

INChO 2006

Problem 1

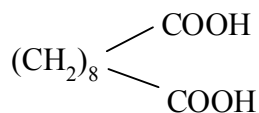
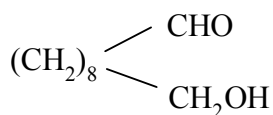
21 marks

Bombykol – An insect pheromone

1.1



1.2

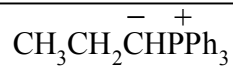


1.3



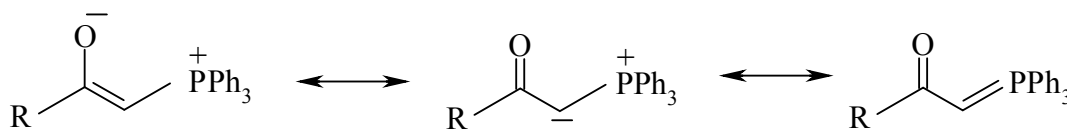
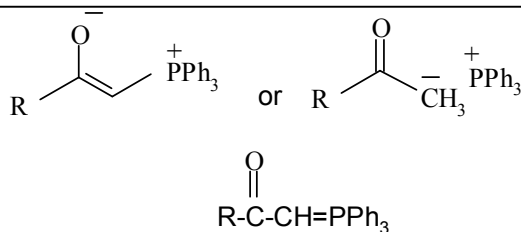
1.4

(a)



D

(b)



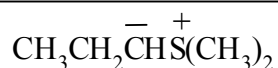
1.5

(b) $p\pi - d\pi$

X

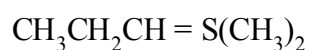
1.6

(a)

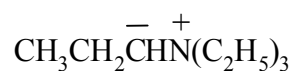


Or

F



(b)

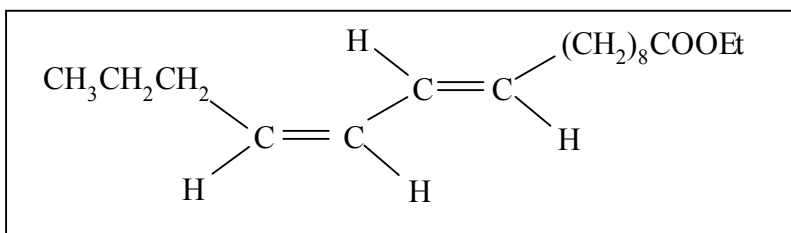
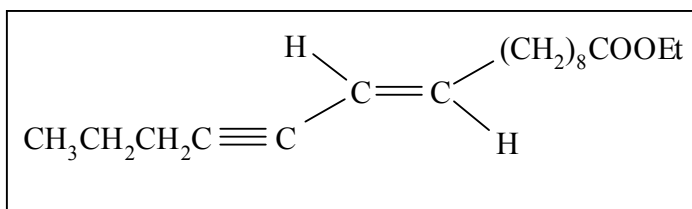
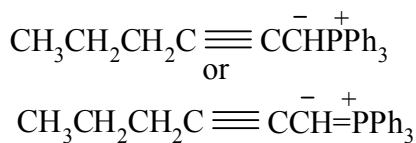


G

1.7

G

1.8



1.9

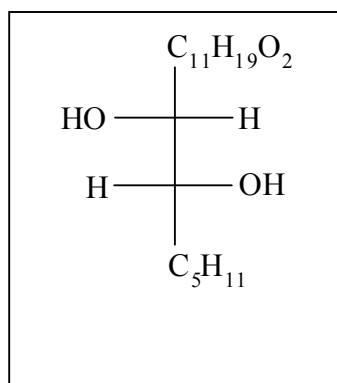
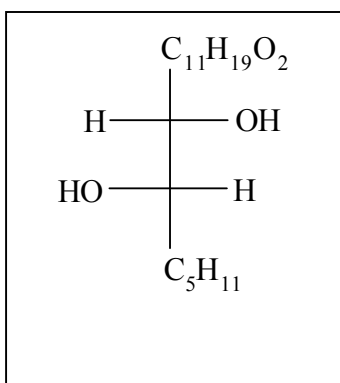
(10E, 12Z)-hexadecadien-1-ol

