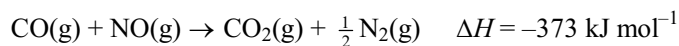


1. Cars are fitted with catalytic converters in order to reduce the pollution caused by the combustion of petrol. Potential pollutant gases include carbon monoxide, nitrogen monoxide and unburnt hydrocarbons. The first two compounds are removed by passing the hot gases over a platinum catalyst.



In the absence of a catalyst, this reaction is extremely slow.

- (a) (i) Define the term **activation energy**.

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(1)

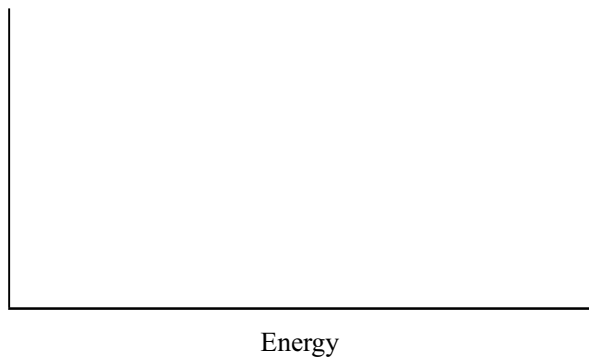
- (ii) Comment on the relative value of the activation energy of this reaction compared with the much faster reaction of nitrogen monoxide with oxygen.

.....

(1)

- (b) (i) Draw a distribution of the molecular energies of gas molecules at two different temperatures, T_1 and a higher temperature T_2 . Label the curves T_1 and T_2 and mark the energy corresponding to the activation energy, E_A .

Fraction of molecules
with a given energy



(3)

- (ii) Use the diagram to explain why the rate of a reaction, such as that between carbon monoxide and nitrogen monoxide, will change as the temperature increases.

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(2)

- (c) The reaction between carbon monoxide and nitrogen monoxide requires a platinum catalyst with a large surface area. Explain the effect of a catalyst on the rate of this reaction and why the surface area needs to be large.

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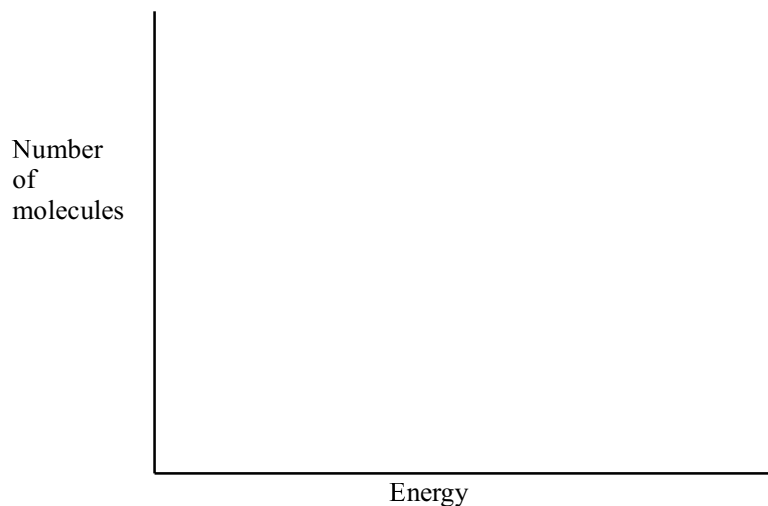
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(4)

(Total 11 marks)

2. The rate of any chemical reaction is increased if the temperature is increased.
- (a) Draw a diagram to represent the Maxwell-Boltzmann distribution of molecular energies at a temperature T_1 and at a higher temperature T_2 .



(3)

- (b) Use your diagram and the idea of activation energy to explain why the rate of a chemical reaction increases with increasing temperature.

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(4)

(Total 7 marks)

3. In a series of experiments to investigate the factors which control the rate of a chemical reaction, aqueous hydrochloric acid was added to calcium carbonate in a conical flask placed on an electronic balance.

The loss in mass of the flask and its contents was recorded for 15 minutes.



Four experiments were carried out.

