

Problem 1

16 marks

Rates of Chemical Reactions and Arrhenius Equation

1.1  $r = 2.0 \times 10^{-6} \times 0.1 = 2.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$   
 $= 1.2 \times 10^{-8} \text{ mol mL}^{-1} \text{ min}^{-1}$

1.2 (iv) the concentration of A decreases with time

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

1.4  $A = 3.14 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   
 $E_a = 193.2 \text{ kJ/mol}$

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

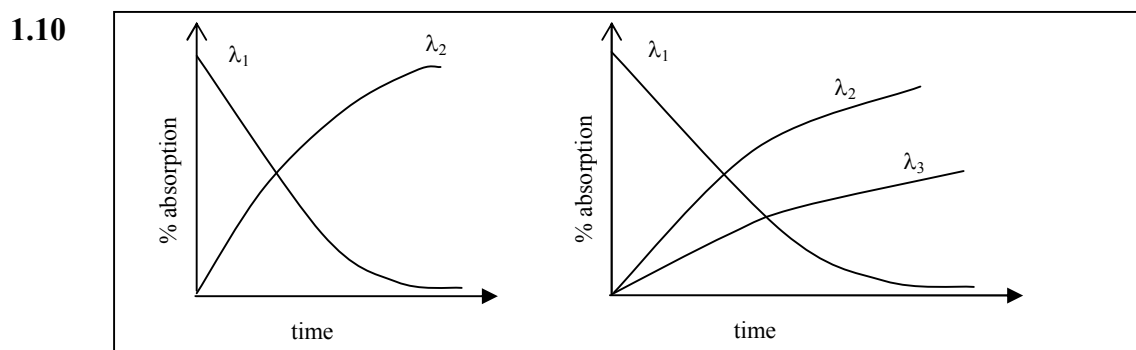
1.6  $E_a(\text{reverse}) = 170.3 \text{ kcal mol}^{-1}$

1.7  $k_2[\text{CH}_3][\text{CH}_3\text{CHO}] = k_3[\text{CH}_3\text{CO}]$   
 $[\text{CH}_3] = (k_1/2k_4)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$

$d[\text{CH}_4] / dt = k_2 (k_1/2k_4)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$

1.8  $E = E_2 + \frac{1}{2} (E_1 - E_4)$

1.9 (ii)  $\text{X} + \text{Y} \rightarrow \text{Z}; \text{Z} \rightarrow \text{W}$



## Problem 2

18 marks

## Electrochemistry

2.1

$$\Lambda(\text{NaOH}) = 221$$

$$\Lambda(\text{NaCl}) = 112$$

$$\Lambda(\text{HCl}) = 403$$

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

2.2

$$\kappa(\text{KCl}) = 0.0812 \text{ S m}^{-1}$$

2.3

Oxidation state of gold = 3

2.4

$$E^\circ_2 = E^\circ_1$$

$$K_2 = (K_1)^2$$

2.5

change in the cell potential is  $-0.01 \text{ V}$ 

2.6

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

Problem 3

14 marks

Molecular Structure and Spectroscopy

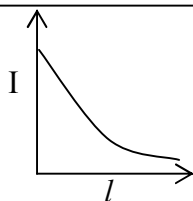
3.1

$$\int_{I_0}^I \frac{dI}{I} = -kc \int_0^{\ell} dx ; \ln \frac{I_0}{I} = k.c.\ell$$

