3. A fixed mass of marble is reacted with dilute hydrochloric acid at a constant temperature. Explain why the rate of the reaction is increased if the lumps of marble are reduced in size.

.....

.....

.....

(2)

(Total 2 marks)

(c) Hydrogen peroxide decomposes more rapidly in the presence of aqueous hydrogen bromide. The decomposition proceeds as shown by the following equations.

$$H_2O_2 + HBr \rightarrow HBrO + H_2O$$

$$HBrO + H_2O_2 \rightarrow H_2O + O_2 + HBr$$

(i) Write an equation for the overall reaction.

.....

(ii) Define the term *catalyst*.

.....

.....

(iii) Give **two** reasons, other than an increase in the reaction rate, why these equations suggest that hydrogen bromide is behaving as a catalyst.

Reason 1 .....

Reason 2 .....

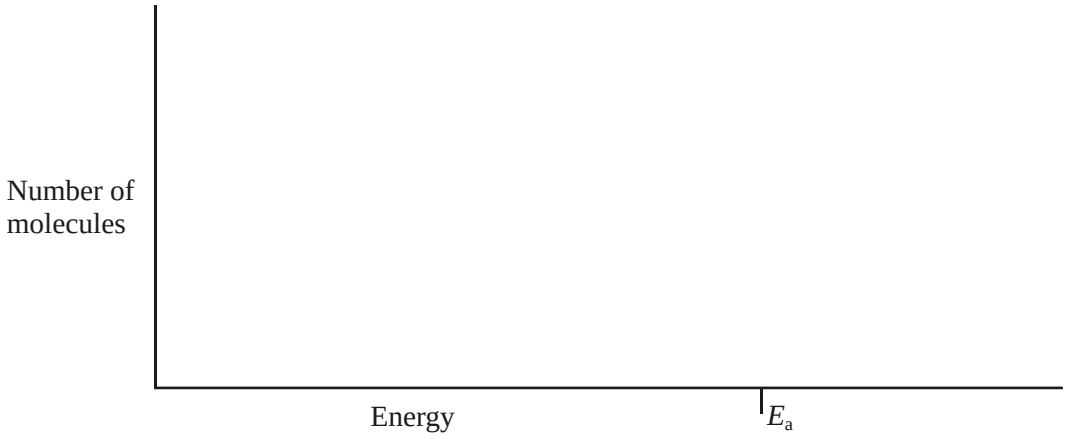
(5)

(Total 10 marks)

5. Gas **G** decomposes as shown in the equation below.

$$G(g) \rightarrow X(g) + Y(g)$$

(a) Draw, on the axes below, a Maxwell–Boltzmann distribution curve for a sample of **G** in which only a small proportion of molecules has energy greater than the activation energy, E_a.



(3)

(b) Define the term *activation energy*.

.....

.....

(2)

(c) At any time, most of the molecules of **G** have energy less than the activation energy. Suggest why, at a constant temperature, most of **G** eventually decomposes.

.....

.....

(2)

(d) State the effect, if any, of adding a catalyst on the time required for **G** to decompose, compared with a similar sample without a catalyst. Explain in general terms how the catalyst has this effect.

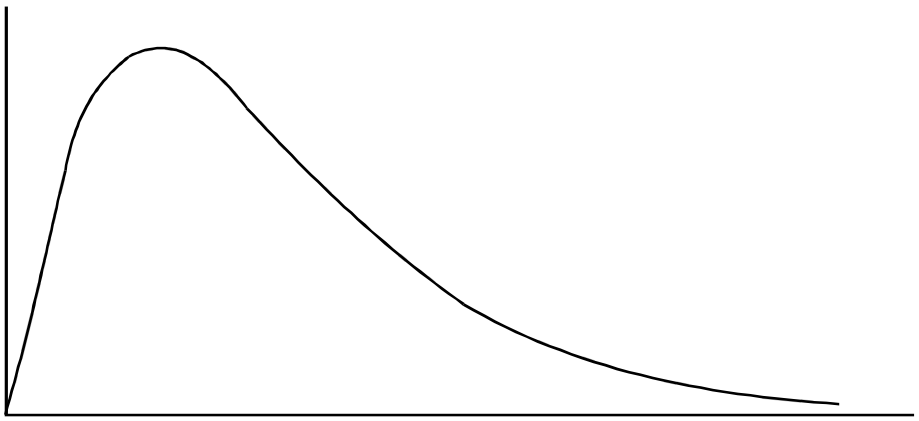
Time for decomposition …….....

