Ref: Examination Study Questions in TEE Chemistry. Nick Lucarelli. (1998) pp 129-147.

REACTION RATE AND EQUILIBRIUM

MULTIPLE CHOICE

- 1. Which of the following statements about reaction rates is correct?
 - The orientation of colliding particles can affect their ability to react.
 - (ii) The initial speed of a reaction depends upon the enthalpy change, ΔH of the reaction.
 - Reacting particles must collide with sufficient energy if they are to react.
 - (a) (i) only
 - (b) (ii) only
 - (c) (iii) only
 - (d) (i) and (iii) only
 - (e) (i), (ii) and (iii)
- 2. Powdered aluminium readily burns when sprinkled through a Bunsen flame yet the same amount of aluminium in strip form is difficult to ignite when heated in the same Bunsen flame. Which of the following gives the best basis for an explanation of the differing reaction rate?
 - (a) collision energy
 - (b) concentration of aluminium
 - (c) concentration of oxygen
 - (d) rate of collision
 - (e) orientation
- 3. Zinc reacts much more rapidly with hot concentrated hydrochloric acid than cold concentrated hydrochloric acid. Which of the following alternatives gives the best explanation for the faster reaction rate?
 - (a) increased rate of collision
 - (b) decreased activation energy
 - (c) alternative reaction pathway
 - (d) heat of reaction
 - (e) increased collision energy
- 4. Which of the substances listed is used as a catalyst in the matching industrial process?

	Industrial process	Substance
(a)	Haber process for synthesis of ammonia	MnO_2
(b)	Contact process for synthesis of sulfuric acid	V_2O_5
(c)	Hall-Heroult process for extraction of aluminium	Na3AlF6 (cryolite)
(d)	Macarthur-Forrest process for extraction of gold	NaCN
(e)	Blast furnace extraction of iron	CaCO ₃ (limestone)

- 5. In the industrial preparation of ammonia by the Haber process the temperature is raised to around 500 °C. Which of the following correctly states the effect of using a high temperature?
 - increases the equilibrium yield of NH₃
 - (ii) increases the rate of formation of NH3
 - (iii) favours the forward reaction forming NH3
 - (a) (i) only
 - (b) (ii) only
 - (c) (iii) only
 - (d) (i), (ii) and (iii)
 - (e) (i) and (iii) only
- The following reaction occurs in a sealed flask.

$$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$
 $\Delta H = -14 \text{ kJ}$

Which of the following will increase the rate of this reaction?

- (a) cooling the vessel
- (b) increasing the pressure
- (c) decreasing the pressure
- (d) adding some base
- (e) using more finely divided CaCO₃(s)
- 7. Which of the following statements about reaction rates is false?
 - Increasing the concentration of reactants increases the reaction rate.
 - (b) The rate of a reaction involving a solid can be increased by finely dividing the solid.
 - (c) Exothermic reactions proceed at a slower rate if the temperature is increased.
 - (d) As a reaction proceeds it may slow down due to decreasing concentration of reactants.
 - (e) Increasing pressure on a gaseous reaction mixture will increase the reaction rate.
- Consider this reaction:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
 $\Delta H = -222 \text{ kJ}$

Which of the following will increase the rate of this reaction?

- (a) lowering the temperature
- (b) lowering the partial pressure of CO(g)
- (c) increasing the partial pressure of O₂(g)
- (d) lowering the surface area of carbon
- (e) lowering the total pressure

The process shown here has reached equilibrium in a closed container at room temperature. 9.

$$Cr_2O_7^{2^-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2^-}(aq) + 2H^+(aq)$$

Which of the following statements concerning this system at equilibrium is true?

