Equivalent solutions may exist

Problem 1 — 17 marks

Thermal and photolytic decomposition of Acetaldehyde

1.1 a)

$$-\frac{d[CH_3CHO]}{dt} = k[CH_3CHO]^{3/2}$$

$$\frac{d[CH_4]}{dt} = \frac{d[CO]}{dt} = k[CH_3CHO]^{3/2}$$

(b)

Order = 3/2

Rate = 8 v

1.2

CH_4, CD_4 and CO

1.3 (a)

Propogation steps : (ii) and (iii)

Termination step: (iv)

(b)

$$[\bullet CH_3] = \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

$$[\bullet CH_3CO] = \frac{k_2}{k_3}\left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^{3/2}$$

(c)

$$\frac{d[CO]}{dt} = k_2\left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^{3/2}$$

1.4 (a)

$CH_3CHO + h\nu \rightarrow \bullet CH_3 + \bullet CHO$
Rate = I_{abs}

$[\bullet CH_3] = (I_{abs}/2k_4)^{1/2} [CH_3CHO]^{3/2}$

$d[CO]/dt = k_2 \times (I_{abs} / 2k_4)^{1/2} [CH_3CHO]^{3/2}$

(b) $\lambda = 317.5$ nm

1.5 (a)

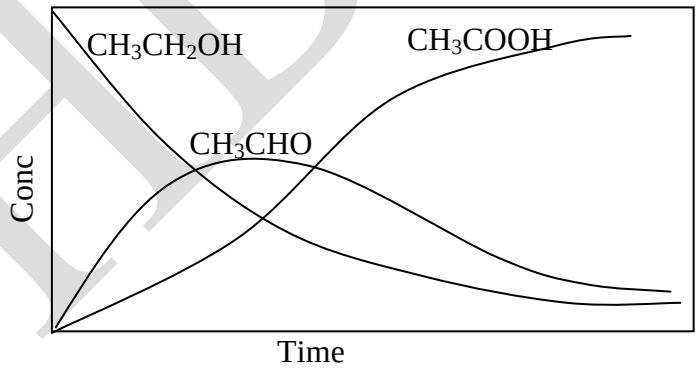
$$E_{thermal} = E_2 + \frac{1}{2}(E_1 - E_4)$$

(b) $E_{photochemical} = E_2 - ½\ E_4$

1.6 (a) $E_{thermal} = 196.46$ kJ mol^{-1}

(b) 5.879×10^{-4} mol dm^{-3} sec^{-1}

1.7 (a)



(b) $[CH_3CHO] = k_5/k_6\ [CH_3CH_2OH]$

Problem 2 19 marks

Chemistry of coordination compounds

2.1

$CuSO_4 + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+} + SO_4^{2-}$
White Blue solution

or balanced equation with $[Cu(H_2O)_4]^{2+}$ entity

$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$
From dil NH_3 Blue ppt.

$Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$
Deep blue soln

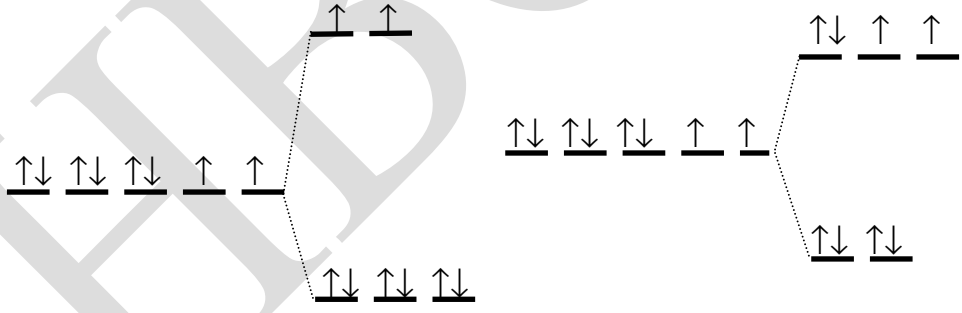
2.2

b] completely filled d-level in Cu(I)

2.3

a] oxidation state of the metal.
b] nature of the ligand.
c] geometry of the complex.

