol

1.5 $\Delta H = -226$ kJ mol^{-1}

1.6 E_a (reverse) = 170.3 kcal mol^{-1}

1.7 $k_2[CH_3][CH_3CHO] = k_3 [CH_3CO]$

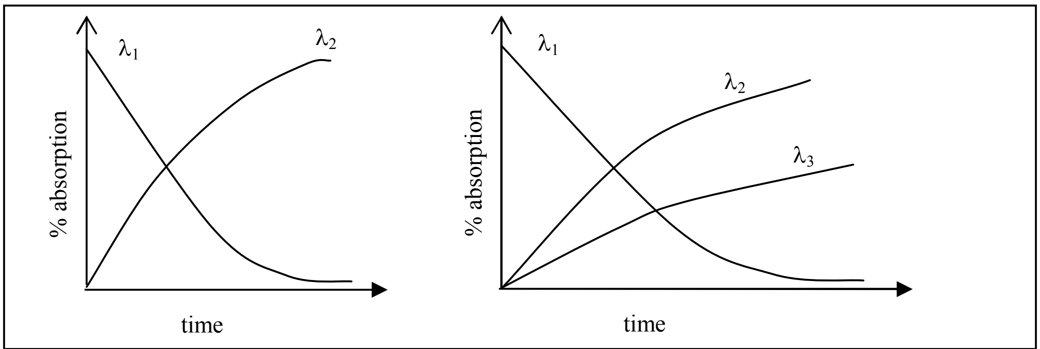
$[CH_3] = (k_1/2k_4)^{1/2} [CH_3CHO]^{1/2}$

$d[CH_4] / dt = k_2 (k_1/2k_4)^{½} [CH_3CHO]^{3/2}$

1.8 $E = E_2 + ½ (E_1 - E_4)$

1.9 (ii) X + Y → Z ; Z → W ☒

1.10



Problem 2 18 marks

Electrochemistry

2.1

$\Lambda(NaOH) = 221$

$\Lambda(NaCl) = 112$

$\Lambda(HCl) = 403$

$\Lambda(H^+ \text{ \& } OH^-) = 512$

2.2

κ (KCl) = 0.0812 S m^{-1}

2.3

Oxidation state of gold = 3

2.4

$E°_2 = E°_1$

$K_2 = (K_1)^2$

2.5

change in the cell potential is – 0.01 V

2.6

It is easier to carry out the oxidation $Cu^+ \rightarrow Cu^{++} + e^-$

Problem 3 14 marks

Molecular Structure and Spectroscopy

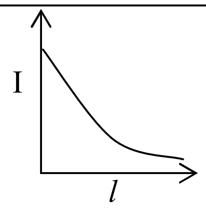
3.1

$$\int_{I_0}^{I} \frac{dI}{I} = -kc\int_{0}^{\ell} dx\,;\ \ln\frac{I_0}{I} = k.c.\ell$$

3.2

$dm^3.mol^{-1}.cm^{-1}$

3.3



3.4

Energy absorbed = 327 kJ mol^{-1}

3.5

$p = 8.8 \times 10^{-22}$ kg.m.s^{-1}

$\upsilon = 9.7 \times 10^{8}$ m.s^{-1}

3.6

$\Delta\vartheta_{min} = 1.1 \times 10^{-28}$ m.s^{-1}

3.7

The general solution of this differential equation is

$x(t) = A \sin \omega t + B\cos \omega t$ where $\omega = (k/\mu)^{1/2}$

$\nu = \omega/2\pi$ cycles/sec = $(1/2\pi)\,(k/\mu)^{1/2}$

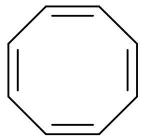
3.8

$k = 512.1\ Nm^{-1}$

Problem 4 **16 marks**

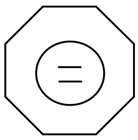
Cyclooctatetraene and Aromaticity

4.1



4.2 (b) a tub-shaped structure X

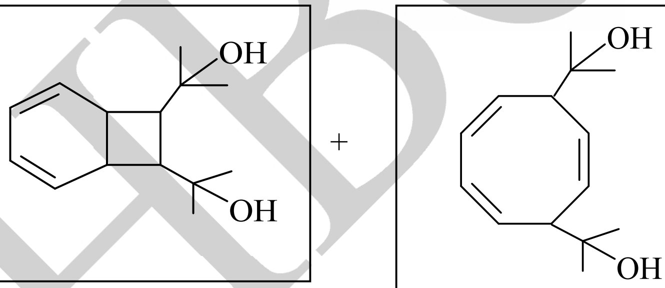
4.3



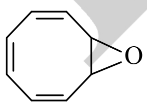
4.4 Planar

4.5 (c) the dianion is aromatic X

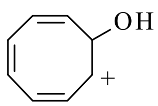
4.6



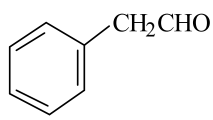
4.7



E

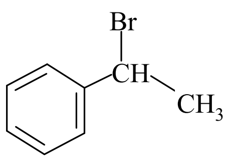


F (intermediate)



G

4.8



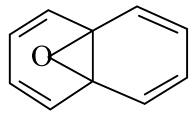
4.9 (a) substitution by an electrophile ✓

(b) addition of bromine ☒

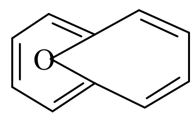
(c) catalytic hydrogenation under mild condition ☒

(d) addition reaction with maleic anhydride ☒

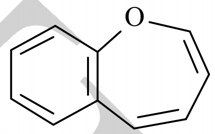
4.10



K (unstable)



