Year 12
Chemistry
Equilibrium and Acid Reactions

2025 Term 1
Work Book Solutions

MATRIX
EDUCATION

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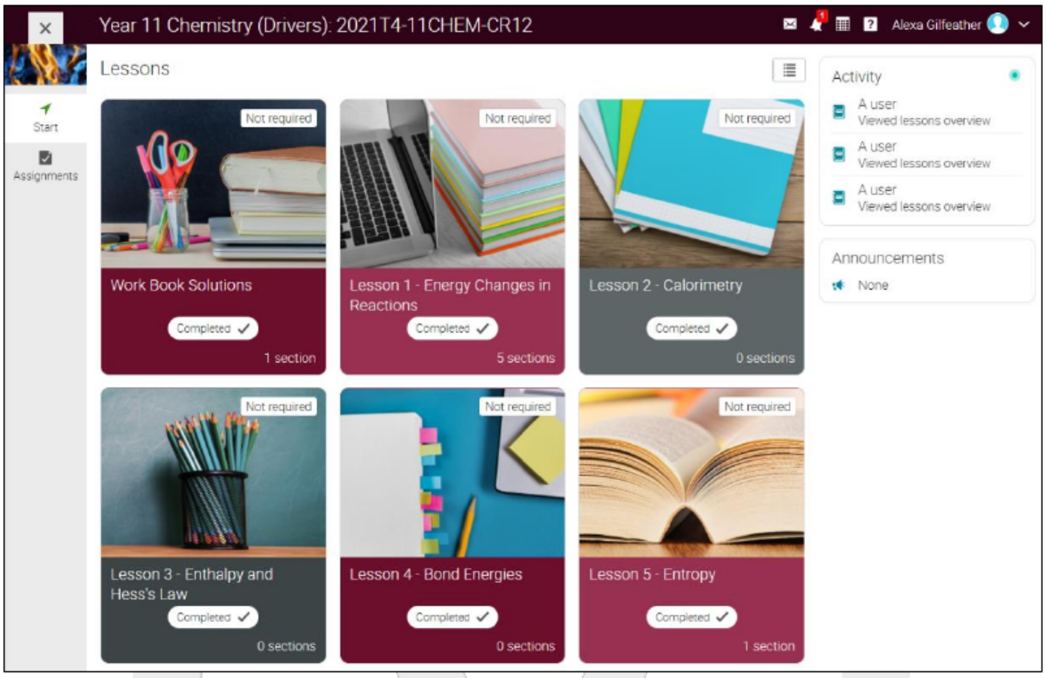

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Part A: Multiple choice questions

Question 1

Which of the following is always true for a system at equilibrium?

(a) The concentrations of reactants and products are equal.

(b) The rate of the forward reaction equals the rate of the reverse reaction.

(c) The forward reaction must be exothermic.

(d) There are no microscopic changes.

Question 2

Which of the following situations represent a system at dynamic equilibrium?

(a) An open can of soft drink.

(b) Rust forming on a bike left in the backyard.

(c) A cake baking in the oven.

(d) A closed bottle of saturated salt solution.

Question 3

Which of the following systems would reach a state of static equilibrium?

(a) A saturated solution of sodium carbonate.

(b) A chemical reaction in which the limiting reactant gets completely used up.

(c) Oxygen is transported around the body by attaching to a protein in the blood called haemoglobin.

(d) Ammonia gas decomposes in a sealed container.

Irreversible reactions that go to completion reach static equilibrium.

Question 4

Which of the following is a characteristic of a reversible system at equilibrium?

(a) The concentration of the products must be greater than the concentration of the reactants.

(b) Neither the forward nor reverse reactions come to a stop.

(c) The rates of the forward and reverse reactions are zero.

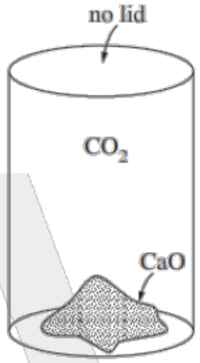
(d) The limiting reagent is completely consumed.

Reversible reactions do not go to completion and reach a dynamic equilibrium state where the forward and reverse reactions continue to occur at the same rate.

Question 5 [HSC Sample Q2]

The conversion of calcium carbonate to calcium oxide and carbon dioxide is a reversible reaction and will reach equilibrium under certain conditions. In which diagram is the system most likely to have reached equilibrium?

A.



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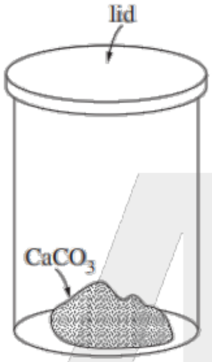

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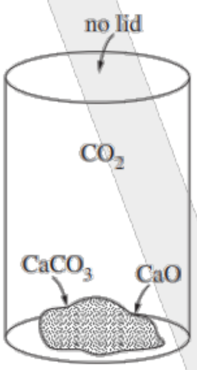

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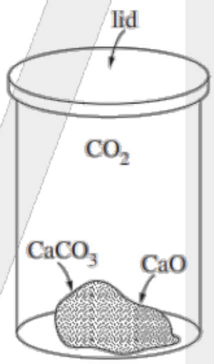


Dynamic equilibrium can only be reached in a closed system, hence A and C are not correct. At dynamic equilibrium, the forward and reverse rates are equal but non-zero, hence all reaction components will be present in the reaction flask.

Question 6

Consider the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{Heat}$$

Which of the following describes the enthalpy, entropy and Gibbs free energy change, in the forward direction, for this reaction at equilibrium?

	Enthalpy	Entropy	ΔG
(a)	increase	increase	>0
(b)	increase	decrease	$= 0$
(c)	decrease	increase	<0
(d)	decrease	decrease	$= 0$

At equilibrium, the free energy change is equal to zero. Since enthalpy decreases for the forward reaction, the entropy change must also decrease for the free energy change to be zero.

Question 7

Consider the following equilibrium reaction:

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightleftharpoons 2Fe_{(s)} + 3CO_{2(g)}$$

The following substances are placed in separate reaction flasks and sealed.

Flask	Substance
1	Fe_2O_3 and Fe
2	CO and CO_2
3	Fe_2O_3 and CO_2
4	Fe and CO_2

In which of the flasks will the equilibrium reaction above be established?

(a) Flask 1

(b) Flask 2

(c) Flask 3

(d) Flask 4

For the forward reaction to occur there must be Fe_2O_3 and CO present together in the flask.

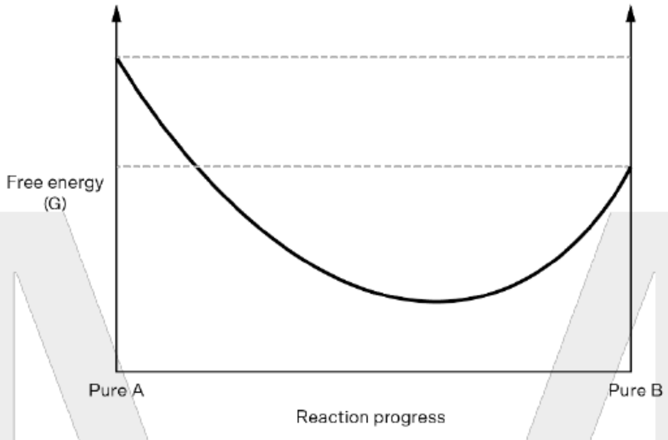
For the reverse reaction to occur there must be Fe and CO_2 present together in the flask.

Only flask 4 has the correct combination.

Question 8

The free energy curve below shows the variation in Gibbs free energy for the reaction:

$$A_{(g)} \rightleftharpoons B_{(g)}$$



Which of the following statements is correct regarding this system?

(a) $\Delta G^{\ominus}$ is positive and products dominate at equilibrium.

(b) $\Delta G^{\ominus}$ is negative and products dominate at equilibrium.

(c) $\Delta G^{\ominus}$ is positive and reactants dominate at equilibrium.

(d) $\Delta G^{\ominus}$ is negative and reactants dominate at equilibrium.

The difference between the two ends of the plot ($\Sigma\Delta G^{\ominus}_{\text{products}} - \Sigma\Delta G^{\ominus}_{\text{reactants}}$) corresponds to $\Delta G^{\ominus}$. Since $\Sigma\Delta G^{\ominus}_{\text{products}} < \Sigma\Delta G^{\ominus}_{\text{reactants}}$, $\Delta G^{\ominus}$ is negative. The position of equilibrium (position with lowest G) lies very close to the products.

Question 9

Nitrogen and oxygen gases were added to a sealed reaction flask and allowed to react to produce nitrogen monoxide according to the equation:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

Which of the following statements is correct regarding this system?

(a) The rate of the forward reaction will reach a maximum when equilibrium is reached.

(b) The concentration of nitrogen will decrease at the same rate as the increase in the concentration of nitrogen monoxide until equilibrium is reached.

(c) The rate of the forward and reverse reactions will both increase until equilibrium is reached.

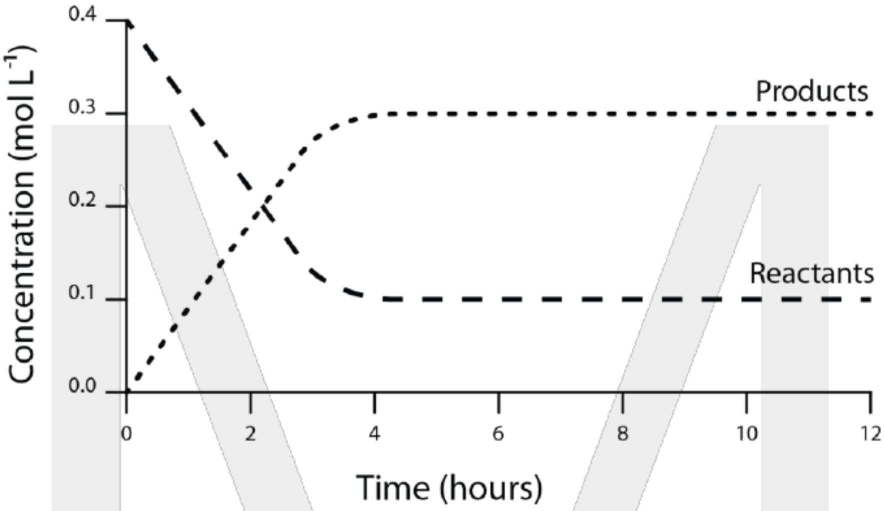
(d) The rate of the reverse reaction will be at its minimum at the start of the reaction.

Rate is proportional to concentration. Since the concentration of nitrogen monoxide will be zero at the start, the rate of the reverse reaction is zero until some nitrogen monoxide is produced. Hence the reverse rate will be at its minimum at the start.

Question 10

The graph below shows how the concentration of reactants and products change over time for the reaction:

$$CH_3COOH_{(aq)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$



From this graph we can determine that

(a) the equilibrium concentrations were 0.2 mol L^{-1}

(b) the forward reaction stopped after four hours

(c) the system reached equilibrium after two hours

(d) the reaction did not go to completion

Equilibrium concentrations are 0.1 and 0.3 M.

Reaction does not stop – it enters state of dynamic equilibrium.

Equilibrium is reached at 4 hours (when concentrations remain constant).

The reactants would be used up if the reaction goes to completion.

Part B: Extended response questions

Question 11

Distinguish between the following

(a) Reversible and irreversible reactions 2

A reversible reaction is one that proceeds in both directions at the same time under certain conditions.

Irreversible reactions go to completion and the reverse reaction does not proceed at any appreciable rate.

(b) Static and dynamic equilibrium 2

Both static and dynamic equilibrium show no macroscopic change and have constant concentrations of their components. However, static equilibrium occurs with irreversible reactions and the rate of reaction at equilibrium (completion) is zero, while dynamic equilibrium occurs with reversible reactions and the rates of the forward and reverse reactions at equilibrium are equal but non-zero.

(c) Open and closed systems 2

Both open and closed systems allow the exchange of energy (in the form of heat or work) with the surroundings, but open systems also allow the exchange of matter.

(d) Spontaneous and non-spontaneous reactions 2

A spontaneous reaction is capable of proceeding under a specific set of conditions in a given direction without the continuous input of energy from an outside source. A non-spontaneous reaction requires the continuous input of energy from an outside source to proceed under a specific set of conditions.

Question 12

Write balanced equations for the following reversible reactions.

(a) Phosphorus trichloride gas and chlorine gas react to form gaseous phosphorus pentachloride. **1**

$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

(b) Solid ammonium chloride decomposes to ammonia and hydrogen chloride gases. **1**

$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

(c) Sulfur dioxide gas combusts to form sulfur trioxide gas. **1**

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

(d) The dissolution of calcium sulfate in water produces calcium and sulfate ions. **1**

$CaSO_{4(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

(e) Iodine trichloride gas is synthesised from chlorine gas and liquid iodine monochloride. **1**

$ICl_{(l)} + Cl_{2(g)} \rightleftharpoons ICl_{3(g)}$

(f) Solid iron(III) chloride and water react to form solid iron(III) hydroxide and a solution of hydrochloric acid. **1**

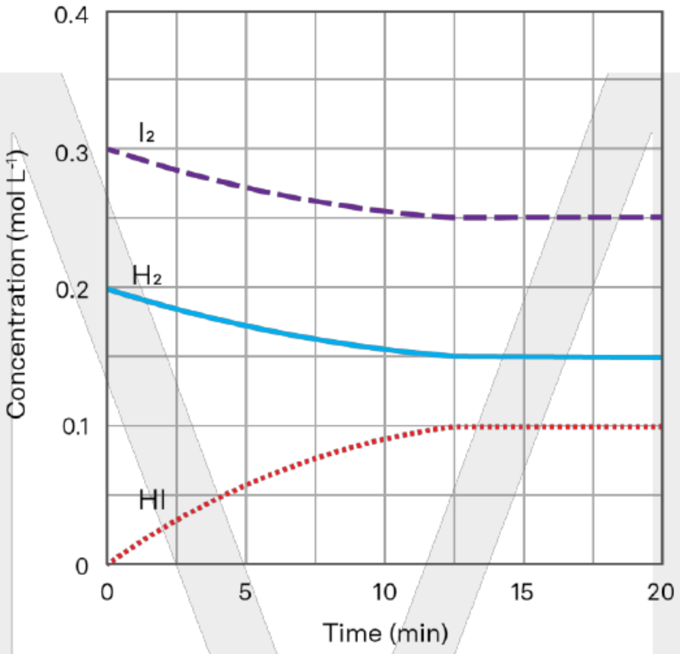
$FeCl_{3(s)} + 3H_2O_{(l)} \rightleftharpoons Fe(OH)_{3(s)} + 3HCl_{(aq)}$

Question 13

Colourless hydrogen gas and purple iodine gas react to form colourless hydrogen iodide. In a sealed container, the system will reach equilibrium.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad \Delta H = -51\ \text{kJ mol}^{-1}$$

The concentrations of reactants and products over time are shown in the graph below.



(a) Identify the time at which equilibrium is reached and justify your answer. 2

Equilibrium is reached at 12.5 minutes as the concentrations remain constant.

(b) State two observations that could be made to indicate that the system has reached equilibrium. Explain your answer. 3

Colour remains constant since the concentration of purple I_2 does not change (it is produced at the same rate as it is consumed). Temperature remains constant since heat is produced at the same rate as it is consumed.

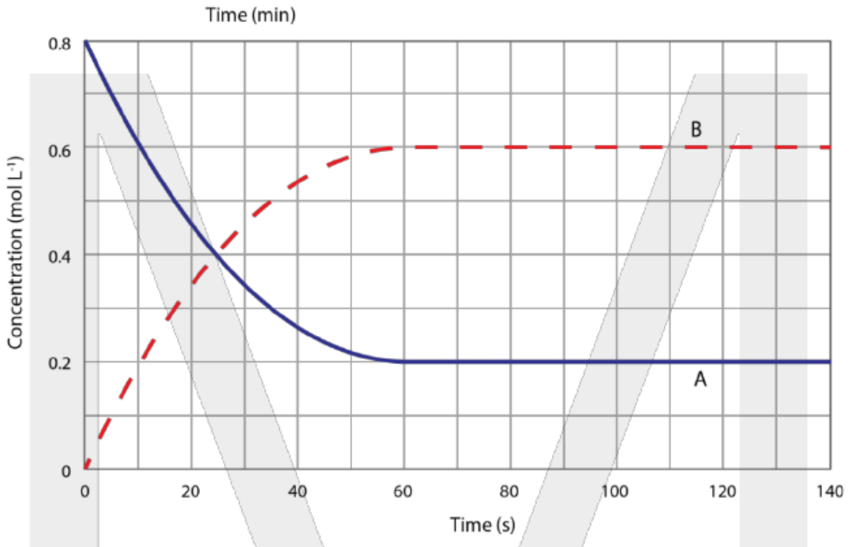
Note: Pressure remaining constant is not a correct answer as the pressure of the system will not change before and after equilibrium is reached.

Question 14

Consider a reversible reaction represented by:

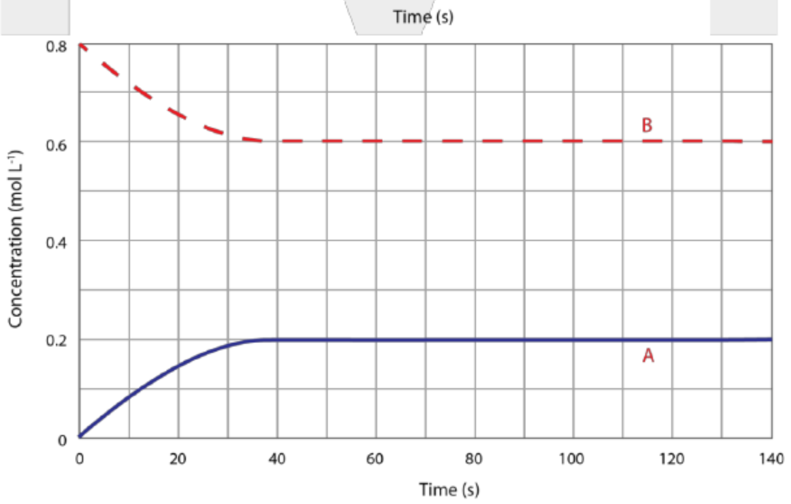
$$A_{(g)} \rightleftharpoons B_{(g)}$$

In one experiment, 0.80 mol L^{-1} of substance A only was introduced into a 5.0 L reaction vessel and the reaction was allowed to reach equilibrium.



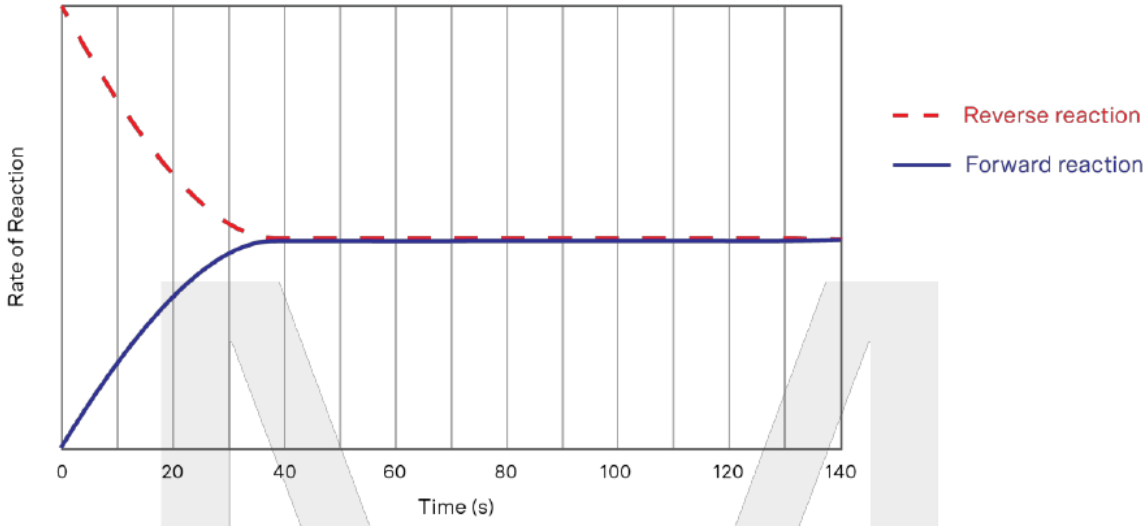
In another experiment, 0.80 mol L^{-1} of substance B only was introduced into a 5.0 L reaction vessel and the reaction was allowed to reach equilibrium. In both experiments, the reaction was carried out under the same conditions.

(a) On the graph below, sketch the curves to show the changes in concentrations of the reactant and product for the second reaction. 2



Note: The system should reach equilibrium faster, but the equilibrium concentrations of A and B should be the same as the graph above as the system will arrive at the same equilibrium position under the same temperature and pressure conditions.

(b) On the graph below, sketch the change in the rates of the forward and reverse reactions for the second experiment as the reaction proceeds towards equilibrium. 2



(c) Explain the changes in the reverse rate of reaction sketched on the graph above. 2

Initially only the reverse reaction proceeds since only B is present. As the reverse reaction proceeds, B is consumed, therefore its concentration decreases and the reverse reaction rate decreases. Eventually, the rate of the reverse does not change as equilibrium is re-established.

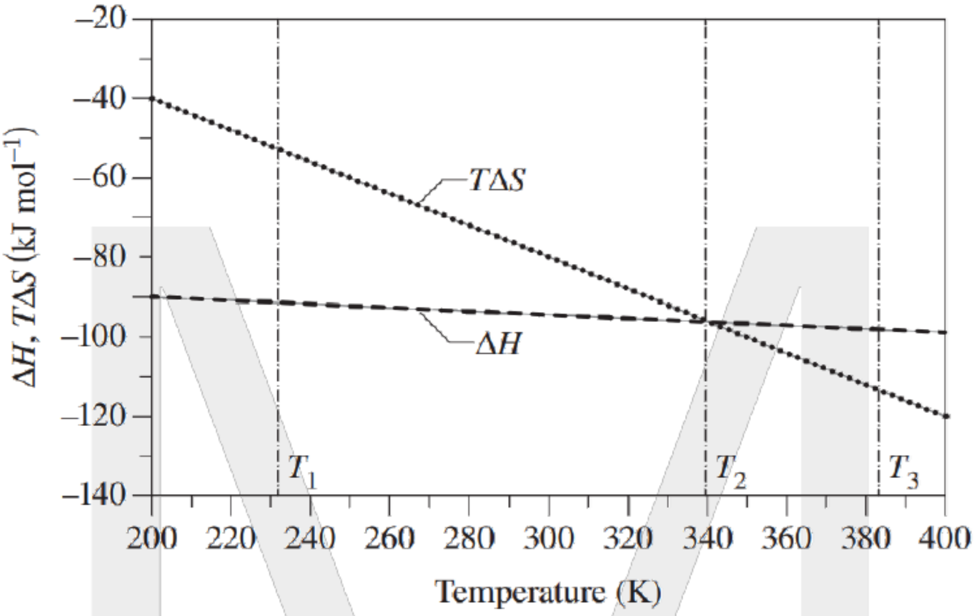
(d) Substance A is a colourless gas whereas substance B is a brown gas. State ONE similarity and ONE difference in the observations between the first reaction and the second reaction as the systems approach equilibrium. Explain your answer. 3

Difference: In the first reaction, the flask will become more intensely coloured as the system approaches equilibrium since the concentration of coloured B gas increases. However, in the second reaction, the colour will fade as the system approaches equilibrium since the concentration of coloured B gas decreases.

Similarity: Both reactions will be the same colour at equilibrium since the concentration of A and B will be the same for both reactions at equilibrium.

Question 15 **[2021 HSC Q33]**

The relationships between ΔH and TΔS with temperature for a chemical system are displayed in the graph.



(a) Calculate ΔG for this system at 300 K. **2**

NESA sample answer:

From graph, TΔS = −78 kJ/mol, ΔH = −93 kJ/mol

ΔG = ΔH − TΔS = −93 − (−78) = −15 kJ/mol

(b) What can be deduced about the system when the temperature is T_1, T_2 and T_3? Support your answer with reference to the graph. **4**

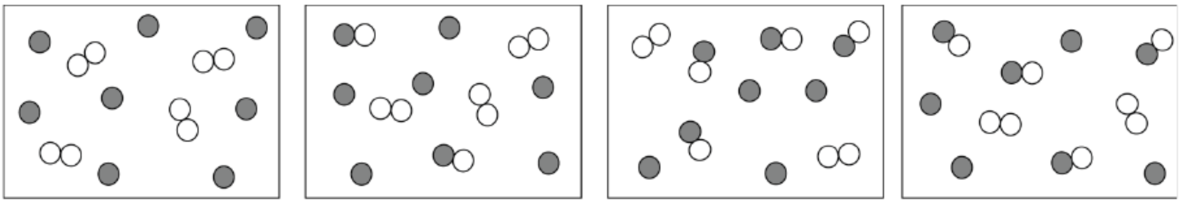
NESA sample answer:

At all three temperatures the reaction is exothermic, as ΔH is negative. The entropy of reaction, ΔS is also negative as TΔS is negative, and T is always positive. From the relationship ΔG = ΔH − TΔS we can see that at T_1, ΔG is negative and therefore the reaction is spontaneous. At T_2 ΔG = 0 and therefore the system is in equilibrium. At T_3, ΔG is positive and therefore the reaction is non-spontaneous.