Explanation …….

.....…….

(3)
(Total 10 marks)

7. (a) Below is a Maxwell–Boltzmann curve showing the distribution of molecular energies for a sample of gas at a temperature *T*.



(i) Label the axes on the diagram above.

(ii) What does the area under the curve represent?

.....

(iii) State why this curve starts at the origin.

.....

(4)

(b) (i) State what is meant by the term *activation energy*.

.....

.....

(ii) The rate of a chemical reaction may be increased by an increase in reactant concentration, by an increase in temperature and by the addition of a catalyst.

State which, if any, of these changes involves a different activation energy. Explain your answer.

Change(s) .....

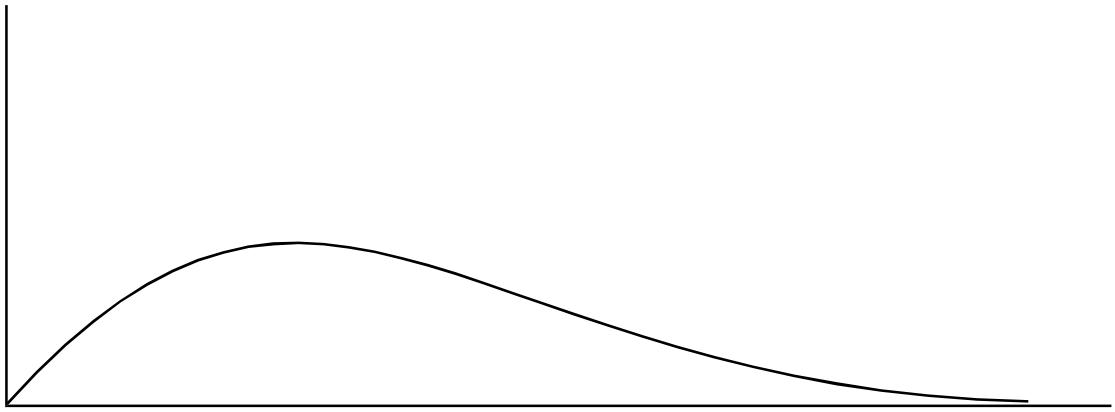
Explanation .....

.....

(5)
(Total 9 marks)

(Total 8 marks)

10. The diagram below represents a Maxwell–Boltzmann distribution curve for the particles in a sample of a gas at a given temperature. The questions below refer to this sample of particles.



(a) Label the axes on the diagram.

(2)

(b) On the diagram draw a curve to show the distribution for this sample at a **lower** temperature.

(2)

(c) In order for two particles to react they must collide. Explain why most collisions do not result in a reaction.

.....

(1)

(d) State one way in which the collision frequency between particles in a gas can be increased without changing the temperature.

.....

(1)

(e) Suggest why a small increase in temperature can lead to a large increase in the reaction rate between colliding particles.

.....

.....

.....

(2)

(f) Explain in general terms how a catalyst works.

.....

.....

.....

(2)

(Total 10 marks)

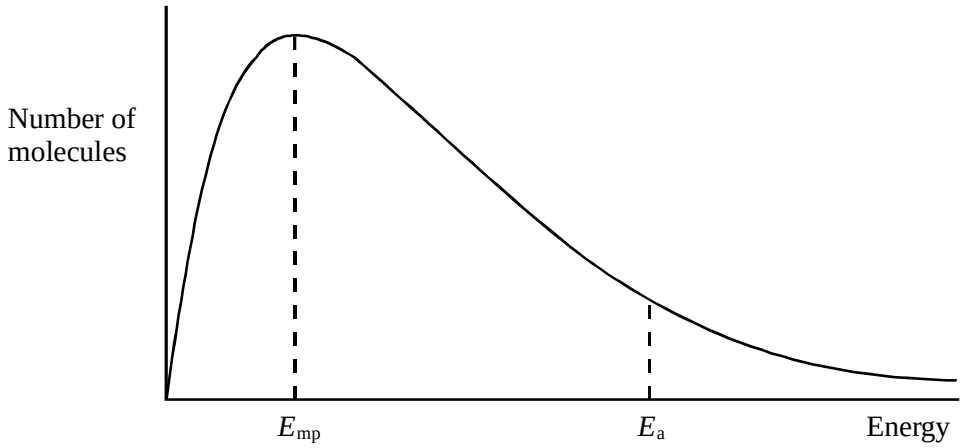
12. (a) State what is meant by the term *activation energy* of a reaction.