L



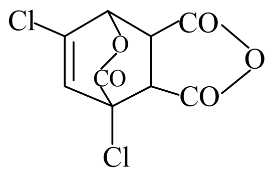
M

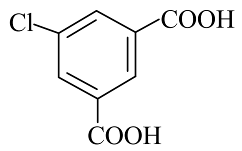
Is **L** aromatic? No X

Problem 5 14 marks

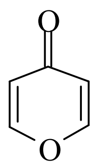
Diels-Alder Reaction

5.1

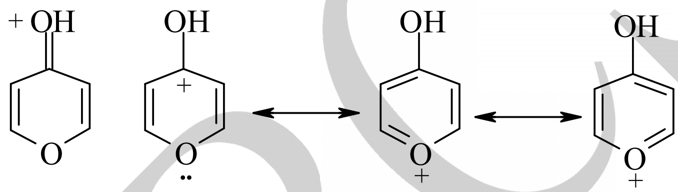




5.2

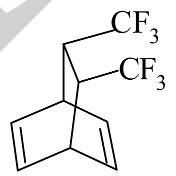


5.3

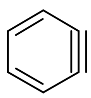


5.4 No ☒

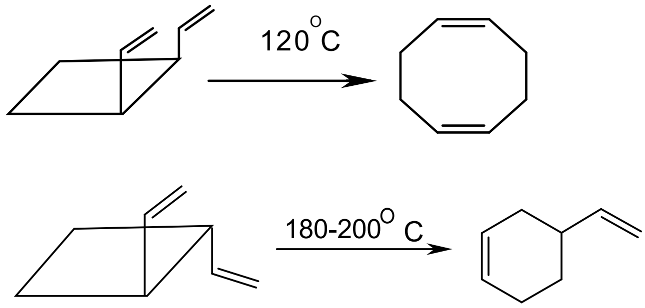
5.5



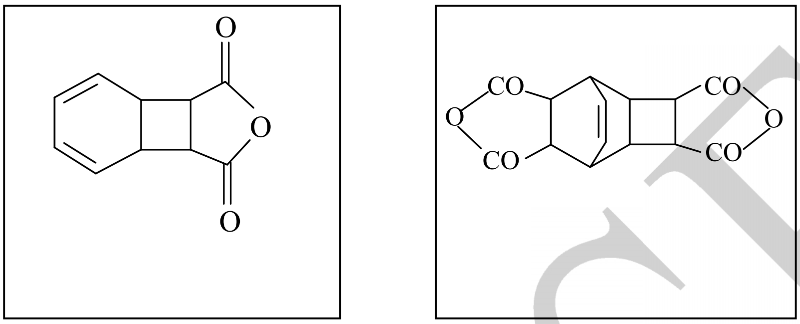
5.6

 + SO_2 + N_2

5.7



5.8



Problem 6 **12 marks**

Chemical Thermodynamics and Kinetic Theory of Gases

6.1

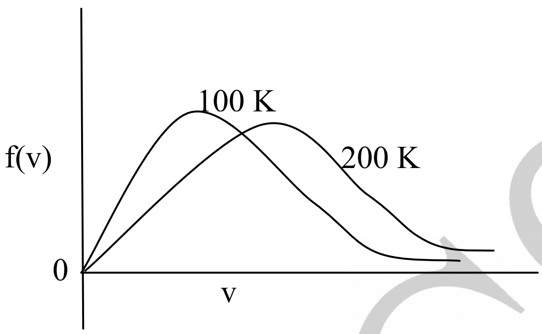
$H_2(g)$ = −120.9 kJ per g

$CH_3OH(l)$ = −19.9 kJ per g

$CH_4(g)$ = −50.1 kJ per g

$C_6H_{14}(g)$ = −453 kJ per g

6.2



6.3

$$v = \left(\frac{2kT}{m}\right)^{1/2}$$

6.4

$$v_{av} = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

6.5

$v_{av} > v_{mp}$

Problem 7 **10 marks**

Halogen Compounds

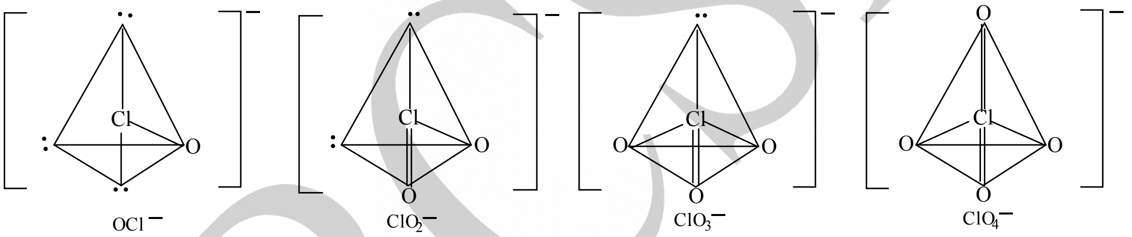
7.1 (c) F – F bond is weakened by strong repulsion between nonbonding electrons in small F_2 molecule [X]

7.2 (c) fluorine reacts with a metal to form a non-reactive metal fluoride film [X]

7.3 $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

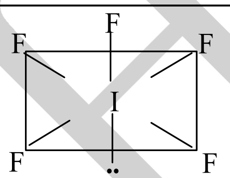
7.4 $HClO_4 > HClO_3 > HClO_2 > HOCl$

7.5



7.6 Due to lack of pπ-dπ bond

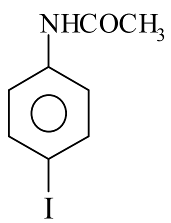
7.7



(Square) pyramidal

5s	5p			5d				
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			

7.8



Problem 8 **16 marks**

Proteins, amino acids, nucleic acids and buffers

8.1

$>CH\text{-}CH_2\text{-}S\text{-}S\text{-}CH_2\text{-}CH<$

(a) $S\text{-}C_2H_4\text{-}OH$ / $S\text{-}C_2H_4\text{-}OH$ (S–S bonded) + $>CH\text{-}CH_2\text{-}SH$

(b) $>CH\text{-}CH_2\text{-}S\text{-}CH_2\text{-}COO^-$

(c) $>CH\text{-}CH_2\text{-}SO_3H$

8.2 .

1) $H_3\overset{+}{N}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C(H)(\overset{+}{N}H_3)\text{-}COOH$

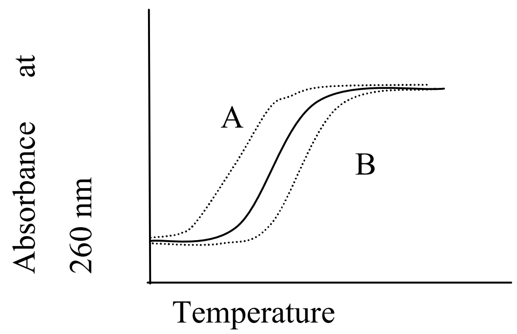
2) $H_3\overset{+}{N}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C(H)(\overset{+}{N}H_3)\text{-}COO^-$

3) $H_3\overset{+}{N}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C(H)(NH_2)\text{-}COO^-$

4) $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C(H)(NH_2)\text{-}COO^-$

8.3 (a) Sample A:
Since the DNA of bacteria isolated from sample (A) will have less number of G-C pairs, it would contain less nmber of H-bond and hence less stable. It would lose the structure first.

(b)



(c) $5'$ AUGUUCGGCUGGCAAUC $3'$

(d) 5 amino acids

(e) 120 * 5 = 600 daltons

8.4 (a) Starting pH of the assay mixture is 7.9. Since the reaction utilizes H^+ ion, the starting pH will be the lowest pH permissible to assay the enzyme activity, i.e. pH – 7.9.

(b) Total concentration of the buffer = 0.1786 M

Final concentration of conjugate acid $[Tris^+]_f$ = 0.0595 M

Final concentration of conjugate base $[Tris^0]_f$ = 0.1191 M

Final pH = 8.3

Problem 9 — 13 marks

Transition Metal Chemistry

9.1

Cr(24): $4s^1\ 3d^5$

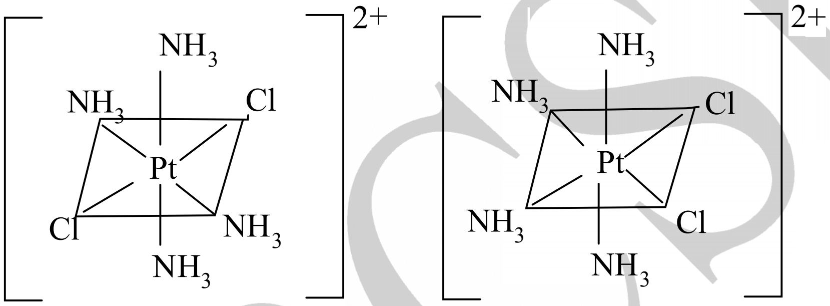
Cu(29): $4s^1\ 3d^{10}$

9.2

Diffuse nature of d orbital and increased nuclear charge due to added protons

9.3

Tetraaminedichloroplatinum(IV)