Question 16

In the following diagrams, the gaseous substances ○○ and ● react to produce ●○.

Eventually the reaction comes to an equilibrium state.



0 min 1 min 2 min 3 min

(a) Identify whether the diagram illustrates a system reaching static or dynamic equilibrium. 1

Dynamic

(b) At which time is equilibrium illustrated? Justify your answer. 2

Equilibrium is reached at 2 minutes as the concentration of each component does not change between 2-3 minutes

(c) Outline the characteristics of a system at equilibrium. 2

The concentrations of all reactants and products stay constant and the rate of the forward reaction equals the rate of the reverse reaction.

(d) Identify 2 differences between static and dynamic equilibrium. 2

Static equilibrium occurs with irreversible reactions- the rate of forward and reverse reactions at equilibrium (completion) are zero, while dynamic equilibrium occurs with reversible reactions and the rates of the forward and reverse reactions at equilibrium are equal but non-zero.

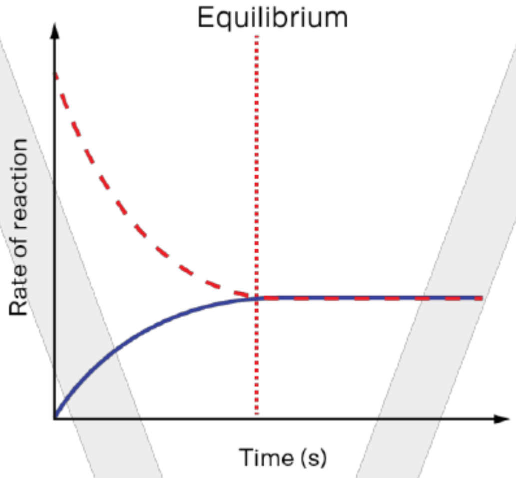
Can also include: No microscopic changes in static equilibrium and microscopic changes occur in dynamic equilibrium.

Question 17

Dinitrogen tetroxide gas decomposes to form nitrogen dioxide gas.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

In an experiment, 2 moles of nitrogen dioxide were introduced into an empty sealed reaction flask at 80 °C. The rates of the forward and reverse reactions over time are shown in the graph below.



(a) On the graph, label the point at which equilibrium is first reached. **1**

(b) State which reaction, forward or reverse, is represented by the dashed line and the solid line. **1**

Dashed line is the reverse reaction and solid line is the forward reaction.

(c) Account for the changes in the forward and reverse rates as seen in the graph. **3**

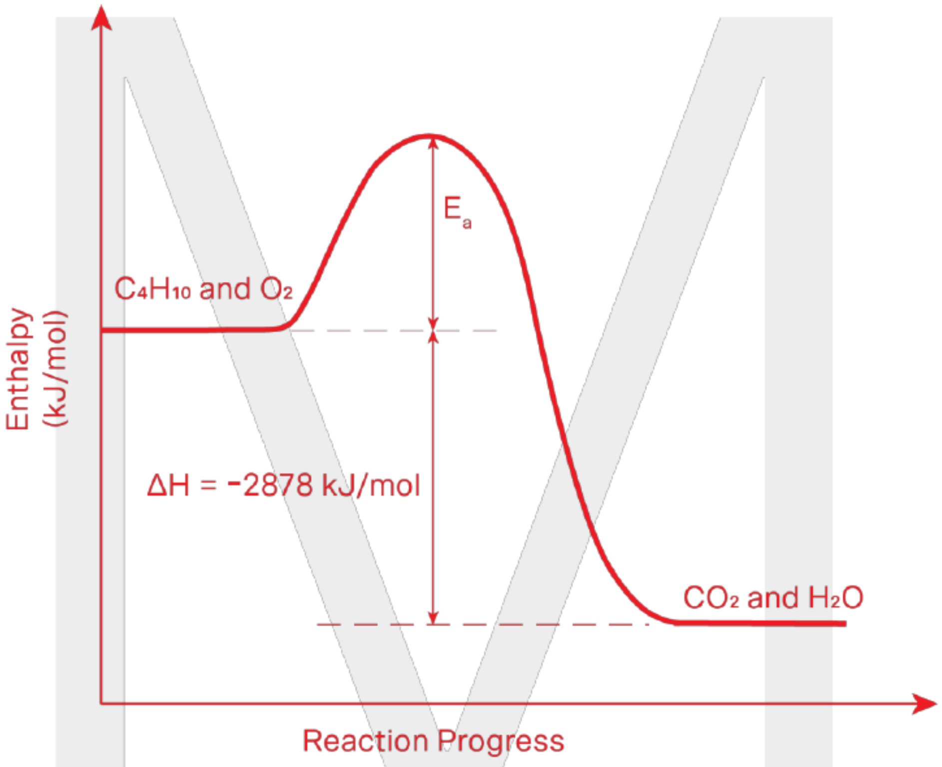
The nitrogen dioxide introduced into the flask will react to form dinitrogen tetroxide. As the concentration of nitrogen dioxide decreases, the rate of the reverse reaction decreases. Initially there is no dinitrogen tetroxide to decompose, but as more is produced, the rate of the forward reaction increases. Eventually, the two rates will become equal and equilibrium is established.

Question 18

(a) Write a balanced equation for the complete combustion of butane gas, C_4H_{10}. **1**

$C_4H_{10(g)} + 13/2O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)}$

(b) The standard enthalpy of combustion of butane is $\Delta H_c^{\ominus} = -2878$ kJ mol^{-1}. Draw an energy profile diagram for the combustion of 1 mole of butane. Label on the diagram the enthalpy change and the activation energy. **3**



(c) Predict whether the reverse reaction is likely to proceed and hence explain the reversibility of this reaction with reference to the activation energy and collision theory. **3**

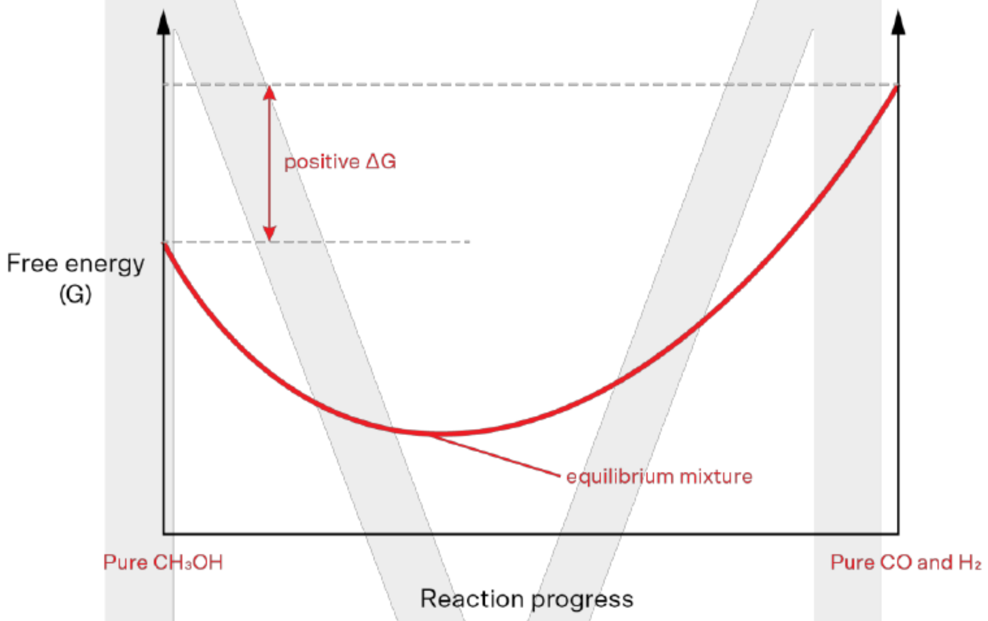
Since the forward reaction is very exothermic, the activation energy of the reverse reaction is very large. This means a large proportion of collisions will have insufficient energy to react in the reverse direction. Thus, the reverse reaction is unlikely to proceed at any appreciable rate and only the forward reaction proceeds. Hence the reaction is considered irreversible.

Question 19

In a closed container, methanol decomposes to form carbon monoxide and hydrogen gas in a reversible reaction:

$$CH_3OH_{(g)} \rightleftharpoons CO_{(g)} + 2H_{2(g)} \qquad \Delta G^{\ominus} = 24.9 \text{ kJ mol}^{-1}$$

(a) At 298 K, reactants dominate in the equilibrium mixture. Sketch a free energy curve on the graph below to show the variation in Gibbs free energy as the reaction progresses at this temperature. 3



(b) With reference to the free energy curve above, explain why the reaction proceeds in both directions, although change in the standard Gibbs free energy of one of the reactions is positive. 3

As products are produced, there is a further decrease to the Gibbs free energy (lowest part of curve) because of an increase in entropy associated with mixing of reactants and product. The reaction will move in the direction of minimising Gibbs free energy, hence both reactions will occur spontaneously.

Question 20

A model can be useful for demonstrating various aspects of a particular scientific phenomenon and explaining complex concepts.

(a) Outline a first-hand investigation you conducted to model a system reaching dynamic equilibrium. 2

1. Two large identical containers were each labelled “Reactants” and “Products”. Half of the Reactant container was filled with water.

2. Water was transferred simultaneously between the two containers using 250 mL beakers.

3. The water level was observed after each transfer. The water transfer was repeated until no more change in the water level was observed.

(b) Assess the validity of the information that could be collected in the investigation outlined in (a). 3

The information collected is valid to a point, in that it reflects some of the characteristics of a closed chemical system at equilibrium. For example, after a number of rounds, the quantity of water in the Reactant and Product containers remained constant, although the water was continually moving between the two containers – this models dynamic equilibrium, where there is no macroscopic change but there is still microscopic change. However, some aspects cannot be captured which compromises the model’s validity. This model can’t model reactions with more than one reactant or product, or where mole ratio isn’t 1:1. It also can’t model changes in observable properties apart from concentration, e.g. colour shifts and temperature changes.

Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Refer to the following information for Questions 21 – 23

A counter swap model was used by some students to model chemical equilibrium. The following procedure was followed.

Step	Description
1	A piece of A4 paper is ruled down the middle. The left half is labelled "Reactant" and the right half labelled "Product". 30 counters are placed on the "Reactant" side.
2	Counters are transferred between the two sides: during each round, 30% of the counters from the "Reactant" side are moved to the "Product" side; at the same time, 50% of the counters from the "Product" side are moved to the "Reactant" side. If a fraction was to be exchanged, the number was rounded up.
3	The counters were transferred for 5 rounds. The number of counters on each side are recorded in a table.
4	Repeat steps 1-3 with 30 counters on the "Product" side instead.

When all the counters began on the reactant side, a ratio of 19 to 11 reactant to product counters was achieved at equilibrium. However, when all of the counters began on the product side, a ratio of 18 to 12 reactant to product counters was achieved at equilibrium.

Question 21

What would be observed when equilibrium is reached in this model?

(a) No counters will be moved from the product to reactant side.

(b) The number of counters on both sides stay constant.

(c) Exchange of counters in both directions result in an increase in the number of reactant counters.

(d) Exchange of counters will stop.

The concentration remains constant at equilibrium. The counters represent the reactants and products; hence their number remains the constant at equilibrium.

Question 22

What can be deduced from the ratio of reactant to product counters?

(a) The reaction modelled by this investigation has a reactant to product stoichiometric ratio greater than 1:1.

(b) The reaction modelled by this investigation has an equilibrium position towards the product side.

(c) The percentage of reactant counters moved increases as equilibrium is reached.

(d) The percentage of reactant counters moved is smaller than the percentage of product counters.

The counter model can't model reactions with more than one reactant or product, or where mole ratio isn't 1:1.

The larger ratio of reactant to product counters means the equilibrium position lies towards the reactant side. This means a smaller percentage of reactant counters is moved.

Question 23

Which of the following is the most likely explanation for the different reactant to product ratios?

(a) The position of equilibrium depends on the initial reaction mixture.

(b) The model has far fewer discrete particles than a real equilibrium system.

(c) The percentage of counters swapped changed between the two experiments.

(d) The students committed an experimental error.

Question 24

Which of the following is not necessarily a characteristic of a reversible system at equilibrium?

(a) It is a closed system, no matter enters or leaves the system.

(b) The rates of the forward and reverse reactions are equal.

(c) The macroscopic properties stay constant.

(d) The concentration of reactants is equal to the concentration of products.

Question 25

For any reversible reaction, a chemical equilibrium may be established by starting a reaction with:

(a) reactants only

(b) products only

(c) equal quantities of reactants and products

(d) all of the above

The system will arrive at the same equilibrium position under the same temperature and pressure conditions, so can be approached from either side.

Question 26

For the reaction, $CAB_4 \rightarrow \frac{1}{2}A_2 + 2B_2 + C$, the change in enthalpy is 90 kJ mol^{-1} and the change in entropy is 200 J K^{-1} mol^{-1}. Which statement is correct regarding the spontaneity of the reaction?

(a) The forward reaction is spontaneous at all temperatures.

(b) The reverse reaction is spontaneous at all temperatures.

(c) The forward reaction is spontaneous at temperatures less than 450 K.

(d) The reverse reaction is spontaneous at temperatures less than 450 K.

$90 - T \times 0.200 < 0$

$T > 450$ K

Thus, for the forward reaction to be spontaneous, the temperature must be greater than 450 K. This means the reverse reaction is spontaneous at temperatures less than 450 K.

Question 27

Which of the following reactions is most unlikely to reach completion?

(a) Sodium reacting with water.

(b) Magnesium reacting with nitric acid.

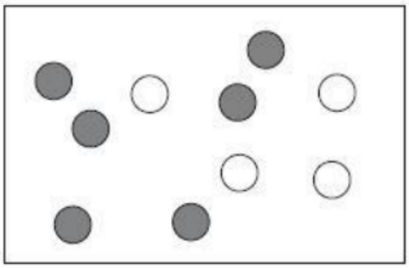
(c) Nitrogen reacting with hydrogen gas.

(d) Ethanol reacting with oxygen gas.

Question 28 **[HSC Sample Q1]**

Particle ● reacts with particle ○ to form the molecule ●○. The system comes to an equilibrium.

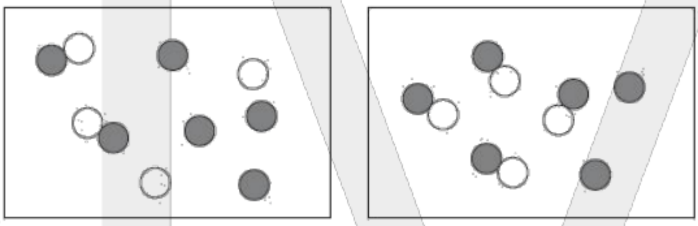
The diagram shows the initial reactants.



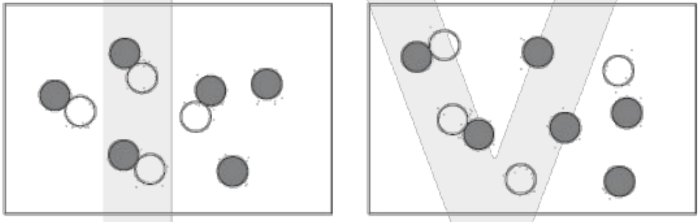
Which combination of diagrams best represents the molecule in a dynamic equilibrium and a static equilibrium?

Dynamic Static

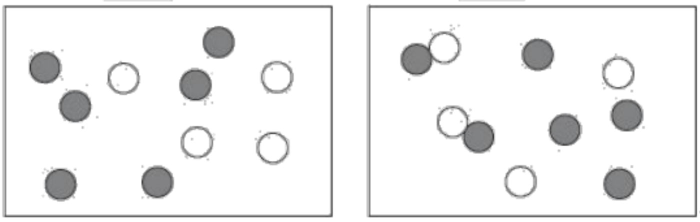
(a)



(b)



(c)



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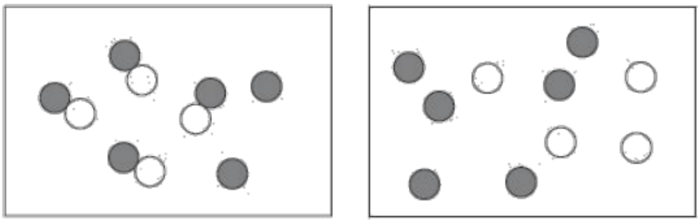
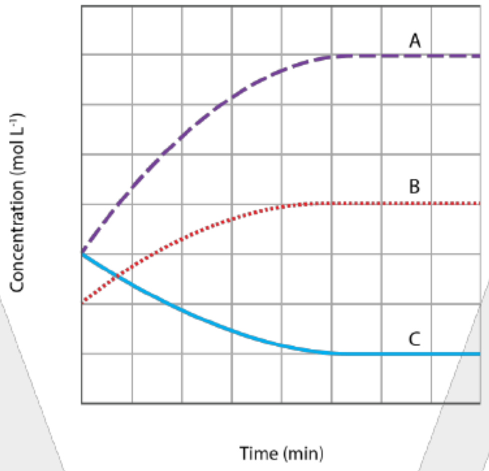


At static equilibrium, the limiting reactant is used up. The white circle is limiting reactant. There are four white circles, so 4 products can be made and 2 black circles remain.

Question 29

The concentration profile diagram shows the changes in concentration for a reversible reaction.



Which of the following equations represents the reaction shown in the diagram above?

(a) $A + B \rightleftharpoons C$

(b) $A \rightleftharpoons B + C$

(c) $2A + C \rightleftharpoons B$

(d) $2A + B \rightleftharpoons C$

A and B must be on the same side of the equations since they move in the same direction. Since the gradient of A is greater than the gradient of B, A must have a greater stoichiometric coefficient in the balanced equation.

Question 30

Consider the following reaction occurring in a beaker:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

Which of the following statements is correct about this system?

(a) The reaction will not go to completion because it is reversible.

(b) Dynamic equilibrium will be reached because the rate of the forward reaction will be equal to the rate of the reverse reaction.

(c) Eventually a static equilibrium will be reached because one of the reactants is a gas which will leave the system.

(d) The temperature of the system will stay constant.

Since the reaction occurs in a beaker, it is an open system. This allows the carbon dioxide gas to escape the reaction, causing the reverse rate to proceed at a very negligible rate. The forward reaction will continue to occur as the system attempts to establish equilibrium. Eventually all the reactant will be used up and the system will be at a static equilibrium.

Question 31

The conversion of diamond to graphite is a spontaneous process at all temperatures. Which of the following correctly describes this process?

(a) An increase in entropy occurs as the reaction proceeds.

(b) The reaction proceeds at a fast rate.

(c) The reaction is endothermic.

(d) The change in Gibbs free energy of the reaction at all temperatures is positive.

Spontaneous processes must have $\Delta G < 0$. In order to be spontaneous at all temperatures (i.e. for $\Delta G < 0$ at all temperatures), reactions must have $\Delta S > 0$ and $\Delta H < 0$.

Question 32

Consider the following reversible reaction:

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$

A solution of $Fe(NO_3)_3$ was mixed with a solution of KSCN. Which of the following statements describes the changes in forward and reverse rates as the reaction proceeds to equilibrium?

(a) Rate of the forward and reverse reactions both increase.

(b) Rate of the forward and reverse reactions both decrease.

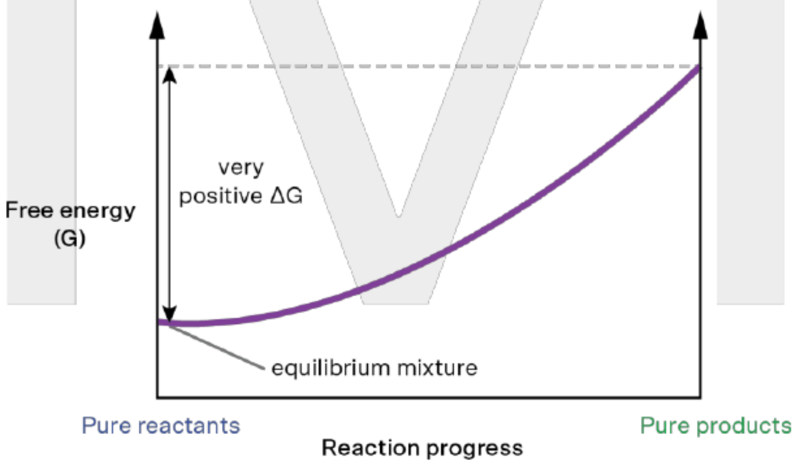
(c) Rate of the forward reaction increases and the rate of the reverse reaction decreases.

(d) Rate of the forward reaction decreases and the rate of the reverse reaction increases.

Only reactants are initially present. As they react to form products, the concentration of reactants decreases, hence the rate of the forward reaction decreases. As more product is produced, the rate of the reverse reaction increases. Eventually, the two rates will become equal and equilibrium is established.

Question 33

The free energy curve below shows the variation in Gibbs free energy of a particular reaction.



What can be concluded about this reaction from the free energy curve?

(a) The forward reaction does not proceed at any appreciable rate.

(b) The reverse reaction is non-spontaneous.

(c) The system will reach dynamic equilibrium very quickly.

(d) Products will dominate in the equilibrium mixture.

The position of equilibrium (position with lowest G) lies very close to the reactants, thus the forward reaction will not occur to any observable extent.

Question 34

Justify the following characteristics of dynamic equilibrium systems:

(a) It must be a closed system. 2

The system must be closed to prevent the exchange of matter with the surroundings which will cause a change in the concentration of one or more reaction components. A change in the concentrations means the system is not at equilibrium.

(b) All reaction components are present in the mixture. 2

At equilibrium, the forward and reverse reactions continue to occur, thus reaction components are continually being consumed and produced. Hence no reaction component will be completely used up.

(c) Concentrations stay constant. 2

For a system at equilibrium, the forward and reverse reaction rates are equal. Since the reaction components are produced at the same rate as they are consumed, there is no change in the concentration.

(d) Microscopic changes occur but there are no macroscopic changes. 2

At equilibrium, the forward and reverse reactions continue to occur, thus there is a change occurring on the microscopic level. However, since there is no change to the concentration of reaction components over time, there are no macroscopic changes.

Question 35

In a closed container, sulfur trioxide decomposes to form sulfur dioxide and oxygen gas in a reversible reaction:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \qquad \Delta H = 99 \text{ kJ mol}^{-1}$$

(a) Initially, 2 mol L^{-1} of sulfur trioxide was present in a sealed reaction flask. Describe how the concentration of each reaction component changes as the system approaches equilibrium. 2

Initially only the forward reaction proceeds. As the forward reaction proceeds, SO_3 is consumed, therefore its concentration decreases. As SO_2 and O_2 are produced, their concentrations increase. Eventually, the concentrations of all reaction components become constant.

(b) State two observations that could be made to indicate that the system has reached equilibrium. Explain your answer. 3

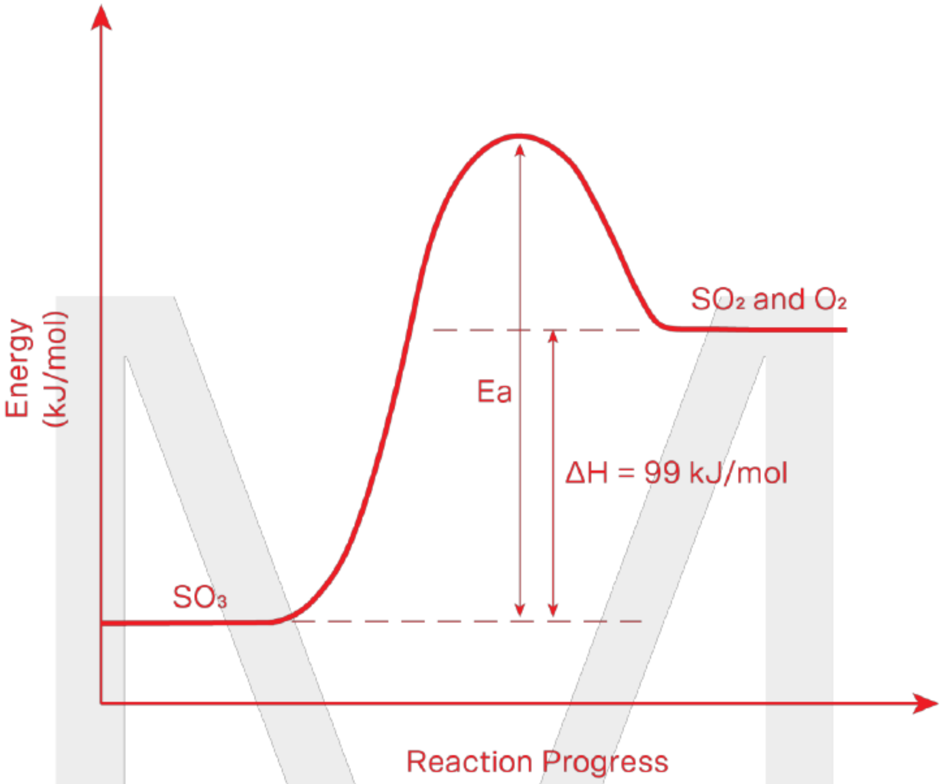
Temperature remains constant since the forward and reverse rates are the same, so heat is produced at the same rate as it is consumed.