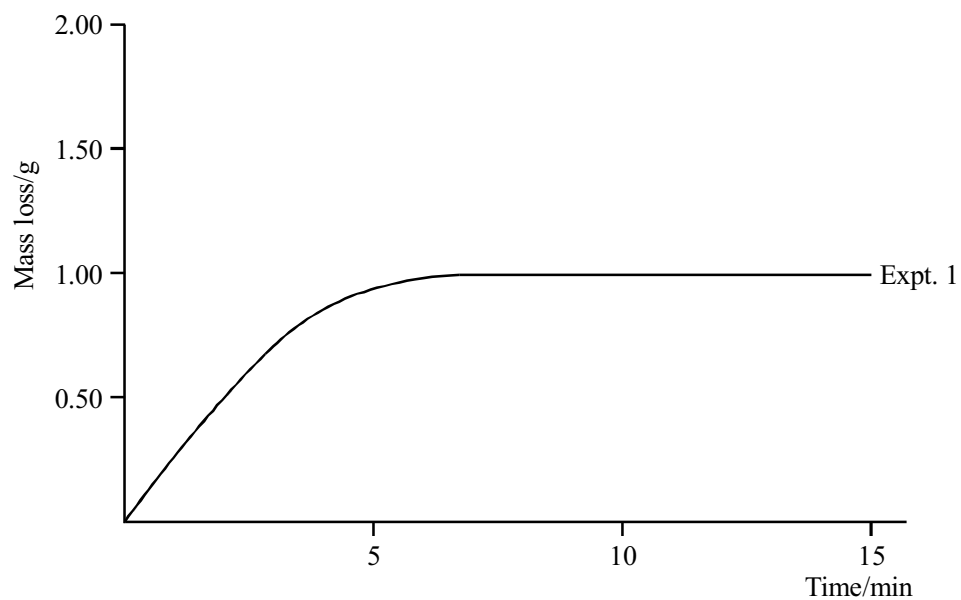
Experiments 1, 3 and 4 were carried out at room temperature (20 °C).

The same mass of calcium carbonate (a large excess) was used in each experiment.

The pieces of calcium carbonate were the same size in Experiments 1, 2 and 4.

Experiment	Calcium carbonate	Hydrochloric acid
1	Small pieces	50.0 cm ³ of 1.00 mol dm ⁻³
2	Small pieces	50.0 cm ³ of 1.00 mol dm ⁻³ heated to 80°C
3	One large piece	50.0 cm ³ of 1.00 mol dm ⁻³
4	Small pieces	50.0 cm ³ of 2.00 mol dm ⁻³

(a) The results of Experiment 1 give the curve shown on the graph below.



(i) Explain why there is a loss in mass as the reaction proceeds.

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(2)

- (ii) Explain the shape of the curve drawn for Experiment 1.

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(2)

- (b) Draw **curves on the graph** to represent the results you would expect for Experiments 2, 3 and 4. Label the curves 2, 3 and 4.

(3)

- (c) (i) Calculate the mass of calcium carbonate which exactly reacts with 50.0 cm³ of 1.00 mol dm⁻³ aqueous hydrochloric acid. $M_r(\text{CaCO}_3) = 100$.

(3)

- (ii) Based on your answer to (c)(i) suggest a suitable mass of calcium carbonate to use in the experiments. Explain your answer.

Suggested mass:

Explanation:

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(2)

(Total 12 marks)

4. (a) (i) State two factors other than a change in temperature or the use of a catalyst that influence the rate of a chemical reaction.

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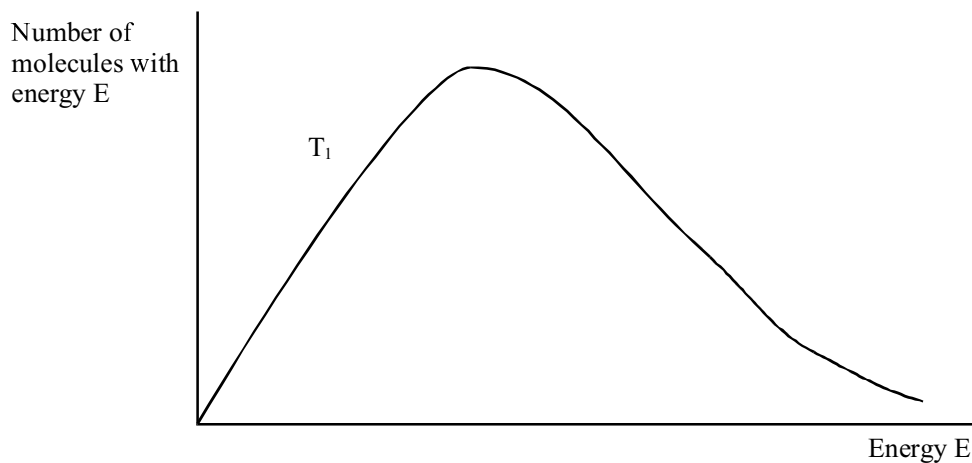
(2)

- (ii) For one of the factors you have chosen explain the effect on the rate.

.....

(2)

- (b) The Maxwell–Boltzmann distribution of molecular energies at a given temperature T_1 is shown below.



- (i) On the same axes draw a similar curve for a reaction mixture at a higher temperature T_2 .

(2)

- (ii) Place a vertical line marked E_a at a plausible value on the energy axis to represent the activation energy for a reaction.