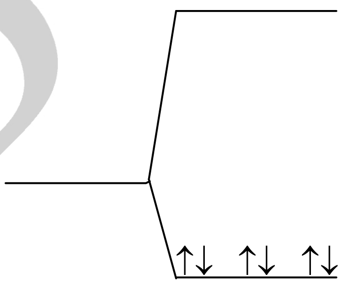


(trans) (cis)

9.4

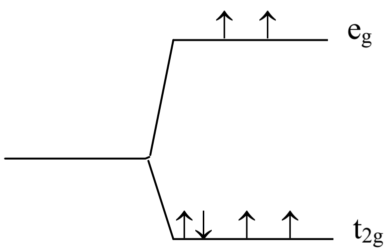
a] $[Co(NH_3)_6]^{3+}$

$Co^{3+} = d^6$



b] $[CoCl_6]^{3-}$

$Co^{3+} = d^6$ (high spin)

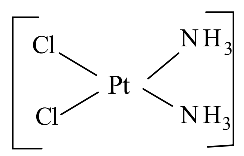


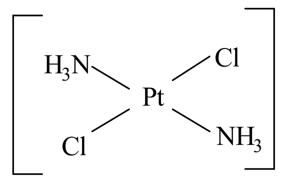
4 unpaired electrons, paramagnetic

$\mu = 2\sqrt{S(S+1)}$, where S =2

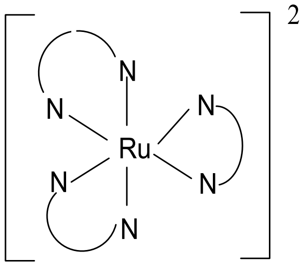
= 4.9 B.M

9.5



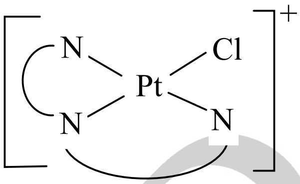


9.6 (a)



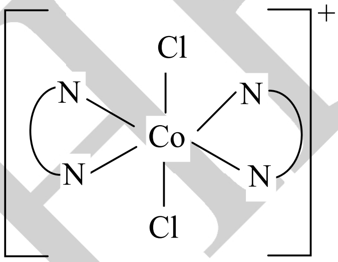
active ☒

(b)



inactive ☒

(c)



inactive ☒

INChO 2006

Problem 1 21 marks

Bombykol – An insect pheromone

1.1 $CH_3CH_2CH_2CHO$

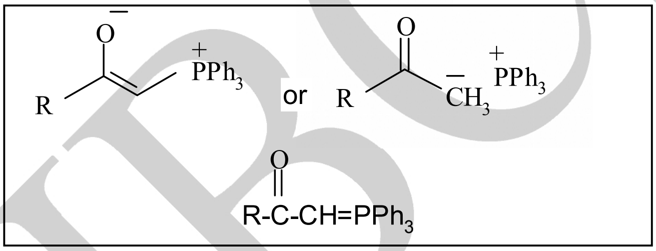
1.2 $(CH_2)_8$ with CHO and CH_2OH ; $(CH_2)_8$ with COOH and COOH

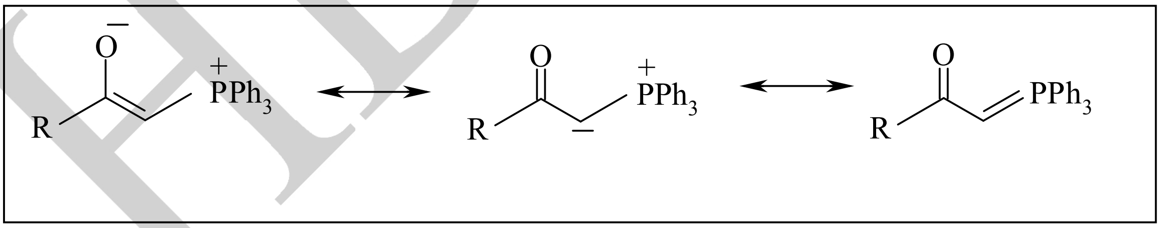
1.3 $CH_3CH_2CH_2CH{=}CHCH{=}CH(CH_2)_8CH_2OH$

1.4 (a) $CH_3CH_2CH_2\overset{+}{P}Ph_3\overset{-}{Br}$; $CH_3CH_2\overset{-}{C}H\overset{+}{P}Ph_3$

D

(b)





1.5 (b) pπ – dπ X

1.6 (a) $CH_3CH_2\overset{-}{C}H\overset{+}{S}(CH_3)_2$

Or **F**

$CH_3CH_2CH = S(CH_3)_2$

(b) $CH_3CH_2\overset{-}{C}H\overset{+}{N}(C_2H_5)_3$

G

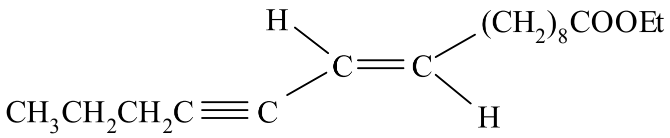
1.7 G

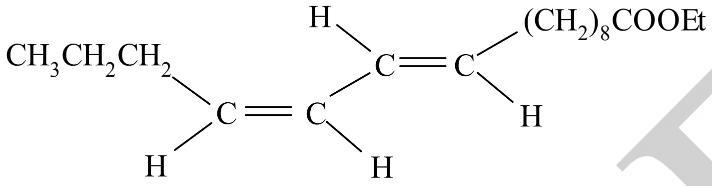
1.8

$CH_3CH_2CH_2C\equiv C\overset{-}{C}H\overset{+}{P}Ph_3$

or

$CH_3CH_2CH_2C\equiv C\overset{-}{C}H{=}\overset{+}{P}Ph_3$

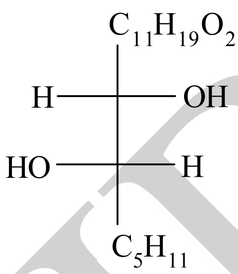


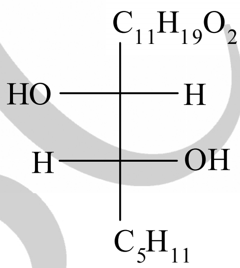


1.9 (10E, 12Z)-hexadecadien-1-ol

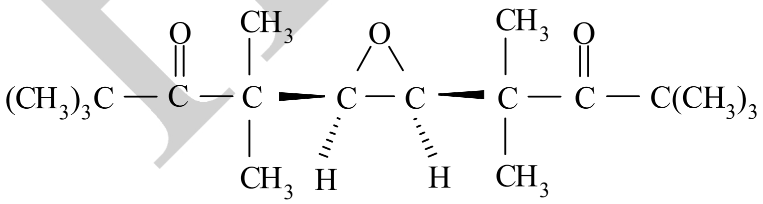
1.10 C_A R C_B S

1.11

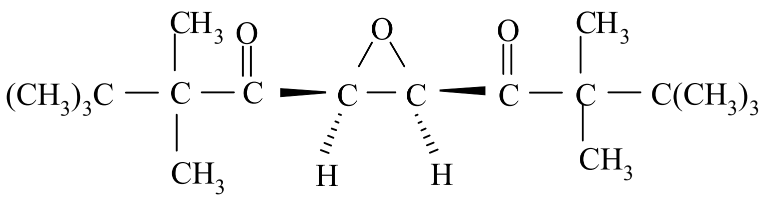




1.12



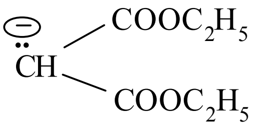
or



Problem 2 **17 marks**

Chemistry of Carbon Acids

2.1

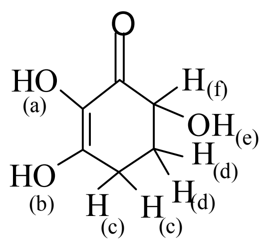


2.2 (i) $CH_3 – CH = CH – COCH_3$

(a) (b) (c) (d)