- Changing the pressure will not affect the equilibrium concentrations. (a)
- (b) Adding a catalyst will favour the products and thus lower the pH.
- (c) Adding a catalyst will favour the products and thus raise the pH.
- (d) Adding NaOH(s) would have no effect on the equilibrium concentrations.
- The Cr₂O₇² (aq) ion is neither being consumed nor produced. (e)
- 10. This reversible reaction has reached equilibrium:

$$Co^{2+}(aq) + 6NH_3(aq) \nearrow Co(NH_3)_6^{2+}(aq)$$

A small sample of CoCl2(s) was then added. As it dissolved the concentration of Co2+(aq) initially increased. When equilibrium is again established, how will the concentration of all species compare to their original concentration, ie prior to addition of CoCl₂(s)?

	Co ²⁺ (aq)	$NH_3(aq)$	Co(NH ₃) ₆ ²⁺ (aq)
(a)	same	lower	higher
(b)	higher	lower	higher
(c)	higher	higher	lower
(d)	lower	lower	higher
(e)	same	higher	lower

11. A mixture of nitrogen, hydrogen and ammonia is present in a sealed container at 300 °C and 1020 kPa. The mixture has reached equilibrium according to the following equation:

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

The system is then compressed (at constant temperature) to half its original volume. Which of the following correctly describes the changes in molar amounts of N2, H2 and NH3 once equilibrium has been re-established?

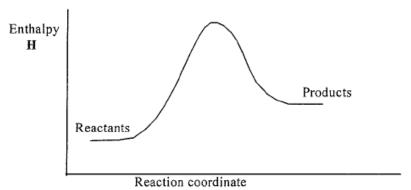
	N_2	H_2	NH_3
(a)	decreased	decreased	increased
(b)	increased	increased	increased
(c)	increased	increased	decreased
(d)	same	same	decreased
(e)	increased	increased	same

 To a sealed container is added some N₂(g), CO₂(g) and H₂O(l). After some time the following chemical equilibrium is established:

$$2CO_2(g) + 2H_2O(l) \gtrsim 3H^+(aq) + HCO_3^- + CO_3^{2^+}(aq)$$

Which of the following changes would increase the equilibrium partial pressure of CO2(g)?

- (a) removing some of the N₂(g)
- (b) adding some base
- (c) adding a source of Ca²⁺(aq)
- (d) increasing the volume of the system
- (e) adding some HCl solution
- A reaction has the following potential energy diagram.



Choose the false statement regarding this reaction.

- (a) It represents an endothermic reaction.
- (b) Enthalpy change for this reaction is positive.
- (c) This reaction would cause a temperature rise.
- (d) The reverse reaction is exothermic.
- (e) Activation energy for the forward reaction is higher than for the reverse reaction.
- 14. Which of the following is a correct statement about activation energy?
 - (a) It is equal to the enthalpy change of a reaction.
 - (b) It is equal to the enthalpy of reactants.
 - (c) It is equal to the enthalpy of products.
 - (d) It is equal to the enthalpy of products minus the enthalpy of reactants.
 - (e) It is equal to the enthalpy of the activated complex (transition state) minus the enthalpy of reactants.

- 15. A small increase in temperature sometimes produces a large increase in reaction rate. Which of the following statements is the **best** explanation for this?
 - (a) The reaction must be endothermic.
 - (b) This increases the rate of collisions between particles.
 - (c) This causes a lowering of the activation energy.
 - (d) The transition state becomes less stable.
 - (e) The colliding particles have higher energy.
- 16. The reaction shown here proceeds rapidly at room temperature:

$$Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_{2}(g)$$

Choose the false statement regarding this reaction.

- (a) The reaction rate increases as the concentration of H⁺(aq) decreases.
- (b) The reaction rate increases if the zinc is powdered.
- (c) The reaction rate may be described in terms of volume of $H_2(g)$ produced per second.
- (d) The reaction rate may be described in terms of the mass of Zn(s) consumed per second.
- (e) The reaction has a low activation energy.
- 17. Which of the following statements concerning the activated complex (transition state) of a chemical reaction is false?
 - (a) The activated complex is an unstable substance.
 - (b) The activated complex always decomposes.
 - (c) The activated complex may decompose to form products.
 - (d) The activated complex for the forward and reverse reaction are different.
 - (e) The activated complex has a higher enthalpy than either reactants or products.
- 18. One of the reactions involved in the manufacture of sulfuric acid is shown here:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + Heat$$

A deliberate effort is made to cool this reaction as it proceeds to equilibrium. Which of the following is the best explanation for doing this?