(1)

- (iii) Use your answers to parts (i) and (ii) to explain why an increase in temperature causes an increase in the reaction rate.

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(3)
(Total 10 marks)

5. (a) (i) Draw a diagram to represent the Maxwell-Boltzmann distribution of molecular energies at a temperature T.



(2)

- (ii) Catalysts are used in the exhausts of modern motor cars to speed up the reaction between polluting gases (carbon monoxide, CO, and dinitrogen oxide, N_2O) before they reach the end of the exhaust pipe.

Use the diagram in (a)(i) to explain how the catalyst achieves this.

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(4)

- (b) State ONE other method of increasing the rate of the reaction between two gases in general. Explain how the collision theory supports your suggested method.

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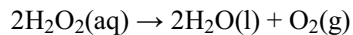
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(3)
(Total 9 marks)

6. Hydrogen peroxide decomposes according to



The reaction is catalysed by solid manganese(IV) oxide, MnO_2 .

- (a) Two experiments are carried out under the same conditions except that in one experiment the manganese(IV) oxide is a fine powder and in the other the same mass of coarse granules is used.

Which experiment would show the faster rate of decomposition? Explain your answer in terms of collision theory.

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(2)

- (b) (i) Draw a labelled Maxwell-Boltzmann distribution of molecular energies in a mixture of gases at two different temperatures T_1 and T_2 , where T_2 is higher than T_1 .



(4)

- (ii) Mark on your graph a suitable value for the activation energy, E_a , for the reaction between the gases. Use your drawing to account for the increase in reaction rate with increasing temperature.

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(3)

- (iii) Use the Maxwell-Boltzmann distribution to explain why a catalyst increases the rate of a reaction at temperature T_1 .

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(2)

(Total 11 marks)

7. Read the passage on 'BUILDING A BETTER BLEACH - A GREEN CHEMISTRY CHALLENGE' straight through and then more carefully. Answer the following questions.

BUILDING A BETTER BLEACH – A GREEN CHEMISTRY CHALLENGE

Your dark red T-shirt has turned everyone else's white washing pink. The problem is how do you remove the stain?

A stain is a colour where you don't want it, but stain removal is not actually removal at all. Instead the stain molecules are altered chemically so they no longer reflect light in the same way as before. We call it bleaching and chemistry is behind the process.

The active ingredient in household bleach, sodium hypochlorite (NaOCl), keeps white clothing white and your toilet sparkling, but how does the bleach act on stain molecules? Bleaching is an example of a redox reaction. The colour of the stain is a property caused by the chemical structure of its molecules. When the bleach removes electrons from a molecule, the chemical structure of the molecule is changed and properties like colour are altered. Any excess sodium hypochlorite is washed away in the rinse water. However, oxidation with such chlorine-based bleaches sometimes adds chlorine atoms to the stain molecules as well as removing electrons. This can lead to the formation of hazardous by-products such as dioxins, which can persist in the environment and accumulate in the food chain.

Non-chlorine bleaches to the rescue

If the release of chlorine-based bleaches on a large scale could be bad for the environment, what else can we use to get rid of the stains? Alternative non-chlorine bleaches are available. They contain hydrogen peroxide or other peroxide compounds. As hydrogen peroxide is a liquid it is not actually present in solid non-chlorine bleaches such as 'Oxi-Clean'. Solid non-chlorine bleaches contain ingredients like perborate or percarbonate - solid compounds which react with water to release hydrogen peroxide. Whilst removing stains, the hydrogen peroxide decomposes to release highly reactive free radicals. These oxidise other molecules by removing electrons or hydrogen atoms from them.

Hydrogen peroxide sounds like our ideal bleach. In addition to its use in household cleaners, stain removers and hair dyes, it is now used in the pulp and paper, textile and laundry industries. Best of all, hydrogen peroxide contains no chlorine atoms so produces no organochlorine pollutants. So why not stop using chlorine-based bleaches altogether?

The challenge of replacing traditional chlorine bleaches with hydrogen peroxide is twofold. Firstly, the peroxide oxidation process can be unselective. This means any molecules in the vicinity that are exposed to the hydrogen peroxide get exposed to free radicals, and some unwanted reactions might accompany the desired oxidation. Secondly, successful bleaching with hydrogen peroxide requires higher temperatures and pressures and longer reaction times than those needed for chlorine-based bleaches. On an industrial scale this means higher costs for energy, equipment and labour.

However, the Institute for Green Oxidation Chemistry at Carnegie Mellon University, in the USA, may have solved our bleaching problems. They have developed some heroic molecules called tetraamido macrocyclic ligands or TAML for short. These molecules function as catalysts in the hydrogen peroxide bleaching process and their presence allows the oxidation to proceed at much lower temperatures and pressures. Like all catalysts, they are not consumed in the process. This could make the process environmentally benign, meaning the materials used are made from renewable resources, the process consumes minimal energy resources and does not release polluting by-products into the environment.