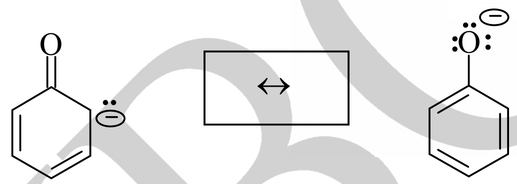
(a)

(ii)

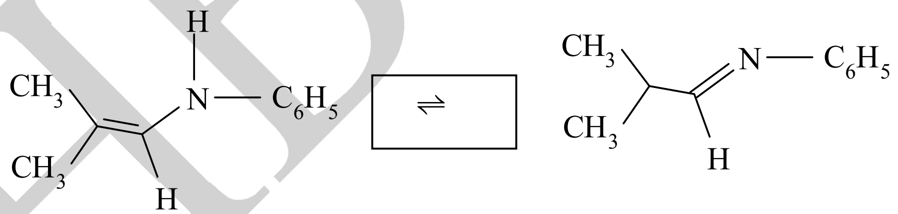


(b)

2.3 (i)

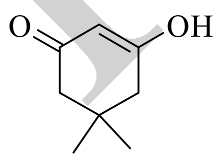


(ii)

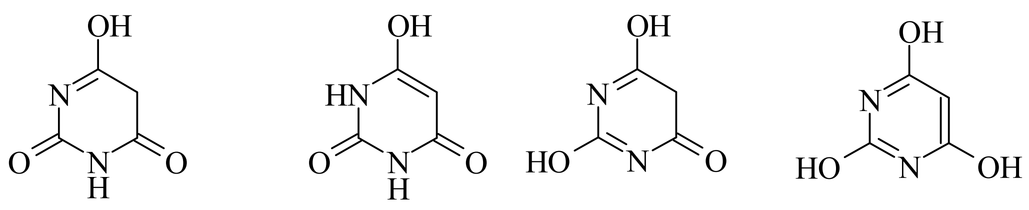


(0.5

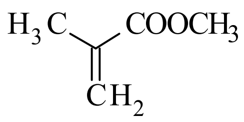
2.4



2.5



2.6

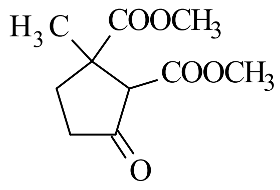


G

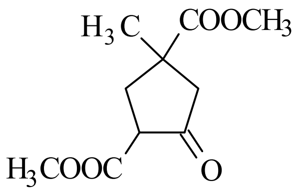
i) KMnO4 /OH$^-$ **H**

iii) CH_3OH / H^+ **I**

$CH_3O^-Na^+$ **J**



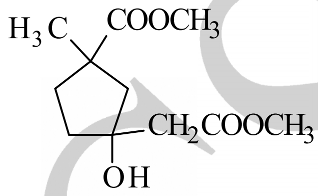
K



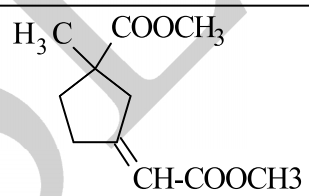
L

i) OH^-/H_2O ii) $H3O^+$ **M**

CH3OH / H+ **N**



O



P

H2-Pt **Q**

C2H5O$^-$ Na$^+$ **R**

S 2 CH_3I

2.7 2

2.8 1,3,3-trimethylbicyclo[2.2.1]heptan-2-one

2.9 Carbonyl group

2.10 (a) iv (b) i (c) ii (d) iii

Problem 3 14 marks

Chemical Kinetics

3.1

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

3.2

$-1/2\ d_{NO2}/dt = dP_{N2}/dt$

3.3

Runs 1 and 2; p_{NO} is doubled while that of H_2 kept constant. Rate changes 4 times. Order with respect to NO is **2**

Runs 3 and 4; p_{H2} is doubled while p_{NO} is kept constant. Rate doubles.

Order with respect to H_2 is **1**

Runs 3 and 5; both p_{NO} and p_{H2} are double. Rate changes 8 times. Confirms the orders

3.4

$Torr^{-2}\ sec^{-1}$

3.5

$-1/2\ d\ NO / dt = kapp\ [P_{H2}]$

3.6

sec^{-1}

3.7

i. Runs 1 and 2: NO is in excess. Hence the reaction will be of first order .

Rate= $k_{app}\ p_{H2}$; $t_{1/2}$ will be independent of p^0_{H2} . Hence it will be the same as for Run 1 = **19.1 sec**

ii. In Runs 3 and 4, H_2 is in excess. Hence the reaction will be of second order.

3.8

From Run 1 (or Run 2) , $k_{app} = 0.693/19.1$
$= 0.036\ sec^{-1}$

but $k_{app} = k\ p^0_{NO}{}^2$;

3.9

The differential rate equation is $- dp\ H_2/ dt = k\ [\ 2p\ H_2]^2]\ [p\ H_2]$ (from the given values of partial pressures and the reaction stoichiometry)

This on integration

3.10

$k = 1.0 \times 10^{-7}\ torr^{-2}\ sec^{-1}$ p^0_{H2} is 10 torr
at $t_{½}$ $[p\ H_2] = ½\ [\ p^0_{H2}\ ]$
Substituting these values, $8 \times 1.0 \times 10^{-7}\ t_{1/2} = 3/ 10^2$

3.11

$[N_2O] = k_2\ [N_2]\ [H_2O_2]/ k_3[H_2]$
$[H_2O_2] = k_1[NO]^2\ [H_2]\ /k_2$

3.12

$-d\ [N_2O]/dt = -d[H_2]/dt = k_3\ [N_2O]\ [H_2]$

3.13

Rate - $k_3\ [N_2O]\ [H_2]$
$[N_2O] = k_2\ [N_2]\ [H_2O_2]\ /k_3\ [H_2]$
substituting for $[H_2O_2]$, $[N_2O] = k_1 / k_3\ [NO]^2$
Hence Rate = $k_1\ k_3\ [NO]^2\ [H_2]/ k_3$

3.14 Yes [X]

Problem 4 — 13 marks

Solubility Equilibria

4.1

$Ag^{+} + Cl^{-} \rightleftharpoons AgCl\downarrow$

$2Ag^{+} + CrO_4^{-2} \rightleftharpoons Ag_2CrO_4\downarrow$

4.2

Amount of Cl^{-} in 100 mL = 0.0035 g

4.3

Indicator range 0.0139 – 0.00277 M

4.4

$[Cl^{-}] = 1.200 \times 10^{-5}$

4.5

$H^{+} + CrO_4^{2-} \rightleftharpoons HCrO_4^{-}$

$2H^{+} + 2\,CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O$

$2H^{+} + CrO_4^{2-} \rightleftharpoons H_2CrO_4$

4.6

From the above calculations, the sodium dihydrogen phosphate and sodium hydrogen phosphate buffer can be used.