(1)

(b) State in general terms how a catalyst increases the rate of a chemical reaction.

(2)

(c) The curve 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 indicated by the symbol E_{mp} and the activation energy by the symbol E_a.



Consider the following changes.

(i) The number of molecules is increased at constant temperature.

(ii) The temperature is decreased without changing the number of molecules.

(iii) A catalyst is introduced without changing the temperature or the number of molecules.

For **each** of these changes state how, if at all, the following would vary:

- the value of the most probable energy, E_{mp}
- the number of molecules with the most probable energy, E_{mp}
- the area under the molecular energy distribution curve
- the number of molecules with energy greater than the activation energy, E_a

(12)
(Total 15 marks)

13. (a) Define the term *activation energy* for a chemical reaction.

(2)

(b) Draw, with labelled axes, a curve to represent the Maxwell–Boltzmann distribution of molecular energies in a gas. Label this curve $\mathbf{T}_1$. On the same axes, draw a second curve to represent the same sample of gas at a lower temperature. Label this curve $\mathbf{T}_2$.

Use these curves to explain why a small decrease in temperature can lead to a large decrease in the rate of a reaction.

(8)

(c) Give **one** reason why most collisions between gas-phase reactants do not lead to a reaction. State and explain **two** ways of speeding up a gas-phase reaction other than by changing the temperature.

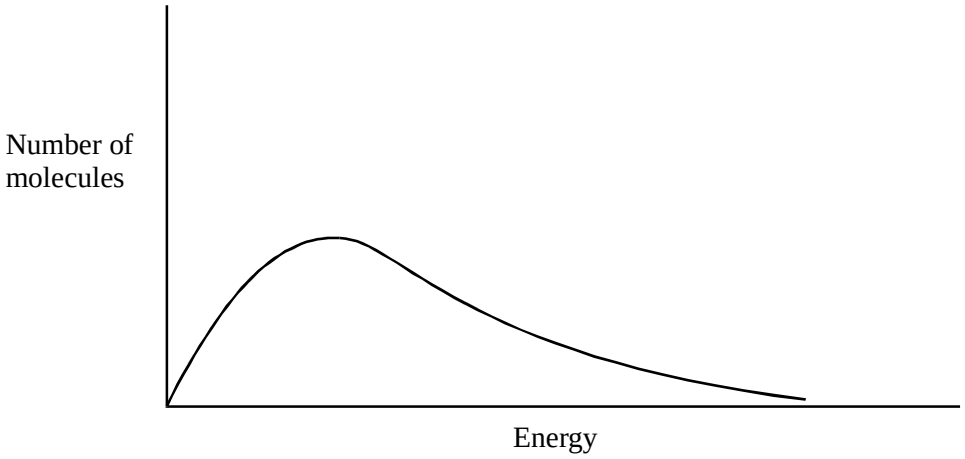
(5)
(Total 15 marks)

14. Draw a Maxwell-Boltzman curve for a sample of gas at a temperature, T_1. On the same axes draw a second curve for the same sample of gas at a higher temperature, T_2. Label the curves and the axes clearly. Explain, using these curves, why an increase in temperature increases the rate of a gas phase reaction.

Suggest how and why the first curve would change if a larger mass of gas were used at temperature T_1.

(Total 10 marks)

15. (a) A sample of a gas was sealed into a flask at temperature *T* and pressure *P*. The Maxwell–Boltzmann distribution of energies for the molecules in this sample is shown below.



(i) Using the axes above, sketch the curve that you would expect if this sample of gas at pressure *P* had been cooled. Label this curve **X**.

(ii) Using the axes above, sketch the curve that you would expect if another sample of the same gas was sealed in the same flask at the original temperature, *T*, but at a higher pressure. Label this curve **Y**.

(4)

(b) Gas **A** decomposes slowly to form gases **B** and **C**. An equilibrium is established as shown by the following equation.

$$A(g) \rightleftharpoons B(g) + C(g) \qquad \Delta H \text{ is positive}$$

(i) In terms of the behaviour of molecules, state what must happen before molecules of **A** can react to form **B** and **C**.

.....

.....