2.4



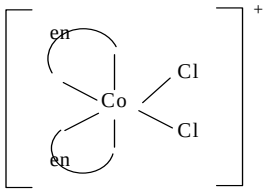
$[Ni(H_2O)_6]^{2+}$ $[NiCl_4]^{2-}$

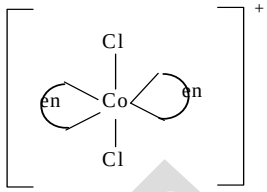
$[Ni(H_2O)_6]^{2+}$ is octahedral. $[NiCl_4]^{2-}$ is tetrahedral

2.5

a] . IUPAC Name : Dichlorobis(ethylenediamine)cobalt(III) ion.
Dichlorobis(ethane-1,2-diamine)cobalt(III) ion
Dichloridobis(ethylenediamine)cobalt(III) ion.
Dichloridobis(ethane-1,2-diamine)cobalt(III) ion

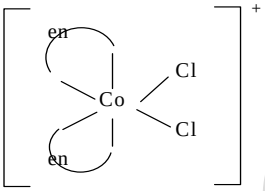
b]. Geometrical isomers:

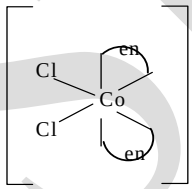




c] cis-$[CoCl_2(en)_2]^+$ is optically active.

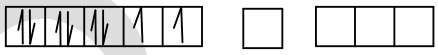
d] Two optical isomers of cis-$[CoCl_2(en)_2]^+$:



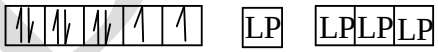


2.6

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



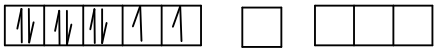
$[NiCl_4]^{2-}$



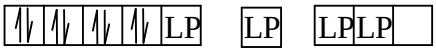
sp^3

sp^3 hybridization
Tetrahedral
Paramagnetic (2 unpaired electrons)

Pt^{2+} [Xe] $5d^8$



$[PtCl_4]^{2-}$



dsp^2

dsp^2 hybridization
Square planar
Diamagnetic (no unpaired electrons)

2.7

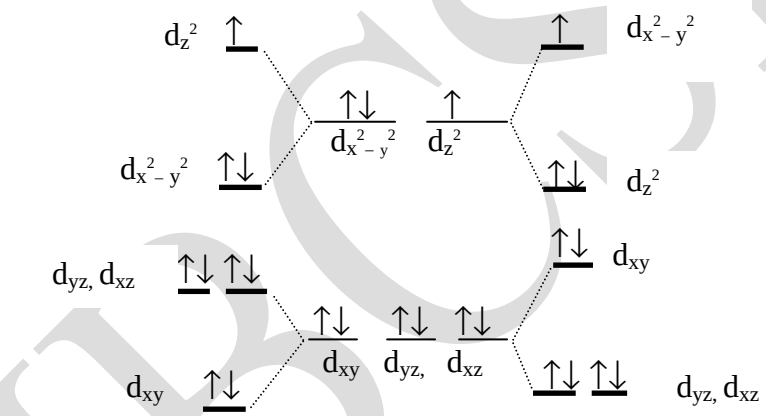
A		**B Δ_o (cm^{-1})**
i) $[CrF_6]^{3-}$		d) 15,000
ii) $[Cr(H_2O)_6]^{3+}$		c) 17,400
iii) $[CrF_6]^{2-}$		b) 22,000
iv) $[Cr(CN)_6]^{3-}$		a) 26,600

2.8

Answer: a) $[Fe(CN)_6]^{3-}$ b) $Ni(CO)_4$

Oxidation state	Fe(III)	Ni(0)
Coordination No.	of Fe(III) : 6	of Ni(II) : 4
EAN of central metal ion	35	36

2.9



Tetragonally distorted octahedron contraction along z-axis

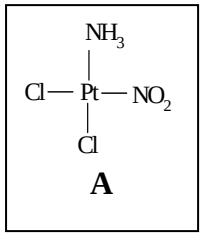
octahedron

Tetragonally distorted octahedron elongation along z-axis

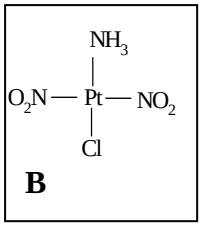
a) (i) by elongation along z-axis.

b) (ii) dx^2-y^2 orbital.

