1 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

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

(1)

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20			

(iii) Explain why K_c for this reaction has no units.

(1)

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(iv) Calculate the numerical value of K_c.

(1)

(b) The esterification reaction above was carried out in the presence of hydrochloric acid as the catalyst.

State the effect on the equilibrium position and the rate of attainment of equilibrium if the concentration of the acid catalyst were to be increased.

(2)

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(c) (i) Identify which bonds are broken and which bonds are made in the esterification reaction.

(2)

Bonds broken:

Bonds made:

(ii) Explain why ΔH for this reaction is not **exactly** zero.
(A calculation is not required.)

(1)

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(d) (i) State the relationship between ΔS_{total} and the equilibrium constant, K, of a reaction.

(1)

*(ii) Use entropy considerations and your answer to (d)(i) to predict any effect of an increase in temperature on the value of the equilibrium constant of a reaction for which ΔH is zero. Assume that ΔS_{system} does not change with temperature.

(3)

(e) An ernative method for preparing ethyl ethanoate is to react ethanoyl chloride with ethanol.

(i) Give the equation for the reaction.

(1)

(ii) Draw the **skeletal** formula of ethyl ethanoate.

(1)

(iii) Ethanoyl chloride also reacts with concentrated ammonia. Draw the **displayed** formula of the organic product of this reaction.

(1)

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3 + NaOH \rightarrow$

(ii) Explain why the reaction in (f)(i) gives a better yield of the alcohol compared with acid hydrolysis of the ethyl ethanoate.

(1)

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(Total for Question = 19 marks)

2 Hydrogen is used in very large quantities as a fuel, as a reducing agent, and in the production of ammonia. Hydrogen is manufactured by steam reforming of methane from natural gas. Two reactions are involved, both being in equilibrium in closed systems.

Reaction I $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +210 \text{ kJ mol}^{-1}$

Reaction II $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H = -42 \text{ kJ mol}^{-1}$

(a) Write the expression for the equilibrium constant, K_p, for reaction **I**.

(1)

(b) Reaction **I** occurs at a temperature of 1000 K and a pressure of 30 atm over a nickel catalyst.

(i) State and explain the effect, if any, **on the value of K_p** of increasing the pressure on the reaction.

(1)

(ii) Explain, in terms of your answers to (a) and (b)(i), why an increase in the pressure leads to a decrease in yield in reaction **I**.

(2)

(iii) Increasing the pressure on this heterogeneously-catalysed reaction **I** has very little effect on the rate of the reaction. Suggest why this is so.

(2)

(c) The expression for K_p for reaction **II** is

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$$

At a particular temperature and 30 atm pressure, a mixture of equal amounts of carbon monoxide and steam react to give an equilibrium mixture where 75 % of the CO has reacted.

Calculate the value of K_p showing your working.

(3)

(d) Carbon dioxide and hydrogen are separated by washing the gas with potassium carbonate solution to give potassium hydrogencarbonate solution, leaving hydrogen in the gas stream. Potassium carbonate is expensive and is regenerated by heating the potassium hydrogencarbonate and liberating the carbon dioxide.

(i) Hydrogen is often claimed to be a non-polluting fuel as it only produces water on burning.

Explain why its manufacture using reactions **I** and **II** does **not** support this claim.

(1)

(ii) Write the equation for the thermal decomposition of potassium hydrogencarbonate.

State symbols are **not** required.

(1)

(e) Although industrial processes are often discussed in terms of equilibria, they are rarely allowed to reach equilibrium.

Suggest why, apart from insufficient reaction time, this is so.

(1)

(Total for Question = 12 marks)