4.7

(0.5 M)(0.5 L)(119.98) = 29.99 g of sodium dihydrogen phosphate

(0.15 M)(0.5 L)(141.96) = 10.65 g of sodium hydrogen phosphate

Problem 5 18 marks

Molecular Hydrogen

5.1

For the reaction II, $K = 1\times10^{-16}$

For the reaction III, $K = 9.743\times10^{4}$

5.2 On the basis of the values obtained for the equilibrium constants of the two reactions which of the statements would be correct?

(i) Reaction II is spontaneous whereas III is not. ☐

(ii) Both reactions II and III are spontaneous. ☐

(iii) When the reactants are mixed in the case of reaction II the reaction will go to completion whereas in the case of reaction III the equilibrium will lie towards left. ☐

(iv) Reaction III is spontaneous whereas II is not. ☐

5.3

No effect on the equilibrium constant, as the temperature is kept constant, the magnitude remains the same

5.4

$$\ln\frac{Kp_2}{Kp_{298}} = \frac{-8.5\ln(T_2/298)}{R} + \frac{0.02575(T_2-298)}{R} + \frac{40853}{R}\left(\frac{1}{T_2}-\frac{1}{298}\right)$$

5.5

$(Kp)_{1200} = 1.592$

5.6

$CO_2 = 26.39\ \% = H_2$

. $CO = 23.1\ \% = H_2O$

5.7

$K_4 = 4.62$ $K_5 = = 7.355$

Problem 6 **10 marks**

Electrochemistry

6.1

$E_{cell} = 1.104 V$

6.2

$\therefore$ Amount of $CuCl_2$ spilt = 0.0095 * 134.45 = 1.366 g

6.3

$[Cu^{2+}]_{final}$ = 0.09482 M

$[Zn^{2+}]_{final}$ = 0.10516 M

6.4

Zero

6.5

E_{cell} = 0.0641 V

6.6

$2Fe \rightleftharpoons 2Fe^{2+} + 4e^-$

$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$

6.7

$2Fe(OH)_2 + ½ O_2 + H_2O \rightarrow 2 Fe(OH)_3$

6.8

Galvanizing is preferred, as $E°_{Zn2+/Zn}$ is more negative than $E°_{Fe2+/Fe}$. Hence when exposed to air Zn will preferentially undergo oxidation as compared to Fe.

Problem 7 — 10 marks

Chemistry of Boron

7.1 $BF_3 > BCl_3 > BBr_3 > BI_3$

7.2 $BF_3 < BCl_3 < BBr_3 < BI_3$

7.3 (a) mismatch between size of boron atom and higher halogen atoms leads to poor overlap of p orbital, which leads to reduction in electron density on boron. ☒

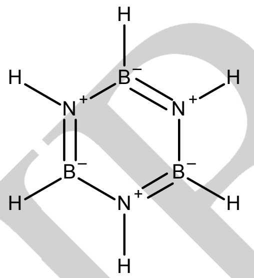
7.4 $F_3B \leftarrow NH_3$

7.5 $B_2H_6 + 2\ NH_3 \rightarrow [H_2B(NH_3)_2]^+ [BH_4]^-$ or equivalent answer

7.6 Diborane molecule has following type of bonds. Mark the correct answer.

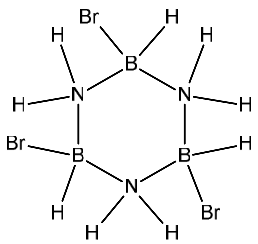
(b) 4 two center- 2 electron bonds and 2 three center- 2 electron bonds [X]

7.7



Dative bond between B-N is also Considered

7.8 $B_3N_3H_9Br_3$



7.9

(1) $(B_{12}H_{12})^{-2}$ Total electrons = 13 pairs

Therefore this is n + 1 case therefore *Closo* structure

(1) B_5H_{11} Total electrons pairs = 8 pairs

Therefore this is n + 3 case therefore *arachno* structure

Problem 8 — 23 marks

Chemistry of chromium and nickel

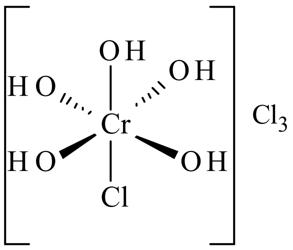
8.1

(1) moles of AgCl = 4.305 /143.5 = 0.03

(2) moles of AgCl= 2.87/143.5 = 0.02

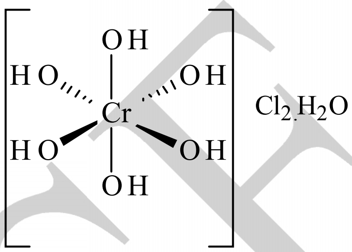
8.2

Complex X



$[Cr(H_2O)_6]Cl_3$
hexaaquachromium(III)chloride

Complex Y



$[Cr(H_2O)_5Cl]Cl_2.H_2O$
chloropentaaquachromium (III)chloride.hydrate

8.3 (a) hydrate [X]

8.4 (a) conductivity of complex X is greater than that of complex Y. [X]

Part B

8.5

$2FeO.Cr_2O_3 + 7Na_2O_2 \longrightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$

(**A** = $NaFeO_2$, **B** = Na_2CrO_4)

8.6

$NaFeO_2 + 2H_2O \longrightarrow NaOH + Fe(OH)_3$

(**A**) — (**C**) Red brown ppt

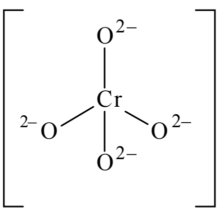
$Na_2CrO_4 + H_2O \longrightarrow CrO_4^{-2} + Na^+$

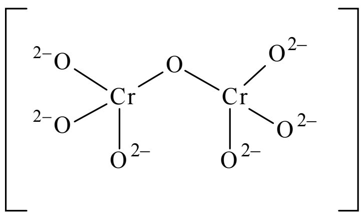
B — yellow **D**

$2CrO_4^{-2} + 2H^+ \longrightarrow Cr_2O_7^{-2} + H_2O$

(**E**) Orange

8.7





8.8 (b) charge transfer transition [X]

8.9

$Cr_2O_7^{-2} + 4Cl^- + 6H^+ \rightarrow 2CrO_2Cl_2$ (**F**) $+ 3H_2O$

$CrO_2Cl_2 + 4OH^- \rightarrow CrO_4^{-2}$ (**G**) $+2Cl^-$ (**H**) $+ 2H_2O$

$CrO_4^{-2} + Pb^{+2} \rightarrow PbCrO_4$ (**I**) $\downarrow$Yellow ppt.