1.10

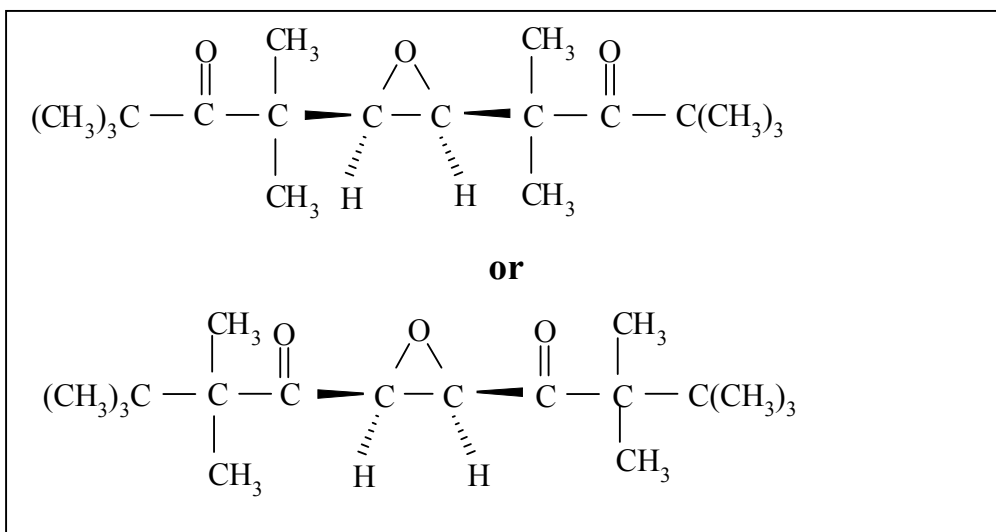
C_A R

C_B S

1.11



1.12

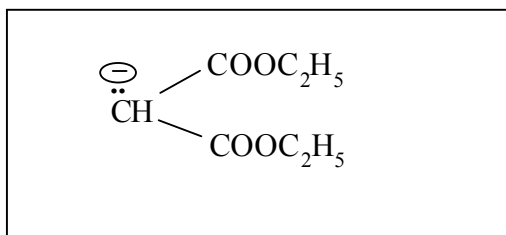


Problem 2

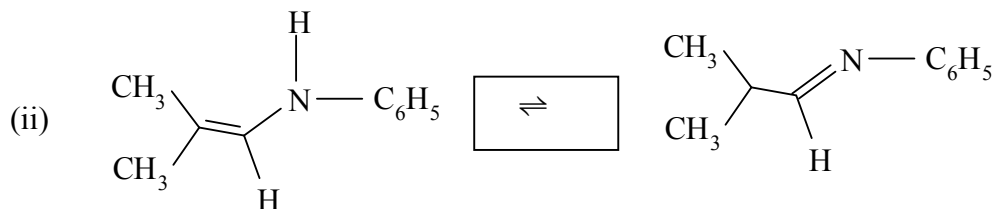
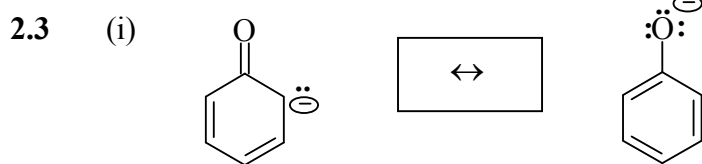
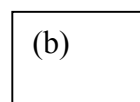
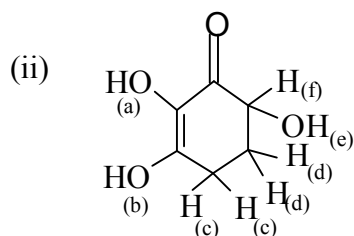
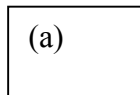
17 marks