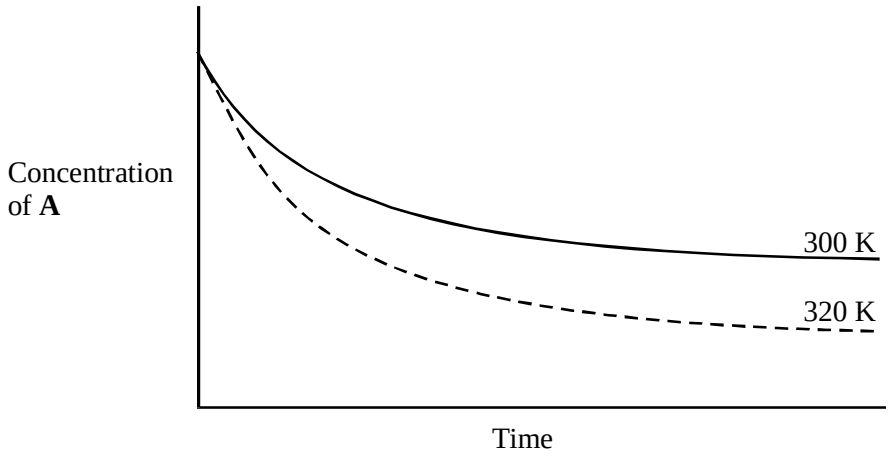
(ii) Explain why the decomposition of **A** is faster at higher temperatures.

.....

.....

(4)

(c) The graphs below show how, starting from **A** alone, the concentration of **A** varies with time at temperatures of 300 K and 320 K for the reversible reaction given in part (b).



(i) Suggest why, as shown on the graphs, the concentration of **A** remains constant after a time.

.....

(ii) Explain why, at 320 K, the concentration of **A** falls to a lower value compared with the reaction at 300 K.

.....

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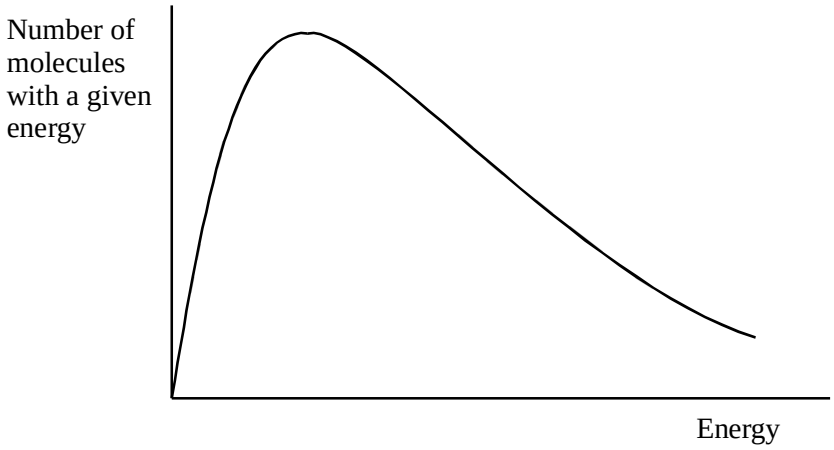
(3)
(Total 11 marks)

20. (a) The diagram below shows the distribution curve for the energies of molecules in a given mass of methane.



(i) If the graph were extended to higher energies, at what point would the curve meet the horizontal axis? Explain your answer.

Point.....

Explanation.....

.....

.....

(ii) Sketch on the diagram a curve for a larger mass of methane at the same temperature.

(iii) A sample of ethane containing the same number of moles as the sample of methane above is at the same temperature and pressure. Describe how the distribution curve for ethane differs, if at all, from that above.

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(5)

(b) Give two requirements for a reaction to occur between two gaseous molecules.

Requirement 1.....

Requirement 2.....

(2)
(Total 7 marks)

21. Methanol can be formed on an industrial scale from carbon dioxide and hydrogen by a reversible reaction as shown below.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

The reaction can be carried out in the presence of a chromium-based catalyst at a temperature of 700 K and a pressure of 30 MPa. Under these conditions, equilibrium is reached when 2% of the carbon dioxide has been converted.

(a) How does the rate of the forward reaction compare with that of the backward reaction when 2% of the carbon dioxide has been converted?

.....…….

(1)

(b) (i) If the pressure was reduced but the temperature was kept the same, deduce what would happen to the equilibrium yield of methanol. Explain your answer.

Yield ……..…….

Explanation ..…….

.....…….

(ii) Give two reasons why, in general, industry prefers to operate processes at pressures lower than 30 MPa.

Reason 1 …..…….

Reason 2 …..…….

(5)

(c) If the chromium-based catalyst was replaced with a more efficient catalyst but other conditions were kept the same, deduce what would happen to the equilibrium yield of methanol. Explain your answer.

