Q1. Hydrogen is produced in industry from methane and steam in a two-stage process.

(a) In the first stage, carbon monoxide and hydrogen are formed.
The equation for this reaction is

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +206 \text{ kJ mol}^{-1}$

(i) Use Le Chatelier's principle to state whether a high or low temperature should be used to obtain the highest possible equilibrium yield of hydrogen from this first stage.
Explain your answer.

Temperature .....

Explanation .....

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(3)

(ii) Le Chatelier's principle suggests that a high pressure will produce a low yield of hydrogen in this first stage.

Explain, in terms of the behaviour of particles, why a high operating pressure is used in industry.

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(2)

(iii) A nickel catalyst is used in the first stage.

Explain why the catalyst is more effective when coated onto an unreactive honeycomb.

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(2)

(b) The second stage is carried out in a separate reactor. Carbon monoxide is converted into carbon dioxide and more hydrogen is formed.

The equation for this reaction is

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -41$ kJ mol^{-1}

Use Le Chatelier's principle to state the effect, if any, of a **decrease** in the total pressure on the yield of hydrogen in this second stage. Explain your answer.

Effect .....

Explanation .....

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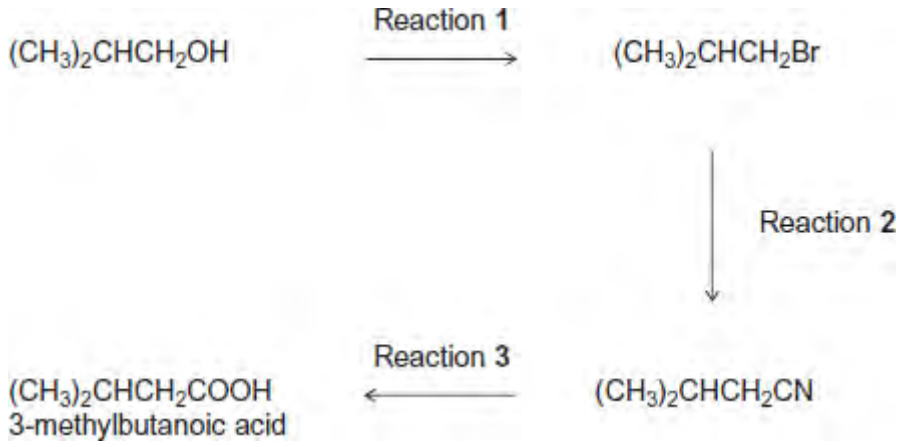
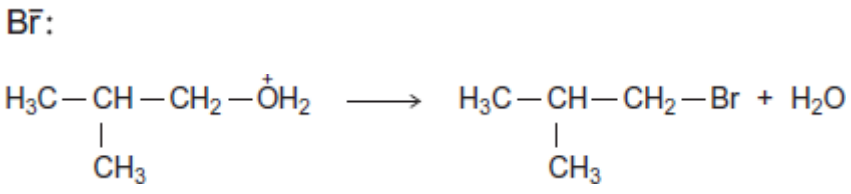
(2)
(Total 9 marks)

Q2. The carboxylic acid 3-methylbutanoic acid is used to make esters for perfumes.
The following scheme shows some of the reactions in the manufacture of this carboxylic acid.



(a) One of the steps in the mechanism for Reaction **1** involves the replacement of the functional group by bromine.

(i) Use your knowledge of organic reaction mechanisms to complete the mechanism for this step by drawing **two** curly arrows on the following equation.



(2)

(ii) Deduce the name of the mechanism in part (i).

Give the IUPAC name of $(CH_3)_2CHCH_2Br$

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(2)

(b) Reaction **3** is an acid-catalysed reaction in which water is used to break chemical bonds when the CN functional group is converted into the COOH functional group. Infrared spectroscopy can be used to distinguish between the compounds in this reaction.

Deduce the name of the type of reaction that occurs in Reaction **3**.

Identify **one** bond in $(CH_3)_2CHCH_2CN$ and a **different** bond in $(CH_3)_2CHCH_2COOH$ that can be used with infrared spectroscopy to distinguish between each compound. For each of these bonds, give the range of wavenumbers at which the bond absorbs.

Use **Table A** on the Data Sheet when answering this question.