8.10

$$2CrO_4^{-2} + 3S_2O_4^{-2} + H_2O + OH^- \longrightarrow 2Cr(OH)_3 + 6SO_3^{-2}$$

8.11

molarity = 0.0148mole/L=0.0148

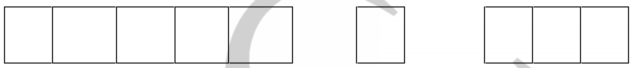
normality = molarity * 3 = 0.0445

S = N X Eq.Wt. = 0.0445 X 116 = 1.72 g/L = 1720 ppm

Part C

8.12

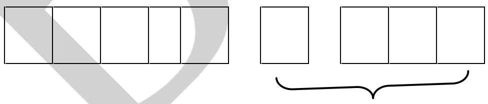
Ni $[Ar]3d^84s^2$



Ni^{+2} $[Ar]3d^8$

$[Ni(Cl)_4]^{-2}$ is paramagnetic

Ni^{+2} in $[NiCl_4]^{-2}$ [Ar]

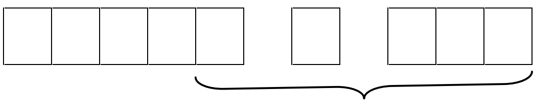


sp^3 hybridisation

sp^3 hybridisation therefore geometry tetrahedral

$[Ni(CN)_4]^{-2}$ is diamagnetic

Ni^{+2} in $[Ni(CN)_4]^{-2}$ [Ar]



dsp^2 hybridisation

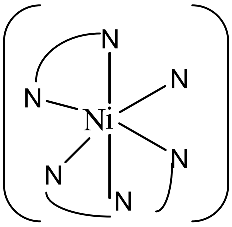
dsp^2 hybridisation therefore sq. planar

8.13

$$[Ni(H_2O)_6]^{+2} + 3en \longrightarrow [Ni(en)_3]^{+2} + 6H_2O$$

8.14 (c) optical

8.15



+2

8.16

J: $[Ni(H2O)_6]^{2+}$	λ max 650 nm
K: $[Ni(en)_3]^{2+}$	λ max 570 nm

8.17 Which of the following statements about the crystal field splitting 10Dq is correct?

(a) 10Dq of en > 10Dq of H_2O ☐

(b) 10Dq of en < 10Dq of H_2O ☐

(c) 10Dq of en = 10Dq of H_2O ☐

INCHO 2007

Problem 1 — 13 Marks

Chemical Kinetics and Reaction Rates

1.1

$$v = k[O_2]^2[NO] \quad \text{or} \quad v = k[NO]^2[O_2]$$

1.2

$$2O_2(g) + NO(g) \rightarrow NO_5$$

$$O_2(g) + 2NO(g) \rightarrow 2NO_2$$

Chemically correct reaction from the above two is

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

1.3

$$v = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

1.4

$$\frac{d[NO_2]}{dt} = \frac{k_1 k_2}{k_{-1}}[NO]^2[O_2]$$

1.5

$$\frac{d[N_2O_2]}{dt} = \frac{k_1}{k_{-1}}[NO]^2[O_2] \quad \text{for } k_{-1} >> k_2[O_2]$$

1.6

NO_3 is a radical species produced in mechanism – 1 and may be detected by an appropriate techniques such as ESR.

1.7

$$K_c = = 6.44 \times 10^5$$

1.8

$$\Delta E = -111.52\,\text{kJ}$$

1.9

The total number of gas molecules diminishes when the reaction proceeds to completion. So ΔS is –ve.

1.10

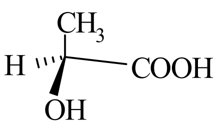
$$[H^+] = k^{1/2}c^{1/2}$$

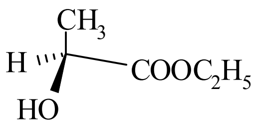
Hence, rate $= \text{const.}[\text{conc. of acid}]^{1/2}$

Problem 2 **16 marks**

Pheromones – A Case of Sulcatol

2.1

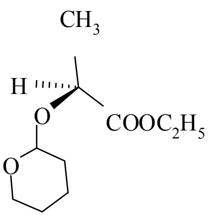




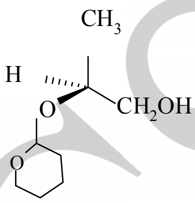
2.2 **I**

2.3 2

2.4



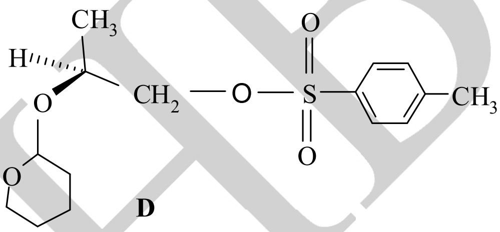
B



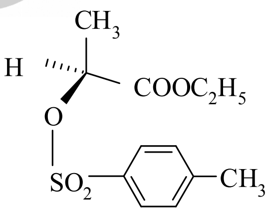
C

2.5 (iii) to increase nucleophilicity of hydroxyl group X

2.6

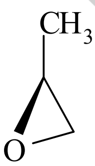


D



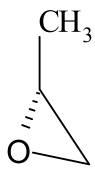
F

2.7



(S)

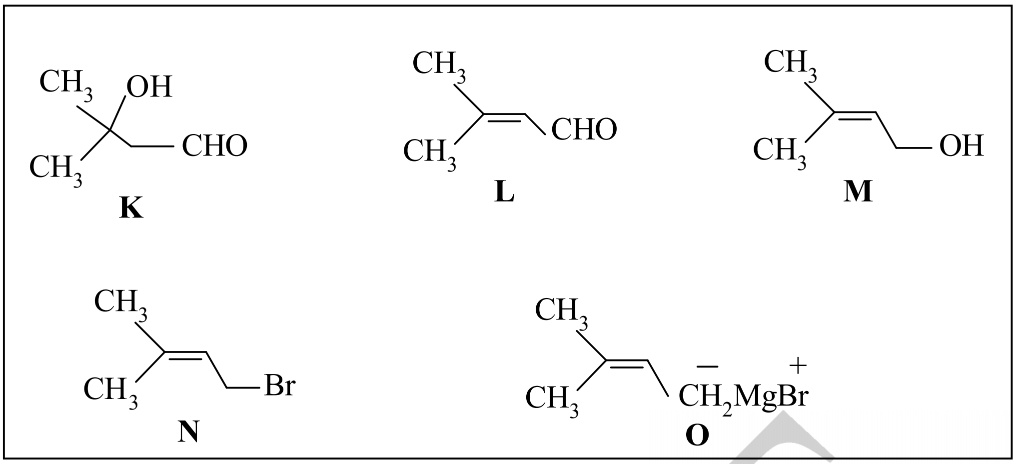
E



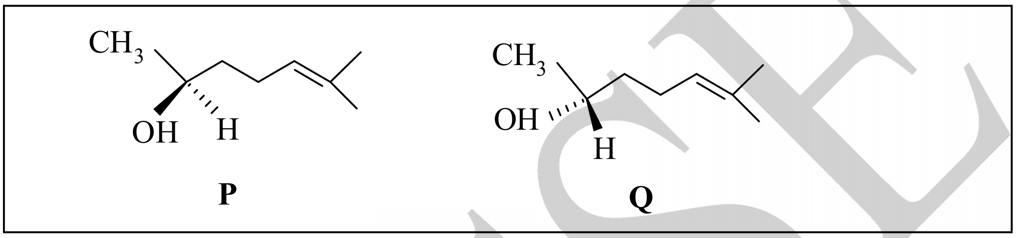
(R)