Yield ……..……..…….

Explanation ..……..……..…….

.....…….

(2)

(d) In the presence of a very efficient copper-based catalyst, this industrial process can be operated at a lower temperature of 500 K and a pressure of 30 MPa. Under these conditions, at equilibrium, more of the carbon dioxide is converted into methanol.

Use this information to deduce the sign of the enthalpy change for the reaction. Explain your deduction.

Sign of enthalpy change……..……

Explanation …..…….

.....…….

(3)

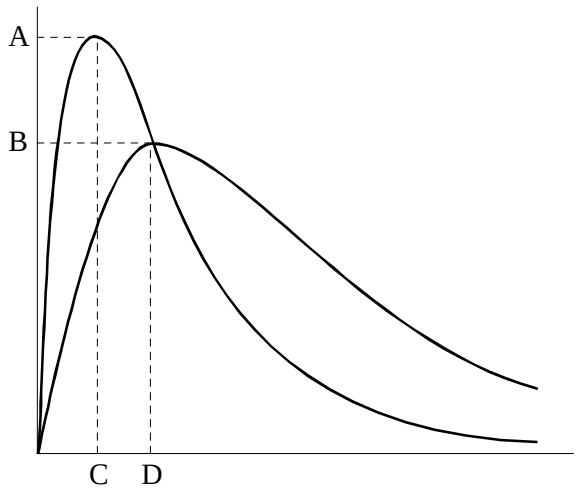
(e) In the processes above, the equilibrium yield of methanol is low. Suggest what is done with the unreacted carbon dioxide and hydrogen.

.....…….

(1)

(Total 12 marks)

22. (a) The diagram below shows the Maxwell-Boltzmann energy distribution curves for molecules of a sample of a gas at two different temperatures.



(i) Label both axes.

(ii) Choose one of the letters on the axes above which represents the most probable energy of the molecules at the lower temperature.

.....

(3)

(b) Give two requirements for a reaction to occur between molecules in the gas phase.

Requirement 1 .....

Requirement 2 .....

(2)

(c) Which has the greater effect on the initial rate of a first-order reaction:

either increasing the temperature of the reaction mixture from 300 K to 309 K (a 3% increase)

or increasing the concentration of the reagent from 1.00 M to 1.03 M (also a 3% increase)?

Briefly explain your answer.

Greater effect .....

Explanation .....

.....

.....

(3)

(Total 8 marks)

23. At high temperatures, nitrogen is oxidised by oxygen to form nitrogen monoxide in a reversible reaction as shown in the equation below.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H^{\ominus} = +180 \text{ kJ mol}^{-1}$$

(b) State and explain the effect of an increase in pressure, and the effect of an increase in temperature, on the yield of nitrogen monoxide in the above equilibrium.

Effect of an increase in pressure on the yield .....

Explanation .....

.....

.....

.....

Effect of an increase in temperature on the yield .....

Explanation .....

.....

.....

(6)

(Total 6 marks)

24. Sulphur dioxide and oxygen were mixed in a 2:1 mol ratio and sealed in a flask with a catalyst. The following equilibrium was established at temperature T_1

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\ominus} = -196 \text{ kJ mol}^{-1}$$

(e) In a further experiment, the amounts of sulphur dioxide and oxygen used, the catalyst and the temperature, T_1, were all unchanged, but a flask of smaller volume was used.

Deduce the effect of this change on the yield of sulphur trioxide and on the value of K_p.

Effect on yield of SO_3 .....

Effect on K_p .....

(2)

26. Hydrogen is produced on an industrial scale from methane as shown by the equation below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^{\ominus} = +205 \text{ kJ mol}^{-1}$$

(a) State Le Chatelier's principle.

.....

.....

(1)

(b) The following changes are made to this reaction at equilibrium. In each case, predict what would happen to the yield of hydrogen from a given amount of methane. Use Le Chatelier's principle to explain your answer.

(i) The overall pressure is increased.

Effect on yield of hydrogen .....

Explanation .....

.....

.....

(ii) The concentration of steam in the reaction mixture is increased.

Effect on yield of hydrogen .....

Explanation .....

.....

.....

(6)

(c) At equilibrium, a high yield of hydrogen is favoured by high temperature. In a typical industrial process, the operating temperature is usually less than 1200 K. Suggest two reasons why temperatures higher than this are not used.

Reason 1 .....

Reason 2 .....