- (i) It increases the equilibrium yield of SO₃ (g).
- (ii) It increases the rate of attainment of equilibrium.
- (iii) This increases the rate of the forward reaction.
- (a) (i) only
- (b) (ii) only
- (c) (iii) only
- (d) (i) and (ii) only
- (e) (ii) and (iii)

- 19. A chemical reaction has reached equilibrium in a closed system. Which of the following observations is least likely for this system?
 - (a) It has a constant colour.
 - (b) It contains equal amounts of reactants and products.
 - (c) Reactions in the system will still be occurring.
 - (d) Its temperature is constant.
 - (e) It has a constant pressure.
- Choose the best statement about a chemical reaction with an equilibrium constant of 1.
 - (a) The reaction goes to completion.
 - (b) Reactants and products have similar concentrations at equilibrium.
 - (c) At equilibrium there will be mainly reactants.
 - (d) The reaction is exothermic.
 - (e) The reaction will quickly reach equilibrium.
- 21. This reaction has reached equilibrium in a closed system. Which of the following conditions has no effect on the equilibrium system?

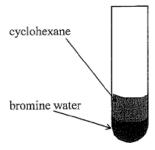
$$CaCO_3(s) + 2H^+(aq) \rightleftharpoons CO_2(g) + H_2O(l) + Ca^{2+}(aq) + Heat$$

- (a) state of subdivision of the CaCO₃(s)
- (b) pressure exerted on the system
- (c) volume of the system
- (d) temperature of the system
- (e) concentration of the H⁺(aq)
- 22. Which of the following conditions affects the value of the equilibrium constant for a reaction?
 - (a) temperature
 - (b) pressure
 - (c) concentration
 - (d) catalyst
 - (e) surface area
- 23. Which of the following gives the best description of the effect a catalyst has on chemical reactions at equilibrium?
 - (a) It lowers the value for the equilibrium constant (K).
 - (b) It favours forward reactions only.
 - (c) It increases the energy of colliding particles.
 - (d) It does not affect the rate of reactions in an equilibrium system.
 - (e) It increases the rate of both forward and reverse reactions.

24. Which of the following set of conditions is closest to that which is used in the manufacture of ammonia by the Haber process?

	Catalyst	Pressure	Temperature
(a)	Yes	3 Atmospheres	50° C
(b)	Yes	300 Atmospheres	500° C
(c)	Yes	3000 Atmospheres	5000° C
(d)	No	3 Atmospheres	50° C
(e)	No	300 Atmospheres	500° C

25. Bromine water and cyclohexene are two immiscible liquids which react to produce 1,2-dibromocyclohexane. The speed of this reaction is increased by shaking the reagents together. Which of the following is the best explanation for the increased rate caused by shaking the reagents?



- (a) An improved orientation for colliding molecules.
- (b) An increased rate of collision between reacting molecules.
- (c) An increase in collision energy.
- (d) A catalytic effect due to shaking.
- (e) A reduced activation energy for the reaction.

SHORT ANSWER

1. Ethene may be produced from ethane according to the following reversible reaction.

 $C_2H_6(g) \rightleftarrows C_2H_4(g) + H_2(g)$ $\Delta H = 120 \text{ kJmol}^{-1}$ (a) State three conditions which would increase the rate of the forward reaction.

(b) State two conditions which would increase equilibrium yield, ie favour products.