H

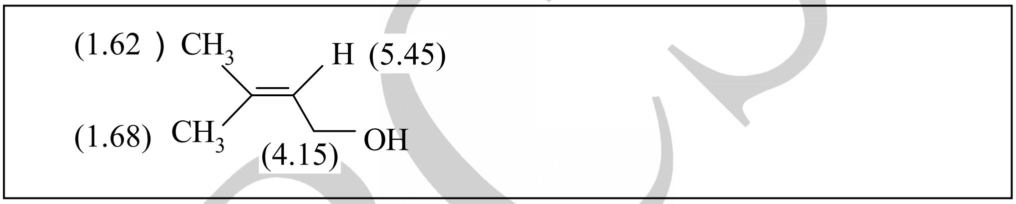
2.8


CH3
OH
CHO
CH3
K
CH3
CHO
CH3
L
CH3
CH3
OH
M
CH3
CH3
Br
N
CH3
CH3
CH2MgBr
O

2.9


CH3
OH
H
P
CH3
OH
H
Q

2.10


(1.62) CH3
H (5.45)
(1.68) CH3
(4.15)
OH

Problem 3 16 Marks

Sea Water

3.1 (c) ice has an open cage-like structure [X]

3.2 Boiling point of sea water = 373.6 K (0.5 mark)

3.3 (A) (b) 1.25 [X]

(B) (c) is stronger than that observed in NaCl [X]

3.4 (A)

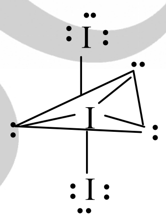
First extraction

Layer	Normality	Amount
Organic	0.04645	0.0590g of I_2/10 mL CCl_4
Aqueous	5.354×10^{-4}	0.0680g of I_2/1000 mL H_2O
Second extraction		
Organic	0.02486	0.03158g of I_2/10 mL CCl_4
Aqueous	2.8677×10^{-4}	0.03642g of I_2/1000 mL H_2O

$K = 0.04645/5.354 \times 10^{-4} = 86.70$

(B) sp^3d and linear

or



tbp with lone pairs at 3 vertices

3.5 (A) Mass of $CaCO_3$ = 1.6 × 50 = 80 g per litre of sea water.

(B) Na^+

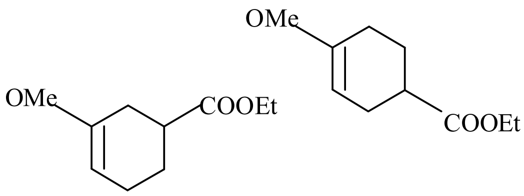
(C) % sites that underwent exchange = 0.08%

3.6 Volume of HCl at STP = 42.56 L.

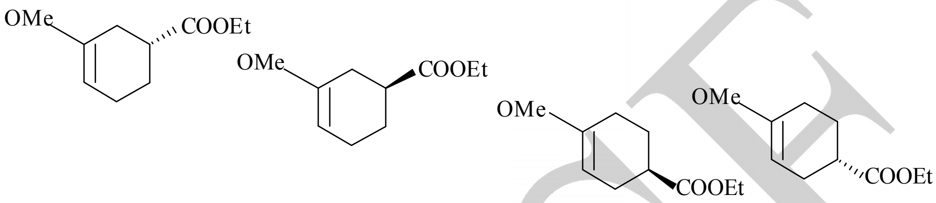
Problem 4 **21 marks**

Cycloaddition Chemistry

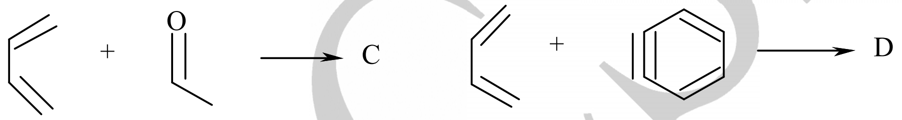
4.1



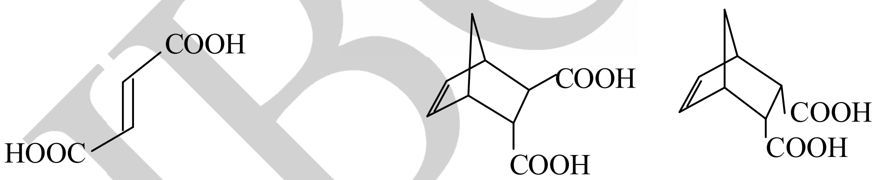
4.2



4.3

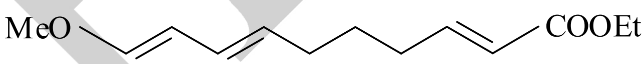


4.4

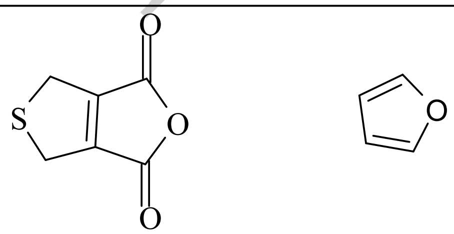


E

4.5



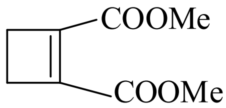
4.6



4.7

H_2/Ni

4.8



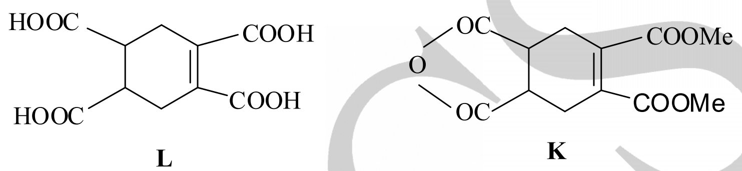
4.9 Equivalent weight of compound **L** is 64.5

4.10 The number of –COOH groups present in compound **L** is 4

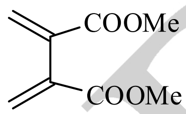
4.11 (ii) cyclohexane ring X

(iv) one double bond X **(1 mark)**

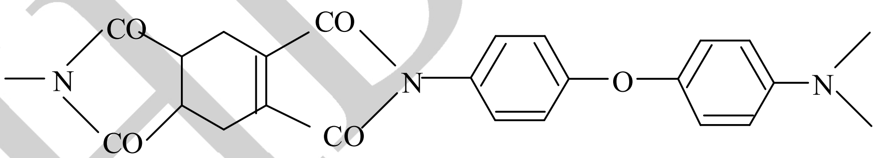
4.12



4.13



4.14



Problem 5 **21 marks**

Acetylene – Production, Structure & Uses

5.1

$$\rho = \frac{PM}{RT} = \frac{101.3\times10^3\times26}{8.314\times10^3\times300} = 1.06\,\text{kg m}^{-3}$$

5.2

Mass of commercial sample = (Since purity = 97 %) = 26.9 kg

5.3

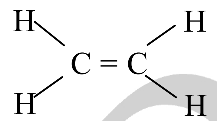
mass of water initially added 124.0 + 17.0 = 141.0 kg

mass of final slurry = 124.0 + 31.0 = 155.0 kg

5.4

Heat liberated on burning 16 kg of acetylene is ~ = 800 $\times10^6$ J

5.5



(sp^2)