Chemistry of Carbon Acids

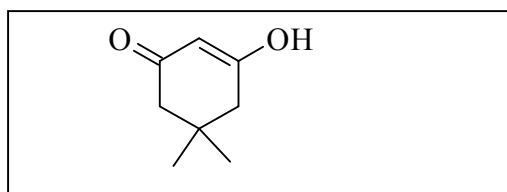
2.1



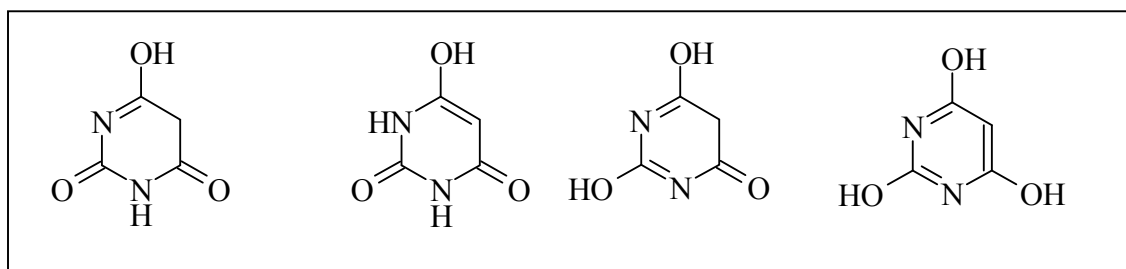
2.2 (i) $\text{CH}_3 - \text{CH} = \text{CH} - \text{COCH}_3$
 (a) (b) (c) (d)



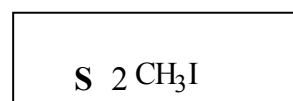
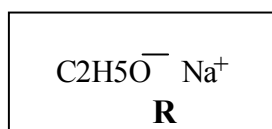
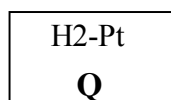
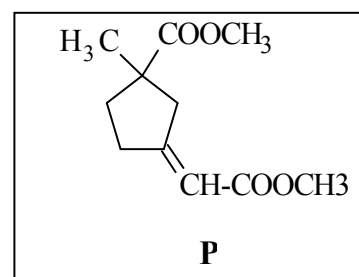
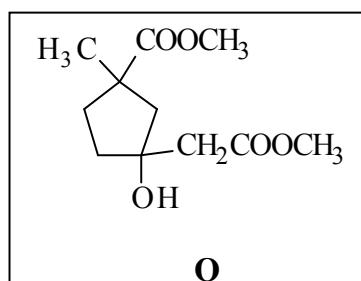
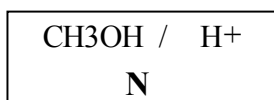
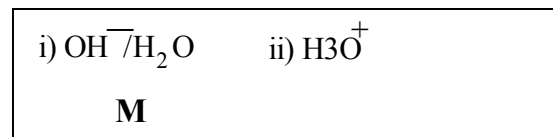
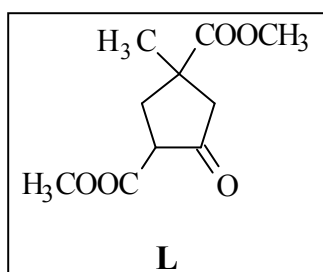
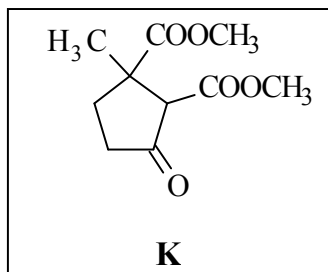
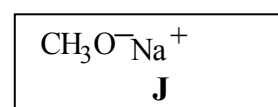
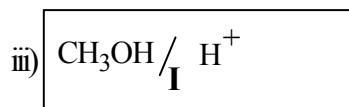
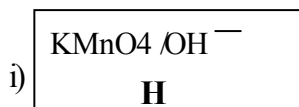
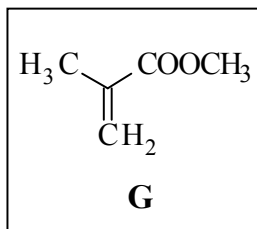
2.4



2.5



2.6



2.7

2

2.8

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

2.9

Carbonyl group

2.10

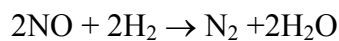
(a) iv (b) i (c) ii (d) iii

Problem 3

14 marks

Chemical Kinetics

3.1



3.2

$$-1/2 \frac{d_{\text{NO}_2}}{dt} = \frac{d_{\text{N}_2}}{dt}$$

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_{H_2} 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_{H_2} are double. Rate changes 8 times. Confirms the orders