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(3)

(c) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an equilibrium is established. The organic product is a pleasant-smelling ester.

$(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons (CH_3)_2CHCH_2COOCH_2CH_3 + H_2O$

an ester

The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than 1 to 1.

(i) Use Le Chatelier's principle to explain why a 1 to 10 mole ratio is used. In your explanation, you should **not** refer to cost.

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(Extra space) .....

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(3)

(ii) Explain how a catalyst increases the rate of a reaction.

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(Extra space) .....

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(2)
(Total 12 marks)

Q3.A study of equilibrium is important for understanding chemical reactions.

(a) State le Chatelier's principle.

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(Extra space) .....

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(1)

(b) Catalysts play an important role in many reactions.

(i) State the meaning of the term *catalyst*.
Explain, in general terms, how catalysts work.

Meaning of the term *catalyst* .....

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How catalysts work .....

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(3)

(Extra space) .....

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(ii) State the effect, if any, of a catalyst on the time taken to reach equilibrium.

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(1)

(iii) State the effect, if any, of a catalyst on the position of an equilibrium.

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(1)

(c) Consider the following equilibrium reactions.

				$\Delta H^{\ominus}$ / kJ mol^{-1}
P	$H_2(g) + I_2(g)$	$\rightleftharpoons$	$2HI(g)$	−10
Q	$CO_2(g) + 3H_2(g)$	$\rightleftharpoons$	$CH_3OH(g) + H_2O(g)$	−49
R	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$	+58
S	$N_2(g) + 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	−92
T	$C_2H_4(g) + H_2O(g)$	$\rightleftharpoons$	$CH_3CH_2OH(g)$	−42

In each of parts (c)(i) to (c)(v), you should record in the box one of the letters, **P, Q, R, S** or **T**, that corresponds to the equilibrium that best fits the information provided. You may use each letter once, more than once or not at all.

(i) A decrease in temperature at constant pressure shifts the position of this equilibrium from right to left.

☐

(1)

(ii) This equilibrium uses concentrated phosphoric acid as a catalyst in a hydration reaction.

(1)

(iii) A decrease in pressure at constant temperature shifts the position of this equilibrium from left to right.

(1)

(iv) There is no change in the position of this equilibrium when the pressure is increased at constant temperature.

(1)

(v) An increase in the concentration of steam at constant temperature and constant pressure shifts the position of this equilibrium from right to left.

(1)
(Total 11 marks)

Q4. The rate of a chemical reaction is influenced by the size of the activation energy. Catalysts are used to increase the rates of chemical reactions but are not used up in the reactions.

(a) Give the meaning of the term *activation energy*.

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(2)

(b) Explain how a catalyst increases the rate of a reaction.

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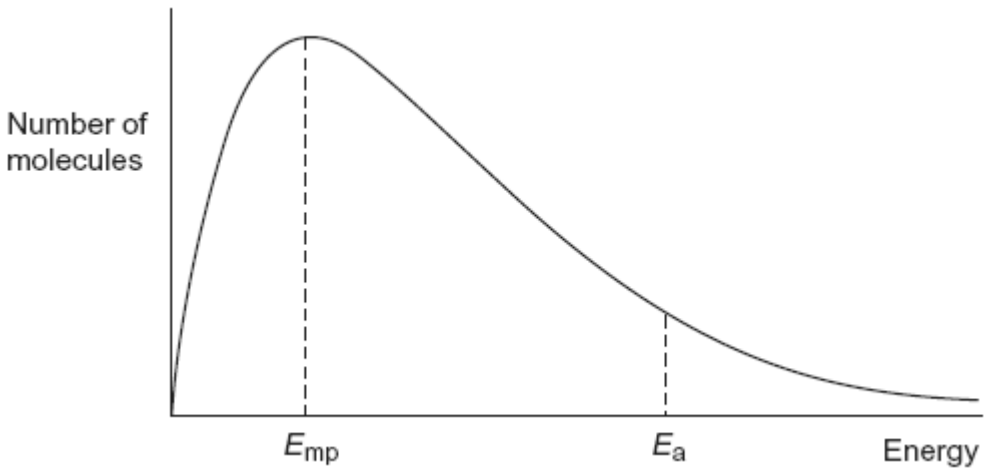
(2)

(c) The diagram below shows the Maxwell–Boltzmann distribution of molecular energies, at a constant temperature, in a gas at the start of a reaction.
On this diagram the most probable molecular energy at this temperature is shown by the symbol E_{mp}
The activation energy is shown by the symbol E_a



To answer the questions (c)(i) to (c)(iv), you should use the words **increases**, **decreases** or **stays the same**. You may use each of these answers once, more than once or not at all.