3.2

$$\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$$

3.3



3.4

$$\text{Energy absorbed} = 327 \text{ kJ mol}^{-1}$$

3.5

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

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

3.6

$$\Delta \mathcal{G}_{\min} = 1.1 \times 10^{-28} \text{ m.s}^{-1}$$

3.7

The general solution of this differential equation is

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

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

3.8

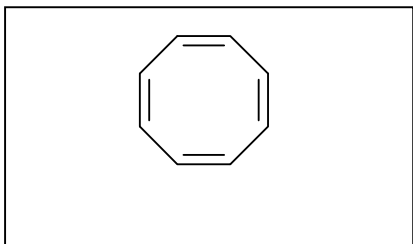
$$k = 512.1 \text{ Nm}^{-1}$$

Problem 4

16 marks

Cyclooctatetraene and Aromaticity

4.1

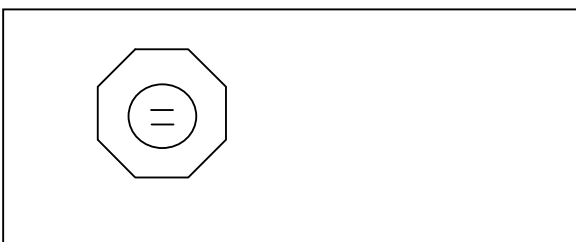


4.2

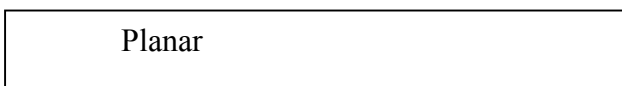
(b) a tub-shaped structure



4.3



4.4

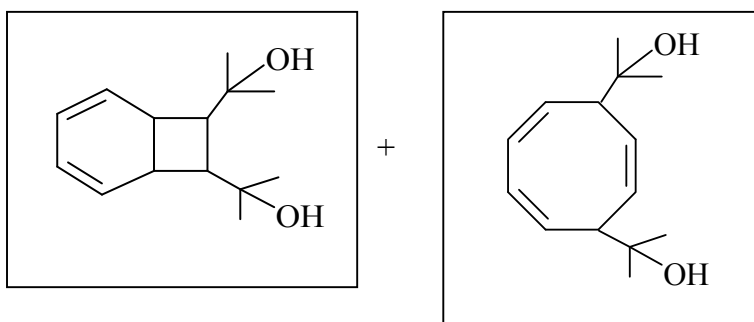


4.5

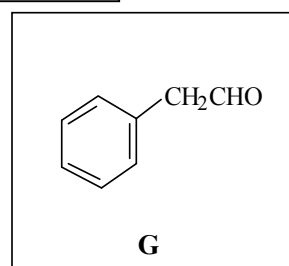
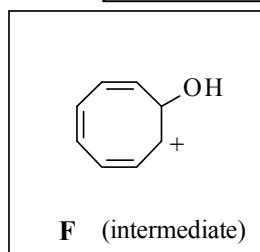
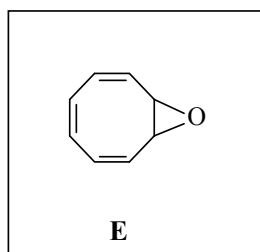
(c) the dianion is aromatic



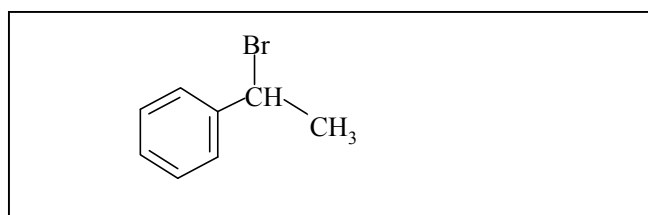
4.6



4.7

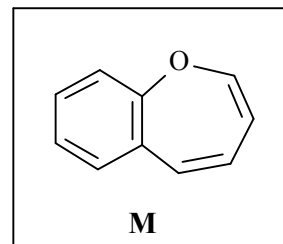
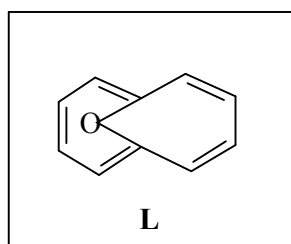
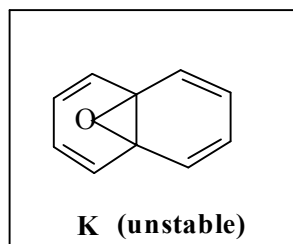


4.8



- 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



Is L aromatic?

No

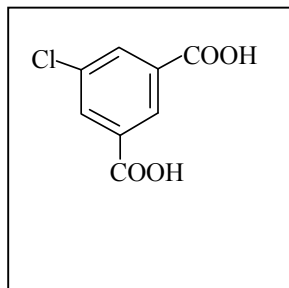
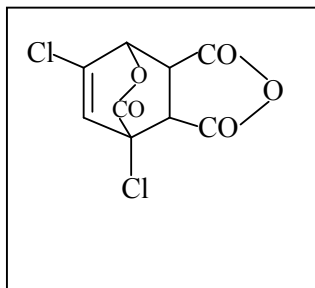
X