Pressure remains constant since the forward reaction (converting 1 mole of gas to 1.5) is proceeding at the same rate as the reverse reaction (converting 1.5 moles of gas to 1).

(c) State how the entropy of the reaction mixture changes as the reaction approaches equilibrium. Explain your reasoning. 2

The entropy increases as the reaction approaches equilibrium. At equilibrium, the free energy change is zero. Since enthalpy increases as the forward reaction approaches equilibrium, the entropy change must also increase for the free energy change to become zero.

(d) Draw an energy profile diagram for the decomposition of 1 mole of sulfur trioxide. Label the enthalpy change and the activation energy on the diagram. 3



(e) Explain the reversibility of this reaction with reference to the activation energies of the forward and reverse reactions. 3

Since the forward reaction is endothermic, the activation energy of the reverse reaction is very small. This means a large proportion of collisions will have sufficient energy to react in the reverse direction. Thus the reverse reaction is likely to proceed at an appreciable rate. Hence the reaction is considered reversible.

Question 36

(a) Outline a first-hand investigation that can conducted to model a system reaching static equilibrium. 3

1. A piece of A4 paper is ruled down the middle. The left half is labelled “Reactants” and the right half labelled “Products”. 12 counters are placed on the reactant side.

2. For each round, 50% of the counters on the “Reactant” side will be moved to the “Products” side. If a fraction was to be exchanged, the number was rounded up.

3. The counters were transferred for 5 rounds. The number of counters on each side are recorded in a table.

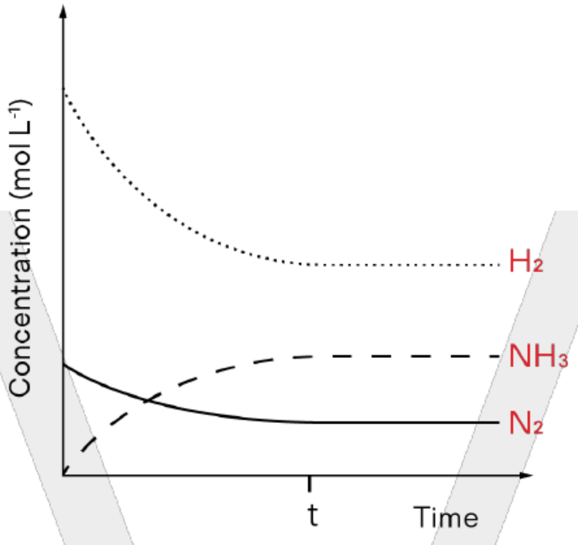
Other answers possible: can outline water tank model

(b) Explain what aspects of static equilibrium were modelled by the procedure outlined in (a). 2

Static equilibrium occurs with irreversible reactions where the reverse reaction does not occur. This is shown by the lack of counters moving from products to reactants. The reaction (movement of counters) proceeds until there is no reactant left (no more reactant counters). There is no reaction (movement of counters) once equilibrium (constant numbers of reactant and product counters) is achieved.

Question 37

The graph shows the variation in concentrations of reactants and product with time for an exothermic reaction between hydrogen gas and nitrogen gas to form ammonia gas.



(a) Write a balanced equation for reversible reaction above. **1**

$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(b) Label on the graph the substances represented by each line. **1**

(c) Explain the changes shown on your graph. **2**

Initially only the forward reaction proceeds. As the forward reaction proceeds, H_2 and N_2 are used up, therefore their concentrations decrease and the forward reaction rate decreases. As NH_3 is produced, its concentration increases and the reverse reaction rate increases. Eventually, the rates of both the forward and reverse become equal hence the concentrations remain constant.

(d) State why the concentrations of reactants and product do not change after time *t*. **1**

The system establishes equilibrium.

(e) What can you say about the activation energies of the forward and reverse reactions? **1**

The forward and reverse reactions must have similar sized activation energies.

Question 38 [NSW DoE Q2(b)]

A model of an open and closed system is set up with 2 identical beakers of water being heated. One beaker has a lid and the other is open. Assess the validity of the model. 3

Beaker 1, with no lid on it, represents an open system. An open system is one which allows both energy and matter to move in and out of the system. This is indicated by the loss of heat (energy) and water (matter), as the water level will continue to drop in beaker 1. It is, therefore, a valid model, as both energy and matter can be transferred to and from the surroundings.

Beaker 2, which has a lid, represents a closed system. In a closed system, energy may still be able to flow between the system and the surrounding, but matter cannot enter or leave the system. In beaker 2, macroscopic changes will occur the until the rate of evaporation is equal to the rate of condensation: $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

This happens when the space above the liquid is saturated with water vapour. From that point, the liquid level will remain constant, demonstrating that matter cannot transfer to and from the surroundings in a closed system.

Thus this experiment is a valid model of the differences between open and closed systems.

Question 39

Phosphorus pentachloride is used in the industrial preparation of many organic phosphorus compounds. The equation below shows its preparation from phosphorus trichloride and chlorine:

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

(a) Calculate the enthalpy change of the above reaction using the data given: 2

$P_{4(s)} + 6Cl_{2(g)} \rightleftharpoons 4PCl_{3(g)}$ $\Delta H = -1280\ kJ\ mol^{-1}$

$P_{4(s)} + 10Cl_{2(g)} \rightleftharpoons 4PCl_{5(g)}$ $\Delta H = -1774\ kJ\ mol^{-1}$

$PCl_{3(l)} \rightleftharpoons 1/4P_{4(s)} + 3/2Cl_{2(g)}$ $\Delta H = 320\ kJ\ mol^{-1}$

$1/4P_{4(s)} + 5/2Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$ $\Delta H = -443.5\ kJ\ mol^{-1}$

$\Delta H = -123.5\ kJ\ mol^{-1}$

(b) The standard entropies of the reactants and products are shown in the table below.

Substance	$S^{\ominus}$ ($J\ K^{-1}\ mol^{-1}$)
$PCl_{3(g)}$	312
$Cl_{2(g)}$	223
$PCl_{5(g)}$	353

Calculate the standard entropy change for this reaction. 1

$\Delta S^{\ominus} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants} = (353) - (312 + 223) = -182\ J\ K^{-1}\ mol^{-1}$

(c) Determine the spontaneity of the reaction at 298 K by calculating the standard free energy change for the reaction. 2

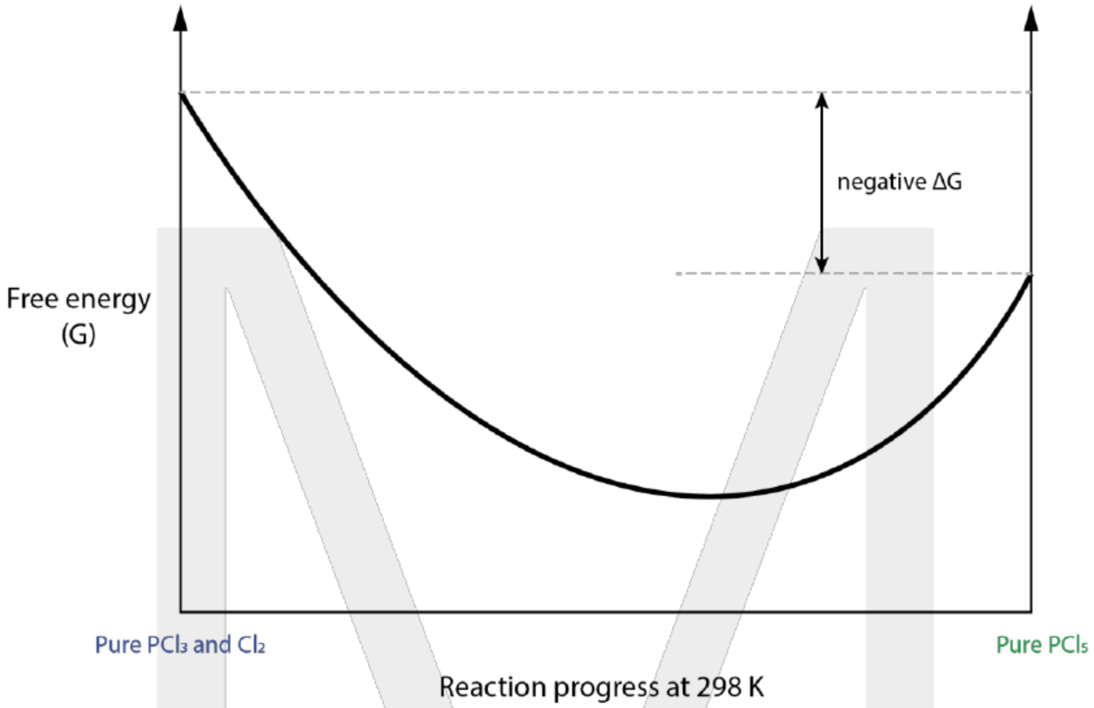
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= -123.5 - 298 \times -182 \times 10^{-3}$

$= -69.3\ kJ\ mol^{-1}$

Reaction is spontaneous at 298 K since $\Delta G^{\ominus} < 0$.

(d) The graph below shows the variation in Gibbs energy against the reaction progress at 298 K. With reference to the free energy curve, explain why the reaction proceeds in the reverse direction. 3



Although the reverse reaction would be predicted to be non-spontaneous at 298 K, owing to the increase in entropy associated with mixing of reactants and product there is a further decrease to the Gibbs free energy (lowest part of curve) as products are produced. The reaction will move in the direction of minimising Gibbs free energy, hence both reactions will occur spontaneously.

Question 40

1.0 g of ethane (C_2H_6) gas was completely burned to form carbon dioxide and water. The heat released from this combustion was used to heat 550 g of water in a calorimeter. The water, initially at a temperature of 17.0 °C, was heated to 38.0 °C.

(a) Write a balanced equation for the complete combustion of ethane. 1

$C_2H_{6(g)} + 7/2O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$

(b) Calculate the amount of heat absorbed by the water. 2

$q(\text{water}) = mc\Delta T$

$= 550 \times 10^{-3} \times 4.18 \times 10^{3} \times (38.0 - 17.0)$

$= 48279\text{ J} = 48.279\text{ kJ}$

(c) Calculate the enthalpy of combustion of ethane. 2

$n(C_4H_{10}) = m / mm = 1.0 / 30.068 = 0.0332579\text{ mol}$

$\Delta H_c = -q / n$

$= -48.279 / 0.0332579$

$= -1451.652972\text{ kJ mol}^{-1} = -1500\text{ kJ mol}^{-1}$ (2 s.f.)

(d) The standard enthalpies of formation are given in the table below. Determine the standard enthalpy of combustion of ethane using the enthalpies of formation. 2

Substance	$\Delta H_f^{\ominus}$ (kJ mol^{-1})
$C_2H_{6(g)}$	−84.67
$CO_{2(g)}$	−393.5
$H_2O_{(l)}$	−285.8

$\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}{}_{\text{products}} - \Sigma\Delta H_f^{\ominus}{}_{\text{reactants}}$

$= (2 \times -393.5 + 3 \times -285.8) - (-84.67) = -1559.7\text{ kJ mol}^{-1}$

(e) Compare the values obtained in (c) and (d). Explain why values differ from one another. 1

In (c), energy was lost to surroundings including the air and calorimeter. This results in the experimental value being smaller in magnitude than the value calculated in (d).

(f) Predict whether the reverse reaction is likely to proceed and hence explain the reversibility of this reaction with reference to the activation energies of the forward and reverse reactions. 3

Since the forward reaction is very exothermic, the activation energy of the reverse reaction is very large. This means a large proportion of collisions will have insufficient energy to react in the reverse direction. Thus the reverse reaction is unlikely to proceed at any appreciable rate and only the forward reaction proceeds. Hence the reaction is considered irreversible.

(g) Calculate the standard entropy change for this reaction using the standard entropies of the reactants and products shown in the table below. 1

Substance	**$S^\ominus$ ($J\ K^{-1}\ mol^{-1}$)**
$C_2H_{6(g)}$	229.5
$O_{2(g)}$	205.0
$H_2O_{(l)}$	69.94
$CO_{2(g)}$	213.7

$\Delta S^\ominus = \Sigma S^\ominus_{products} - \Sigma S^\ominus_{reactants}$

$= (2 \times 213.7 + 3 \times 69.94) - (229.5 + 7/2 \times 205.0)$

$= -309.8\ J\ K^{-1}\ mol^{-1}$

(h) Determine the temperature range for which this reaction is spontaneous. 2

For spontaneous reactions $\Delta G < 0$, thus $\Delta H - T\Delta S < 0$

$-1559.73 - (T \times -309.8 \times 10^{-3}) < 0$

$T < 1559.73 / 0.3098$

$T < 5035$ K (4 s.f.)

Year 12
Chemistry
Equilibrium and Acid Reactions

Work Book 2
Le Chatelier’s principle

MATRIX
EDUCATION

Part A: Multiple choice questions

Question 1

Consider the following system initially at equilibrium:

$$NO_{(g)} + Cl_{2(g)} \rightleftharpoons NOCl_{2(g)} \qquad \Delta H = +21 \text{ kJ mol}^{-1}$$

Which of the following changes would NOT result in the production of additional $NOCl_{2(g)}$?

(a) Decreasing the system's volume

(b) Decreasing the temperature

(c) Removal of $NOCl_{2(g)}$ from the system

(d) Addition of Cl_2

Decreasing volume shifts equilibrium towards the side with less gas moles (right)

Decreasing the temperature favours the exothermic reverse reaction

Removal of product shifts equilibrium to the right

Addition of $Cl_{2(g)}$ shifts equilibrium to the right

Question 2

The following equilibrium reaction was established in a closed container:

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

Which of the following correctly describes the effect of increasing the volume of the container?

	Yield	Rate
(a)	increase	increase
(b)	increase	decrease
(c)	decrease	increase
(d)	decrease	decrease

Yield: Equilibrium shifts to side with more gas moles (LHS), hence yield decreases

Rate: Decreases concentration of all species, hence collision frequency decreases

Question 3

Which of the following reactions will the equilibrium be unaffected by a change in the volume at constant temperature?

(a) $C_3H_{8(g)} + 5O_{2(g)} \rightleftharpoons 3CO_{2(g)} + 4H_2O_{(g)}$

(b) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

(c) $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$

(d) $CO_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2O_{(g)}$

Same number of moles of gas on both sides, therefore neither the forward or reverse reaction will be favoured to minimise the disturbance.

Question 4

Consider the following equilibrium reaction:

$$2H_{2(g)} + C_{(s)} \rightleftharpoons CH_{4(g)} \qquad \Delta H = 74 \text{ kJ mol}^{-1}$$

Which one of the following will result in the largest increase in percentage of carbon converted to methane gas?

(a) Decreasing the temperature

(b) Addition of a catalyst

(c) Increasing the concentration of hydrogen gas in the mixture

(d) Increasing the volume of the reaction vessel

Decreasing the temperature will shift equilibrium in the exothermic direction (left)

Addition of a catalyst causes no shift to equilibrium

Increasing H_2 causes equilibrium to shift right to remove some added H_2

Increasing volume shifts equilibrium towards the side with more gas moles (left)

Question 5

When a solution containing $Co(H_2O)_6^{2+}{}_{(aq)}$ is added to a solution of chloride ions, the following equilibrium is established.

$$\underset{\text{(pink)}}{Co(H_2O)_6^{2+}{}_{(aq)}} + 4Cl^-{}_{(aq)} \rightleftharpoons \underset{\text{(blue)}}{CoCl_4^{2-}{}_{(aq)}} + 6H_2O_{(l)}$$

Which of the following statements about the colour of the solution is not true?

(a) Diluting the solution with water will make solution turn pink.

(b) If the reaction is exothermic, heating the solution will make it turn blue.

(c) If the reaction is endothermic, cooling the solution will make it turn pink.

(d) Adding a large amount of solid potassium chloride to the solution will make it turn blue.

Adding water will shift equilibrium to the left, forming more of the pink species.

Heating will shift equilibrium to endothermic side, making more of the pink species.

Cooling will shift equilibrium to exothermic side, making more of the pink species.

KCl will dissolve to add Cl^-, shifting equilibrium right to form more of the blue species.

Question 6

In an experiment to investigate the effect of adding and removing reactants on an equilibrium, a mixture of Fe^{3+} and SCN^- was poured into 3 test tubes. 0.5 mL of concentrated iron(III) nitrate solution was added to tube 1, 0.5 mL of concentrated sodium hydroxide solution was added to tube 2 and 0.5 mL of water was added to tube 3. What was the purpose of tube 3?

(a) To keep the other test tubes cool.

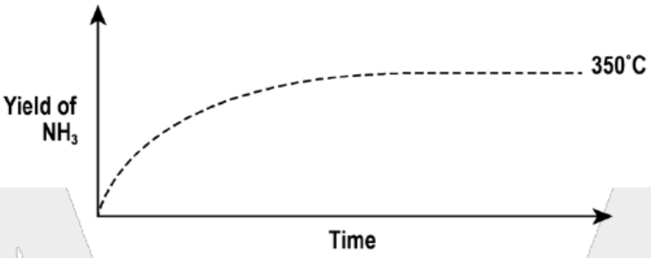
(b) To ensure there is a backup in case a test tube is spilled.

(c) To act as a control.

(d) To check if the reaction has reached a static equilibrium.

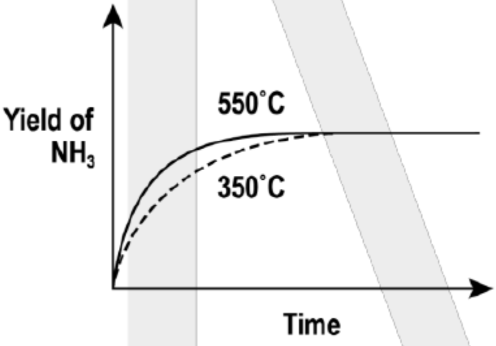
Question 7

The graph below shows the yield of ammonia produced at 350 °C and 250 atm via the Haber process. The synthesis of ammonia is reversible and exothermic.

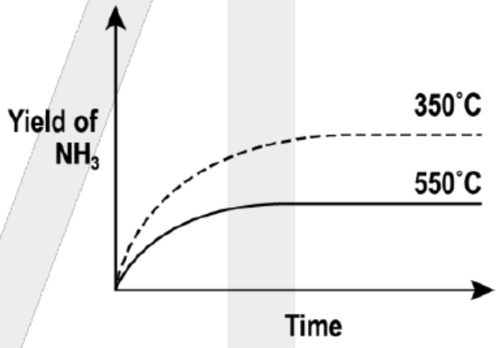


Which of the following illustrates the relative yield of ammonia produced at a temperature of 550 °C, if all other conditions are kept the same?

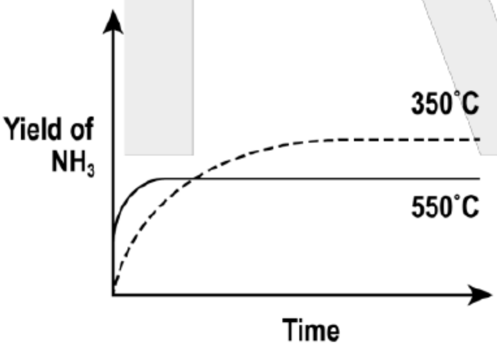
(a)



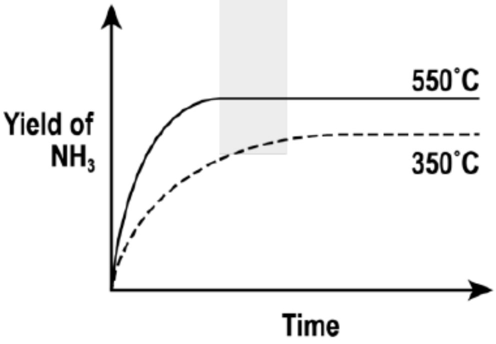
(b)



(c)



(d)



Higher temperature = lower yield (equilibrium shift in the reverse endothermic direction) and higher rate.

Question 8

The equation describes an equilibrium reaction occurring in a closed system.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons 2C_{(g)} \qquad \Delta H = -132\ \text{kJ mol}^{-1}$$

Under which set of conditions would the highest yield of $C_{(g)}$ be obtained?

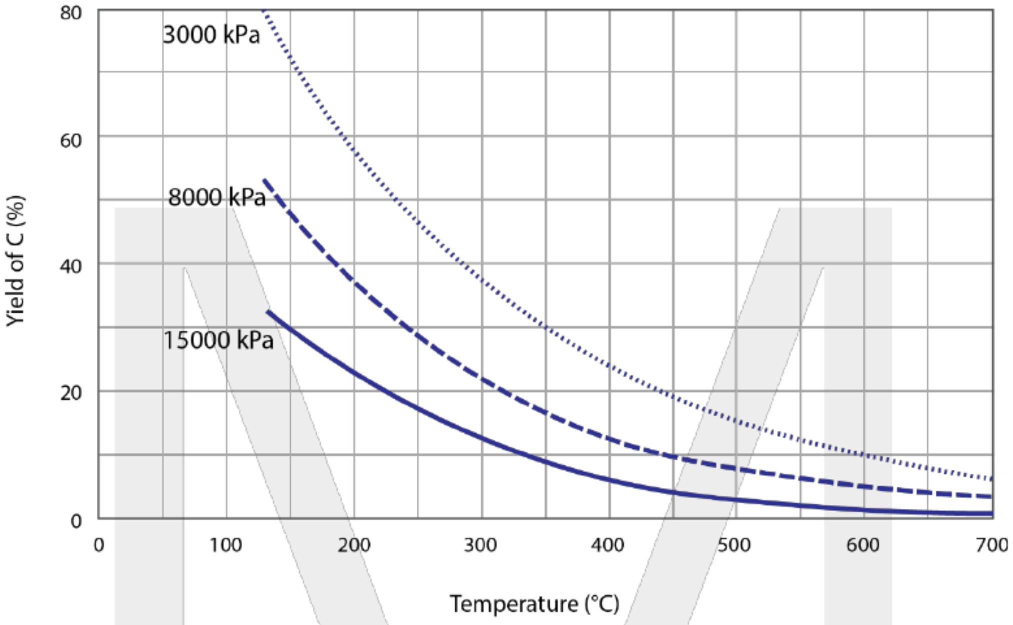
	Temperature (K)	Pressure (kPa)
(a)	300	100
(b)	300	200
(c)	500	100
(d)	500	200

The forward reaction is exothermic, hence is favoured by low temperatures.

The right-hand side has less gas moles, hence formation of products is favoured by high pressures.

Question 9

This graph represents the yield of an equilibrium reaction at different temperature and pressure conditions inside a reaction vessel.



Which of the following reactions could produce the trends shown in the graph?

(a) $A_{(g)} + B_{(s)} \rightleftharpoons 4C_{(g)}$ $\Delta H = +250$ kJ

(b) $2A_{(g)} + B_{(s)} \rightleftharpoons 3C_{(g)}$ $\Delta H = -250$ kJ

(c) $2A_{(g)} + B_{(s)} \rightleftharpoons C_{(g)}$ $\Delta H = +250$ kJ

(d) $4A_{(g)} + 2B_{(s)} \rightleftharpoons 3C_{(g)}$ $\Delta H = -250$ kJ

From graph, yield of C decreases with increasing temperature therefore reaction is exothermic ($\Delta H < 0$).

Yield of C increases with decreasing pressure therefore there are more moles of gas on product side.

Only (b) fulfils both criteria.

Question 10

The following reaction is exothermic.

$$\underset{\text{(pale yellow)}}{Fe^{3+}_{(aq)}} + SCN^{-}_{(aq)} \rightleftharpoons \underset{\text{(deep red)}}{[Fe(SCN)]^{2+}_{(aq)}}$$

Which row correctly describes the effect of the following changes?