So bleaching using TAML activated peroxide would be an ideal example of green chemistry in action. Made from naturally occurring biochemicals, TAML catalysts reduce energy costs and prevent pollution. In addition their highly selective nature means they can ‘hunt and destroy’ dye molecules in solution preventing dye transfer to other clothes, which may mean in the future TAML could protect you and your pink-clothed family from further laundry mishaps.

[613 words]

(Source: adapted from *Chem matters — Demystifying Everyday Chemistry* by Kathryn Parent, April 2004)

- (a) Name sodium hypochlorite, NaOCl, using Stock notation.

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(1)

- (b) Explain what is meant by a **free radical**.

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(1)

- (c) TAMLs can act as catalysts in the peroxide bleaching process. Explain how catalysts increase the rate of a reaction.

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(2)

- (d) Describe the THREE key features of an **environmentally benign** process.

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(2)

- (e) Suggest why **accumulation** of dioxins in the food chain may be harmful to people.

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(1)
(Total 7 marks)

8. (a) (i) Draw a Maxwell-Boltzmann distribution of molecular energies in a gas at a temperature T .



(2)

- (ii) Add a curve to your diagram to show the distribution at a higher temperature and label it T_H .

(1)

- (iii) Mark on your diagram a line at a suitable place for the activation energy, E_a , for a reaction.

(1)

- (b) (i) Use your answer to (a) to explain, in terms of the **frequency** and **energy** of collisions, why an increase in temperature increases the rate of a reaction.

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(4)

- (ii) Suggest whether the frequency of the collisions or the energy of collisions is more important in increasing the rate.

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(1)

(Total 9 marks)

9. (a) This part of the question is about the hydrolysis of halogenoalkanes.

2 cm³ of ethanol is added to each of three separate test-tubes.

Three drops of 1-chlorobutane are added to the first, three drops of 1-bromobutane to the second, and three drops of 1-iodobutane are added to the third test-tube.

2 cm³ portions of hot aqueous silver nitrate solution are added to each test-tube.

A precipitate forms immediately in the third test-tube, slowly in the second testtube and extremely slowly in the first test-tube. In each reaction the precipitate is formed by silver ions, Ag⁺(aq), reacting with halide ions formed by hydrolysis of the halogenoalkane.

- (i) Why was ethanol added to each test-tube?

.....

(1)

- (ii) The mechanism of this reaction is similar to that of the reaction between halogenoalkanes and aqueous hydroxide ions.

What feature of a water molecule enables it to act as a nucleophile in this reaction? Suggest the mechanism for the reaction between water and 1-iodobutane. (You may represent 1-iodobutane as RCH_2I).

Feature of water molecule

.....

Mechanism

(4)

- (iii) What is the colour of the precipitate in the third test-tube?

.....

(1)

- (iv) Name the precipitate which forms slowly in the **first** test-tube.

.....

(1)

- (v) Ammonia solution is added to the precipitate in the **first** test-tube. Describe what you would observe.

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(1)

- (vi) Suggest, why the rates of hydrolysis of the three halogenoalkanes are different, in terms of bonding and kinetics.

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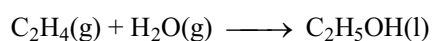
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(3)

- (b) One method of the manufacture of alcohols is to react steam with an alkene.
For example



Suggest TWO reasons why this method is preferred to the hydrolysis of halogenoalkanes.

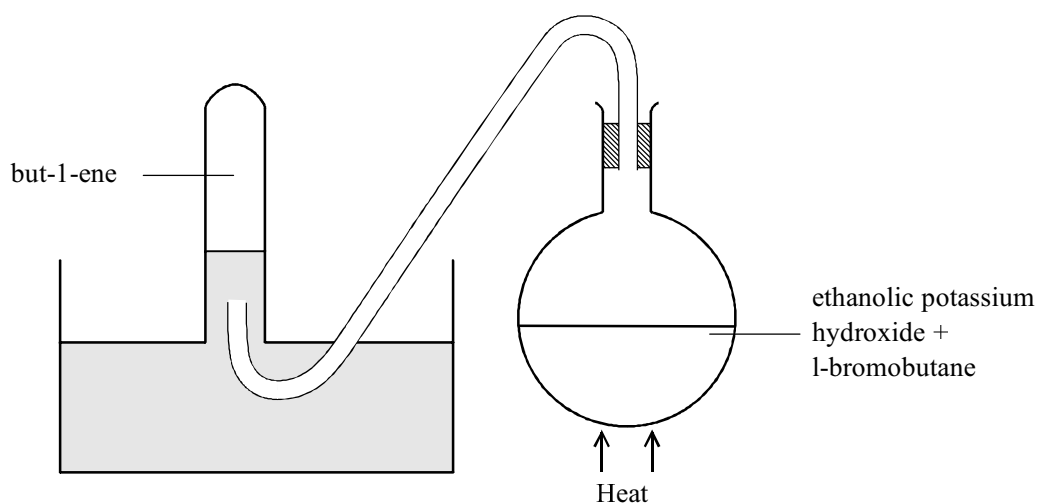
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(2)