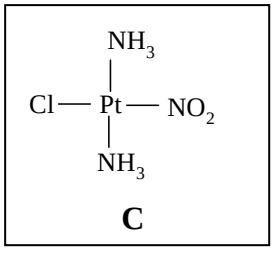
2.10



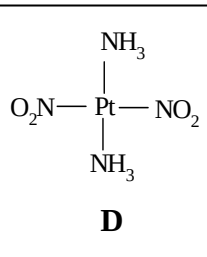
A



B



C



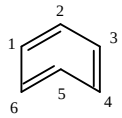
D

Problem 3 **14 marks**

Chemistry of isomeric benzenes

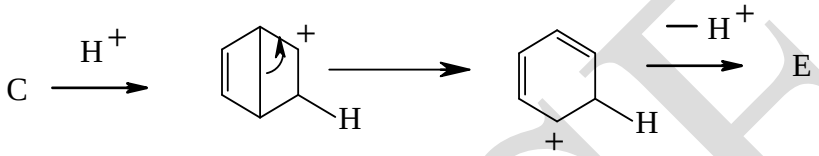
3.1

Z,Z,E -1,3,5-cyclohexatriene

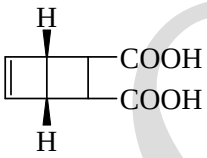


(D)

3.2

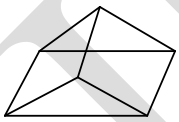


3.3



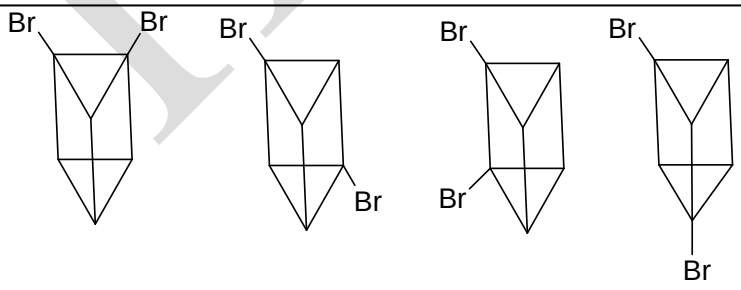
F

3.4



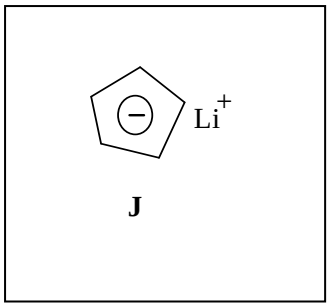
H

3.5



3.6 (b) Three X

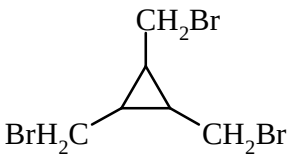
3.7



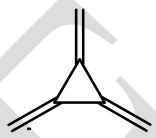
J

K

3.8

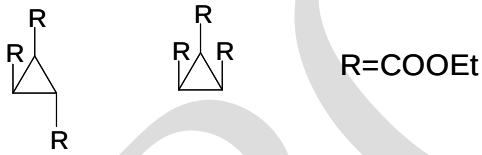


M

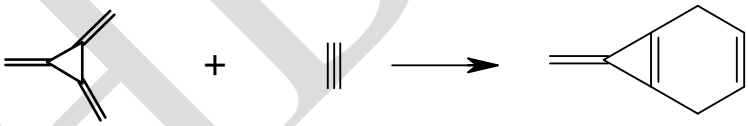


N

3.9



3.10



N **O**

Problem 4 10 marks

s-Block Elements

4.1 a) only one valence electron [X]

b) large atomic size [X]