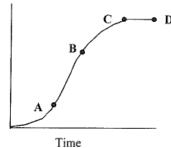
 The preparation of hydrogen gas in the laboratory uses the reaction of zinc granules with hydrochloric acid solution.

$$Zn(s) + 2H^{+}(aq) \rightarrow H_{2}(g) + Zn^{2+}(aq)$$

$$\Delta H = -154 \text{ kJ}$$

A student investigated the rate of this reaction by preparing a mixture of HCl(aq) and excess zinc granules. The total volume of hydrogen produced over time was then measured and recorded. These results were graphed and a sketch of this is shown at right.





Complete the table to describe how the rate of reaction is changing in the various time intervals indicated. Describe them as *increasing*, *decreasing*, *steady or zero*. Also give an explanation for the changing rate in each of the intervals listed.

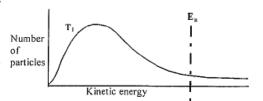
Interval	Rate	Why the rate of reaction is changing as described
from the start up to A		
between B and C		
between C and D		

3. The graph at right shows the distribution of kinetic energy for reacting particles at a temperature of T₁. The activation energy for this reaction (Ea) is also indicated.

Sketch onto this graph the distribution of

Sketch onto this graph the distribution of kinetic energy for the same particles at a higher temperature, T₂.

Use your graph to help explain the effect of increasing temperature on reaction rate.



4.	One step	in the synthesis	of nitric acid	l involves the	following	reversible reaction
• •	One step	m me symmesis	or mure acre	i mivorves me	gillwoning	reversible reaction

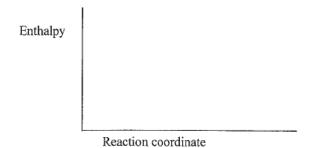
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
 $\Delta H = -114 \text{ kJ}$

Assume this reaction has reached equilibrium in a closed container at constant temperature and pressure.

- (a) What happens (increase, no change, decrease) to the equilibrium yield of NO₂(g) if the following occur?
- (i) The volume of the container is increased _____
- (ii) More oxygen is added to the container _____
- (iii) A suitable catalyst is added
- (b) What happens initially (increase, no change, decrease) to the rate of the forward reaction if the following changes are made?
- (i) The temperature of the container is increased
- (ii) More NO₂(g) is added into the container
- (iii) A suitable catalyst is added to the container
- 5. The following equation shows one step in the synthesis of liquid hydrocarbons from methane:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$
 $\Delta H = 206 \text{ kJ}$

Given the reaction is very slow under normal laboratory conditions, sketch an enthalpy change diagram for the reaction. Clearly label ΔH, reactants, products and activation energy.



A student prepared a solution of the weak monoprotic acid HF by dissolving 0.100 mole of it in 6. water and making its volume up to 1.00 L in a volumetric flask.

What is the molar concentration of HF(aq) molecules if ionisation does not occur? (a)

Answer			
2 2220 1102	. =		

Being a weak acid, partial ionisation of HF(aq) molecules will occur. Write an (b) equation to represent the formation of H+(aq) and F-(aq) by ionisation of HF(aq).

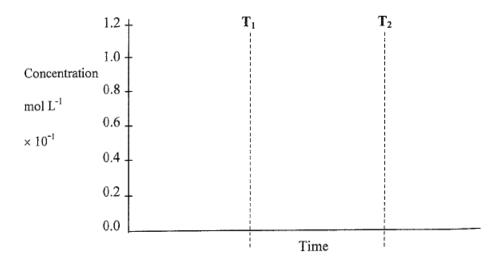
Equation	
	_

(c) Write an expression for the equilibrium constant for the reaction in (b).

When equilibrium has been achieved the concentration of H+(aq) and F-(aq) is (d) 0.025 mol L-1 in each case. What will be the actual concentration of HF(aq) molecules

1 22 1 1 10	
when equilibrium is achieved?	

On these axes show the changes in concentration of HF(aq), H+(aq) and F'(aq) from (e) when the solution is first made until equilibrium is achieved at time T1. Ensure your graph is suitably labelled to distinguish HF(aq), H+(aq) and F-(aq).