(i) State how, if at all, the value of the most probable energy (E_{mp}) changes as the total number of molecules is increased at constant temperature.

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(1)

(ii) State how, if at all, the number of molecules with the most probable energy (E_{mp}) changes as the temperature is decreased without changing the total number of molecules.

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(1)

(iii) State how, if at all, the number of molecules with energy greater than the activation energy (E_a) changes as the temperature is increased without c hanging the total number of molecules.

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(1)

(iv) State how, if at all, the area under the molecular energy distribution curve changes as a catalyst is introduced without changing the temperature or the total number of molecules.

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(1)

(d) For each of the following reactions, identify a catalyst and name the organic product of the reaction.

(i) The fermentation of an aqueous solution of glucose.

Catalyst .....

Name of organic product .....

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(2)

(ii) The hydration of but-2-ene.

Catalyst .....

Name of organic product .....

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(2)

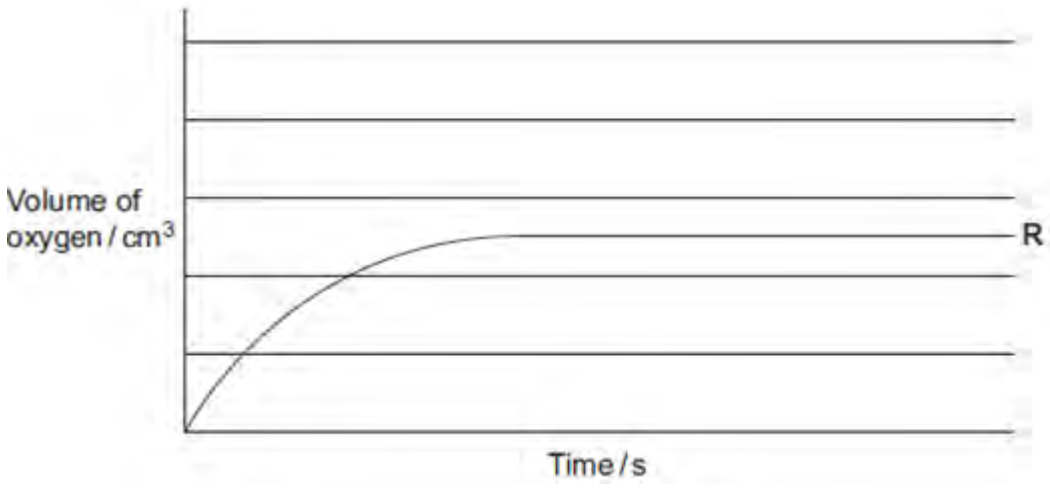
(Total 12 marks)

Q5. A student carried out an experiment to determine the rate of decomposition of hydrogen peroxide into water and oxygen gas.

The student used 100 cm^3 of a 1.0 mol dm^{-3} solution of hydrogen peroxide at 298 K and measured the volume of oxygen collected.
Curve **R**, in each of **Figures 1**, **2** and **3**, shows how the total volume of oxygen collected changed with time under these conditions.

(a) Draw a curve on **Figure 1** to show how the total volume of oxygen collected will change with time if the experiment is repeated at 298 K using 100 cm^3 of a 2.0 mol dm^{-3} solution of hydrogen peroxide.