4.2

Inhalation $2\ KO_2 + 2\ H_2O \rightarrow 2\ KOH + H_2O_2 + O_2$

Exhalation $KOH + CO_2 \rightarrow KHCO_3$

or $4\ KO_2 + 2\ CO_2 \rightarrow 2K_2CO_3 + 3O_2$

or $2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$

4.3

I $4\ Li + O_2 \rightarrow 2\ Li_2O$

II $Cs + O_2 \rightarrow CsO_2$

4.4

i) Bond order = 1

ii) diamagnetic [X]

4.5

$Na + (x + y)\ NH_3 \rightarrow [Na(NH_3)_x]^+ + [e(NH_3)_y]^-$

OR

$Na + NH_3 \rightarrow Na^+ + e^-_{solvated\ /\ (am)}$

4.6 b) It is paramagnetic in nature [X]

c) On standing this solution slowly liberates hydrogen resulting in the formation of sodium amide [X]

4.7 c) half the number of tetrahedral [X]

4.8 b) cyclohexane [X]

c) diisopropyl ether [X]

4.9 a) ionization energy of alkali metal [X]

b) electron gain enthalpy of halogen [X]

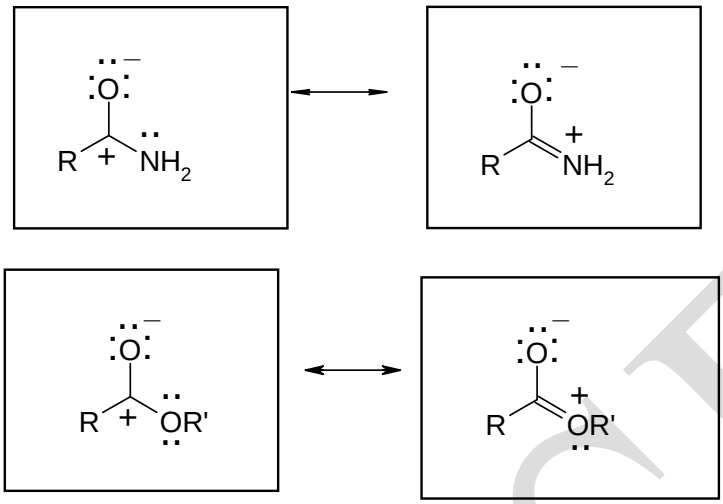
d) sizes of cations and anions [X]

4.10 LiF

Problem 5 17 marks

Carboxylic acid derivatives

5.1



5.2 (c) Amide > Ester > Acid Chloride X

5.3 Amide X

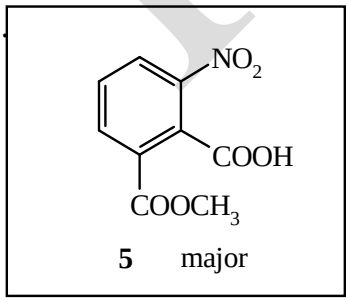
5.4

1650 cm^{-1}	A
1750 cm^{-1}	C
1800 cm^{-1}	B

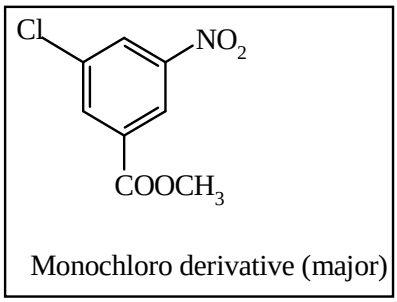
5.5 CH_3CH_2COCl X

5.6 Best C Poorest B

5.7

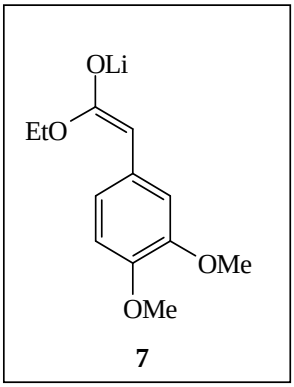


5 major



Monochloro derivative (major)