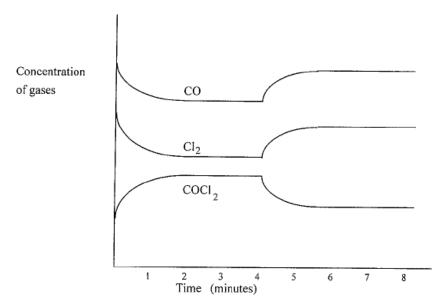


At the time labelled T2 the student adds some hydrochloric acid to the solution of (f) $\mathrm{HF}(aq)$ so that the total $\mathrm{H}^+(aq)$ concentration rises immediately to 0.05 mol L^{-1} . Continue your graph from T1 past time T2 showing how the concentration of the three species HF(aq), H+(aq) and F-(aq) changes until a new equilibrium is established. Assume there is negligible volume change on addition of the hydrochloric acid.

Phosgene (COCl₂) is prepared according to the following reversible reaction: 7.

$$CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$$

A mixture containing these three gases is introduced into a closed system in the presence of a charcoal catalyst. The following graph shows how the concentration of each of these gases varies with time.



(a) Describe the system three minutes after mixing?

(b) Write an expression for the equilibrium constant of this reaction.

(c) Four minutes after mixing, the temperature of the system is increased to a constant but higher value. From the system's response shown on the graph above, deduce whether the reaction as written is endothermic or exothermic and explain your answer.

Answer		 	***	
Explana	ition			

8.	Consid	ler this equilibrium process shown below:
		$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l) + 90 \text{ kJ}$
	(a)	Write the equilibrium constant expression.
	(b)	Sketch an enthalpy change diagram for this reaction. Label the axes, reactants, products, activation energy and enthalpy change.
(c)		dict the effect of the following changes on this equilibrium. Write favour reactants, our products or no change.
(i)	Inc	reasing the pressure on the system
(ii)	Lov	vering the temperature
(iii)	Ado	ling a small amount of CH ₃ OH(l) (negligible volume change)
(iv)	Ado	ling a catalyst
9.	reaction	en can be produced in the laboratory from hydrogen peroxide through the following on. Use your knowledge of the collision theory as a basis for explaining the observed on reaction rate when the following changes are made to the reaction shown here:
		$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ $\Delta H = -948 \text{ kJ}$
	(a)	When heated with a Bunsen, oxygen is produced much more quickly than when left at room temperature.

Reaction rate and equilibrium 141

	quickly than without it. The MnO ₂ (s) does not appear to be consumed during the confidence of the reaction.
c)	Using a more concentrated solution of H ₂ O ₂ causes a more rapid reaction.

- 10. The economic production of ammonia from nitrogen and hydrogen gas by the Haber process is achieved by applying the principles of equilibrium and reaction rates. Temperature, pressure and catalysts are three conditions which are carefully controlled in this process.
 - (a) Complete the table below to show your knowledge and understanding of this.
 - Circle the alternative which comes closest to the conditions of temperature, pressure and catalyst which is used.
 - (ii) Describe the effect of these conditions on equilibrium yield of NH₃ and rate of production of NH₃, ie write increase, decrease or no effect.

	Conditio	ns used our choice)	Effect on rate of formation of NH ₃	Effect on equilibrium yield of NH ₃	
temperature	5 °C	50 °C,			
degrees Celsius	500°C	5000 ° C			
pressure	3.5 atm	35 atm			
(atmospheres)	350 atm	3500 atm			
catalyst	V ₂ O ₅	Fe/FeO			
	MnO ₂	Pt			

(b)	Using Le Chatelier's principle explain the effect of pressure on the equilibrium yield o NH_3 in the Haber process.