3.4

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

3.5

$$-1/2 \frac{d \text{NO}}{dt} = k_{\text{app}} [\text{P}_{\text{H}_2}]$$

3.6

$$\text{sec}^{-1}$$

3.7

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

Rate= $k_{\text{app}} p_{\text{H}_2}$; $t_{1/2}$ will be independent of $p_{\text{H}_2}^0$. 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

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

$$\text{but } k_{\text{app}} = k p_{\text{NO}}^2 ;$$

3.9

The differential rate equation is $-dp_{\text{H}_2}/dt = k [2p_{\text{H}_2}]^2 [p_{\text{H}_2}]$ (from the given values of partial pressures and the reaction stoichiometry)

This on integration

3.10

$$k = 1.0 \times 10^{-7} \text{ torr}^{-2} \text{ sec}^{-1} \quad p_{\text{H}_2}^0 \text{ is } 10 \text{ torr}$$

$$\text{at } t_{1/2} \quad [p_{\text{H}_2}] = \frac{1}{2} [p_{\text{H}_2}^0]$$

$$\text{Substituting these values, } 8 \times 1.0 \times 10^{-7} t_{1/2} = 3/10^2$$

3.11

$$[\text{N}_2\text{O}] = k_2 [\text{N}_2] [\text{H}_2\text{O}_2] / k_3 [\text{H}_2]$$

$$[\text{H}_2\text{O}_2] = k_1 [\text{NO}]^2 [\text{H}_2] / k_2$$

3.12

$$-d[\text{N}_2\text{O}]/dt = -d[\text{H}_2]/dt = k_3 [\text{N}_2\text{O}] [\text{H}_2]$$

3.13

$$\text{Rate} = k_3 [\text{N}_2\text{O}] [\text{H}_2]$$

$$[\text{N}_2\text{O}] = k_2 [\text{N}_2] [\text{H}_2\text{O}_2] / k_3 [\text{H}_2]$$

$$\text{substituting for } [\text{H}_2\text{O}_2], \quad [\text{N}_2\text{O}] = k_1 / k_3 [\text{NO}]^2$$

$$\text{Hence Rate} = k_1 k_3 [\text{NO}]^2 [\text{H}_2] / k_3$$

3.14

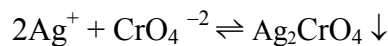
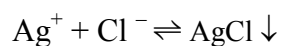
Yes

Problem 4

13 marks

Solubility Equilibria

4.1



4.2

Amount of Cl^- in 100 mL = 0.0035 g

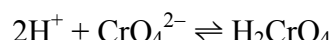
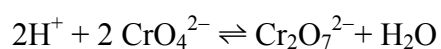
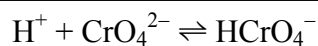
4.3

Indicator range 0.0139 – 0.00277 M

4.4

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

4.5



4.6

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

4.7

$$(0.5 \text{ M})(0.5 \text{ L})(119.98) = 29.99 \text{ g of sodium dihydrogen phosphate}$$

$$(0.15 \text{ M})(0.5 \text{ L})(141.96) = 10.65 \text{ g of sodium hydrogen phosphate}$$

Problem 5

18 marks

Molecular Hydrogen

5.1

For the reaction II, $K = 1 \times 10^{-16}$
 For the reaction III, $K = 9.743 \times 10^4$

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

$$\frac{\ln K_{p_2}}{K_{p_{298}}} = \frac{-8.5 \ln(T_2/298)}{R} + \frac{0.02575(T_2 - 298)}{R} + \frac{40853}{R} \left(\frac{1}{T_2} - \frac{1}{298} \right)$$

5.5

$$(K_p)_{1200} = 1.592$$

5.6

$\text{CO}_2 = 26.39\% = \text{H}_2$
 $\text{CO} = 23.1\% = \text{H}_2\text{O}$

5.7

$$K_4 = 4.62 \quad K_5 = 7.355$$

Problem 6

10 marks

Electrochemistry

6.1

$$E_{\text{cell}} = 1.104 \text{ V}$$

6.2

$$\therefore \text{Amount of CuCl}_2 \text{ spilt} = 0.0095 * 134.45 = 1.366 \text{ g}$$