	Increasing temperature	Addition of Fe^{3+}
(a)	colour darkens	colour darkens
(b)	colour lightens	colour darkens
(c)	colour darkens	colour lightens
(d)	colour lightens	colour lightens

Increasing temperature will shift the equilibrium in the endothermic direction (Le Chatelier's principle). This is the reverse reaction hence colour will lighten.

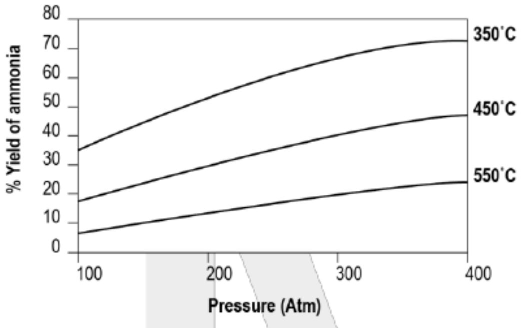
Addition of Fe^{3+} will shift the equilibrium right, hence colour will darken.

Question 11

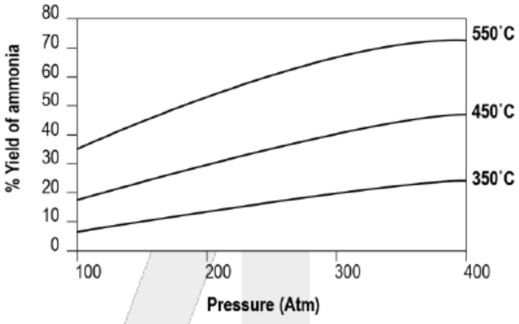
Which of the following graphs shows the relationship between temperature, pressure and yield of ammonia produced via the Haber process?

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H < 0$$

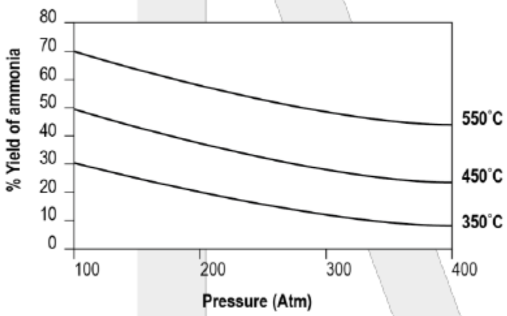
(a)



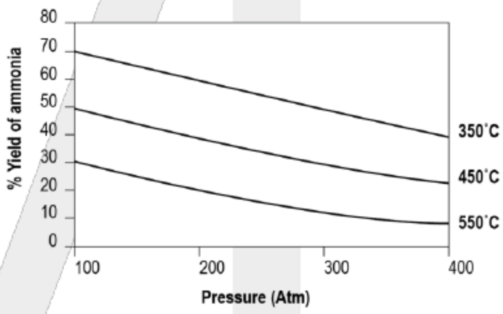
(b)



(c)



(d)



(a) shows increasing yield with increasing pressure, and increasing yield with decreasing temperature, which is in line with the predictions from Le Chatelier's principle.

Part B: Extended response questions

Question 12

Colourless nitrogen monoxide and oxygen was placed in a 1.0 L container and the following equilibrium was established with brown nitrogen dioxide:

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = -112 \text{ kJ mol}^{-1}$$

Explain what effect the following influences have on the equilibrium and colour of the reaction mixture.

(a) An increase in temperature 3

Increasing temperature disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift in the endothermic direction when heated, to remove the added heat to minimise the disturbance. This is the reverse direction, so the equilibrium will shift to the left. This decreases the concentration of brown NO_2 hence the colour will fade.

(b) An increase in volume 3

Increasing volume causes a decrease in pressure which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift to the side with more gas moles, to increase the pressure and minimise the disturbance. Hence the equilibrium will shift to the left. This decreases the concentration of brown NO_2 hence the colour will fade.

(c) Addition of an inert gas (at constant volume) 2

Addition of an inert gas at constant volume does not disturb the equilibrium, hence the equilibrium will not change and there will be no change to the colour of the reaction mixture.

Question 13

Consider the following equilibrium:

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)} \qquad \Delta H = 44 \text{ kJ mol}^{-1}$$

(a) With reference to the characteristics of a dynamic equilibrium, explain why wet clothes left in a closed bag do not dry but when the bag is left opened the clothes will begin to dry. **4**

Wet clothes in a closed bag is a closed system, so the above dynamic equilibrium will be established. Since the rate of the forward and reverse reactions are equal, there would be no observable change in amount of liquid water, so the clothes remain wet.

Wet clothes in an open bag is an open system. The gaseous water diffuses away from the clothes, removing it from the equilibrium mixture. According to Le Chatelier's principle, the equilibrium will shift continuously to the right to replace the gaseous water to minimise the disturbance. Therefore, all of the liquid water will be converted to gaseous water and escape the bag, leaving dry clothes.

(b) Explain why wet clothing causes rapid hypothermia (drastically decreasing body temperature) in cold conditions. 2

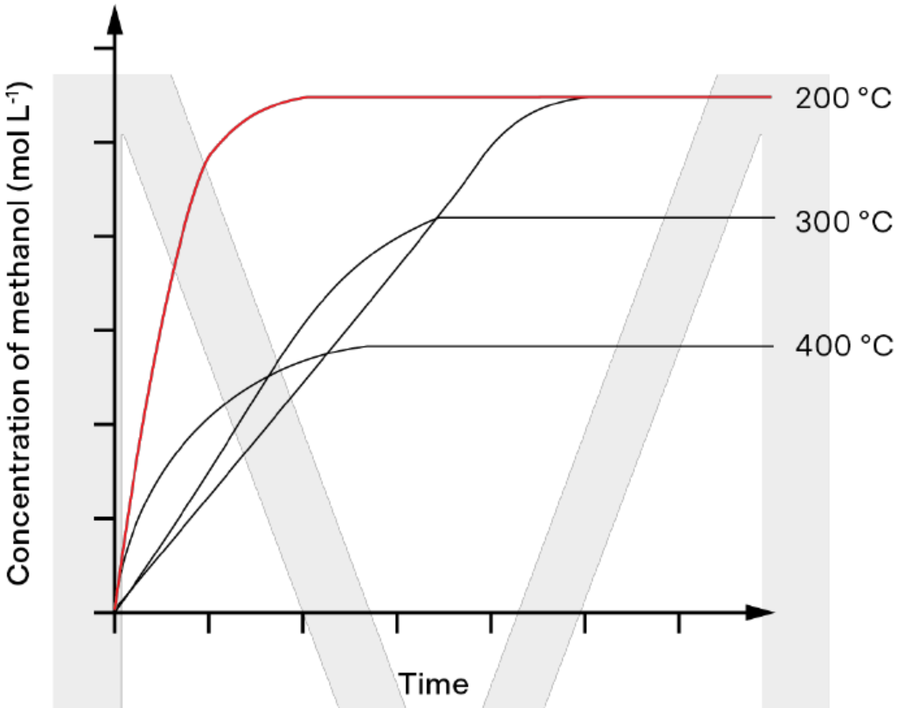
The evaporation of water is endothermic, thus as the process occurs, energy is absorbed from the surrounding (body), causing the temperature of the surrounding to decrease.

Question 14

Methanol can be prepared industrially according to the following equation:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

The graph below represents the formation of methanol at various temperatures in the absence of a catalyst.



(a) Explain why the curves:

(i) are initially steep. **2**

Initially, the system only contains CO and H_2, and no methanol. Therefore initially, there are many collisions between the reactants, resulting in a high rate for the forward reaction (production of methanol).

(ii) level off with time. **3**

As the CO and H_2 are used up, their concentrations decrease, which means less collisions and slowing down of the forward reaction. The concentration of methanol increases as it gets produced, causing an increased rate of the reverse reaction. Eventually the rates of the forward and reverse reactions become equal, resulting in a constant concentration of methanol (flat part of the graph).

(iii) have different gradients. 2

With increasing temperature, the rate of methanol production increases as the particles have increased kinetic energy. This causes more collisions as well as a higher proportion of collisions with sufficient energy to react.

(b) Is the formation of methanol endothermic or exothermic? Explain your answer. 3

Exothermic. Decreasing the temperature of the system causes the equilibrium concentration of methanol to be higher according to the graph. According to Le Châtelier's principle, decreasing the temperature causes the equilibrium to shift in the exothermic direction to produce more heat to minimise the disturbance, so the formation of methanol is exothermic.

(c) Sketch on the graph above the formation of methanol at 200 °C in the presence of a catalyst. 1

Question 15

The reaction below is one of the main steps in the commercial production of sulfuric acid.

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad \Delta H = -99 \text{ kJ mol}^{-1}$$

(a) What changes to the reaction conditions, in terms of temperature, pressure and use of a catalyst, would a manufacturer need to implement to increase the yield of SO_3? Explain your answer. 3

Decrease in temperature: According to Le Chatelier's principle, low temperatures favour the exothermic reaction to add heat and minimise the disturbance. Since the forward reaction is exothermic, a low temperature increases the yield of SO_3.

Increase in pressure: Increased pressure disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift to the side with less gas moles to reduce pressure and minimise the disturbance. Hence a higher yield of SO_3 is achieved at high pressures.

No change to use of a catalyst: increases the rate of both the forward and reverse reactions equally. Thus there is no disturbance to the equilibrium and hence no change in yield.

(b) Outline the effect of temperature, pressure, and the presence of a catalyst on the time taken for the reaction to reach equilibrium. 3

Increased temperature increases kinetic energy of molecules, thus increasing frequency of collisions as well as the proportion of collisions with the necessary activation energy. The rate is increased and equilibrium is reached more quickly.

Increased pressure: brings molecules closer together and increases frequency of collisions. Equilibrium is reached more quickly.

Presence of a catalyst: lowers the activation energy by providing an alternate reaction pathway and increases the rate of reaction. Equilibrium reached more quickly.

(c) Suggest a practical method for determining whether a particular mixture of sulfur dioxide, sulfur trioxide and oxygen is at equilibrium. 2

Monitor one of the following:

concentration of any of the reaction components

change in temperature

change in pressure

If the system is at equilibrium, the temperature and pressure should remain constant. If the system is NOT at equilibrium and the forward reaction is still dominant, the system will be producing heat and pressure will be decreasing (1.5 moles of gas are turning into 1 mole); if the reverse reaction is still dominant, the inverse will occur. At equilibrium, the rates of the forward and reverse reactions are equal, so heat is being used and produced at the same rate (no overall change in temperature), and pressure will be constant (no overall change in number of gas molecules).

Question 16

Acid rain containing sulfuric acid attacks a marble statue according to the following reaction:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightleftharpoons CaSO_{4(s)} + CO_{2(g)} + H_2O_{(l)}$$

Discuss how the equilibrium is affected in the above scenario by the fact that CO_2 is gaseous. 3

The gaseous CO_2 diffuses away from the reaction site, thus removing the product from the equilibrium mixture. According to Le Chatelier's principle, the equilibrium will shift continuously to the right to replace the CO_2, minimising the disturbance. Hence the reaction never reaches equilibrium (and this is why we normally use a forward arrow rather than an equilibrium arrow for this reaction).

Question 17

To qualitatively analyse an equilibrium reaction, a group of students made up an aqueous solution of iron(III) nitrate, which is pale yellow, and potassium thiocyanate, a colourless solution. They added these solutions together to form iron(III) thiocyanate which is an intense deep red colour. The flask initially became slightly hot.

(a) Write a balanced net ionic equation for equilibrium above. **1**

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$

(b) The solution was divided between 3 test tubes and the equilibrium mixture was investigated by the addition of different solutions to each test tube. Predict the outcomes observed by the students with the following changes and explain your answer.

(i) More of the solution containing iron(III) nitrate was added. **2**

Iron(III) nitrate dissolves to produce Fe^{3+} ions, increasing its concentration which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift right to remove some of the added Fe^{3+} ions and minimise the disturbance. Thus the concentration of $[Fe(SCN)]^{2+}$ increases and the solution will appear more red.

(ii) More of the solution containing potassium thiocyanate was added. **2**

Potassium thiocyanate dissolves to produce SCN^- ions, increasing its concentration which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift right to remove some of the added SCN^- ions and minimise the disturbance. Thus the concentration of $[Fe(SCN)]^{2+}$ increases and the solution will appear more red.

(iii) A solution containing sodium hydroxide was added (iron(III) hydroxide is insoluble). **2**

Addition of sodium hydroxide decreases the concentration of Fe^{3+} ions which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift left to produce more Fe^{3+} ions and minimise the disturbance. Thus the concentration of $[Fe(SCN)]^{2+}$ decreases and the solution will appear less red.

(c) Outline a procedure the students could follow to qualitatively observe the effect of temperature on this reversible reaction. 3

1. To a 50 mL beaker, add 0.5 mL of 0.1 M $Fe(NO_3)_3$, 0.5 mL of 0.1 M KSCN and 15 mL distilled water. Swirl to mix.

2. Transfer 4 mL to each of 3 test tubes labelled A, B and C.

3. Leave tube A as a control.

4. Place tube B in an ice bath or refrigerator.

5. Place tube C in a hot water bath. Record observations after 15 minutes.

(d) State the expected observations from the method outlined in (c). 2

Tube A: No colour change

Tube B: More red

Tube C: Less red

Note: Since the flask initially became hot and only the forward reaction occurs initially, the forward reaction must be exothermic.

(e) Outline the risks associated with the above investigation. 2

Iron(III) nitrate is irritating to the eye, skin and respiratory system.

Potassium thiocyanate is toxic and can cause headaches and nausea if ingested or inhaled.

Hot bath can cause burns to skin.

Question 18

The industrial production of hydrogen involves the following two reactions.

Reaction I: $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$ $\Delta H = +206 \text{ kJ mol}^{-1}$

Reaction II: $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ $\Delta H = -41 \text{ kJ mol}^{-1}$

(a) Write "increase", "decrease" or "no change" in the table to identify the expected effect of each change on the equilibrium yield of hydrogen in each reaction. 3

Change	Effect on H_2 yield in reaction I	Effect on H_2 yield in reaction II
addition of steam	increase	increase
increase in temperature	increase	decrease
addition of a suitable catalyst	no change	no change

(b) Explain the effect of decreasing volume at constant temperature on the hydrogen equilibrium yield in each reaction. 4

For Reaction I, decreasing the volume will increase the pressure of the system which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift to the left, the side with less gas moles, to reduce the pressure and minimise the disturbance. Hence H_2 yield decreases.

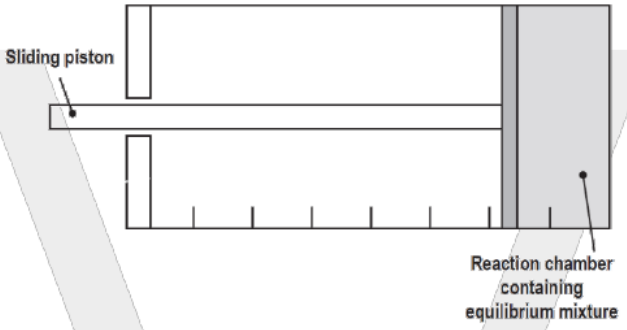
For Reaction II, there are 2 moles of gas on each side, hence decreasing the volume of the system will not disturb the equilibrium. Thus, there will be no shift and no change to the yield of H_2.

Question 19

Colourless dinitrogen tetroxide (N_2O_4) decomposes to form brown nitrogen dioxide (NO_2).

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

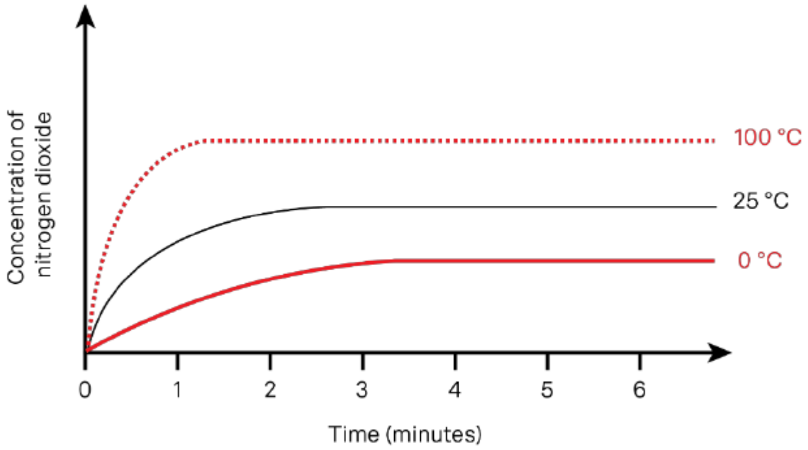
In an investigation, a student placed dinitrogen tetroxide into a reaction chamber as shown below and allowed the system to reach equilibrium under different temperatures.



The colour of the equilibrium mixture was recorded.

Temperature (°C)	Pressure (kPa)	Colour
0	1.0	Light brown
25	1.0	Brown
100	1.0	Dark brown

The graph represents the change in concentration of NO_2 as the reaction proceeds to equilibrium at 25 °C.



(a) On the graph above sketch two curves showing the change in concentration of NO_2 as the reaction proceeds to equilibrium at 0°C and at 100 °C. 2

(b) Deduce whether the forward reaction is exothermic or endothermic, explaining your reasoning. 3

According to Le Chatelier's principle, increasing the temperature causes the equilibrium to shift in the endothermic direction to remove added heat to minimise the disturbance. Since the container became more brown with higher temperatures, this means more NO_2 was formed, and the equilibrium had shifted to the right. Hence the forward reaction is endothermic.

(c) Keeping the temperature constant, the sliding piston was now moved, doubling the volume. The system was allowed to reach equilibrium. Describe what the student would observe. 3

Increasing the volume initially causes a decrease in concentration of all species, hence initially there will be a lighter brown colour observed as $[NO_2]$ is initially decreased.

Increasing the volume causes a decrease in pressure. According to Le Chatelier's principle, this change in pressure disturbs the equilibrium and the equilibrium shifts right to the side with more moles of gas in order to minimise the disturbance by increasing the overall pressure. As a consequence, the mixture would then become more brown as $[NO_2]$ increases as the equilibrium shifts to attain a new equilibrium.

Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 20

Which of the following changes will not cause a shift in the equilibrium of a system?

(a) Increasing the pressure of the system

(b) Addition of a catalyst

(c) Decreasing the temperature of the system

(d) Removal of one reaction species from the system

Increasing pressure shifts equilibrium towards the side with less gas moles.

Addition of a catalyst causes no shift to equilibrium as both forward and reverse rates are increased and there is no disturbance to the equilibrium.

Decreasing temperature will shift equilibrium in the endothermic direction.

Removing reaction species will shift equilibrium to replace species.

Question 21

The Haber process for the production of ammonia is an exothermic reaction.

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Which set of conditions would achieve the maximum yield of ammonia?

(a) High temperature and low pressure

(b) High temperature and high pressure

(c) Low temperature and high pressure

(d) Low temperature and low pressure

The forward reaction is exothermic, hence is favoured by low temperatures.

The right-hand side has less gas moles, hence formation of products is favoured by high pressures.

Question 22

Phosgene is synthesised from the reaction of carbon monoxide and chlorine:

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)} \qquad \Delta H = -9.93 \text{ kJ mol}^{-1}$$

Which of the following statements is correct?

(a) Use of a catalyst will increase the proportion of phosgene in the equilibrium mixture at constant temperature and pressure.

(b) Increasing the volume at a constant temperature will increase the proportion of phosgene in the equilibrium mixture.

(c) Increasing the temperature will increase the proportion of phosgene in the equilibrium mixture.

(d) Decreasing the concentration of chlorine will result in a decrease in the proportion of phosgene in the equilibrium mixture.

Addition of a catalyst causes no shift to equilibrium as both forward and reverse rates are increased and there is no disturbance to the equilibrium. Hence the proportion of phosgene remains the same.

Increasing volume shifts equilibrium towards the side with more gas moles (reverse direction). Hence the proportion of phosgene decreases.

Increasing temperature will shift equilibrium in the endothermic direction (reverse direction). Hence the proportion of phosgene decreases.

Removing reaction species will shift equilibrium to replace species. Removal of Cl_2 shifts equilibrium to the left; hence the proportion of phosgene decreases.

Question 23

The following endothermic reaction occurs when steam reacts with carbon at very high temperatures.

$$H_2O_{(g)} + C_{(s)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

Which set of temperature and pressure conditions will ensure the efficient production of hydrogen?

(a) Low temperature and low pressure

(b) Low temperature and high pressure

(c) High temperature and moderate pressure

(d) Moderate temperature, and high pressure

Endothermic therefore high temperature will increase both rate and yield.

Low pressures will increase yield (more gas moles on RHS), although rate is reduced.

Question 24

Nitrogen and oxygen gases react together at 600 °C to form an equilibrium mixture with nitrogen monoxide as given below.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad \Delta H = +180 \text{ kJ mol}^{-1}$$

If the temperature of the reaction is decreased and the volume kept constant, which correctly describes the changes to the concentrations of the reactants and products?

(a) Concentration of N_2 and O_2 increases and concentration of NO decreases.

(b) Concentration of N_2 and O_2 decreases and concentration of NO increases.

(c) Concentrations of reactant and products will both decrease.

(d) Concentrations of reactant and products remains the same as only the rate of the reaction will change.

According to Le Chatelier's principle, a decrease in temperature shifts equilibrium to the exothermic direction to produce more heat and minimise the disturbance. This is the reverse direction, hence the concentrations of reactants increase while concentration of products decrease.

Question 25

Which of the following changes will shift this equilibrium reaction in the forward direction?

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad \Delta H = 52\ \text{kJ mol}^{-1}$$

(a) Increasing the pressure of the system

(b) Increasing the temperature of the system

(c) Addition of a suitable catalyst

(d) Removal of iodine from the system

(b) shifts equilibrium to the right to remove the added heat according to Le Chatelier's principle.

(a) and (c) do not change equilibrium position, (d) will shift equilibrium to the left.

Question 26

For the following equilibrium, explain the effect that each change will have on the equilibrium with reference to Le Chatelier's principle.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H < 0$$

(a) The volume of the system is decreased. 2

Decreasing the volume of the system will cause an increase in pressure in the system which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift to the side with less gas moles to reduce pressure in order to minimise the disturbance. Thus the equilibrium will shift in the forward direction.

(b) SO_3 is removed as it forms. 2

Removal of SO_3 decreases the concentration of SO_3 in the equilibrium mixture, thus disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift to the right to replace SO_3, minimising the disturbance.

(c) The reaction is performed at a higher temperature. 2

Increasing temperature disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift in the endothermic direction, to the left, to remove some of the added heat to minimise the disturbance.

Question 27

In an aqueous solution containing chloride ions, cobalt(II) ions exists as a mixture of two complex ions at equilibrium:

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^{-}{}_{(aq)} \rightleftharpoons [CoCl_4]^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

(pink) (blue)

(a) Outline a suitable method to qualitatively investigate the effect of adding and removing reactants from this equilibrium. The laboratory has the following materials available. 3

- 0.1 M cobalt(II) nitrate solution
- Concentrated hydrochloric acid
- 0.1 M silver nitrate solution

Note: Silver chloride (AgCl) is insoluble.

1. Add 10.0 mL of 0.1 M $Co(NO_3)_2$ solution to a 50 mL beaker. Add concentrated hydrochloric acid in approximately 0.5 mL increments until the solution turns purple when evenly mixed.

2. Transfer 3 mL of this equilibrium mixture into 3 separate test tubes and label A, B and C, respectively. Note the initial colour of solution in each test tube.

3. Leave the solution in test tube A as a control.

4. Add 1 mL of concentrated HCl was to test tube B.

5. Add 0.1 M silver nitrate solution to test tube C.

6. Record the final colour of the solution in each test tube.

(b) State an observation that could be made to indicate that the system has reached equilibrium. Explain your answer. 2

Colour should remain constant since the concentration of the coloured reactant and product does not change at equilibrium.

Temperature remains constant since heat is produced at the same rate as it is consumed.

(c) Provide the expected observations from the method outlined in (a) and explain your answer. 4

Addition of concentrated HCl increases the concentration of Cl^- ions, which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift right to remove some of the added Cl^- ions and minimise the disturbance. Thus the concentration of $[CoCl_4]^{2-}$ increases and the solution in tube B will appear more blue.

Addition of silver nitrate decreases the concentration of Cl^- ions which disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift left to produce more Cl^- ions and minimise the disturbance. Thus the concentration of $[Co(H_2O)_6]^{2+}$ decreases and the solution in tube C will appear more pink.

Tube A is a control, thus no change in colour will be observed.

(d) Outline the safety precautions associated with this investigation. 2

Substance	Hazard
Cobalt(II) nitrate	Toxic by ingestion, body tissue irritant, suspected carcinogenicity and reproductive toxicity, toxic to aquatic life, oxidising
Concentrated hydrochloric acid	Highly toxic by ingestion or inhalation and is severely corrosive to skin and eyes
Silver nitrate	Corrosive, oxidising

Use safety goggles, gloves and lab coat when handling, perform experiment near water source so spills on skin can be quickly rinsed off. Have a weak base on hand for neutralising acid spills on the bench. Keep away from flammable materials.