(2)

(Total 9 marks)

27. Methanol can be synthesised from carbon monoxide by the reversible reaction shown below.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91 \text{ kJ mol}^{-1}$$

The process operates at a pressure of 5 MPa and a temperature of 700 K in the presence of a copper-containing catalyst. This reaction can reach dynamic equilibrium.

(a) By reference to rates and concentrations, explain the meaning of the term *dynamic equilibrium.*

.....

.....

(2)

(b) Explain why a high yield of methanol is favoured by high pressure.

.....

.....

(2)

(c) Suggest **two** reasons why the operation of this process at a pressure much higher than 5 MPa would be very expensive.

Reason 1.....

Reason 2.....

(2)

(d) State the effect of an increase in temperature on the equilibrium yield of methanol and explain your answer.

Effect.....

Explanation.....

.....

.....

(3)

(e) If a catalyst were not used in this process, the operating temperature would have to be greater than 700 K. Suggest why an increased temperature would be required.

.....

(1)
(Total 10 marks)

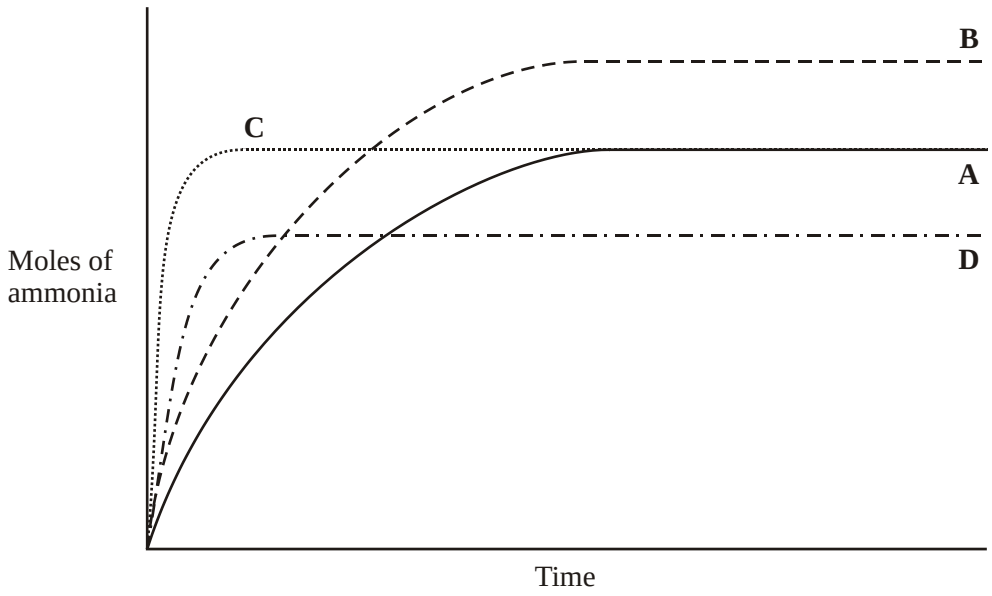
28. The equation for the formation of ammonia is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Experiment **A** was carried out starting with 1 mol of nitrogen and 3 mol of hydrogen at a constant temperature and a pressure of 20 MPa.

Curve **A** shows how the number of moles of ammonia present changed with time.

Curves **B**, **C** and **D** refer to similar experiments, starting with 1 mol of nitrogen and 3 mol of hydrogen. In each experiment different conditions were used.



(a) On curve **A**, mark the point that represents the time at which equilibrium is first reached. Label this point **X**.

(1)

(b) State Le Chatelier's principle.

.....

.....

(1)

(c) Use Le Chatelier's principle to identify which one of the curves **B**, **C** or **D** represents an experiment carried out at the same temperature as experiment **A** but at a higher pressure. Explain why this curve is different from curve **A**.

Curve .....

Explanation .....

.....

.....

.....

(4)

(d) Identify which one of the curves **B**, **C** or **D** represents an experiment in which the conditions are the same as in experiment **A** except that a catalyst is added to the reaction mixture. Explain your choice of curve.

Curve .....

Explanation .....

.....

.....

(3)
(Total 9 marks)

29. When carbon monoxide reacts with steam at 670 K, the following homogeneous dynamic equilibrium is established.

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

(a) (i) Explain why this reaction is described as a *homogeneous* reaction.

.....

(ii) State what is meant by the term *dynamic equilibrium*.

.....

.....

.....

(3)

(b) State the effect, if any, of the following changes on the concentration of hydrogen in the equilibrium mixture. In each case, explain your answer.

(i) An increase in the concentration of steam

Effect.....