H — C ≡ C — H (sp)

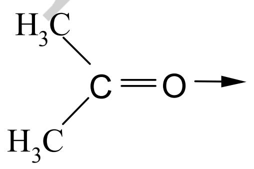
$CH_2 = C = CH_2$ (sp^2 for terminal and sp for central atom)

5.6 c) increasing s character with increasing unsaturation [X]

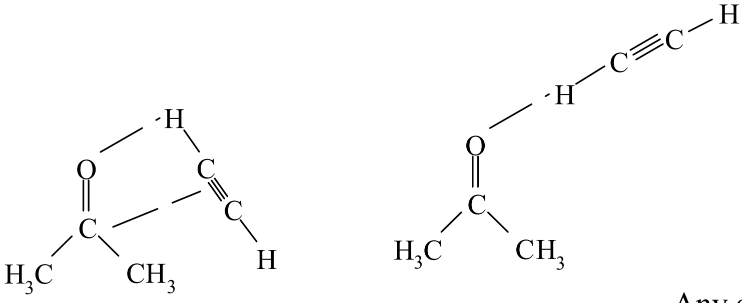
5.7 i) Hydrogen in acetylene [X]

ii) acetone [X] water [X]

iii)



iv)



Any other logical choice

5.8

percentage conversion of C_2H_2 = 40 %

5.9

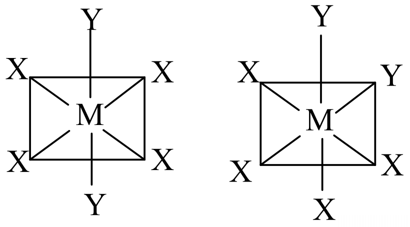
5% of initial water decomposed

Problem 6 33 marks

Transition Metal Chemistry

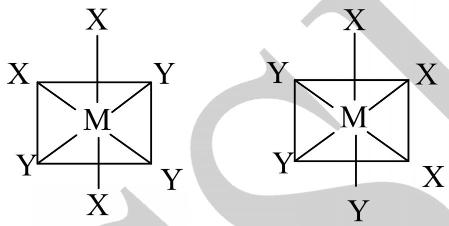
6.1

(i) MX_4Y_2



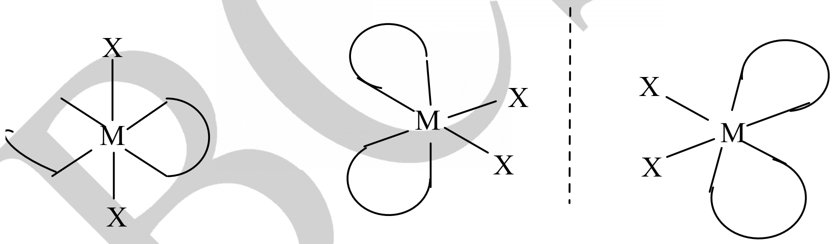
trans *cis*

(ii) MX_3Y_3



mer *fac*

(iii) $M(en)_2X_2$ (en: ethylenediamine) Represent en by ∩



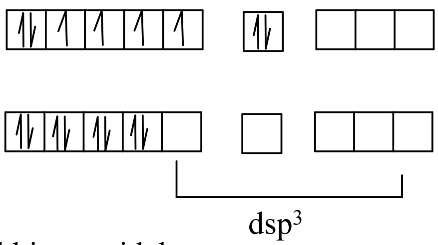
m*eso* *enantiomers*

diastereomers

6.2 (i) $Fe(CO)_5$

Fe [Ar]$3d^6$ $4s^2$ $4p^0$ (free metal) [Ar]

$Fe(CO)_5$ [Ar]

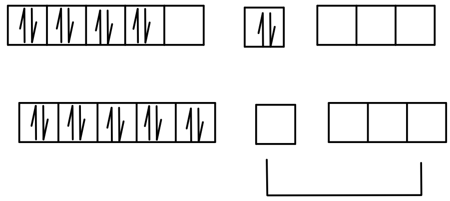


$Fe(CO)_5$ - dsp^3 hybridization, geometry = trigonal bipyramidal

(ii) $Ni(CO)_4$

Ni [Ar] $3d^8$ $4s^2$ $4p^0$ (free metal) [Ar]

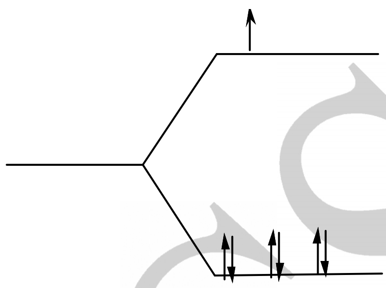
$Ni(CO)_4$ [Ar]



$Ni(CO)_4$ -sp^3 hybridization, geometry = tetrahedral geometry sp^3

6.3 (i) $K_4[Co(CN)_6]$

(i) Co^{2+} d^7

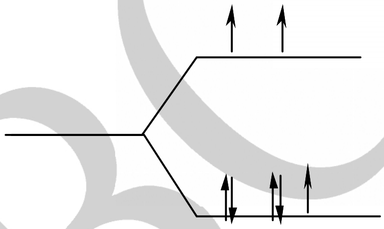


1 unpaired electron

Magnetic moment 1.73 BM

(ii) $K_4[Co(ox)_3]$

(ii) Co^{2+} d^7



3 unpaired electron

Magnetic moment 3.87 BM

6.4 i) Oxidation state of M III

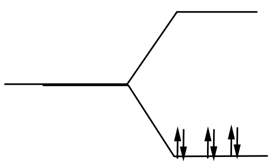
ii) Number of d electrons present 6

iii) Identify M Co

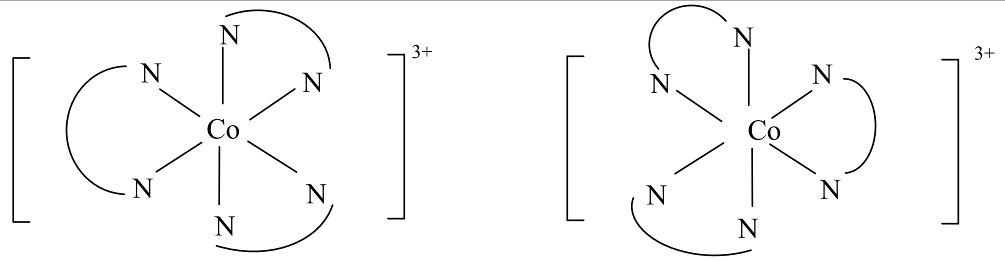
iv) No X

The complex is diamagnetic

d^6



(v)



6.5 TiO_2 has Ti^{4+} hence d^0 electronic configuration. Here d-d* transition is not possible hence it is color less. Fe_2O_3 has Fe^{3+} d^5 system hence, d-d* transition is possible.

6.6

$[Co(NH_3)_6]Cl_3$	: Hexamminecobalt (III) chloride
$K_4[Fe(CN)_6]$	: Potassium hexacyanoferrate (III)
$Fe(C_5H_5)_2$	: Bis(cyclopentadienyl)iron(II)

6.7