- (c) 1-bromobutane reacts with an ethanolic solution of potassium hydroxide on heating to form but-1-ene. A diagram of the apparatus that could be used to carry out this reaction and to collect the gaseous but-1-ene is shown below.



- (i) State the hazard when the heating is stopped.

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(1)

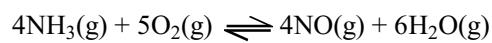
- (ii) How would you minimise the risk associated with this hazard?

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(1)

(Total 15 marks)

10. Ammonia reacts with oxygen, in a reversible, **exothermic reaction**, as shown in the equation below. This is the first stage in the manufacture of nitric acid.



- (a) (i) State and explain the effect of an increase in pressure on the **position** of this equilibrium.

.....

(2)

- (ii) State and explain the effect of an increase in temperature on the **position** of the equilibrium.

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(2)

- (b) (i) State and explain the effect of an increase in pressure on the **rate** of the reaction.

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.....

(3)

- (ii) State and explain the effect of an increase in temperature on the **rate** of the reaction.

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.....

(3)

- (c) (i) Name the catalyst used in the reaction, during the manufacture of nitric acid.

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(1)

- (ii) Explain the effect of a catalyst on the rate of the reaction.

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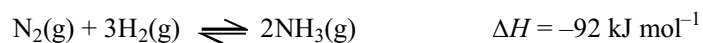
(3)

- (iii) Suggest why the catalyst is in the form of a gauze or mesh.

.....

(1)
 (Total 15 marks)

11. The reaction in the Haber Process that is used to produce ammonia is a homogeneous dynamic equilibrium:



- (a) State the meaning of the terms:

- (i) dynamic equilibrium;

.....

(2)

- (ii) homogeneous.

.....

(1)

- (b) Give, with a reason in each case, the effect of the following on the **position** of the equilibrium above:

- (i) an increase in pressure;

.....

(2)

- (ii) an increase in temperature.

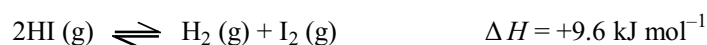
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(2)
(Total 7 marks)

12. (a) A mixture of hydrogen iodide, hydrogen and iodine (all in the gaseous state) establishes dynamic equilibrium if a constant temperature is maintained.



- (i) Explain the meaning of the term **dynamic equilibrium**.

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(2)

- (ii) How, if at all, would the proportion of hydrogen iodide present at equilibrium change if the temperature were to be increased? Justify your answer.

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(2)

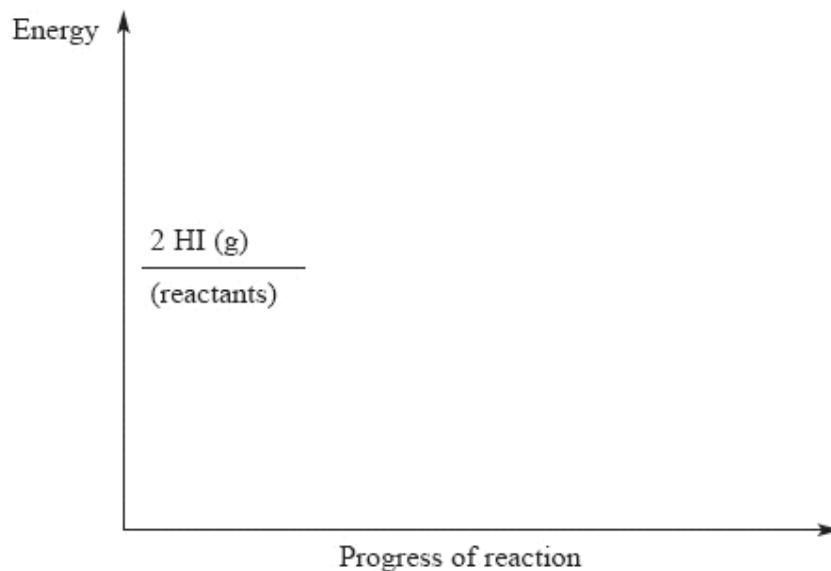
- (iii) The reaction is catalysed by metals such as gold and platinum. How, if at all, would the proportion of hydrogen iodide present at equilibrium change if the reaction were to be catalysed? Justify your answer.