Explanation.....

.....

(ii) A decrease in the temperature

Effect.....

Explanation.....

.....

(6)

(c) State and explain the effect, if any, of a catalyst on the position of this equilibrium.

Effect.....

Explanation.....

(3)
(Total 12 marks)

30. The industrial process for converting ammonia into nitric acid is carried out in three stages.

Stage 1	$4NH_3(g) + 5O_2(g)$	$\rightleftharpoons$	$4NO(g) + 6H_2O(g)$	$\Delta H^{\ominus} = -950\ kJ\ mol^{-1}$
Stage 2	$2NO(g) + O_2(g)$	$\rightleftharpoons$	$2NO_2(g)$	$\Delta H^{\ominus} = -114\ kJ\ mol^{-1}$
Stage 3	$3NO_2(g) + H_2O(l)$	$\rightleftharpoons$	$2HNO_3(aq) + NO(g)$	$\Delta H^{\ominus} = -117\ kJ\ mol^{-1}$

(a) Consider the reaction in **Stage 1** above.

(i) State how the temperature should be changed in order to increase the yield at equilibrium in this reaction. Explain your answer.

Temperature change.....

Explanation.....

.....

(ii) State how the pressure should be changed in order to increase the yield at equilibrium in this reaction. Explain your answer.

Pressure change.....

Explanation.....

.....

(4)

(b) The **Stage 1** reaction is carried out by passing ammonia and air over a platinum gauze at a temperature of 900°C and a pressure of 700kPa.

(i) What are the advantages of using this temperature and this pressure?

Temperature.....

Explanation.....

(ii) Give two reasons why the catalyst is used in the form of a gauze.

Reason 1.....

Reason 2.....

(4)

(c) The reaction by which NO is formed directly from nitrogen and oxygen is shown below.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H^{\ominus} = +180 \text{ kJ mol}^{-1}$$

(i) Give the name for the enthalpy change for this reaction.

.....

.....

(ii) Explain fully the meaning of the symbol $^{\ominus}$

.....

.....

.....

(iii) Suggest why reactions between nitrogen and oxygen are often considered to be environmentally unfriendly.

.....

.....

(iv) Explain why the decomposition of NO into its elements is favoured by a low temperature.

.....

.....

(7)

(d) By considering the reactions in **Stage 2** and **Stage 3,** suggest how the overall yield of nitric acid could be increased without altering either the temperature or the pressure chosen for each of the three stages.

.....

.....

(2)

(Total 17 marks)

32. (a) Hydrogen used in the Haber Process is produced in the following dynamic equilibrium reaction.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(i) In terms of rates and of concentrations, what does the term *dynamic equilibrium* mean?

Rates .....

Concentrations .....

(ii) State how an increase in pressure will affect the equilibrium yield of hydrogen. Explain your answer.

Equilibrium yield .....

Explanation .....

.....

(iii) The equilibrium yield of hydrogen is reduced when the reaction is carried out at a lower temperature. What can be deduced about the enthalpy change in this reaction?

.....

(iv) Explain why the equilibrium yield is unchanged when a catalyst is introduced.

.....

.....

(8)

(b) Ammonia is produced in the Haber Process according to the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H_f^{\ominus} = -92 \text{ kJ mol}^{-1}$$

Typical operating conditions are 450 °C and 20 MPa (200 bar).

(i) Explain why 450 °C is a compromise temperature.

.....

.....

.....

.....

(ii) Explain why 20 MPa is a compromise pressure.

.....

.....

.....

.....

(6)
(Total 14 marks)

33. Methanol, CH_3OH, is a convenient liquid fuel.

(a) An experiment was conducted to determine the enthalpy of combustion of liquid methanol. The energy obtained from burning 2.12 g of methanol was used to heat 150 g of water. The temperature of the water rose from 298 K to 362 K. (The specific heat capacity of water is 4.18 J K^{-1} g^{-1})

(i) Define the term *standard enthalpy of combustion*.

(ii) Use the data above to calculate a value for the enthalpy of combustion of one mole of liquid methanol.

(7)

(b) Methanol can be synthesised from methane and steam by a process that occurs in two stages.

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

Stage 2 $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\Delta H^{\ominus} = -91 \text{ kJ mol}^{-1}$

(i) Explain why, in *Stage 1*, a higher yield of hydrogen and carbon monoxide is **not** obtained if the pressure is increased.