5.8



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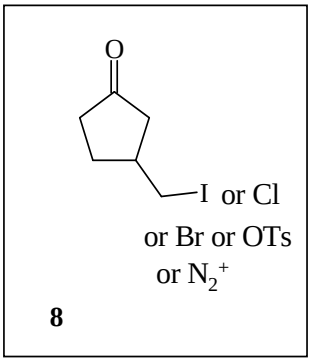

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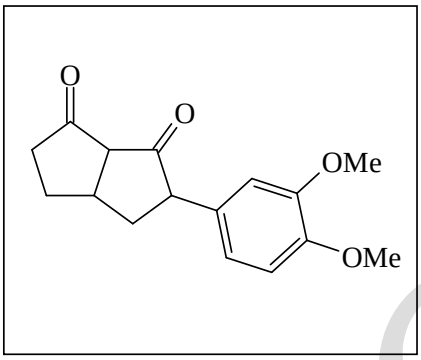
5.9



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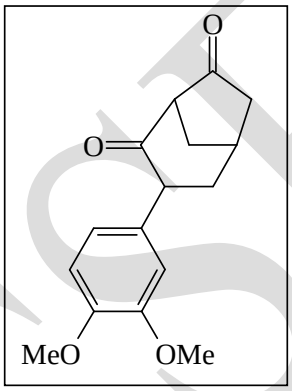

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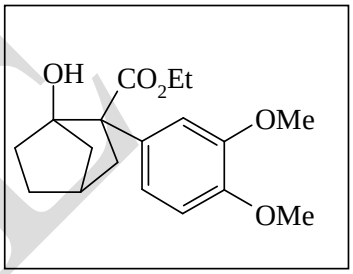

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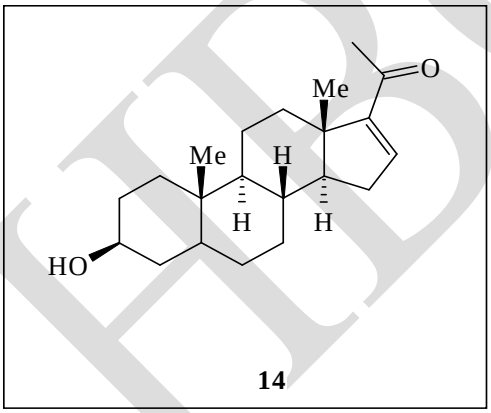
5.10

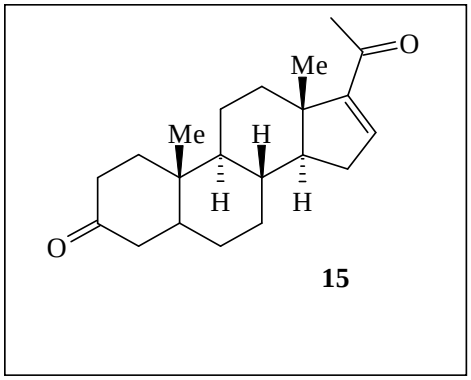


14

5.11 (i) 9

(ii) Both are S

5.12



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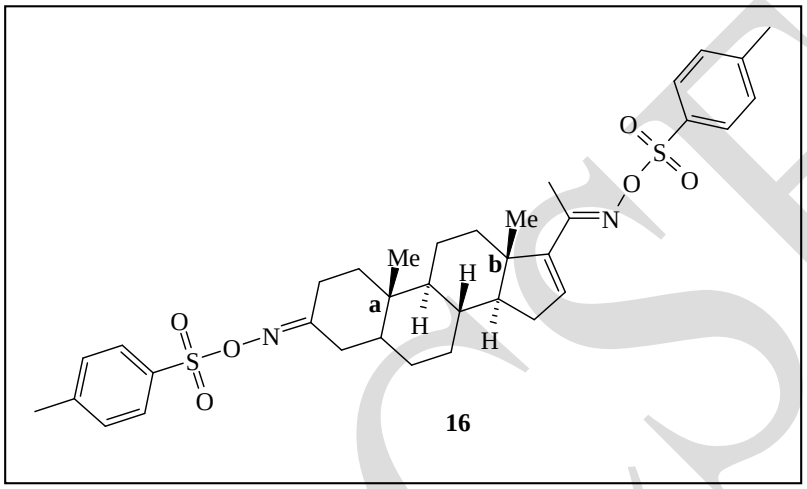
5.13