Problem 5

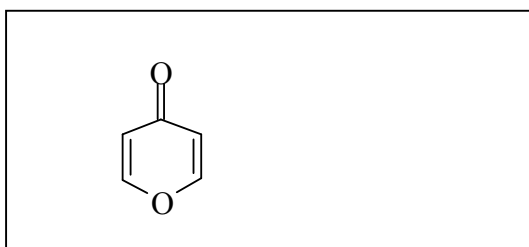
14 marks

Diels-Alder Reaction

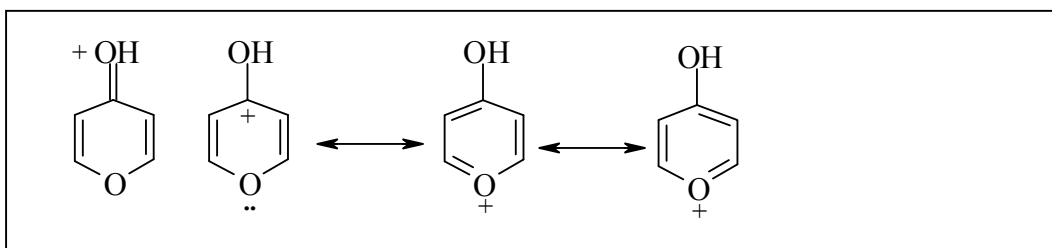
5.1



5.2



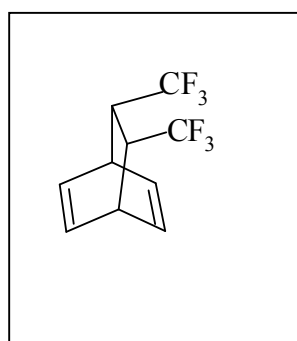
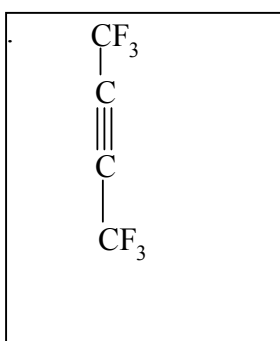
5.3



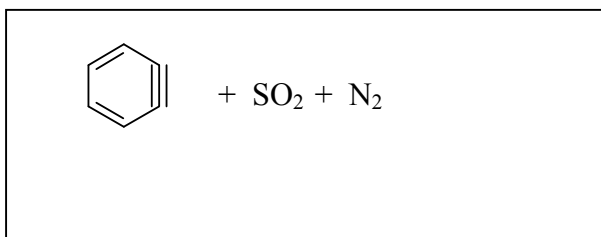
5.4

No

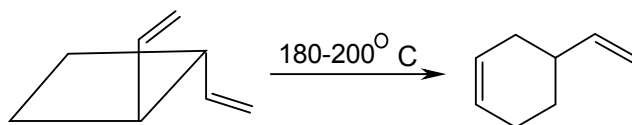
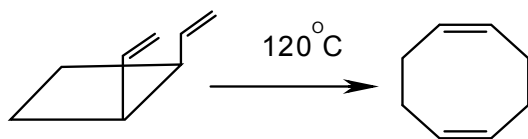
5.5



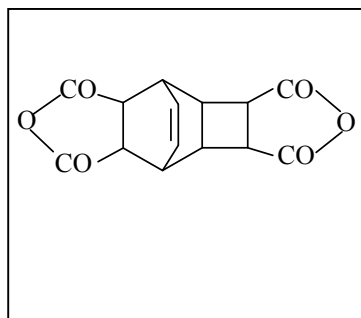
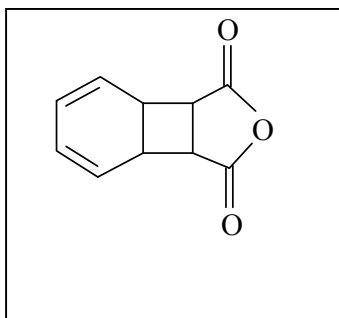
5.6



5.7



5.8



Problem 6

12 marks

Chemical Thermodynamics and Kinetic Theory of Gases

6.1

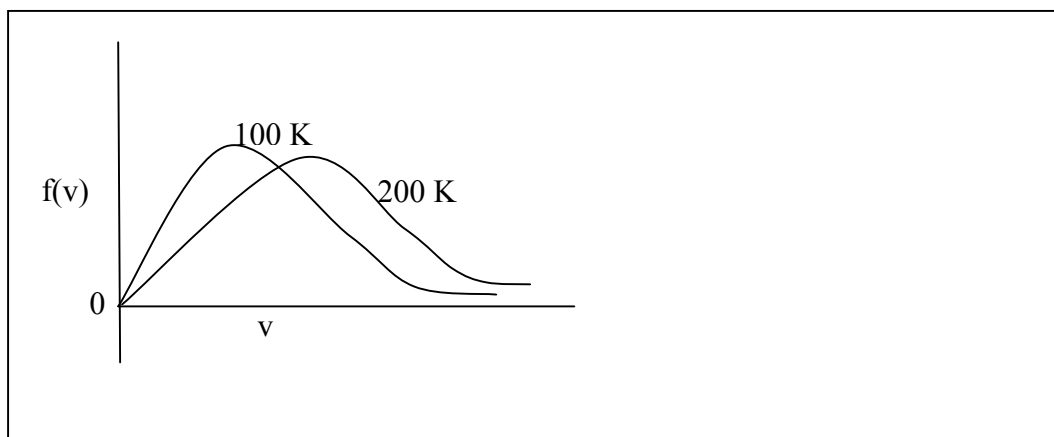
$$\text{H}_2(\text{g}) = -120.9 \text{ kJ per g}$$