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(1)

- (b) Part of an energy profile for this reaction is shown below. It is not intended to be to scale.



Complete the profile showing:

- the products;
- the progress of **both** uncatalysed and catalysed reactions;
- labelled arrows to indicate the activation energies of **both** the uncatalysed and catalysed reactions.

(4)
(Total 9 marks)

13. This question is concerned with alkenes including ethene and buta-1,3-diene, $\text{CH}_2 = \text{CHCH} = \text{CH}_2$.

- (a) (i) The typical reactions of alkenes are addition reactions, for example their reactions with bromine.

Explain why the reaction of ethene with bromine is described as an addition reaction.

.....

(1)

- (ii) Why should this reaction be carried out in the absence of sunlight or ultra-violet radiation?

.....
.....

(1)

- (iii) Explain how, in this reaction, the bromine molecule is able to act as an electrophile, even though it is normally non-polar.

(2)

- (b) (i) When 1 mole of bromine molecules is added to 1 mole of buta-1,3-diene, the principal product is 1,4-dibromobut-2-ene, $\text{CH}_2\text{BrCH}=\text{CHCH}_2\text{Br}$, a compound which exists as two geometric isomers.

Draw the **displayed** formulae of both of these two isomers.

(2)

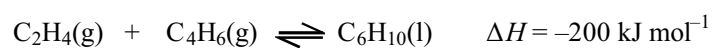
- (ii) State why geometric isomerism is possible in 1,4-dibromobut-2-ene.
[You may find it helpful to refer to the formulae you have drawn above].

.....

(1)

- (c) It has been suggested that cyclohexene, another alkene, could be made by a reaction between ethene and buta-1,3-diene.

Using molecular formulae, the reaction could be represented by the equation



- (i) Draw the **displayed** formula of cyclohexene.

(1)

- (ii) Decide whether high or low temperature and pressure would give the higher proportion of cyclohexene at equilibrium. Justify your choice in each case.

Temperature

.....

Pressure

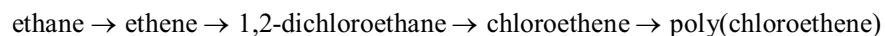
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(2)

(Total 10 marks)

14. The industrial processes involved in the production of poly(chloroethene) are summarised in the flow chart:



- (a) (i) Ethane is converted to ethene by dehydrogenation.

Write a balanced equation, including state symbols, for this equilibrium reaction.

(1)

- (ii) Explain why conditions of high pressure are less favourable for ethene production.

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(2)

- (b) Draw a labelled diagram of an ethene molecule, showing the electron density distribution in the σ and π bonds between the carbon atoms.

(2)

- (c) Give a chemical test which would distinguish between ethane and ethene.

State the result of your test with ethene.

Test

Result

(2)

- (d) 1,2-dichloroethane is formed from ethene by reaction with chlorine.

State the type and mechanism of this reaction.

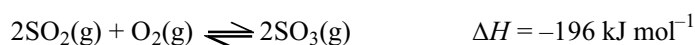
Type

Mechanism

(2)

(Total 9 marks)

15. A step in the Contact Process, for the manufacture of sulphuric acid, is the catalytic oxidation of sulphur dioxide:



If sulphur dioxide and oxygen are heated to a temperature of 450 °C and at a pressure of 2 atm in the presence of a catalyst of vanadium(V) oxide, a dynamic equilibrium is reached in which about 98 % of the sulphur dioxide is converted into sulphur trioxide.

- (a) (i) Explain the meaning of the term **dynamic equilibrium**.

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(2)

- (ii) State the effect on the percentage of sulphur dioxide converted, if extra oxygen is added to the system in equilibrium.

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(1)

- (iii) State the effect on the percentage of sulphur dioxide converted, if the catalyst is removed from the system in equilibrium.

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(1)

- (b) Use your understanding of kinetics and equilibria to justify the temperature used to obtain an economic yield in the manufacture of sulphuric acid.

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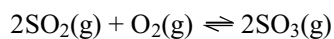
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(4)
(Total 8 marks)

16. One stage in the manufacture of sulphuric acid is the exothermic reaction



- (a) In a closed container this mixture of gases would be in dynamic equilibrium. State the meaning of the words **dynamic** and **equilibrium** in this context.

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(2)

- (b) (i) State the conditions of temperature and pressure used industrially for the manufacture of SO_3 .

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(2)

- (ii) Justify the choice of **temperature** for this reaction in terms of yield and rate.

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(3)

- (iii) The yield of products would be greater if a higher pressure were to be used for the reaction.

Suggest a reason why a higher pressure than you have given in (i) is **not** used.

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(1)

- (c) (i) Calculate ΔH for the forward reaction, given the enthalpies of formation below.