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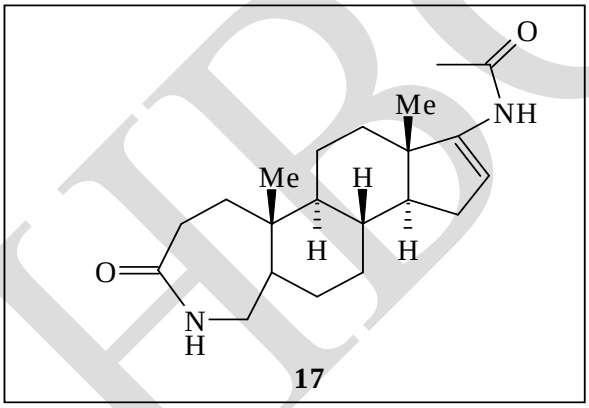
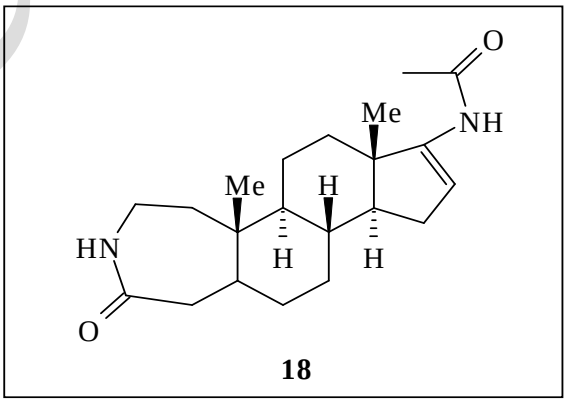
5.14



17



18

Problem 6 17 marks

Chemical Thermodynamics

6.1 2930 J

6.2 Kp = 0.7030

Kp = Kc

6.3 $X_{CO} = 0.342$, $X_{H_2} = 0.458$, $X_{H_2O} = 0.092$, $X_{CO_2} = 0.108$

$X_{CO} = 34.95\%$, $X_{H_2} = 45.41\%$, $X_{H_2O} = 9.59\%$, $X_{CO_2} = 10.06\%$

6.4 $\Delta H_{1400} = 31258\ J$

6.5 a) Kp will increase with increase in temperature X

6.6 Air intake (engine;m^3s^{-1}) = $V_A = 4 \times 9.902 \times 10^{-3}\ m^3s^{-1} = 0.0396\ m^3s^{-1}$

6.7 $T_1 = 2060K$

$T_2 = 708\ K$

6.8

Compound	**Molar composition of gases after leaving the bed (Mol $\times 10^{-4}$)**
N_2 (g)	407.64
O_2 (g)	38.55
CO (g)	0.78
CO_2 (g)	44.14
H_2O (g)	49.44

Problem 7 10 marks

7.1

V= 87.5 mL

7.2

$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

$Ka = [H_3O^+][CH_3COO^-]/[CH_3COOH]$

7.3

$$[H_3O^+] = -\frac{Ka \pm \sqrt{Ka^2 + 4KaC_T}}{2}$$

7.4

pH = 2.88

7.5 a)

$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$
$$CH_3COO^- + H_2O \leftrightarrow OH^- + CH_3COOH$$

b)

$$[CH_3COOH]_{eq} = C_T - [H_3O^+] + [OH^-]$$
$$[CH_3COO^-]_{eq} = [CH_3COONa] + [H_3O^+] - [OH^-]$$

c)

$$[H_3O^+] = Ka\frac{C_T}{[CH_3COONa]}$$

d)

pH = 3.80

7.6

pH = 8.73