$$\text{CH}_3\text{OH}(\text{l}) = -19.9 \text{ kJ per g}$$

$$\text{CH}_4(\text{g}) = -50.1 \text{ kJ per g}$$

$$\text{C}_6\text{H}_{14}(\text{g}) = -453 \text{ kJ per g}$$

6.2



6.3

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

6.4

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

6.5

$$v_{\text{av}} > v_{\text{mp}}$$



Problem 7

10 marks

Halogen Compounds

7.1 (c) F – F bond is weakened by strong repulsion between nonbonding electrons in small F<sub>2</sub> molecule

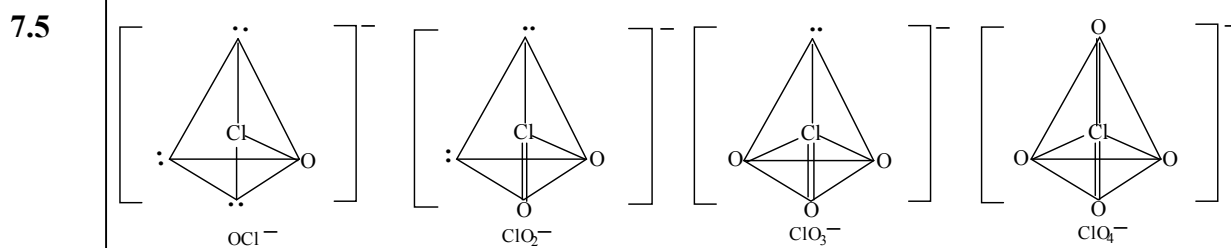
X

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

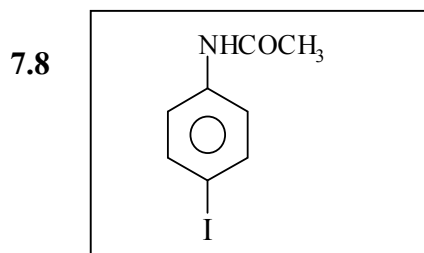
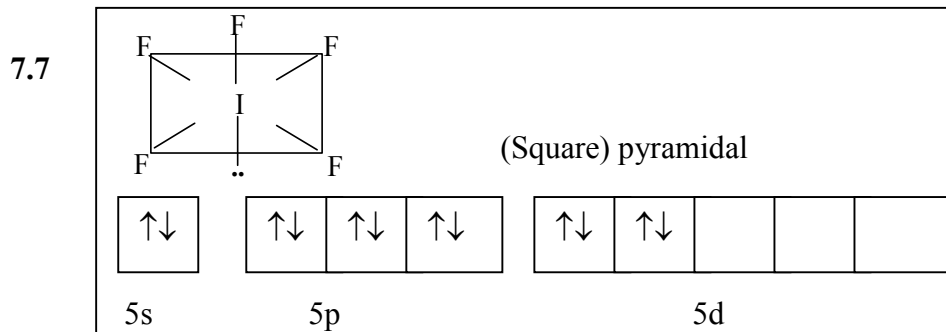
X

7.3 SiF<sub>4</sub> > SiCl<sub>4</sub> > SiBr<sub>4</sub> > SiI<sub>4</sub>

7.4 HClO<sub>4</sub> > HClO<sub>3</sub> > HClO<sub>2</sub> > HOCl



7.6 Due to lack of pπ-dπ bond

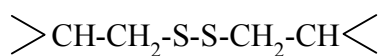


Problem 8

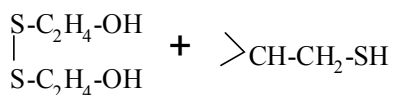
16 marks

Proteins, amino acids, nucleic acids and buffers

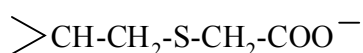
8.1



(a)