142 Unit 7 11. One of the reactions for the manufacture of sulfuric acid by the Contact process is shown here: $2SO_2(g)$ + O₂(g) ⇄ $2SO_3(g)$ $\Delta H = -198 \text{ kJ}$ The following questions are about this reaction. What is the significance of the two arrows? (a) (b) The equilibrium constant for this reaction has a very small value at room temperature. What does this indicate about the equilibrium yield of $SO_3(g)$ at room temperature? In the industrial manufacture of sulfuric acid this reaction is carried out at a temperature (c) of around 450 °C. What is the effect on the equilibrium yield of SO₃(g) and speed of its formation at this higher temperature (compared of normal temperature). Explain your answer in terms of Le Chatelier's principle and the Collision theory. Effect on equilibrium yield of SO₃(g) Explanation in terms of Le Chatelier's principle

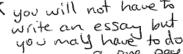
Effect on speed of formation of SO₃(g) _______

Explanation in terms of Collision theory ______

EXTENDED ANSWER

When answering the following extended answer questions, use appropriate equations, diagrams and illustrative examples of the chemistry you are describing. Arrange your material as clearly and coherently as possible. Your answer should be presented in about 11/2-2 pages.

1. Write an essay on catalysis, including the following aspects.



- write an essay but you will not have to write an essay but you may have to do what are catalysts and how do they effect chemical reactions? Highlight your answer with an example from your laboratory work with an example from your laboratory work.
- Use your knowledge of the collision theory to explain the effect of catalysts.
- Describe two industrial applications of catalysts.
- 2. Many chemical reactions involve equilibrium processes. Describe the meaning of "equilibrium" as it applies to chemical reactions. Certain conditions are capable of affecting a system at equilibrium. Note these and describe their effect on chemical equilibrium. Also discuss the application of equilibrium principles in the Haber process (manufacture of ammonia). Note: Do not describe the entire Haber process.

ANSWERS - UNIT 7

MULTIPLE CHOICE

1	D	6	E	11	A	16	A	21	A
2	D	7	C	12	E	17	D	22	Α
3	E	8	C	13	C	18	A	23	Ε
4	В	9	A	14	E	19	В	24	В
5	R	10	B	15	E	20	В	25	В

SHORT ANSWER

1.	(a)	(i) - (iii)	High temperature, high pressure, catalyst, increase partial pressure of $C_2H_6(g)$.
	(b)	(i) - (ii)	High temperature, low pressure, reduced partial pressure of $C_2H_4(g)$ or $H_2(g)$.

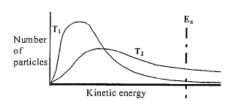
		The second secon
2.	Start to A	This reaction is exothermic thus heat is produced as it progresses. This heat causes an
		increase in temperature and a corresponding increase in rate as more particles have

energy greater than activation energy.

The acid (limiting reagent) is almost consumed, thus the concentration of H+(aq) is low From B to C rate decreases very low. This causes a decrease in the rate of collisions and hence rate decreases.

The acid is fully consumed, thus the concentration of H+(aq) is now zero. Therefore the From C to D rate is zero rate of collisions is zero and hence the rate of reaction is zero.

3.

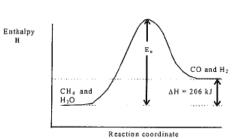


At the higher temperature $(T_2 > T_1)$ a greater percentage of particles have a kinetic energy greater than the activation energy (Ea). This means a greater percentage of collisions have an energy equal to or greater than the activation energy. Thus a greater percentage of the collisions are successful and hence the reaction rate increases:

- 4. (a)
- (i) decrease
- (ii) increase
- (iii) no change

- (b)
- (i) increase
- (ii) no change
- (iii) increase

5.



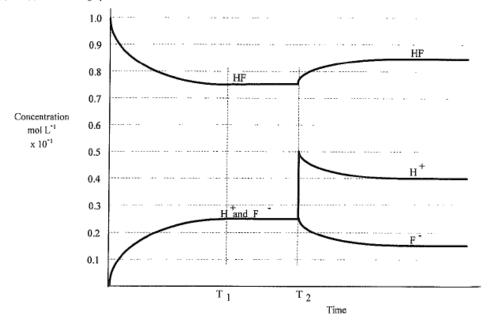
Note: The slow rate of reaction under normal conditions indicates this reaction has a high activation energy.