(e) Suggest a method to determine whether the forward reaction is exothermic or endothermic. 2

Increase the temperature of the solution and monitor the colour change. Heating favours the endothermic reaction. If the solution becomes more blue upon heating, the forward reaction was favoured and is endothermic. If the solution becomes more pink upon heating, the reverse reaction was favoured, hence forward reaction is exothermic.

Question 28

The Haber process can be summarised with the following chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

(a) With reference to Le Chatelier's principle, explain what happens to the product yield when ammonia is liquefied. 3

Liquefying the ammonia gas decreases the concentration of $NH_{3(g)}$. According to Le Chatelier's principle, this will disturb the equilibrium and cause the equilibrium to shift to the right to replenish the $NH_{3(g)}$ to minimise the disturbance. Thus there will be an increase in the yield of ammonia.

(b) Explain why temperature and pressure conditions are important for optimising both the yield and rate of the Haber process. 4

Hint: Your answer should include

How the temperature affects the yield, with reference to Le Chatelier's principle

How the temperature affects the rate, with reference to collision theory

How the pressure affects the yield, with reference to Le Chatelier's principle

How the pressure affects the rate, with reference to collision theory

Temperature:

According to Le Chatelier's principle, high temperatures favour the endothermic reaction to remove heat and minimise the disturbance. Since the forward reaction is exothermic, a high temperature decreases the yield of ammonia.

However, high temperatures result in an increased rate of reaction as increased kinetic energy causes more effective collisions. The opposite is the case at low temperatures.

As a result, a compromise must be made between high and low temperatures due to their opposite effects on yield and reaction rate. This is done by utilising a moderate temperature.

Pressure:

Increased pressure disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift to the side with less gas moles to reduce pressure and minimise the disturbance. Hence a higher yield of ammonia is achieved at high pressures.

Due to all the species of the reaction being gaseous, an increase in pressure increases the rate of reaction as the reaction components are brought closer together resulting in an increase in the frequency of collisions.

Hence high pressures are optimal for both reaction rate and yield.

Note: Although high pressures are optimal for both reaction rate and yield, maintaining these pressures is both expensive and possibly dangerous. Low pressures result in lower yield and reaction rate. Thus pressure must be monitored and maintained carefully in industry to ensure maximum efficiency whilst maintaining safety.

Question 29

Colourless hydrogen iodide was placed inside a sealed container and the following equilibrium reaction was established with colourless hydrogen and purple iodine gases:

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

The container was cooled and the intensity of the purple colour increased. Deduce whether the forward reaction is exothermic or endothermic, explaining your reasoning. 3

Cooling disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium will shift in the exothermic direction to produce more heat in order to minimise the disturbance. Since the container became more purple when cooled, this means more I_2 was formed, and the equilibrium had shifted to the right. Hence the forward reaction is exothermic.

Question 30

Phosgene, $COCl_2$, is used for the production of plastics and polycarbonate. One method of production of phosgene is via the reversible exothermic reaction between carbon monoxide and chlorine gases. At 8 °C, phosgene condenses to form a liquid.

(a) Write a balanced equation for the production of phosgene. 1

$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$

(b) Identify two methods that could be utilised in industry to maximise the production of phosgene. Justify your answer. 4

Any two of the following with an explanation:

Decrease temperature (increased yield but decreased rate)

Increase pressure

Increase concentration of a reactant (or both)

Removal of the product i.e. removal of phosgene by liquefying below 8 °C and opening the tap

Catalyst (doesn't affect yield but increases speed at which yield is reached)

Note: rate arguments are included due to wording of question: how industry could maximise production.

Question 31

(a) Outline a procedure that could be used to qualitatively analyse the effects of adding and removing reactants from the following equilibrium reaction.

$$2CrO_4{}^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \rightleftharpoons Cr_2O_7{}^{2-}{}_{(aq)} + H_2O_{(l)}$$

(yellow) (orange)

Note: Barium chromate ($BaCrO_4$) is insoluble, while barium dichromate ($BaCr_2O_7$) is soluble.

3

1. Mix 10 mL of 0.1 M sodium chromate and 10 mL of 0.1 M nitric acid in a 50 mL beaker.

2. Transfer 6 mL of the equilibrium mixture into each of 3 test tubes. Label them A–C.

2. To test tube A, add 1 mL of 2 M sodium chromate. Record the colour.

3. To test tube B, add 1 mL of 2 M barium nitrate. Record the colour.

4. Keep test tube C as a control.

(b) State the expected observations from the method outlined in (a). 2

Tube A: colour turns more orange

Tube B: colour turns more yellow

Tube C: colour remains light orange

Question 32

An aqueous solution of nickel(II) ions is green. When mixed with ammonia solution, an equilibrium mixture with blue nickel-ammonia complex is formed.

$$Ni^{2+}_{(aq)} + 6NH_{3(aq)} \rightleftharpoons [Ni(NH_3)_6]^{2+}_{(aq)}$$

(green) (blue)

(a) Explain the colour change observed when solid nickel(II) nitrate is added to the equilibrium solution. 3

Nickel(II) nitrate dissolves to produce Ni^{2+} ions, increasing its concentration. This disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium shifts right to remove some of the added Ni^{2+} ions and minimise the disturbance. As a result, more $[Ni(NH_3)_6]^{2+}$ will form and the solution will become more blue.

(b) Hydrochloric acid reacts with ammonia to form ammonium chloride. Explain the colour change observed when hydrochloric acid is added to the equilibrium solution. 3

Addition of hydrochloric acid decreases the concentration of NH_3 and disturbs the equilibrium. According to Le Chatelier's principle, the equilibrium shifts left to produce more NH_3 and minimise the disturbance. As a result, more Ni^{2+} will be produced and the solution will become more green.

Question 33

You have performed a first-hand practical investigation involving an equilibrium reaction.

(a) Outline the procedure you used. **3**

1. 0.5 mL of 0.1 M $Fe(NO_3)_{3(aq)}$ and 0.5 mL of 0.1 M $KSCN_{(aq)}$ were added to a 50 mL beaker. Then 15 mL of distilled water was added to the beaker and the solution was evenly mixed.

2. 3 mL of this solution was transferred into 4 separate test tubes and labelled A, B, C and D, respectively. The initial colour of solution in each test tube was noted.

3. The solution in test tube A was used as a control.

4. 1 mL of 0.1 M $Fe(NO_3)_{3(aq)}$ was added to test tube B.

5. 1 mL of 0.1 M $KSCN_{(aq)}$ was added to test tube C.

6. 1 mL of 0.1 M $NaOH_{(aq)}$ was added to test tube D.

7. The final colour of the solution in each test tube was recorded.

(b) Explain how you qualitatively analysed the equilibrium reaction. **4**

The change in colour of the solution was used to analyse the equilibrium reaction.

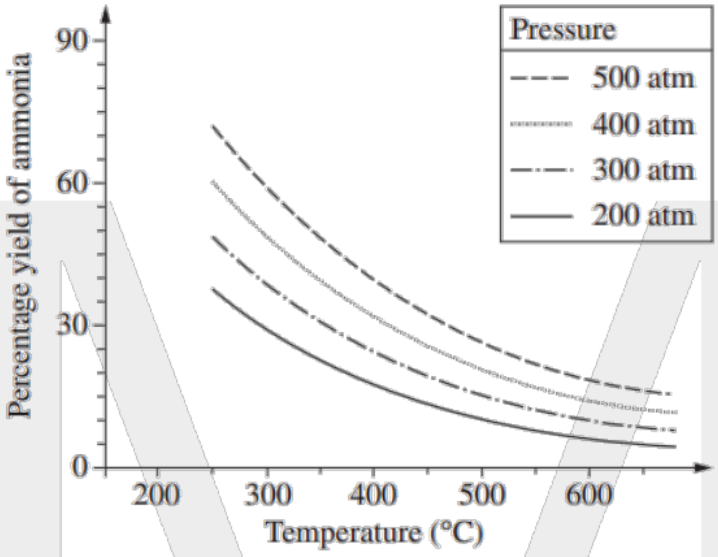
$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$

(yellow) (red)

The initial colour of the solution in the test tubes was orange. The colour of the solution in tube A did not change as the equilibrium was not disturbed. The colour of the solution in tube B became a more intense red. This is because the concentration of $Fe^{3+}_{(aq)}$ was increased, causing the equilibrium to shift right to remove some of the added $Fe^{3+}_{(aq)}$ (Le Chatelier's principle). Thus the concentration of $[Fe(SCN\ ]^{2+}_{(aq)}$ increased causing a more intense red colour. The final colour of the solution in tube C also became a more intense red. This is because concentration of $SCN^{-}_{(aq)}$ was increased, causing the equilibrium to shift right to use up some of the added $SCN^{-}_{(aq)}$ (Le Chatelier's principle). Therefore, the concentration of $[Fe(SCN)]^{2+}_{(aq)}$ increased, intensifying the red colour. The final colour of the solution in tube D became a less intense red. This is because the added $OH^{-}_{(aq)}$ ions reacted with the $Fe^{3+}_{(aq)}$, causing a decrease in the concentration of $Fe^{3+}_{(aq)}$ and a shift in equilibrium to the left to produce more $Fe^{3+}_{(aq)}$ (Le Chatelier's principle). Therefore the concentration of $[Fe(SCN)]^{2+}_{(aq)}$ decreased causing a less intense red colour.

Question 34 **[2015 HSC Q30 modified]**

The graph shows the percentage yield of ammonia produced from nitrogen and hydrogen at different temperatures and pressures via the Haber process.



Industrially, the Haber process is conducted at 450 °C and 250 atm in the presence of an iron oxide catalyst.

Explain the conditions used industrially in the Haber process with reference to the graph. 5

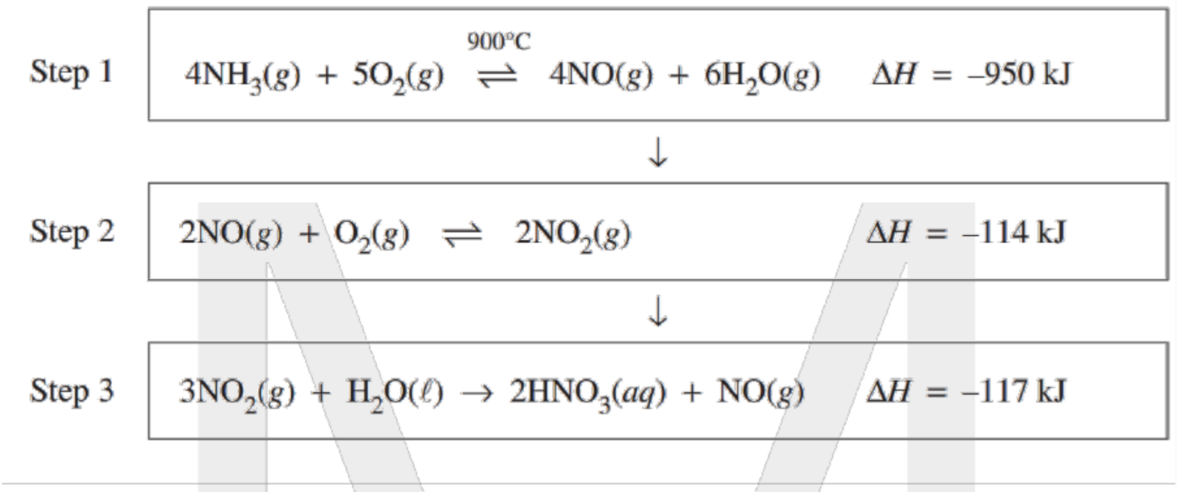
The following reaction produces ammonia in the Haber process: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

The reaction is exothermic. Hence, if temperature is lowered, the equilibrium would shift to the right to minimise the disturbance (Le Chatelier's principle), increasing the yield. This is shown by the downward slope of the graphs. However, the rate is unfeasibly low at low temperatures; hence a moderate temperature of 450 °C is used. An iron oxide catalyst is used in industry to increase the rate at this relatively low temperature.

There are less gas moles on the product side, so if pressure is increased, the equilibrium would shift right to minimise the disturbance (Le Chatelier's principle) and increase yield. This is shown in the graph as the 500 atm curve lies above the 200 atm curve, for example. However, high pressures are expensive and unsafe, hence a compromise of 300 atm is used in industry. Additionally, a 1:3 ratio of N_2 to H_2 is used to avoid build-up of excess reactant, and NH_3 is removed via liquefaction which pushes the equilibrium to the right, increasing yield.

Question 35 **[2011 HSC Q30]**

The flow chart outlines the sequence of steps in the Ostwald process for the manufacture of nitric acid.



Step 1 $4NH_3(g) + 5O_2(g) \overset{900°C}{\rightleftharpoons} 4NO(g) + 6H_2O(g) \quad \Delta H = -950\ kJ$

↓

Step 2 $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114\ kJ$

↓

Step 3 $3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g) \quad \Delta H = -117\ kJ$

Explain the reaction conditions required at each step of the Ostwald process to maximise the yield and production rate of nitric acid. 6

Hint: Plan your response before you start writing it.

Step 1 in the process is very exothermic as increasing the temperature will force the reaction in the reverse direction. However, as indicated, the reaction occurs at 900 °C. This high temperature is necessary to keep up the rate of reaction. To compensate for the high temperature, it would be appropriate to decrease the pressure. This would force the reaction in the forward direction, as there are more moles of product than moles of reactants. Removing NO as it forms would speed up the reaction.

In Step 2, the temperature isn't as critical as the ΔH is only −114 kJ. NO_2 is more stable than NO in the presence of O_2. For this reaction, an increase in pressure is necessary in order to force the reaction to the product side, producing more NO_2. NO_2 should also be removed as it forms to keep the reaction proceeding in the forward direction.

Step 3 is not an equilibrium reaction; therefore, increasing the temperature will increase the rate of reaction, producing more HNO_3 despite it also being exothermic reaction.

Catalysts should be used in all steps to also speed up the rate of reaction.

Year 12
Chemistry
Equilibrium and Acid Reactions

Work Book 3
Qualitative analysis of equilibrium

MATRIX
EDUCATION

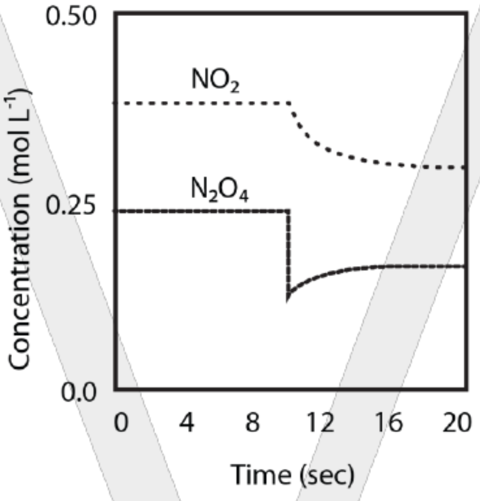
Part A: Multiple choice questions

Question 1

The decomposition of dinitrogen tetroxide can be summarised by the following equilibrium equation:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

The graph below shows the concentration of reaction components at equilibrium until a disturbance occurs and a new equilibrium is found.



The disturbance shown in this graph was caused by:

(a) the removal of N_2O_4 gas

(b) an increase in the temperature

(c) a shift to the left

(d) an increase in the volume of the container

Spike downwards means species has been removed

Equilibrium shifts to the left side as shown by the increase in N_2O_4 and decrease in NO_2 after the disturbance. The shift is consistent with the predictions from Le Chatelier's principle.

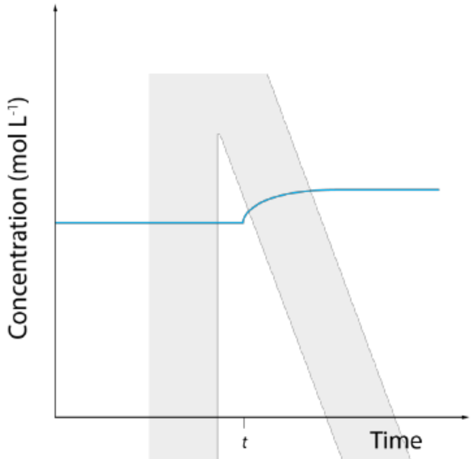
Question 2

Consider the following equilibrium:

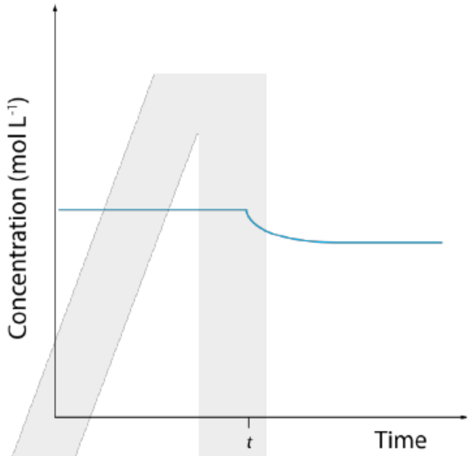
$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad \Delta H = +175 \text{ kJ mol}^{-1}$$

Which of the following correctly represents the change in concentration of carbon dioxide as the temperature is increased at time *t*?

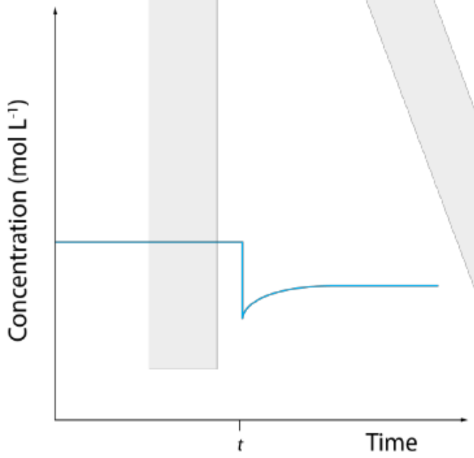
(a)



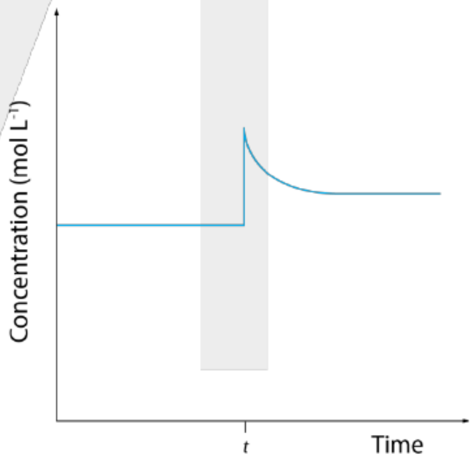
(b)



(c)



(d)



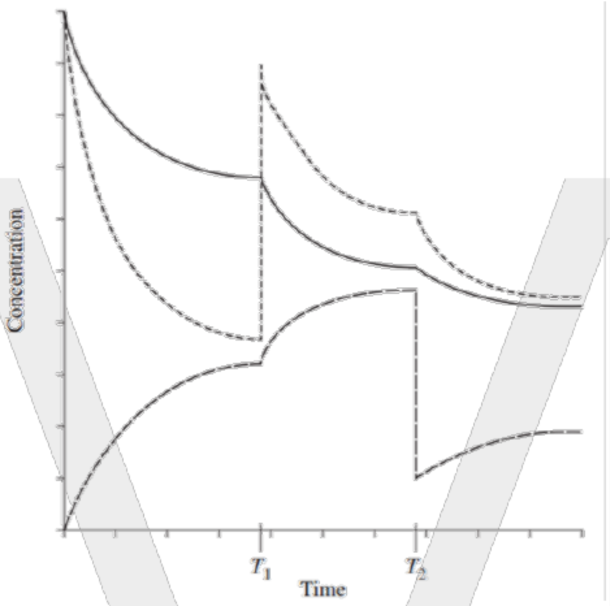
No spikes for change in temperature

According to Le Chatelier's principle, the equilibrium will shift in the endothermic direction when heated, to remove the added heat to minimise the disturbance. This is the forward direction, so the concentration of $CO_{2(g)}$ increases.

Question 3 **[2012 HSC Q16]**

The graph shows the concentrations over time for the system:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$



What has happened at times T_1 and T_2?

	T_1	T_2
(a)	H_2 added	CH_3OH removed
(b)	CO added	CH_3OH removed
(c)	H_2 added	CO removed
(d)	CO added	CO and H_2 removed

Bottom long-dash line is CH_3OH as it forms as the other two species are used up.

Solid line is CO as it is consumed at half the rate as the short-dash line, which is H_2

T_1 – upward spike in short-dash line only = addition of H_2

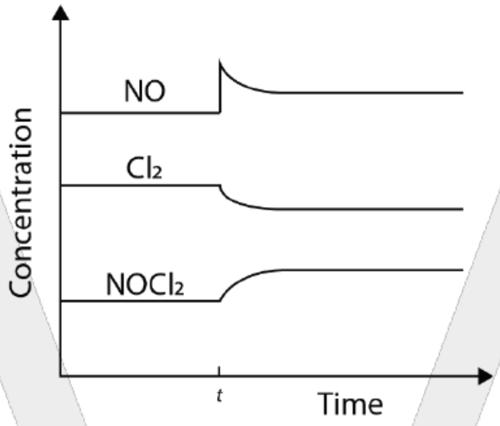
T_2 – downward spike in long-dash line only = removal of CH_3OH

Question 4

Nitrosyl chloride (NOCl) decomposes according to the following equilibrium reaction:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g} \qquad \Delta H \text{ is positive}$$

A concentration-time graph for this system is shown below.



What event occurred at time *t* to cause the change in equilibrium concentrations?

(a) The pressure was decreased at a constant temperature.

(b) The temperature was increased at a constant volume.

(c) A catalyst was added at a constant temperature and volume.

(d) NO gas was added at a constant volume and temperature.

Upward spike in one species only signals addition of that component.

Equilibrium shifts to the left afterwards, consistent with addition of NO (Le Chatelier's principle).

Question 5

Consider the following equilibrium reaction:

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

Which of the following describes the change in the rate of the forward reaction when carbon monoxide gas is added to the system and as the system returns to a new equilibrium?

(a) The rate of the forward reaction will increase until a new equilibrium is reached.

(b) The rate of the forward reaction will decrease until a new equilibrium is reached.

(c) The rate of the forward reaction will increase initially and then decrease until a new equilibrium is reached.

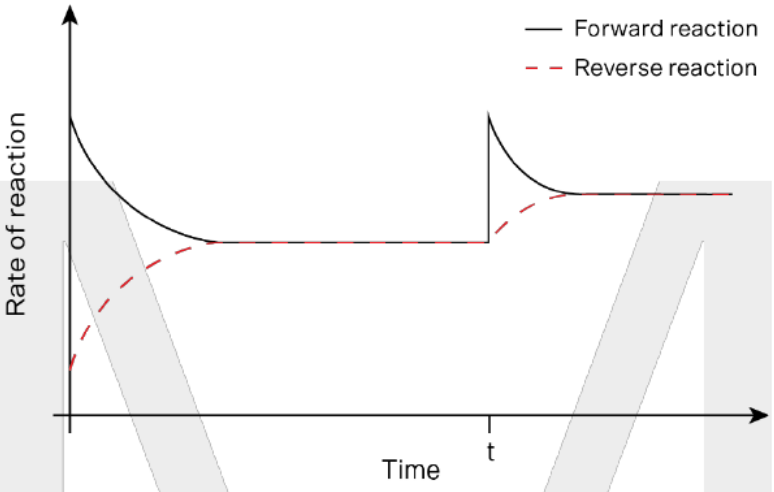
(d) The rate of the forward reaction will decrease initially and then increase until a new equilibrium is reached.

Addition of CO will result in more collisions between reactants, hence rate of the forward reaction increases. As the forward reaction proceeds, the concentration of the reactants decrease, thus rate will decrease until a new equilibrium is established.

Question 6

Consider the rate-time diagram for the following equilibrium reaction:

$$Cl_{2(g)} + SbCl_{3(g)} \rightleftharpoons SbCl_{5(g)}$$



What disturbance occurred at time t?

