1. Consider the esterification reaction

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

(a) (i) Give the expression for K_c.

(1)

(ii) An equilibrium mixture from the above reaction contains 0.90 mol of ethyl ethanoate, 0.90 mol of water, 0.10 mol of ethanoic acid, and 2.1 mol of ethanol. It has a volume of 235 cm^3. Calculate K_c to 2 significant figures, having regard for the units.

(3)

(iii) State, giving a reason, what would happen to the equilibrium composition if more ethanoic acid were to be added to the equilibrium mixture.

……

……

(2)

(b) The reaction employs an acid catalyst, usually a little sulphuric acid. State, with a reason, the effect on the equilibrium position if the concentration of the acid catalyst were to be increased.

……

……

(2)

(c) (i) Using the concept of mean bond enthalpies show that ΔH for the esterification reaction is zero.

(2)

(ii) State, with a reason, the effect of an increase in temperature on the equilibrium composition of this reaction.

……

……

……

(2)

(iii) Explain why, when esters are hydrolysed in the laboratory, they are heated under reflux with dilute sodium hydroxide solution rather than with dilute sulphuric acid.

……

……

……

(2)

(Total 14 marks)

2. (a) Define

(i) pH : ……

(1)

(ii) K_w : ……

(1)

(b) Calculate the pH of 0.100 mol dm^{-3} sodium hydroxide solution at 25 ºC. The value of K_w at this temperature is 1.0×10^{-14} mol^2 dm^{-6}.

(2)

(c) 100 cm^3 of 0.100 mol dm^{-3} sodium hydroxide solution was added to 100 cm^3 of 0.200 mol dm^{-3} ethanoic acid.

(i) Find the concentration of ethanoic acid in the mixture.

(2)

(ii) Calculate the concentration of sodium ethanoate in the mixture.

(2)

(iii) Calculate the pH of the mixture at 25 ºC; K_a for ethanoic acid at this temperature is 1.80×10^{-5} mol dm^{-3}.

(2)

(iv) State and explain what happens if a small amount of hydrochloric acid is added to this mixture.

……

……

……

(3)

(d) When the solutions in part (c) are mixed, 560 J of heat energy is evolved. If hydrochloric acid of the same concentration is used instead of ethanoic acid, 580 J of heat energy is evolved. Suggest reasons for the difference.

……

……

……

……

(3)

(Total 16 marks)

3. Benzene reacts with concentrated nitric acid in the presence of concentrated sulphuric acid at about 50 ºC in an electrophilic substitution reaction to give nitrobenzene.

(a) (i) Give the equation representing the overall reaction.

(1)

(ii) Give the equation representing the formation of the electrophile.

……

(1)

(iii) Give the mechanism for the reaction of the electrophile with benzene.

(3)

(b) In an experiment to determine the kinetics of this reaction, it is found that the attack of the electrophile on the benzene ring is the rate determining step. The following data shows the effect of changing the concentrations on the rate:

[benzene] (relative)	**[electrophile] (relative)**	**Rate (relative)**
1	1	1
1	2	2
2	1	2
2	2	4

(i) What is the order with respect to

benzene ……

the electrophile? ……

(2)

(ii) Write a rate equation for the reaction.

……

(1)

(iii) In some electrophilic substitution reactions of aromatic compounds, the rate determining step is the production of the electrophile. In such cases what would be the order of the reaction with respect to the aromatic compound?

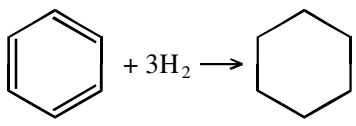
……

(1)

(c) The equation representing the hydrogenation of ethene is

$H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3 \quad \Delta H = -120 \text{ kJ mol}^{-1}$

(i) Assuming that benzene consists of a ring with three double bonds, predict the enthalpy change for the reaction



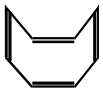
……

(1)

(ii) The enthalpy of hydrogenation of benzene is actually –205 kJ mol^{-1}. What can you deduce from this and your answer to part (i) about the stability of the benzene ring? Use an enthalpy level diagram to illustrate your answer.

(2)

(iii) The compound cyclo–octatetraene



has an enthalpy of hydrogenation of –480 kJ mol^{-1}; the molecule, unlike that of benzene, is not flat. Suggest in terms of the possibility of orbital overlap why cyclo–octatetraene does not show the same type of stability as benzene, despite superficial similarities in their structures.

……

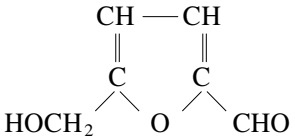
……

……

(2)

(Total 14 marks)

4. The pleasant smell that betrays the making of toast or of caramel comes from the compound hydroxymethylfurfural which is a product of heating sugars. The structure of the molecule is:



(a) (i) What would you see if this compound were shaken with a solution of bromine dissolved in an organic solvent?

……

(1)

(ii) Suggest a structure for the product which is obtained from this reaction.

(2)

(b) In each case state a reagent you could use, and the observations you would make, to show the presence in hydroxymethylfurfural of

(i) the hydroxyl group;

……

……

(2)

(ii) the aldehyde group.

……

……

(2)

(c) If hydroxymethylfurfural is heated with potassium dichromate(VI) solution which has been acidified with dilute sulphuric acid, the compound **X** obtained contains 46.1% carbon, 2.56% hydrogen, and 51.3% oxygen by mass. The ring structure remains intact.

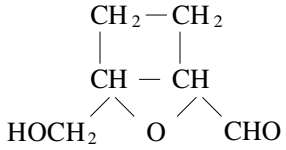
(i) Calculate the empirical formula of **X**.

(2)

(ii) Draw the structural formula for **X**, given that its relative molecular mass is 156.

(2)

(d) Hydroxymethylfurfural can react with hydrogen in the presence of a catalyst to give compound **Y** which has the structure:



(i) What volume of hydrogen would be required to convert 3.15 g of hydroxymethyl–furfural into compound **Y**?

(The molar volume of any gas at the temperature and pressure of the experiment is 24 dm^3. The relative molecular mass of hydroxymethylfurfural is 126.)

(3)

(ii) Explain why compound **Y** is chiral.

……

……

(2)

(Total 16 marks)