- 6. (a) 0.100 mol L⁻¹
- (b) $HF(aq) \rightleftharpoons H^{\dagger}(aq) + F^{\dagger}(aq)$

 $HF(aq) + H_2O(l) \rightleftharpoons H_3O^*(aq) + F'(aq)$

- (c) $K = \frac{[F^*][H^+]}{[HF]}$
- (d) 0.075 mol L⁻¹

(e) and (f) Refer to the graph below.



- 7. (a) The system is at equilibrium. (b) $K = \frac{[COCl_2]}{[CO] \times [Cl_2]}$
 - (c) Answer: Exothermic

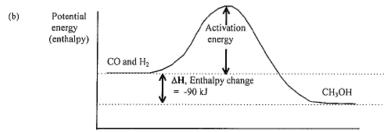
Explanation: The new equilibrium has favoured reactants. Since an increase in temperature favours an endothermic process then the reverse process is endothermic. Hence the forward process is

exothermic.

8. (a) $K = \frac{1}{[CO] \times [H_2]^2}$

(iii)

no change



Reaction coordinate

- (c) (i) favour products (ii) favour products
- Using a Bunsen increases the temperature of the reaction mixture. At higher temperatures particles have greater kinetic energy. This means a greater percentage of collisions have an energy equal to or greater than the activation energy. Thus a greater percentage of the collisions are successful and the reaction rate increases producing O₂(g) more quickly.

(iv)

(b) MnO₂ is a catalyst for the decomposition of H₂O₂. A catalyst provides a reaction pathway with a lower activation energy. As a result a greater percentage of collisions have an energy equal to or greater than the activation energy. Thus more collisions are successful and hence the reaction rate increases.

no change

- (c) The higher concentration of H₂O₂ particles causes an increase in the rate of collisions between these particles and hence an increase in the rate of reaction.
- 10. (a) Temperature: 500 °C increases rate decrease yield
 Pressure: 350 atm increases rate increases yield
 Catalyst: Fe/FeO increases rate no effect on yield
 - (b) Le Chatelier's principle states, if a system is at equilibrium and a change in conditions is imposed on the system then the system will re-establish a new equilibrium in such a way as to partially counteract the imposed change. The formation of ammonia involves a reduction in the total number of moles of gas (4 mol to 2 mol) and therefore a reduction in the total pressure. Thus when the imposed change is an increase in pressure, this system will counteract the change by forming more products, ie increasing the yield of NH₃(g).
- (a) This shows the formation of SO₃(g) is an equilibrium process. The two arrows represent the forward and reverse reaction of the equilibrium process.
 - (b) This indicates a low yield of SO₃(g) under normal conditions.
 - (c) Effect on yield: reduces yield

Explanation: Le Chatelier's principle states, if a system is at equilibrium and a change in conditions is imposed on the system then the system will re-establish a new equilibrium in such a way as to partially counteract the imposed change. The imposed change is an increased temperature (450 °C instead of 25 °C) which the system counteracts by favouring the endothermic reaction (this absorbs heat and reduces temperature). For this system the endothermic reaction is the decomposition of SO₃ thus reducing the yield of SO₃.

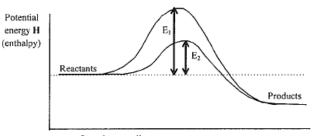
Effect on rate: increases rate

Explanation: At higher temperatures the SO_2 and O_2 particles have greater kinetic energy. This means a greater percentage of collisions between these particles have an energy equal to or greater than the activation energy. Thus a greater percentage of the collisions are successful in producing SO_3 and hence the reaction rate increases. [This effect is even greater for the endothermic reaction and explains the overall decrease in yield of SO_3 described above.]