(a) Addition of a catalyst

(b) Addition of Cl_2

(c) Addition of $SbCl_5$

(d) A decrease in the volume

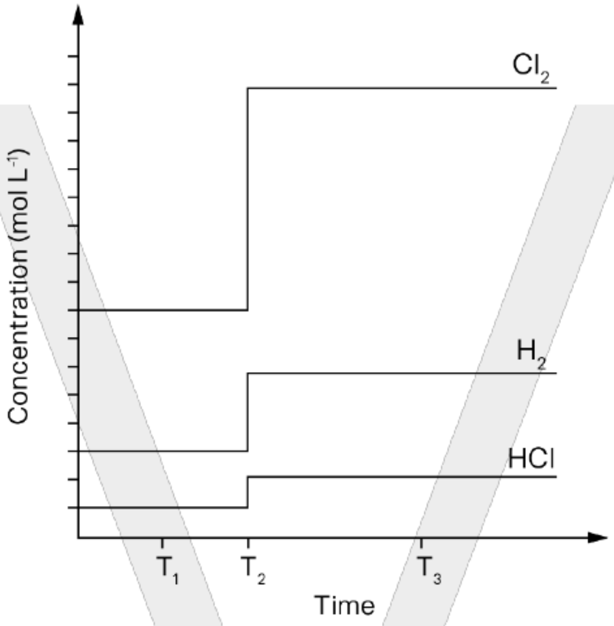
Upward spike in forward rate means its rate is increased. The only change that could cause an instantaneous increase to the rate of the forward reaction with no effect of the rate of the reverse reaction would be the addition of reactant(s).

Question 7

Consider the following equilibrium:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

The concentration profile diagram below shows the concentrations of the reaction components at equilibrium until a change was made to the system.



Which of the following is consistent with the information given in the diagram above?

(a) The moles of HCl at equilibrium is greater at T_3 than T_1.

(b) A catalyst was added to the equilibrium mixture at T_2.

(c) The rate of the forward reaction is greater than the rate of the reverse reaction at T_3.

(d) The rate of production of HCl at T_3 is double the rate of production of HCl at T_1.

Since all concentrations doubled at T_3, the rate of production of HCl is doubled compared to T_1.

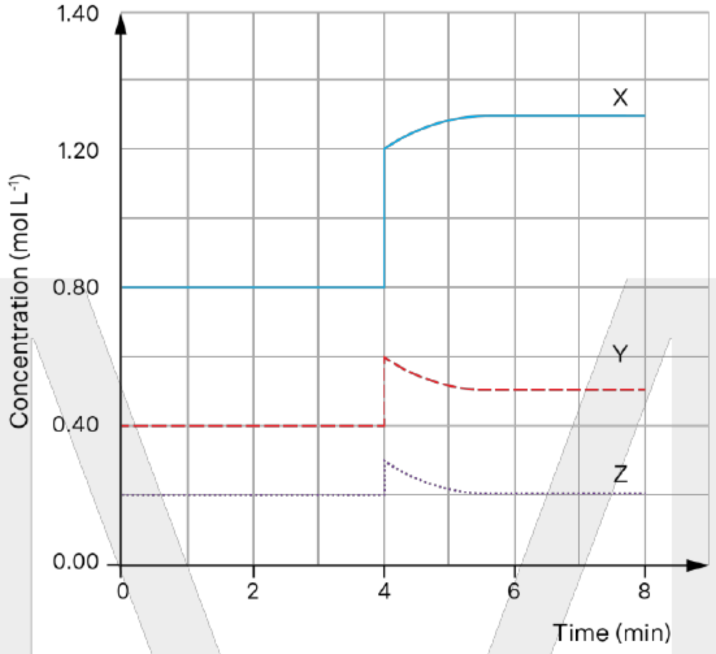
(a) is not correct. The only change that could cause an increase to the concentration of all species is a decrease in volume. However, because there are the same number of gaseous particles on both sides of the equation, the system remains at equilibrium and thus no shift occurs when the volume decreases. Hence there is no effect on the moles H_2, Cl_2 and HCl.

(b) is not correct as a catalyst has no impact on the concentrations of the species.

(c) is not correct as the system is at equilibrium at T_3, hence the forward and reverse rates are equal.

Use the following information to answer questions 8 and 9.

The graph below shows the changes in the concentration of 3 gaseous species over time.



Question 8

Which equation represents the described equilibrium reaction?

(a) $X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$

(b) $4X_{(g)} \rightleftharpoons 2Y_{(g)} + Z_{(g)}$

(c) $4X_{(g)} + 2Y_{(g)} \rightleftharpoons Z_{(g)}$

(d) $X_{(g)} + Y_{(g)} \rightleftharpoons Z_{(g)}$

Y and Z must be on the same side of the equation since they move in the same direction. The gradient of Y and Z are the same, therefore, there is a 1:1 stoichiometry for Y and Z.

Question 9

A disturbance occurs at 4 minutes. Which statement is consistent with the data presented?

(a) At 4 minutes, the volume increased by one-third of the initial volume.

(b) At 4 minutes, the volume increased by two-thirds of the initial volume.

(c) At 4 minutes, the volume decreased by one-third of the initial volume.

(d) At 4 minutes, the volume decreased by two-thirds of the initial volume.

As the concentration of all species increases at 4 minutes, the volume of the gaseous system must have decreased. Considering the concentration change of any one component, and assuming initial volume is 1 L, $V_2 = C_1V_1 / C_2 = 2/3$. Hence volume has decreased by 1/3.

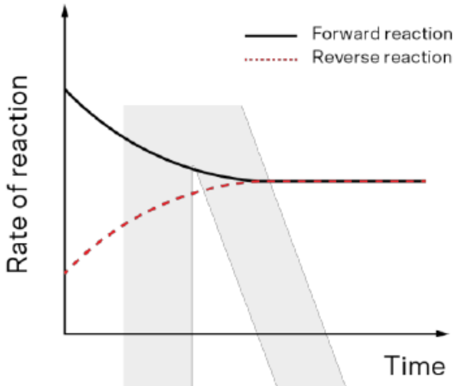
Question 10

Consider the equilibrium below:

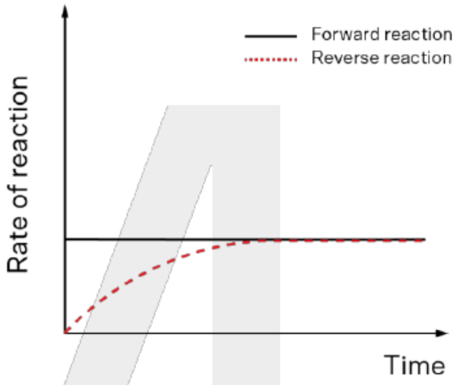
$$X + Y \rightleftharpoons Z$$

Which of the following graphs represents the system establishing equilibrium by shifting towards the left?

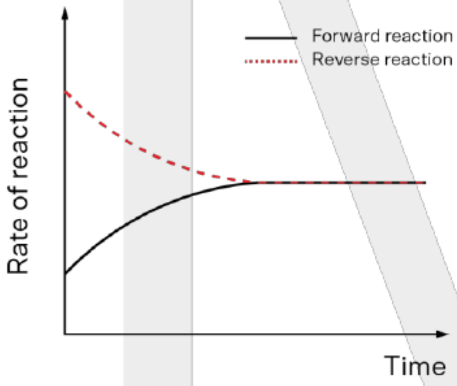
(a)



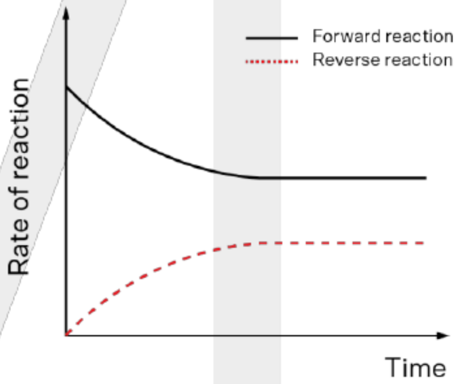
(b)



(c)



(d)



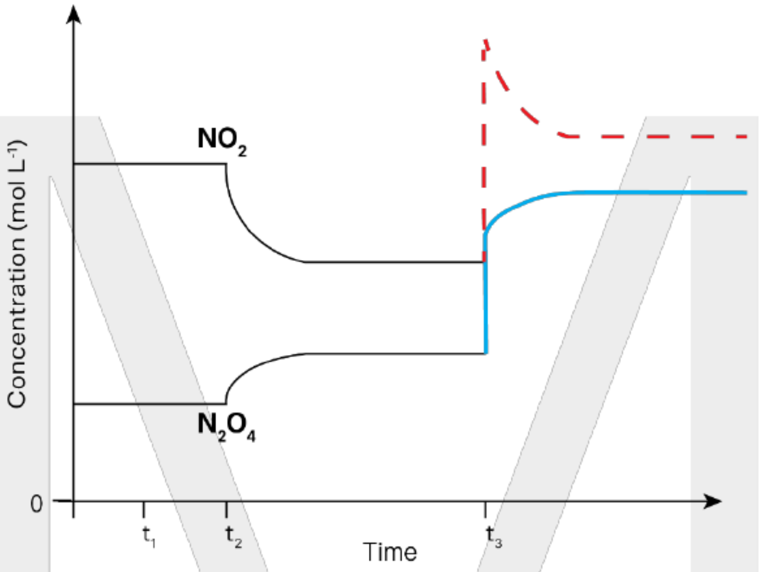
A shift to the left means the reverse rate is faster relative to the forward rate.

Part B: Extended response questions

Question 11

Consider the following diagram for the equilibrium:

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = +57\ \text{kJ mol}^{-1}$



(a) Identify the stress applied at time t_2. Explain your answer. 3

At t_2 there is a decrease in the concentration of products and an increase in reactants with no spikes in concentrations, thus the equilibrium shifted to the left, in the exothermic direction, when temperature was changed. According to Le Chatelier's principle, a decrease in temperature will cause the equilibrium to shift to the exothermic side to produce more heat and minimise the disturbance. Therefore the stress at time t_2 is a decrease in temperature.

(b) At time t_3 the volume of the reaction vessel was reduced.

(i) Sketch on the graph how the concentrations would change from t_3. 2

(ii) Explain the changes shown on your graph. 3

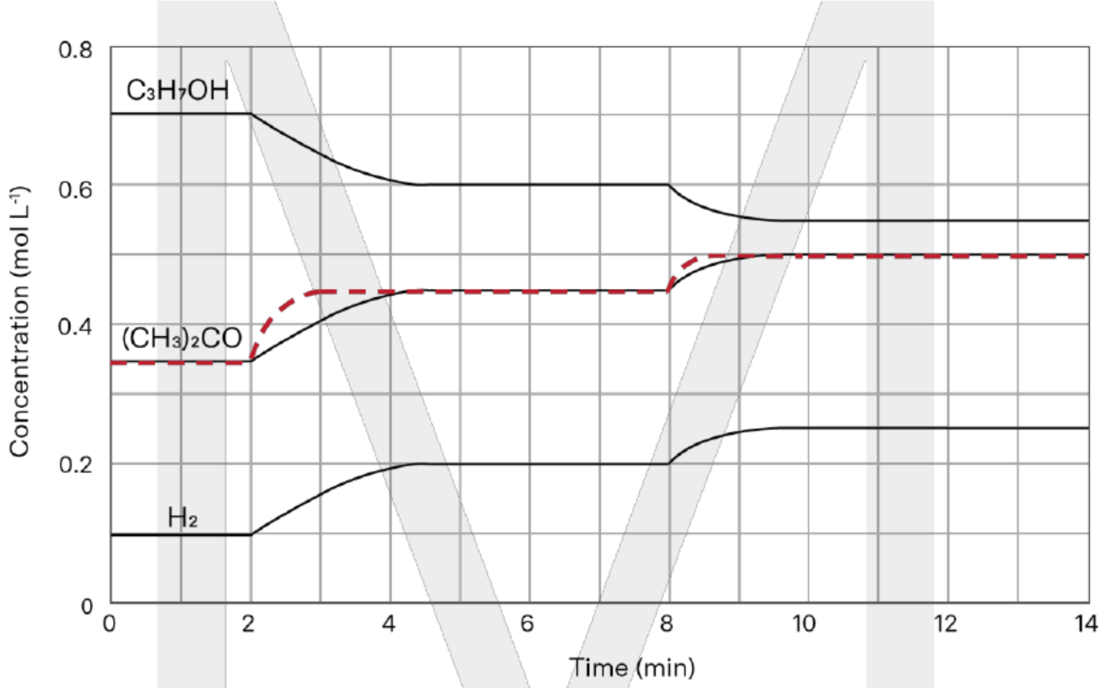
Decreasing volume causes the concentration of all components to increase (spike up). According to Le Chatelier's principle, the equilibrium will shift to the side with less gas moles (left), to decrease the pressure and minimise the disturbance. This decreases the concentration of NO_2 and increases the concentration of N_2O_4. Eventually, the rates of the forward and reverse become equal and the concentrations remain constant.

Question 12

Acetone ($(CH_3)_2CO$) is a common chemical used in nail polish removers. It can be prepared from propan-2-ol (C_3H_7OH) according to the equation:

$$C_3H_7OH_{(g)} \rightleftharpoons (CH_3)_2CO_{(g)} + H_{2(g)}$$

As a part of an investigation, the concentration of the equilibrium mixture was monitored continuously. The temperature of the system was increased at 2 minutes and then again at 8 minutes. A concentration-time graph for this system is shown below.



(a) Determine whether the forward reaction is exothermic or endothermic, explaining your reasoning. 3

According to Le Chatelier's principle, increasing the temperature causes the equilibrium to shift in the endothermic direction to remove some of the added heat to minimise the disturbance. Since more acetone was produced with higher temperatures, the equilibrium shifted right. Thus the forward reaction is endothermic.

(b) Suggest one other method that could be employed to increase yield of acetone. 1

Any one of: increase volume/decrease pressure, remove acetone/H_2, added propanol

(c) When a copper-zinc catalyst is used, the rate of reaction increases. On the graph above sketch another curve showing the changes in the concentration of acetone as the reaction proceeds to equilibrium in the presence of a catalyst. 1

Question 13

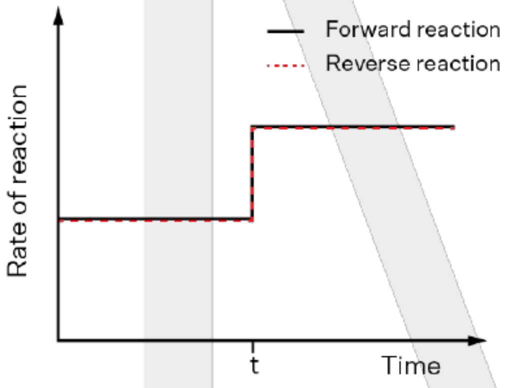
Consider the following equilibrium reaction occurring in a closed system.

$$2X_{(g)} \rightleftharpoons Y_{(g)} + W_{(g)}$$

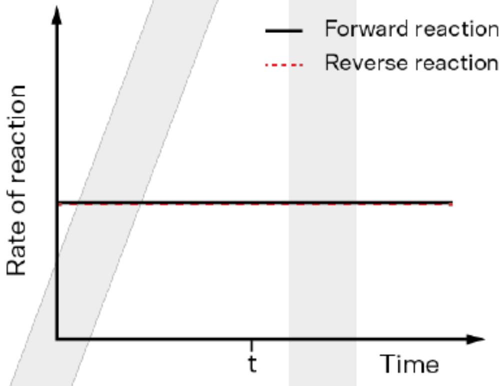
The reaction was repeated a number of times, with different stresses occurring at time t. The stresses include:

- (i) Addition of X
- (ii) Addition of a catalyst
- (iii) Addition of argon gas (at constant volume)
- (iv) Decreased pressure (at constant temperature)

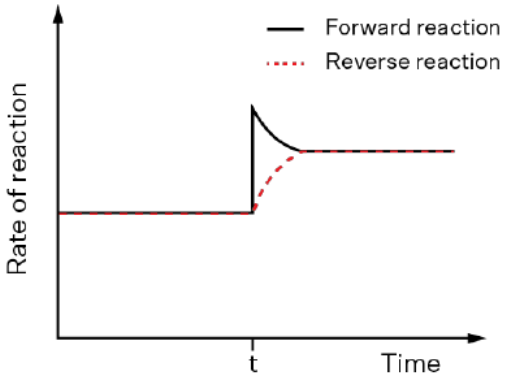
For each of the graphs below, state which of the stresses is consistent with the rate changes shown. 2



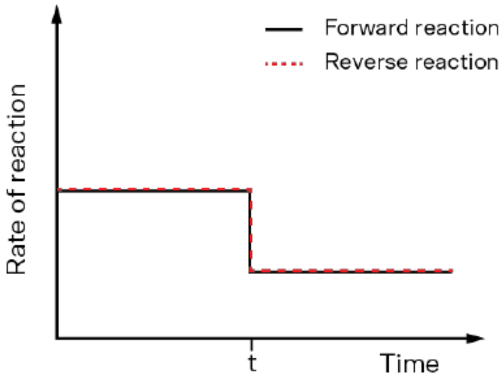
Addition of a catalyst



Addition of argon



Addition of X



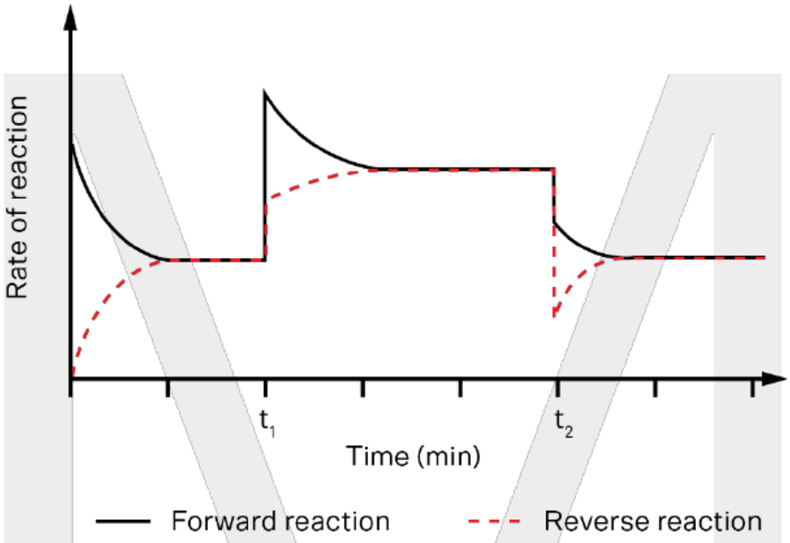
Decreased pressure

Question 14

Consider the following equilibrium system:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad \Delta H = -206 \text{ kJ mol}^{-1}$$

Stresses are made to the equilibrium system at various times as shown in the rate vs time graph below.



Identify and explain each of the stresses at t_1 and t_2 that have shaped the graph above. **4**

At t_1, the volume was decreased (or pressure increased). When the volume decreases, the concentrations of all gaseous species increase, which increases the rate of both the forward and reverse reactions due to a higher frequency of collisions. However, the forward reaction involves a greater number of particles colliding, hence the rate of the forward reaction is increased by a greater extent.

At t_2, the temperature was decreased. When temperature decreases, the rates of both reactions decrease as less collisions exceed the activation energy. However, the endothermic reaction has a higher activation energy, hence there is a greater percentage decrease in the number of collisions exceeding the activation energy of the endothermic reaction. Thus the rate of the reverse endothermic reaction decreases more than the rate of the forward exothermic reaction.

Question 15 **[2019 HSC Q25]**

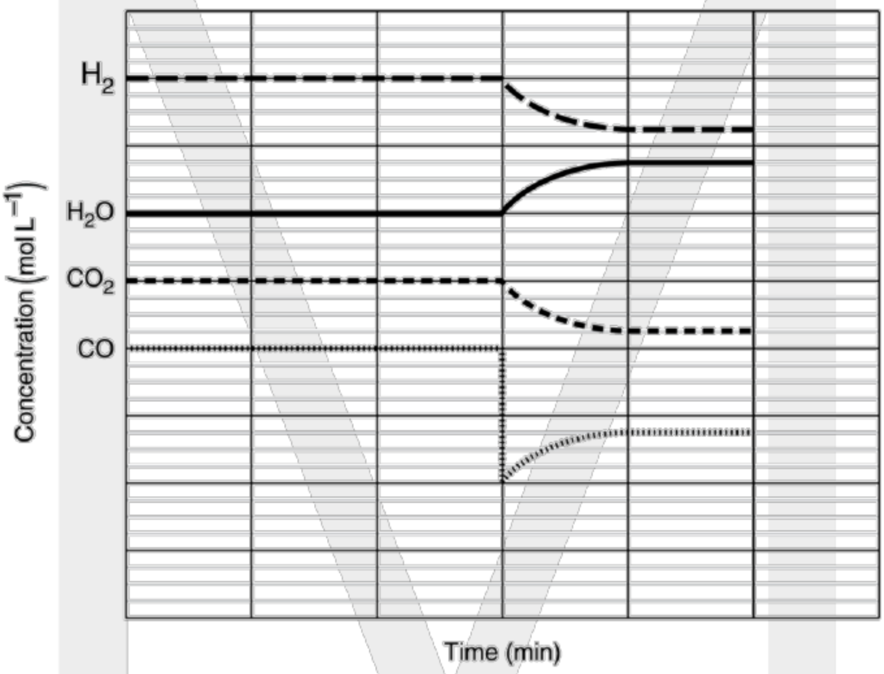
The concentrations of reactants and products as a function of time for the following system were determined.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

At time *T*, some $CO_{(g)}$ was removed from the system.

(a) The concentration of CO after time *T* is shown. 2

Sketch the concentrations after time T for the remaining species.



(b) Using collision theory, explain the change in the concentration of CO after time *T*. 3

At time T, the concentration of CO was decreased.

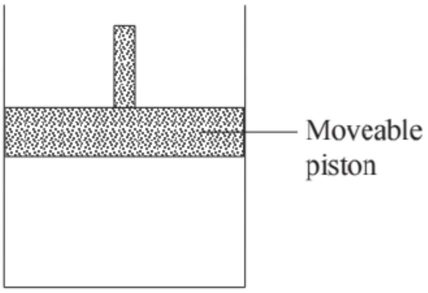
A decrease in the concentration of CO results in a decrease in the rate of the forward reaction due to fewer collisions between CO and H_2O molecules.

The rate of the reverse reaction is now greater than the forward reaction so the concentrations of $H_{2(g)}$ and $CO_{2(g)}$ decrease. As this occurs, the concentrations of $CO_{(g)}$ and $H_2O_{(g)}$ gradually increase.

The rate of the forward reaction subsequently increases until at some point the rate of the reverse reaction will be the same as the rate of the forward reaction as equilibrium is established.

Question 16 **[2023 HSC Q33]**

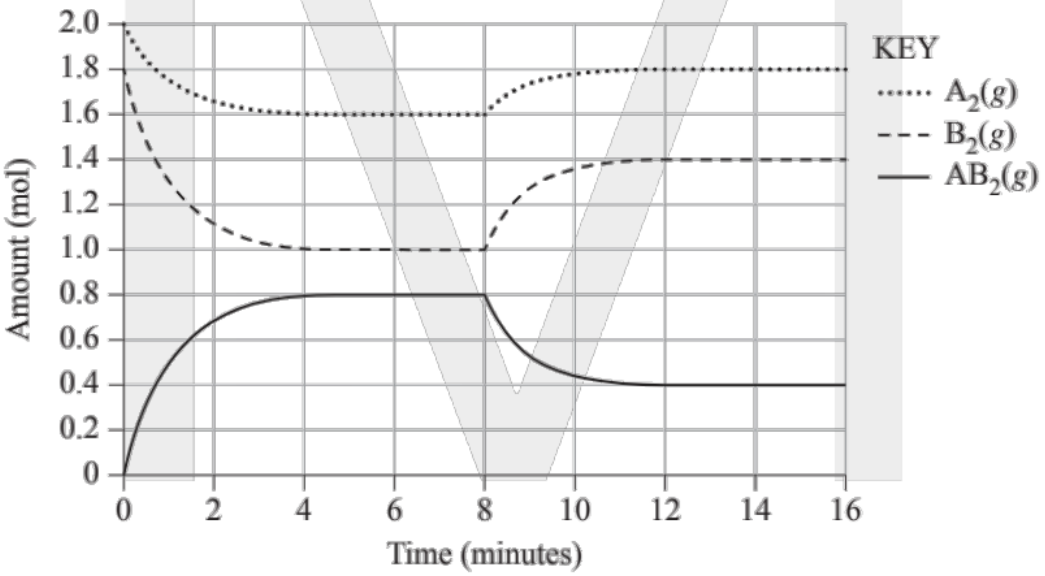
Gases A_2 and B_2 are placed in a closed container of variable volume, as shown.



The reaction between these substances is as follows.

$$A_{2(g)} + 2B_{2(g)} \rightleftharpoons 2AB_{2(g)} \qquad \Delta H = -10 \text{ kJ mol}^{-1}$$

The following graph shows changes in the amounts (in mol) of these three substances over time in this container.



(a) Explain what is happening in this system between 6 minutes and 8 minutes. **2**

Between 6-8 minutes, the system is at dynamic equilibrium. At dynamic equilibirum, the rate of the forward reaction is equal to the rate of the reverse reaction, hence the moles of the reaction componenets remain constant.