	$\Delta H_f / \text{kJ mol}^{-1}$
$\text{SO}_2(\text{g})$	-297
$\text{SO}_3(\text{g})$	-395
$\text{O}_2(\text{g})$	0

(2)

(ii) State why the enthalpy of formation of oxygen, $O_2(g)$, is zero.

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(1)

(d) (i) State the **formula** of the catalyst used in the industrial process.

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(1)

(ii) Draw an enthalpy level diagram to show the reaction profiles of the uncatalysed and catalysed reactions.

(3)

(iii) Explain how the catalyst increases the reaction rate.

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(2)

- (e) Suggest why the sulphur trioxide produced is passed into concentrated sulphuric acid rather than water to form sulphuric acid at the end of the process.

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(1)
(Total 18 marks)

17. (a) Define the term **standard enthalpy of formation**.

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(3)

- (b) The dissociation of phosphorus pentachloride is a reversible reaction.



- (i) Use the values of enthalpy of formation given to calculate ΔH for the forward reaction.

	$\Delta H_f /$ kJ mol^{-1}
$\text{PCl}_5(\text{g})$	- 399
$\text{PCl}_3(\text{g})$	- 306

(1)

- (ii) Explain, with reasons, the effect that raising the temperature would have on the composition of the equilibrium mixture.

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(2)

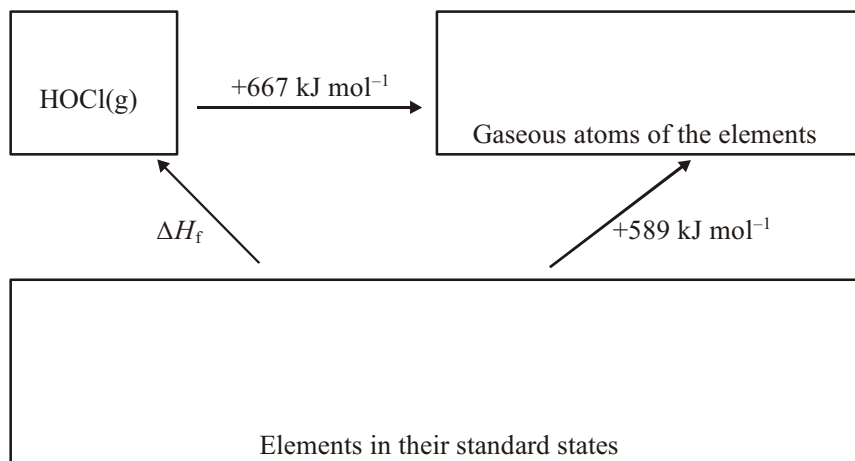
- (iii) Other than by changing the temperature, suggest how the amount of PCl_5 present at equilibrium could be increased. Give a reason for your answer.

.....

(2)

(Total 8 marks)

18. The Hess cycle below can be used to estimate the enthalpy change of formation, ΔH_f , of the unstable gaseous compound with the formula HOCl(g) .



- (a) (i) Insert formulae, with state symbols, into the appropriate boxes, to show the correct quantities of each element.

(1)

- (ii) Use the cycle to calculate a value for the enthalpy change of formation, ΔH_f , [HOCl(g)].

(1)

- (iii) Assuming that the H—O bond energy is $+464 \text{ kJ mol}^{-1}$, calculate a value for the O—Cl bond energy.

(1)

- (b) (i) Draw a 'dot and cross' diagram for the HOCl molecule showing outer electrons only.

(2)

- (ii) Predict the HOCl bond angle. Justify your answer.

Angle

Justification

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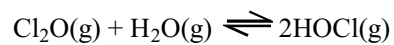
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(2)

- (c) HOCl(g) can be made from chlorine(I) oxide by the reversible reaction



What effect, if any, would an increase in pressure have on the proportion of HOCl(g) at equilibrium? Justify your answer.

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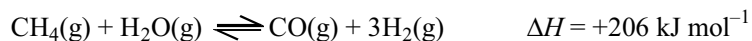
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(2)
(Total 9 marks)

19. Hydrogen gas is manufactured by passing methane and steam over a heated catalyst.



Explain the effect, if any, on the equilibrium yield of hydrogen by using:

- (i) a higher pressure

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(2)

- (ii) a higher temperature

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(2)

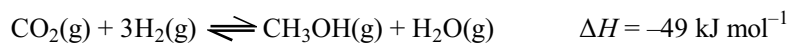
- (iii) a catalyst.

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(1)

(Total 5 marks)

20. The main reactions involved in the conversion of synthesis gas to methanol in both methods are



Compare the old and the new methods by considering their operating conditions.

Discuss ONE advantage of the old method and THREE advantages of the new method. Justify your answers.

(i) Advantage of old method.

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.....
.....