EXTENDED ANSWER

CATALYSIS

- Catalysts are substances that increase the rate of a chemical reaction.
- These substances are consumed and produced during the course of a reaction and so there is no net change in the
 amount of catalyst over time.
- Some examples of catalysts used in the laboratory are:
 - ⇒ MnO₂(s) catalysing the decomposition of H₂O₂
 - ⇒ H₂SO₄(l) acts as a catalyst for esterification reactions.
- For a reaction to occur particles must collide with energy greater than or equal to the activation energy.
- A catalyst enables a reaction to proceed via an alternative pathway of lower activation energy.



E₁ shows the activation energy for the reaction without a catalyst.

E₂ shows the activation energy for the reaction with a catalyst.

Reaction coordinate

- In the presence of a catalyst a greater proportion of collisions have energy greater than or equal to the activation energy. For this reason a greater percentage of the collisions are successful and the reaction rate increases.
- Two industrial applications of catalysts include:
 - ⇒ Contact process for the manufacture of H₂SO₄ uses the catalyst V₂O₅ to speed up the complete oxidation of SO₂ gas.

$$V_2O_5$$

 $2SO_2(g) + O_2(g) \stackrel{\longrightarrow}{\rightarrow} 2SO_3(g)$

⇒ Haber process for manufacture of NH₃ uses an Fe/FeO catalyst.

Fe/FeO

$$N_2(g) + 3H_2(g) \stackrel{\longrightarrow}{\rightarrow} 2NH_3(g)$$

 In each of the above examples the use of catalysts increases the economic viability of the process by speeding up the relevant reactions.

2. CHEMICAL EQUILIBRIUM

Meaning of equilibrium

- Chemical equilibrium involves a balance between two opposing reactions. These reactions are referred to as the forward and reverse reaction.
- At equilibrium the rate of the forward reaction equals the rate of the reverse reaction.
- In a system at equilibrium there are no changes in macroscopic properties such as pressure, temperature, concentration, or colour of the system (ie these properties remain constant).
- Chemical equilibrium can only arise for a chemical reaction occurring in a closed system, that is one where neither
 matter nor energy can enter or leave the system.

Conditions affecting equilibrium

- The relative concentrations of each species in a system at equilibrium may be altered by changes to:
 - ⇒ the concentration of any one species in the system
 - ⇒ the total pressure on the system
 - ⇒ the temperature of the system.
- Temperature: Increasing temperature favours the endothermic process as this consumes heat thus counteracting the
 increased temperature. Reducing temperature has the opposite effect ie favours the exothermic process.
- Altering temperature has the effect of changing the value of the equilibrium constant.
- Pressure: Increasing the total pressure (by reducing volume) favours the side of the reaction with fewest gaseous
 molecules. By responding this way the system partially counteracts the increased pressure. Decreasing pressure
 favours the side of the reaction with most gaseous molecules.

Reaction rate and equilibrium 147

- Concentration: Increasing the concentration of one species favours the consumption of that species and shifts the
 equilibrium away from that species. Decreasing the concentration of one species favours the formation of that
 species and shifts the equilibrium towards that species.
- Le Chatelier's principle summarises the effect of these alterations on an equilibrium system, "if a system is at
 equilibrium and a change in conditions is imposed on the system then the system will re-establish a new
 equilibrium in such a way as to partially counteract the imposed change".

Applying the principles of equilibrium - The Haber process

 Uses high pressure. This favours the formation of fewer gas molecules as this partially counteracts the increased pressure. Thus high pressure favours the formation of NH₃(g) increasing its yield.

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

(4 molecules) \rightleftharpoons (2 molecules)

- Uses reduced concentration of NH₃. To achieve this NH₃(g) is frequently removed from the equilibrium mixture.
 This favours its replacement and forms more NH₃(g) and thus increases the yield of NH₃(g).
- Equilibrium considerations would dictate the use of low temperatures as the forward reaction [formation of NH₃(g)] is exothermic. However a moderate temperature is used as this allows a faster reaction rate, resulting in a more economic process despite the reduced yield of NH₃(g).