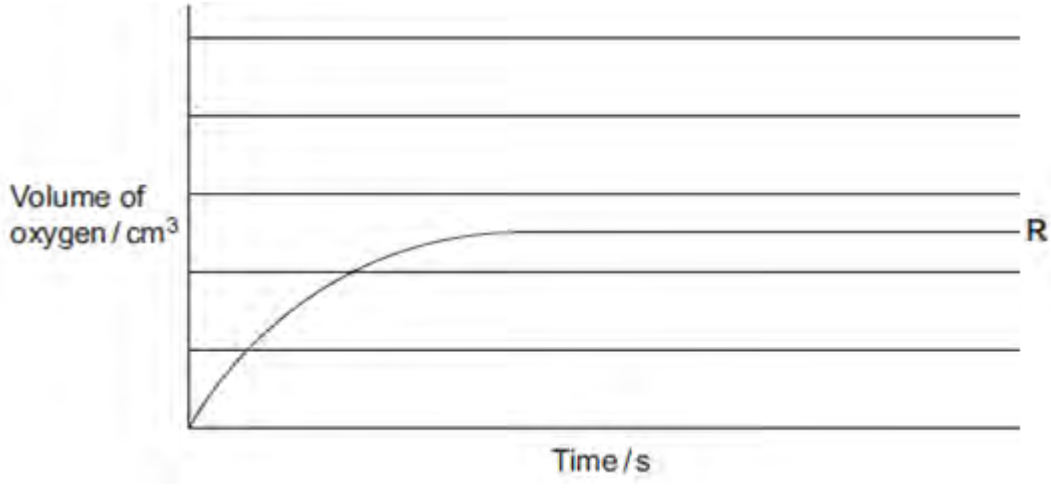
Figure 1



(2)

(b) Draw a curve on **Figure 2** to show how the total volume of oxygen collected will change with time if the experiment is repeated at 298 K using 100 cm^3 of a 0.4 mol dm^{-3} solution of hydrogen peroxide.

Figure 2

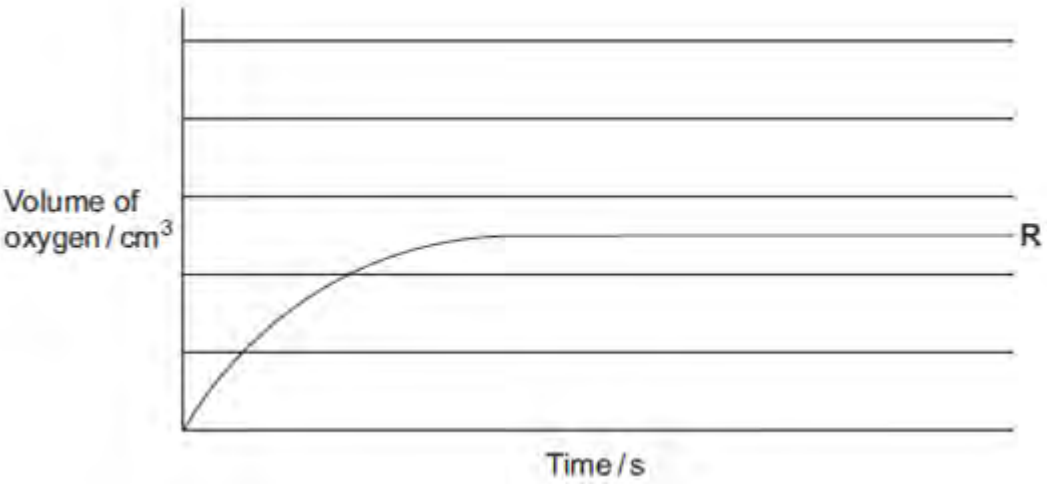


(2)

(c) Draw a curve on **Figure 3** to show how the total volume of oxygen collected will

change with time if the **original** experiment is repeated at a temperature higher than 298 K.
You should assume that the gas is collected at a temperature of 298 K.

Figure 3



(2)

(d) Explain why the slope (gradient) of curve **R** decreases as time increases.

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(Extra space) .....

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(e) The student discovered that hydrogen peroxide decomposes at a faster rate when a few drops of aqueous hydrogen bromide are added to the solution.
The student found on the Internet that this decomposition is thought to proceed in two steps as shown by the following equations.

Step **1** $H_2O_2 + HBr \longrightarrow HBrO + H_2O$

Step **2** $HBrO + H_2O_2 \longrightarrow H_2O + O_2 + HBr$

(i) Write an equation for the overall reaction.

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(1)

(ii) Give **one** reason, other than the increase in rate of reaction, why the student was able to deduce that hydrogen bromide behaves as a catalyst in this two-step reaction.

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(1)