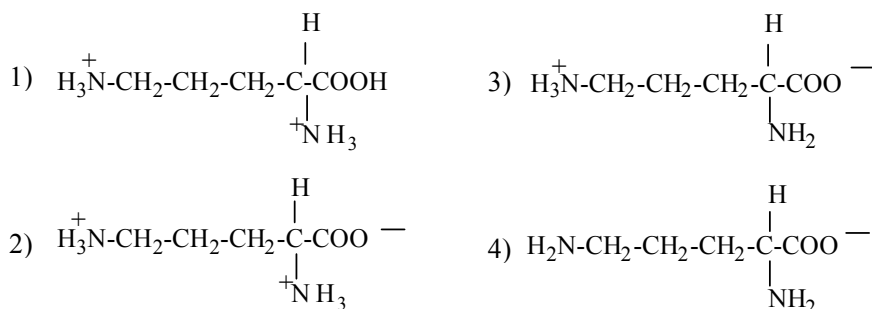
(b)



(c)



8.2



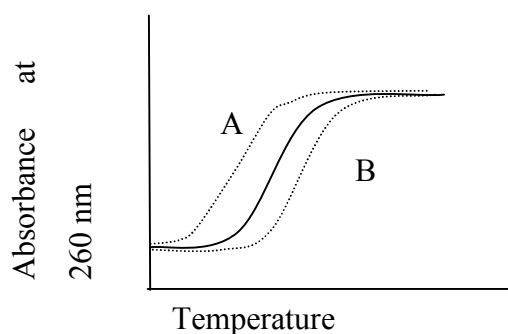
8.3

(a)

Sample A:

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

(b)



(c)  $5' \text{ AUGUUCGGCUGGCAAUC } 3'$

(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  $\text{H}^+$  ion, the starting pH will be the lowest pH permissible to assay the enzyme activity, i.e. pH – 7.9.

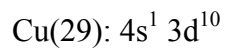
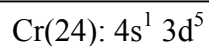
(b) Total concentration of the buffer = 0.1786 M  
 Final concentration of conjugate acid  $[\text{Tris}^+]_f = 0.0595 \text{ M}$   
 Final concentration of conjugate base  $[\text{Tris}^0]_f = 0.1191 \text{ M}$   
 Final pH = 8.3

Problem 9

13 marks

Transition Metal Chemistry

9.1

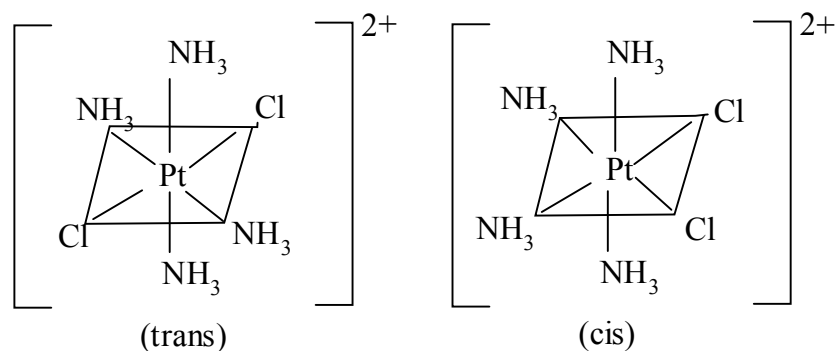


9.2

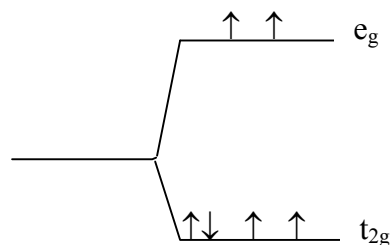
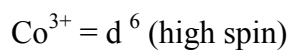
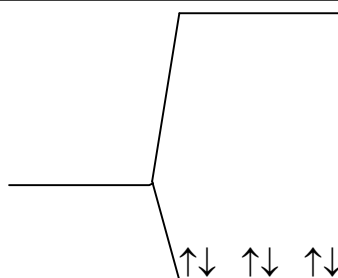
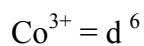
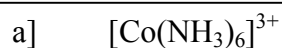
Diffuse nature of d orbital and increased nuclear charge due to added protons

9.3

Tetraaminedichloroplatinum(IV)



9.4

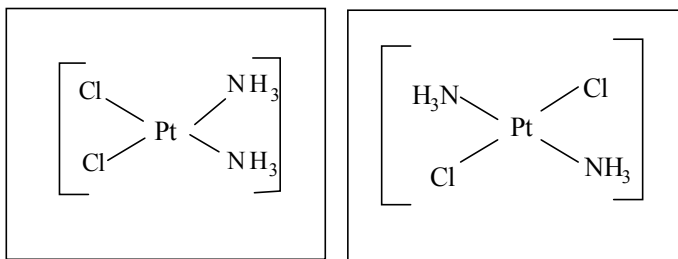


4 unpaired electrons, paramagnetic

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

$$= 4.9 \text{ B.M}$$

9.5



9.6