(1)

(ii) Advantages of new method.

Advantage 1

.....
.....

Advantage 2

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.....

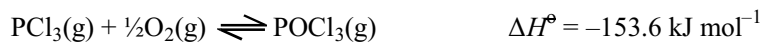
Advantage 3

.....
.....

(3)

(Total 4 marks)

21. (i) Phosphorus trichloride reacts with oxygen to form phosphorus oxychloride in an equilibrium reaction.



Suggest how you would adjust the temperature and pressure to increase the yield of this reaction. Justify your answer in each case.

Temperature

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.....

.....

Pressure

.....

.....

.....

(2)

- (ii) State the effect of the adjustments you propose in part (i) on the rate of the reaction.

Temperature

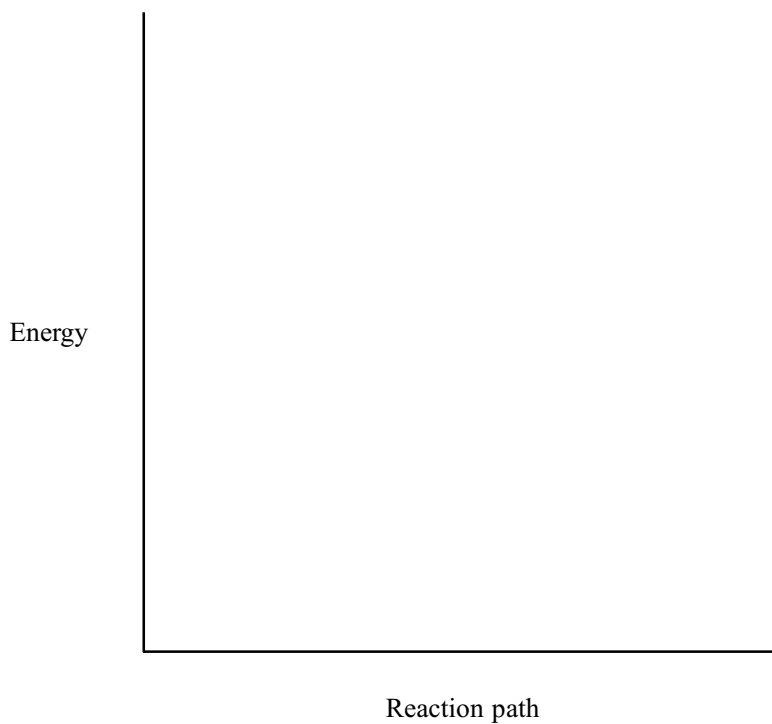
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Pressure

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(2)

- (iii) On the axes below, sketch the energy profiles of the reaction in (c)(i) with and without a catalyst. Label the profiles.

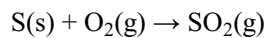


(2)
(Total 6 marks)

22. This question is about the manufacture of sulphuric acid, H_2SO_4 .

- (a) The first stage in the manufacture of sulphuric acid is the combustion of sulphur.

The following equation shows the reaction taking place when the standard enthalpy of combustion of sulphur is measured.



Define the term **standard enthalpy of combustion**.

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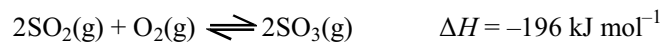
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(3)

- (b) In the second stage of the manufacture of sulphuric acid, sulphur dioxide is oxidised to sulphur trioxide as shown in the following equation:



- (i) Explain, in terms of collision theory, why the rate of a reaction is increased by increasing the temperature and by the addition of a catalyst.

Temperature

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.....

Catalyst

.....

.....

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.....

.....

(4)

- (ii) State and explain the effect, if any, of increasing the temperature on the equilibrium yield of sulphur trioxide.

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(2)

- (iii) State and explain the effect, if any, of an increased pressure on the equilibrium

yield of sulphur trioxide.

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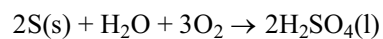
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(2)

- (c) The following equation represents the overall reaction for the manufacture of sulphuric acid from sulphur, oxygen and water.

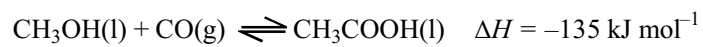


Use the data below to calculate the enthalpy change for this reaction.

Substance	ΔH_f^\ominus / kJ mol^{-1}
$\text{H}_2\text{O (l)}$	-286
$\text{H}_2\text{SO}_4 (\text{l})$	-814

(2)
(Total 13 marks)

23. Almost two thirds of the world's ethanoic acid is made using the following equilibrium reaction, with the aid of an iridium complex as a catalyst.



Which of the following changes in conditions would increase the equilibrium yield of ethanoic acid?

- A increase pressure
- B decrease pressure
- C increase temperature
- D add a catalyst

(Total 1 mark)