(ii) *Stage 2* is carried out at a compromise temperature of 500K. By considering what would happen at higher and lower temperatures, explain why 500 K is considered to be a compromise for *Stage 2*.

(5)

(c) The standard enthalpies of combustion of carbon monoxide and of hydrogen are -283 kJ mol^{-1} and -286 kJ mol^{-1}, respectively. Use these data and the enthalpy change for *Stage 2* to calculate a value for the standard enthalpy of combustion of gaseous methanol.

(3)

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(Total 15 marks)

34. When ammonia gas is heated, a homogeneous, dynamic equilibrium is established between ammonia and its constituent elements. This decomposition is endothermic.

(a) Explain the terms *homogeneous*, *dynamic* and *equilibrium*.
Write an equation for this decomposition and derive an expression for the equilibrium constant, K_c

(5)

(b) State and explain the conditions under which a high equilibrium concentration of hydrogen would be obtained.

(4)

(c) The decomposition of ammonia might in the future be used as an industrial method for the manufacture of hydrogen.
Explain why an industrial chemist might decide to use conditions different from those you have given in part (b) if large quantities of hydrogen were to be produced by this decomposition. Discuss the effect that using a catalyst would have on the equilibrium yield and on the amount of hydrogen which could be produced in a given time.

(6)
(Total 15 marks)

35. Hydrogen is produced by the reaction between steam and methane when the following dynamic equilibrium is established.

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

(a) Use Le Chatelier's principle to predict the separate effects of an increase in temperature and of an increase in pressure on the yield of hydrogen obtained in the above reaction. In each case, explain your answer.

(6)

(b) State how, and explain why, the use of a catalyst might or might not change the equilibrium yield of hydrogen, and also the amount of hydrogen produced, in a given time.

(4)

(Total 10 marks)

36. (a) Define the term *activation energy* for a reaction.

.....

.....

(2)

(b) Give the meaning of the term *catalyst.*

.....

.....

(2)

(c) Explain in general terms how a catalyst works.

.....

.....

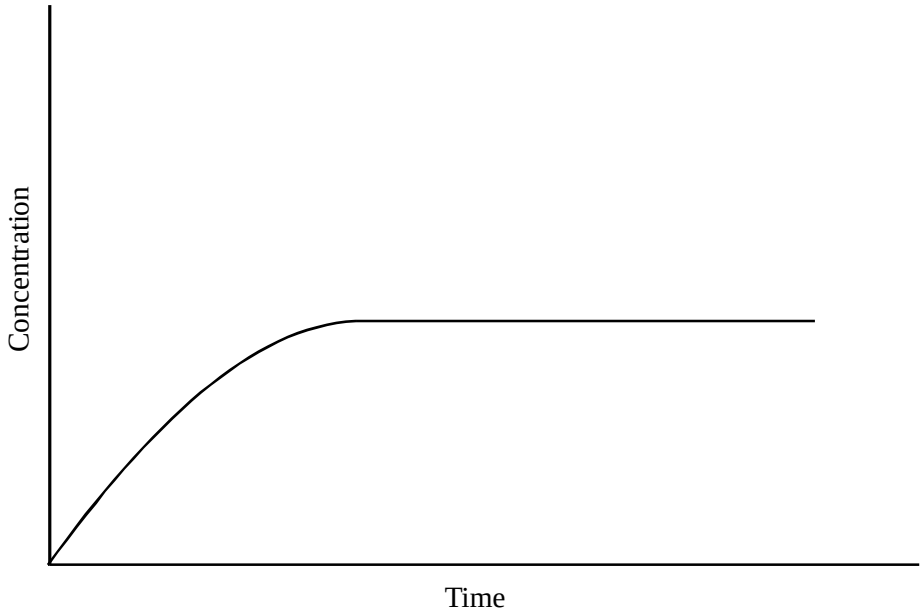
(2)

(d) In an experiment, two moles of gas **W** reacted completely with solid **Y** to form one mole of gas **Z** as shown in the equation below.

$$2W(g) + Y(s) \rightarrow Z(g)$$

The graph below shows how the concentration of **Z** varied with time at constant

temperature.



(i) On the axes above, sketch a curve to show how the concentration of **W** would change with time in the same experiment. Label this curve **W**.

(ii) On the axes above, sketch a curve to show how the concentration of **Z** would change with time if the reaction were to be repeated under the same conditions but in the presence of a catalyst. Label this curve **Z.**

(iii) In terms of the behaviour of particles, explain why the rate of this reaction decreases with time.

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.....

(6)
(Total 12 marks)