6.3

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

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

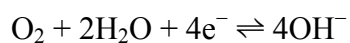
6.4

Zero

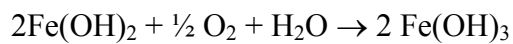
6.5

$$E_{\text{cell}} = 0.0641 \text{ V}$$

6.6



6.7



6.8

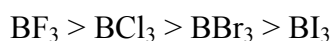
Galvanizing is preferred, as $E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ is more negative than $E^\circ_{\text{Fe}^{2+}/\text{Fe}}$. Hence when exposed to air Zn will preferentially undergo oxidation as compared to Fe.

Problem 7

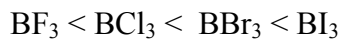
10 marks

Chemistry of Boron

7.1



7.2



7.3

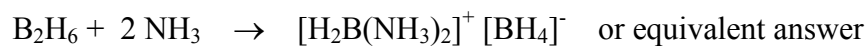
- (a) mismatch between size of boron atom and higher halogen atoms leads to poor overlap of p orbital, which leads to reduction in electron density on boron.



7.4



7.5



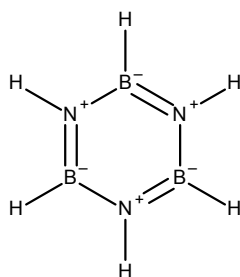
7.6

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

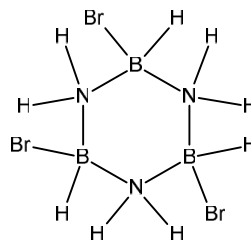
X

7.7



Dative bond between B-N is also Considered

7.8



7.9

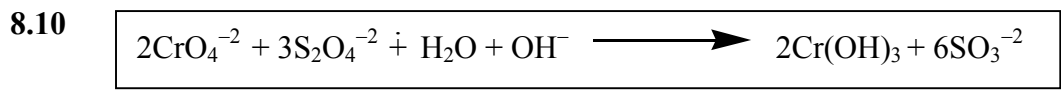
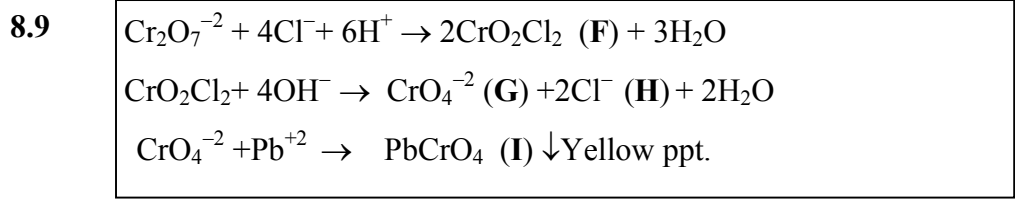
(1) $(B_{12}H_{12})^{-2}$ Total electrons = 13 pairs

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

8.8 (b) charge transfer transition X




8.11 molarity = 0.0148 mole/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

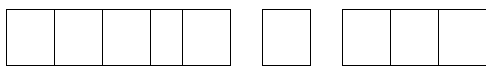
Ni $[\text{Ar}]3d^84s^2$



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

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

Ni^{+2} in $[\text{NiCl}_4]^{-2}$ $[\text{Ar}]$

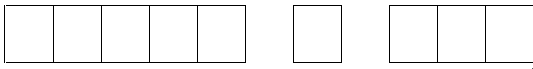


sp^3 hybridisation

sp^3 hybridisation therefore geometry tetrahedral

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

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



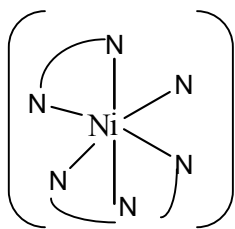
dsp^2 hybridisation

dsp^2 hybridisation therefore sq. planar



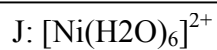
8.14 (c) optical

8.15

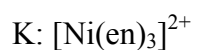


+2

8.16



λ_{max} 650 nm



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