(b) Explain TWO different factors that could result in the disturbance at 8 minutes. **4**

The disturbance at 8 minutes does not have any immediate effect on the moles of A_2, B_2 and AB_2. Hence, the disturbance must be a change in temperature or volume. After the disturbance at 8 minutes, the moles of A_2 and B_2 increases and the moles of AB_2 decreases. This means a shift in the reverse direction occurs to counteract the disturbance.

The reverse direction is endothermic, hence an increase in temperature could have occurred at 8 minutes. According to Le Chatelier's principle, an increase in temperature shifts the equilibrium in the endothermic direction to remove added heat and minimise the disturbance.

The reverse direction has more moles of gas, hence an increase in volume or decrease in pressure could have occurred at 8 minutes. According to Le Chatelier's principle, a decrease in pressure shifts the equilibrium in the direction with more moles of gas to increase pressure and minimise the disturbance.

Question 17

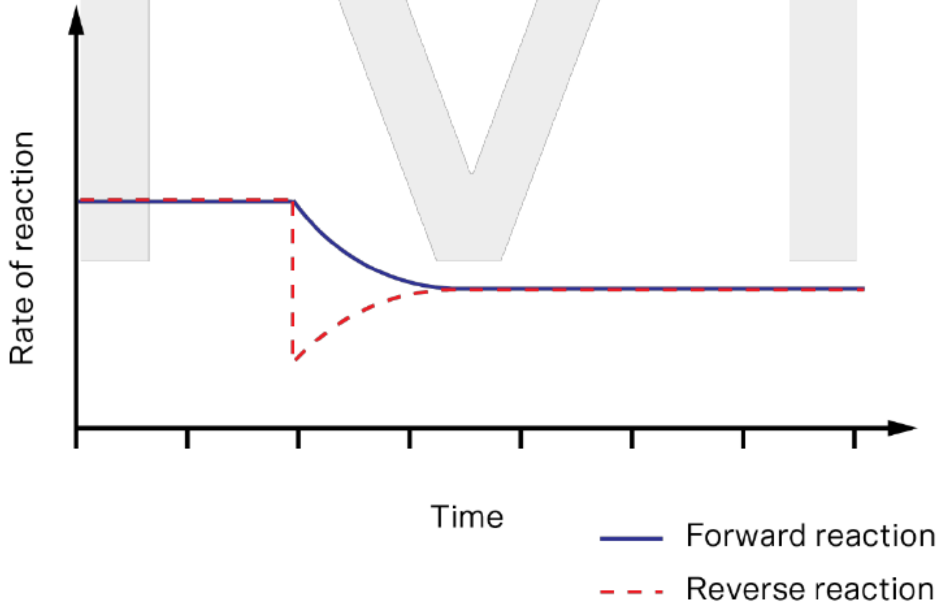
Consider a system containing PCl_3, Cl_2 and PCl_5 that has come to equilibrium.

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)} \qquad \Delta H = -123.5 \text{ kJ mol}^{-1}$$

(a) Describe what happens at the molecular level when PCl_3 is added to this system and explain how the system returns to equilibrium. Assume that the temperature and volume of the system remain unchanged. 3

The addition of PCl_3 leads to a greater number of collisions between PCl_3 and Cl_2, increasing the rate of the forward reaction while the reverse reaction is relatively unaffected. Since the forward rate > reverse rate, the equilibrium shifts to the right. Over time, the concentration of PCl_3 and Cl_2 decreases, leading to less collisions between reactant molecules and a decrease in the rate of the forward reaction. Conversely, more PCl_5 is formed, hence there is an increase in the rate of the reverse reaction. Eventually both rates become equal and a new equilibrium is established.

(b) Complete the rate vs time graph illustrating the changes in the forward and reverse rates of reaction when PCl_5 is removed from the system at equilibrium and when the system attains a new equilibrium. 2



(c) What is the relative size of the activation energy for the forward reaction compared to the reverse reaction in the above equilibrium reaction? **1**

The forward reaction is exothermic, hence the activation energy of the forward reaction is smaller than the activation energy of the reverse reaction.

(d) Explain, with reference to collision theory, how increasing the temperature would affect the position of equilibrium. **3**

Increasing the temperature increases both the rate of the forward and reverse reactions as more collisions exceed the activation energy. However, since the activation energy for the reverse reaction is greater than the forward reaction, the proportional increase in the number of collisions exceeding activation energy will be higher for the reverse reaction. Therefore, the rate of the reverse reaction will increase more than the forward reaction, causing the equilibrium to shift in the reverse direction.

(e) Explain, in terms of reaction rates, what happens to the equilibrium mixture when the pressure of the system increases at constant temperature. **3**

When the pressure of the system increases at constant temperature, the gaseous particles are brought closer together and collision frequency increases, which increases the rate of both the forward and reverse reactions. However, the forward reaction involves a greater number of particles colliding, hence the rate of the forward reaction is increased by a greater extent. Hence, equilibrium shifts in the forward direction until a new equilibrium is established, resulting in an increase in the concentration of PCl_5 and decrease in concentration of PCl_3 and Cl_2.

Question 18

Consider the equilibrium system containing hydrogen iodide, hydrogen and iodine gases inside an expandable reaction vessel:

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

At time t, an inert gas was added to the equilibrium mixture at constant pressure and temperature.

(a) Explain what effect this will have on the:

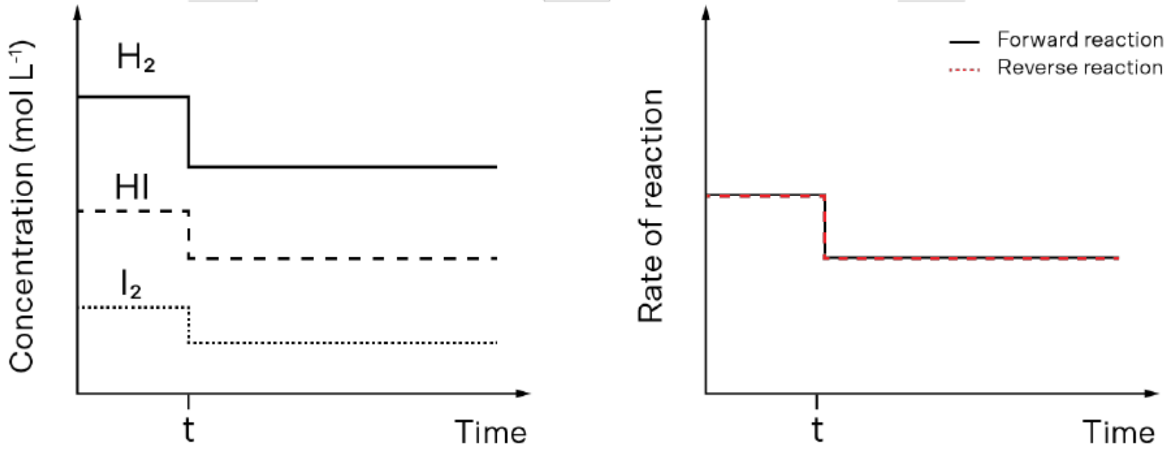
(i) rate of forward reaction and reverse reaction 3

When inert gas is added at constant pressure and temperature, the volume of the system increases. As a result, the frequency of collisions of both the forward and reverse reactions decrease, leading to decreased rates of both the forward and reverse reactions. Since both reactions involve the collision of the same number of particles, both rates decrease by the same extent. As time passes, the forward rate and reverse rate remain equal, but at a lower value than the previous equilibrium state.

(ii) equilibrium position 2

Since both reactions involve the collision of the same number of particles, the forward and reverse rates remain equal when the volume of the system increases. Thus, the equilibrium position will not shift as the system remains at equilibrium.

(b) Complete the graphs below to show the changes that occur to the concentrations of each species and the forward and reverse rates. 2

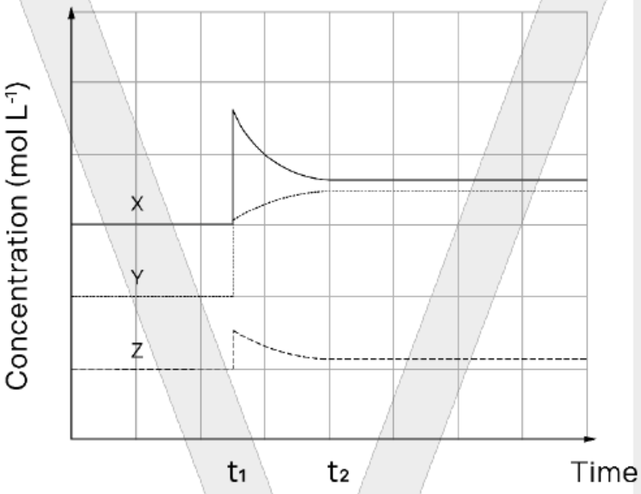


Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 19

Three gases X, Y and Z were added to a closed container and equilibrium was established. At time t_1, the equilibrium was disturbed, and a new equilibrium was established at t_2. The concentration of each gas is plotted against time. Which equation represents the described equilibrium reaction?



(a) $X_{(g)} + Y_{(g)} \rightleftharpoons Z_{(g)}$

(b) $3X_{(g)} + Z_{(g)} \rightleftharpoons Y_{(g)}$

(c) $X_{(g)} \rightleftharpoons 2Y_{(g)} + Z_{(g)}$

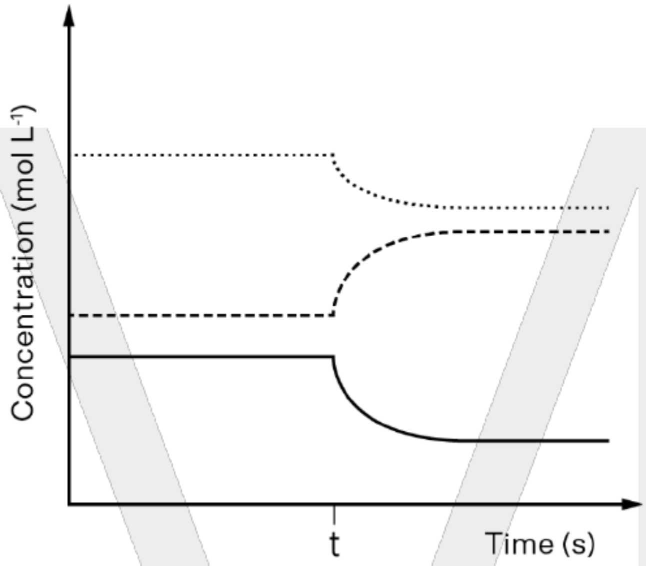
(d) $2X_{(g)} \rightleftharpoons Z_{(g)} + Y_{(g)}$

X and Z must be on the same side of the equation since they move in the same direction. Since the gradient of X is greater than the gradient of Z, X must have a greater stoichiometric coefficient in the balanced equation.

Question 20

The graph below shows the concentration of reaction species of the following reversible reaction:

$$2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + 2Br_{2(g)}$$



At time t, the temperature of the system was decreased. Which correctly describes the forward reaction and the immediate change in the rate of the forward reaction?

(a) Exothermic and forward rate increases

(b) Exothermic and forward rate decreases

(c) Endothermic and forward rate increases

(d) Endothermic and forward rate decreases

The dashed line represents the concentration of NOBr. The equilibrium shifts left when temperature decreases as the concentration of NOBr increases after time t. Decreasing the temperature will shift equilibrium in the exothermic direction, hence the reverse reaction must be exothermic and the forward reaction is endothermic.

A decrease in temperature decreases kinetic energy, therefore less molecules with sufficient energy collide, hence rate in both directions decreases.

Refer to the following information for Questions 21 & 22

Consider the following equilibrium:

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

Some $CO_{2(g)}$ is removed from this system at equilibrium.

Question 21

Which of the following correctly identifies the immediate change to the rates of the forward and reverse reactions?

	Forward rate	Reverse rate
(a)	increases	no change
(b)	increases	decreases
(c)	no change	decreases
(d)	no change	increases

Removal of $CO_{2(g)}$ decreases its concentration. This means less collisions between the products will occur, decreasing the rate of the reverse reaction, while the forward reaction is unaffected.

Question 22

Which of the following correctly identifies the change to the rates of the forward and reverse reactions after the new equilibrium is established, compared to the rates before the disturbance?

	Forward rate	Reverse rate
(a)	increased	increased
(b)	increased	decreased
(c)	decreased	increased
(d)	decreased	decreased

As equilibrium is re-established, the forward rate and reverse rate remain equal, but at a lower value than the previous equilibrium state.

Question 23

The equation describes an equilibrium reaction occurring in a closed system.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons 2C_{(g)}$$

The volume of the reaction flask was decreased when the system was at equilibrium.

Which correctly describes the change in the shape of the graphs of the different substances in the concentration profile diagram when the disturbance occurs?

(a) The concentration of A and B spike up and the concentration of C spikes down.
(b) The concentration of A and B spike down and the concentration of C spikes up.
(c) The concentration of all components spike down.
(d) The concentration of all components spike up.

When the volume of the flask is reduced, the concentrations of all components will be increased.

Question 24

The Haber process for the production of ammonia is given below.

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92\text{ kJ mol}^{-1}$$

Which of the following will increase the rate of reaction?

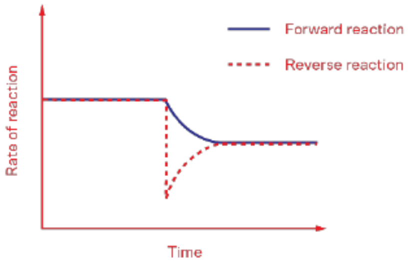
(a) Decreasing the concentration of $NH_{3(g)}$
(b) Increasing the volume of the system
(c) Decreasing the temperature of the system
(d) Increasing the temperature of the system

Decreasing the $[NH_{3(g)}]$ decreases the rate of the reverse but has no effect on the forward rate.

Increasing the volume of the system decreases concentration/pressure of the system which decreases both rate and yield.

Decreasing the temperature of the system decreases the rate of reaction.

Increase in temperature increases kinetic energy, therefore more molecules with sufficient energy collide more frequently, hence increases rate in both directions.

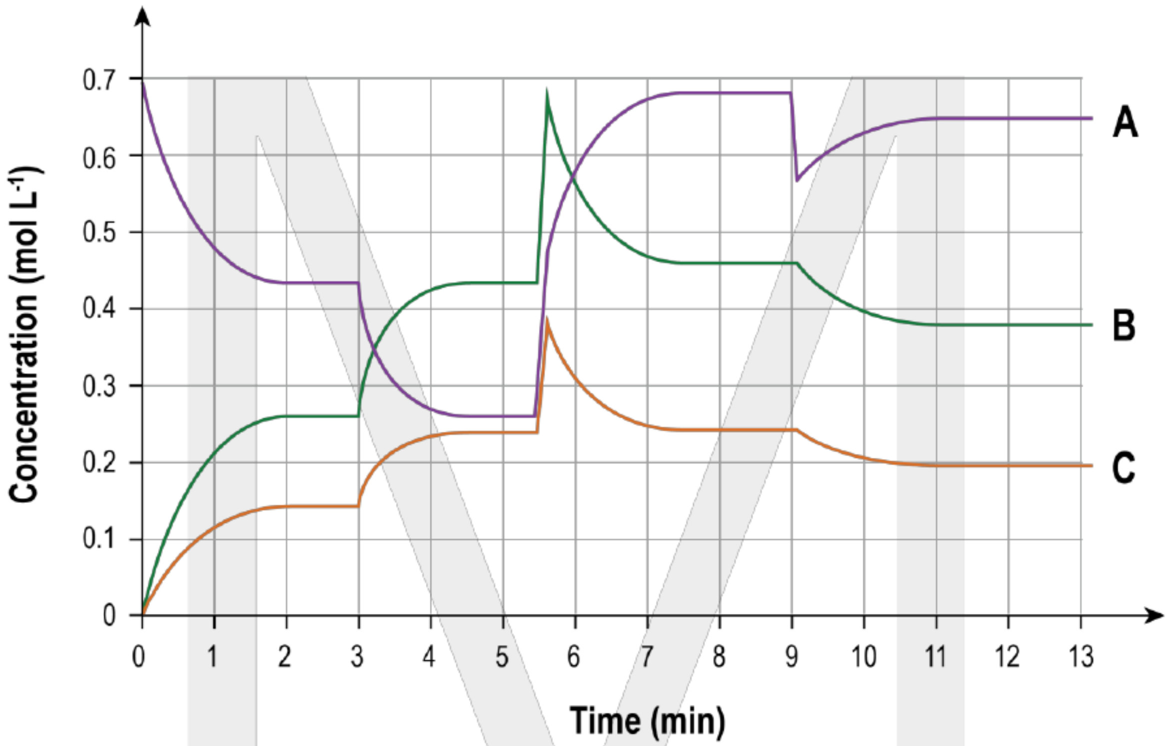


Question 25

Sulfur trioxide, sulfur dioxide and oxygen exist in equilibrium:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)} \qquad \Delta H > 0$$

The changes in the concentrations of the reaction components in a closed system over time are shown below.



(a) Identify each of the species A, B and C from the graph. 1

A: SO_3, B = SO_2, C = O_2 (from mole ratios and direction of change)

(b) Identify and explain each of the changes that have shaped the graph above. 6

0–2 min: SO_3 was placed in a container and decomposed to form SO_2 and O_2. As the forward reaction proceeds, the concentration of SO_3 decreases and the forward reaction slows. As SO_2 and O_2 are formed, their concentration increases and the reverse rate increases.

2–3 min: The reaction has reached equilibrium. Since the forward and reverse rates are equal, the production and consumption of any component occurs at equal rates, hence the concentrations all remain the same.

3 min: An increase in temperature disturbs the equilibrium.

3–4.5 min: According to Le Chatelier's principle, the equilibrium shifts in the forward endothermic direction to remove added heat to minimise the disturbance. This results in a decrease in SO_3 concentration and increases in the concentrations of SO_2 and O_2.

4.5–5.5 min: A new equilibrium has been established.

5.5 min: The volume of the system is decreased, disturbing the equilibrium.

5.5–7.5 min: According to Le Chatelier's principle, the equilibrium shifts in the reverse direction towards the side with less gas moles to minimise the disturbance. This results in an increase in SO_3 concentration and decreases in the concentrations of SO_2 and O_2.

7.5–9 min: A new equilibrium has been established.

9 min: SO_3 is removed from the system, disturbing the equilibrium.

9–11 min: According to Le Chatelier's principle, the equilibrium shifts in the reverse direction to replace the removed SO_3 to minimise the disturbance. This results in an increase in SO_3 concentration and decreases in the concentrations of SO_2 and O_2.

11–13 min: A new equilibrium has been established.

Question 26

When 0.5 mol L^{-1} solutions of silver nitrate and iron(II) nitrate are mixed together, the following equilibrium is established:

$$Ag^{+}_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$$

(a) With reference to Le Chatelier's principle, explain how the equilibrium amount of silver ions is affected by the addition of chloride ions to the system which react to form insoluble silver chloride. 3

Addition of chloride ions will cause a decrease in the concentration of silver ions as it will be reacted to form insoluble silver chloride. According to Le Chatelier's principle, this will disturb the equilibrium and the equilibrium will shift to the left in order to replace the silver ions and minimise the disturbance. Thus the equilibrium amount of silver ions will initially decrease and then increase until a new equilibrium is established.

(b) With reference to collision theory, explain how the equilibrium amount of silver atoms is affected by the addition of solid iron(III) nitrate to the system. 3

Addition of iron(III) nitrate increases the concentration of Fe^{3+}. This means more collisions between the products will occur, increasing the rate of the reverse reaction, while the forward reaction is relatively unaffected. Hence the equilibrium will shift to the left. Thus the equilibrium amount of silver metal will decrease until a new equilibrium is established.

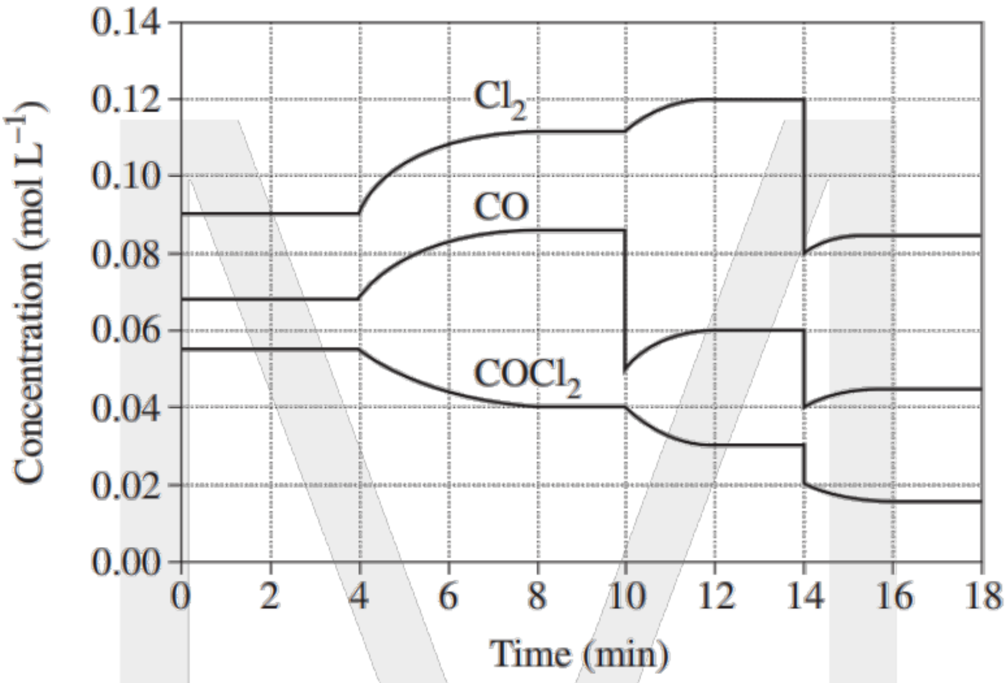
(c) Explain how the equilibrium will be affected by adding a suitable catalyst to the reaction. 2

The addition of a catalyst increases the rate of both the forward and reverse reaction equally. Thus there is no disturbance to the equilibrium and the equilibrium position remains the same.

Question 27 **[2009 HSC Q23]**

The graph shows the variation in concentration of reactant and products as a function of time for the following system.

$$COCl_{2(g)} \rightleftharpoons Cl_{2(g)} + CO_{(g)} \qquad \Delta H = +108 \text{ kJ}$$



Identify and explain each of the changes in conditions that have shaped the curves during the time the system was observed. 6

Sample answer:

Concentrations vary at 4 to 8 minutes, 10 to 12 minutes and 14-16 minutes.

At 4 to 8 minutes the system is moving to the right. There is no indication that Cl_2 or CO have been initially removed or that $COCl_2$ was initially added, hence the temperature has been changed. The reaction is endothermic to the right, so this means heat has been added (temperature has been raised).

The sharp drop in [CO] at 10 minutes means that CO has been removed. The system then moves to the right, seen as an increase in [CO] and [Cl_2] and a decrease in [$COCl_2$].

At 14 min all concentrations abruptly decrease, all by a 2/3 factor hence the volume of the system has increased. As the right side is proportionally more affected than the left hand side, the system moves to the right to compensate, hence [CO], [Cl_2] increases and [$COCl_2$] decreases.

Answers could include:

- Where the graph shows horizontal lines for concentrations, equilibrium has been achieved.

- Discussion on the rate of change

- Discussion on equilibrium states

- Change at 14 min may have occurred because of mechanical or chemical removal of all species, but this is very unlikely.

Question 28

Nitrogen, hydrogen and ammonia come to equilibrium in a closed container.

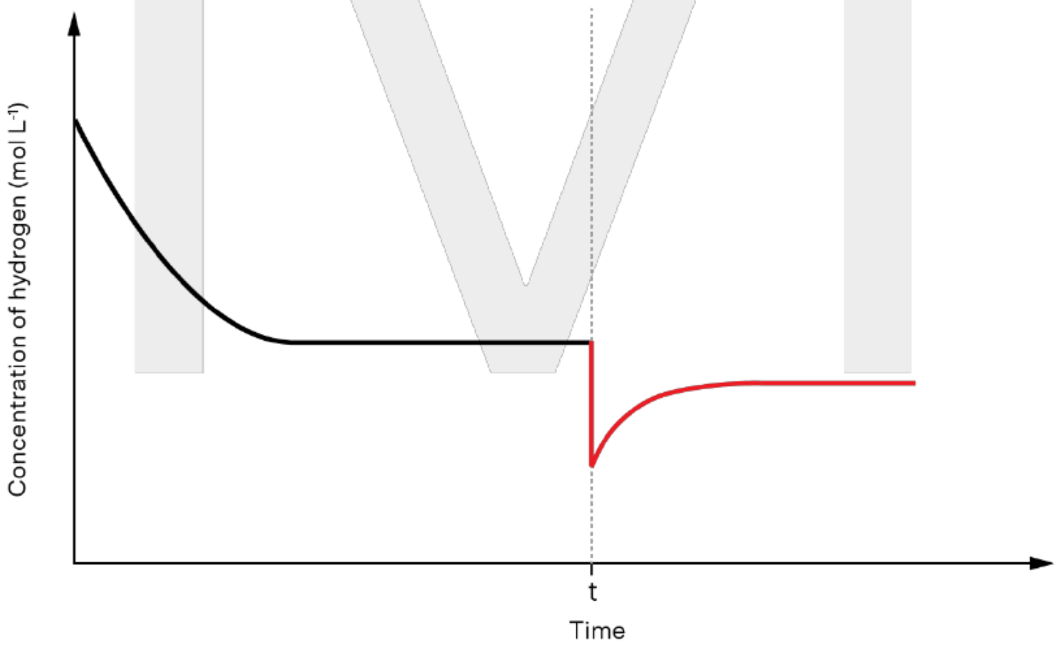
$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

(a) With reference to Le Chatelier's principle, explain any changes to the concentrations of the reaction species when the volume of the container is doubled. 3

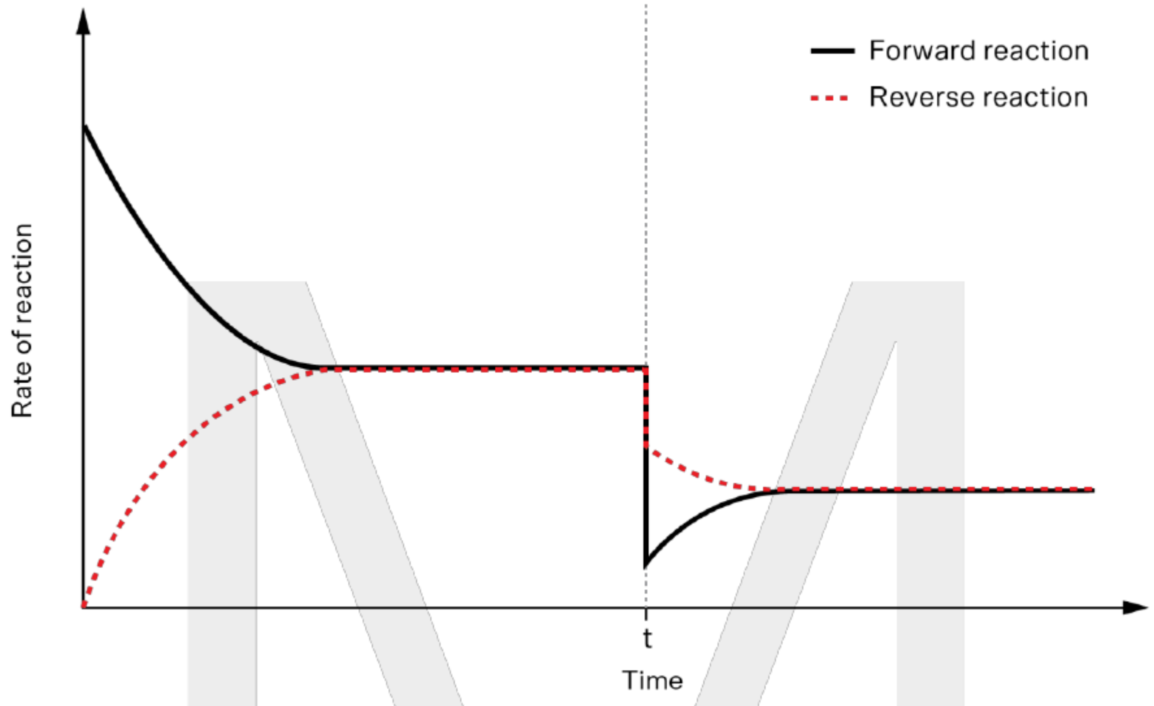
Initially, the concentration of all reaction species would decrease as the volume of the container increases. However, the increase in volume decreases the pressure which disturbs the equilibrium. According Le Chatelier's principle, the equilibrium will shift in the reverse direction to the side with more gaseous moles to increase pressure and minimise the disturbance. So $[H_2]$ and $[N_2]$ would then start to increase while $[NH_3]$ would decrease until equilibrium is re-established.

(b) The volume of the container is doubled at time *t*.

(i) On the graph below, show the impact of this disturbance on the concentration of hydrogen as the system reaches a new equilibrium. 2



(i) On the graph below, show the impact of this disturbance on the forward and reverse reaction rates as the system reaches a new equilibrium. 2

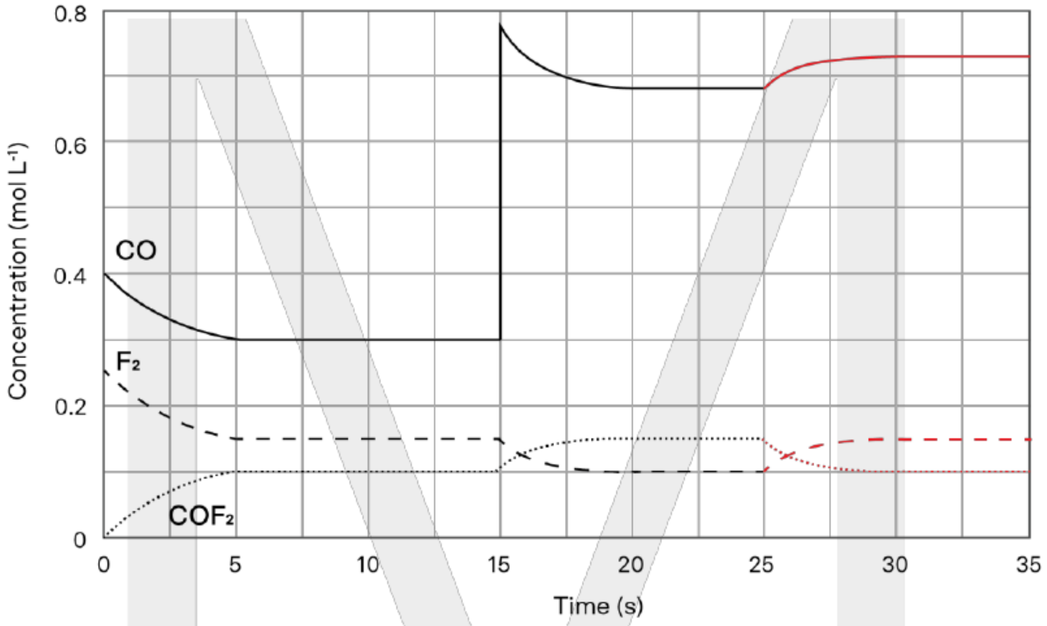


Question 29

Carbon monoxide can react with fluorine to produce carbon oxyfluoride. In a sealed reaction vessel, the reaction reaches equilibrium.

$$CO_{(g)} + F_{2(g)} \rightleftharpoons COF_{2(g)} \qquad \Delta H < 0$$

The changes in the concentrations of the reaction components in a closed system over time are shown below.



(a) Identify and explain each of the changes that have shaped the graph above. **4**

0–5 min: CO and F_2 were placed in a container and reacted to form COF_2. As the forward reaction proceeds, the concentration of CO and F_2 decreases and the forward reaction rate decreases. As COF_2 is produced, its concentration increases and the reverse rate increases.

5–15 min: The reaction has reached equilibrium. Since the forward and reverse rates are equal, the production and consumption of any component occurs at equal rates, hence the concentrations all remain the same.

15 min: An increase in the concentration of carbon monoxide disturbs the equilibrium.

15–20 min: According to Le Chatelier's principle, the equilibrium shifts in the forward direction to remove some of the added CO to minimise the disturbance. This results in a decrease in the concentration of CO and F_2, and an increase in the concentrations of COF_2.

20–25 min: A new equilibrium has been established.

(b) With reference to Le Chatelier’s principle, explain what happens to the concentrations of the reaction species when temperature is increased at t = 25 s. 3

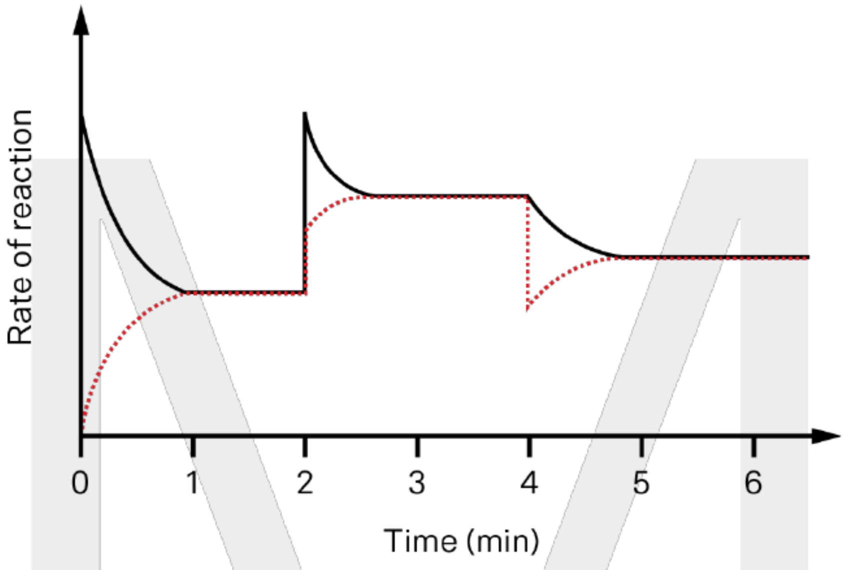
Increasing the temperature disturbs the equilibrium. According to Le Chatelier’s principle, the equilibrium will shift in the reverse endothermic direction to consume the heat in order to minimise the disturbance. This decreases the concentration of COF_2 and increases the concentration of CO and F_2.

(c) On the graph above, show the impact of the disturbance at t = 25 s on the concentrations of each substance as the system reaches a new equilibrium at t = 30 s. 2

Question 30

The graph shows the change in the reaction rate of the following equilibrium system as changes are made to the system over an interval of 6 minutes.

$$2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad \Delta H = -427\ \text{kJ mol}^{-1}$$



(a) At 2 minutes, the temperature of the reaction was increased. State which reaction, forward or reverse, is represented by the solid line and the dotted line. 1

Solid line = reverse reaction dotted line = forward reaction

(b) Identify the disturbance that occurred at 4 minutes. 1

Removal of $O_{3(g)}$

(c) Explain how the changes in the forward and reverse rates of reaction support the disturbance identified in (b). 3

Removal of $O_{3(g)}$ decreases its concentration. Thus less collisions between the reactants will occur, decreasing the rate of the forward reaction, while the reverse reaction is unaffected. This is illustrated in the graph at 4 minutes.

Since the forward rate < reverse rate, the equilibrium shifts left. As a result, the concentration of O_2 decreases, meaning less collisions occur between O_2 molecules and the rate of the reverse reaction will decrease. As more O_3 is formed, more collisions between the reactants occur, hence the forward reaction increases. This is seen between 4-5 minutes. Eventually both rates become equal and a new equilibrium is established, as shown in the graph after 5 minutes.

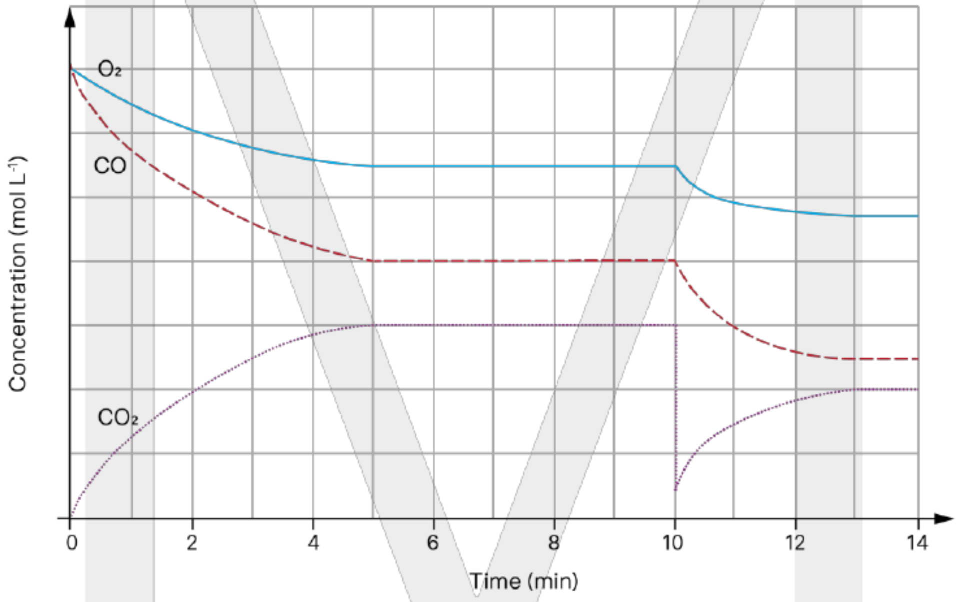
Question 31

Consider the exothermic reaction between carbon monoxide and oxygen gases to form carbon dioxide gas.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} \qquad \Delta H = -128 \text{ kJ mol}^{-1}$$

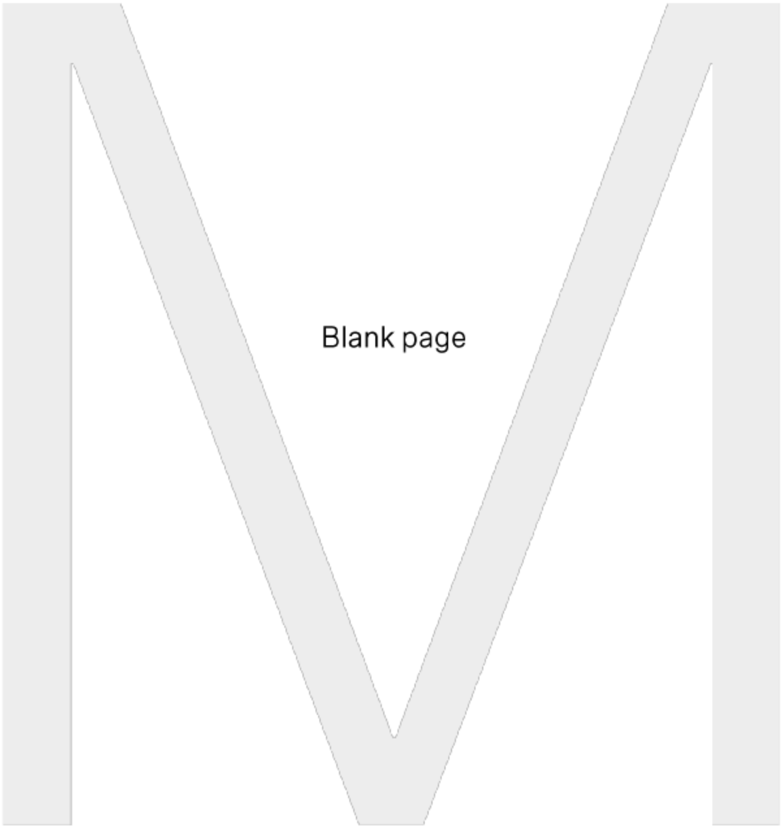
Initially, 0.50 mol L^{-1} of carbon monoxide and oxygen gas each were introduced into a reaction vessel and allowed to react until equilibrium was reached after 5 minutes. At 10 minutes some of the carbon dioxide was removed from the reaction vessel via fractional distillation. Equilibrium was re-established after 13 minutes.

(a) Sketch the changes in the concentrations of reactants and products described above. 3



(b) Explain the changes shown on your graph. 4

Initially only the forward reaction proceeds. As CO and O_2 are used up, their concentration decreases and the forward reaction rate decreases. As CO_2 is produced, its concentration increases and the reverse reaction rate increases. Eventually, the forward and reverse rates become equal, and the reaction reaches equilibrium. Since the production and consumption of any component occurs at equal rates, the concentrations all remain the same. Removal of CO_2 causes its concentration to decrease. According to Le Chatelier's principle, the equilibrium will shift right to produce more CO_2 to minimise the disturbance. This decreases the concentration of CO and O_2. Eventually, the forward and reverse rates become equal and the concentrations remain constant.



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Year 12
Chemistry
Equilibrium and Acid Reactions

Work Book 4
Equilibrium constant 1

MATRIX
EDUCATION

Part A: Multiple choice questions

Question 1

Which of the following changes will affect the value of the equilibrium constant?

(a) Adding a catalyst

(b) Adding more of one reactant

(c) Conducting the reaction at a higher temperature

(d) Increasing the volume of the reaction vessel

The only factor that changes the equilibrium constant is temperature.

Question 2

The reaction of ammonia gas and hydrogen chloride gas results in the following equilibrium:

$$NH_{3(g)} + HCl_{(g)} \rightleftharpoons NH_4Cl_{(s)}$$

The equilibrium expression for this reaction is:

(a) $K = \frac{[NH_4Cl]}{[NH_3][HCl]}$

(b) $K = \frac{[NH_3][HCl]}{[NH_4Cl]}$

(c) $K = [NH_3][HCl]$

(d) $K = \frac{1}{[NH_3][HCl]}$

Only gases and aqueous species appear in the equilibrium expression.

Question 3

Nitrogen monoxide gas can be synthesised from nitrogen and oxygen gases. The equilibrium expression for this reaction is:

(a) $K = \frac{[N_2][O_2]}{[NO]^2}$

(b) $K = \frac{[NO]^2}{[N_2][O_2]}$

(c) $K = \frac{[NO]}{[N_2][O_2]}$

(d) $K = \frac{[N_2][O_2]}{[NO]}$

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

$K_{eq} = \frac{[products]}{[reactants]}$, the concentration of each component is raised to the power of its stoichiometric coefficient.

Question 4

The following reversible reaction is occurring in a closed reaction vessel.

$$A_{(l)} + B_{(s)} \rightleftharpoons C_{(g)} \qquad \Delta H < 0$$

Which of the following changes will cause a shift in the equilibrium and increase the yield of C?

(a) Adding more A to the system

(b) Increasing the temperature of the system

(c) Increasing the volume of the reaction vessel

(d) Removing some B from the system

The equilibrium constant expression is $K = [C]$. Hence addition of A and removal of B does not change the K value and thus will not disturb and shift the equilibrium.

Increasing the temperature will shift the equilibrium to the endothermic side which is the reverse reaction. Hence yield would decrease.

When the volume of the reaction vessel increases, the concentration of C will decrease, hence $Q < K$. Thus the equilibrium will shift forward to produce more C and re-establish equilibrium.

Question 5

On the basis of the equilibrium constant values, which of the following reactions does the equilibrium position lie most to the right?

(a) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $K = 5.4 \times 10^{-6}$

(b) $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ $K = 1.0 \times 10^{-13}$

(c) $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$ $K = 2.1 \times 10^{3}$

(d) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $K = 5.0 \times 10^{-31}$

Since, $K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$, the larger the value of K, the greater the concentration of products compared to reactants, hence the further the equilibrium lies towards the right.

Question 6

Consider the following reaction:

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}{}_{(aq)} \qquad \Delta H < 0$$

The equilibrium constant K for this reaction at 300 K is 140. Which of the following correctly describes the change in value of K when the reaction is conducted at 500 K?

(a) The value of K increases

(b) The value of K decreases

(c) The value of K stays the same

(d) The value of K decreases but then increases

According to Le Chatelier's principle, an increase in temperature shifts the equilibrium position to the endothermic direction to remove some of the added heat to minimise the disturbance. This is the reverse direction, hence the concentration of reactants will increase and concentration of products will decrease.

Since $K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$, the value of K decreases.

Question 7

In the reversible reaction:

$$4AB_{3(g)} + 5C_{2(g)} \rightleftharpoons 4AC_{(g)} + 6B_2C_{(g)}$$

The equilibrium concentrations measured at 298 K are:

$[AB_3] = 0.25 \text{ mol L}^{-1}$ $[C_2] = 0.40 \text{ mol L}^{-1}$ $[AC] = 0.30 \text{ mol L}^{-1}$ $[B_2C] = 0.40 \text{ mol L}^{-1}$

The equilibrium constant for this reaction at 298 K is closest to:

(a) $K = 0.83$

(b) $K = 1.4$

(c) $K = 2.2$

(d) $K = 0.91$

$$K = \frac{[AC]^4[B_2C]^6}{[AB_3]^4[C_2]^5} = \frac{(0.30)^4(0.40)^6}{(0.25)^4(0.40)^5} = 0.82944$$

Question 8

Consider the reversible reaction:

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

At 510 K, the equilibrium constant *K* for this reaction is 0.497. Which is the closest value for the equilibrium constant for the decomposition of phosphorus pentachloride at 510 K?

(a) $K = 0.497$

(b) $K = 0.705$

(c) $K = 1.42$

(d) $K = 2.01$

The *K* value for the reverse reaction is the inverse of the forward reaction:

$$\frac{1}{K} = \frac{1}{0.497} = 2.012$$

Question 9

A reversible reaction and its equilibrium expression are shown below.

$$2X \rightleftharpoons Y + 2Z \qquad K = [Y][Z]^2$$

Which of the following situations could be true?

(a) X, Y and Z are all aqueous

(b) X is a gas, Y and Z are aqueous

(c) X is a solid, Y and Z are aqueous

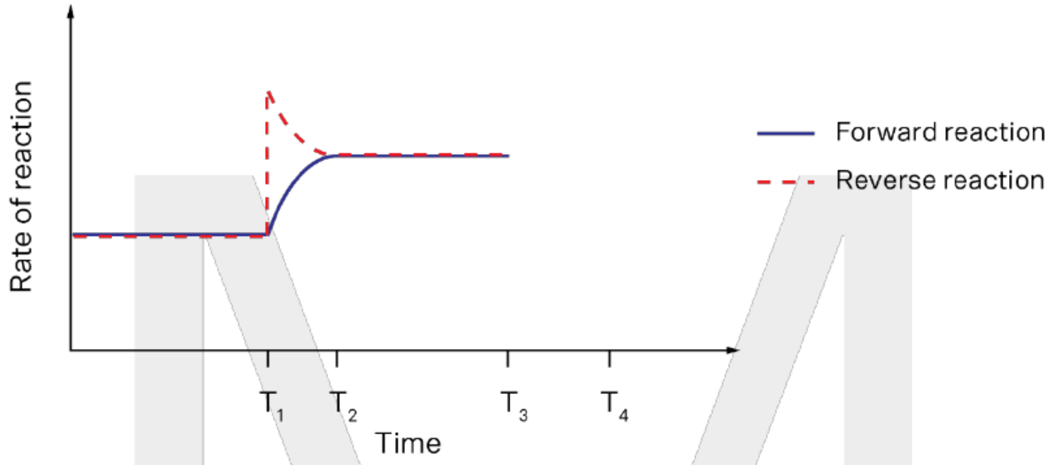
(d) X is a gas, Y and Z are liquid

Since X does not appear in the equilibrium expression, it must be a pure solid or liquid.

Refer to the following information for Questions 10 – 11

Consider the graph below that shows the rate of the forward and reverse reactions versus time for the following equilibrium reaction:

$$A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)} \qquad \Delta H > 0$$



Question 10

A disturbance was made to the equilibrium mixture at T_1 and equilibrium was re-established at T_2. Which of the following is consistent with the information provided in the graph?

(a) At T_1, reactants are removed from the reaction vessel.

(b) The amount of products at equilibrium before T_1 is greater than the amount of products at equilibrium from T_2 to T_3.

(c) The disturbance at T_1 has no effect on the equilibrium constant.

(d) A catalyst is added to the equilibrium mixture at T_1.

The only change that could cause an instantaneous increase to the rate of the reverse reaction at T_1 with no effect of the rate of the forward reaction would be the addition of products. Hence (a) and (d) are not correct. The addition of products to the equilibrium at T_1 means the amount of products at equilibrium after the disturbance at T_1 is greater than the amount of products before T_1. Thus (b) is not correct. The only factor that can change the value of the equilibrium constant is a change in temperature.

Question 11

Another disturbance was made to the equilibrium mixture at T_3 and equilibrium was re-established at T_4. This disturbance caused a change in the equilibrium constant. If the rate of the reverse reaction at T_4 was lower than at T_2, which of the following correctly shows the change in the equilibrium system from T_2 to T_4?

	Equilibrium constant	Total energy
(a)	Increased	Increased
(b)	Increased	Decreased
(c)	Decreased	Increased
(d)	Decreased	Decreased

The only factor that can change the value of the equilibrium constant is a change in temperature. Since the rate of the reverse reaction at T_4 is lower, the temperature must have decreased. The equilibrium will shift in the reverse exothermic direction to counteract the decreased temperature. Hence [reactants] increase and [products] decrease.

Part B: Extended response questions

Question 12

The following equilibrium between the gases methane, hydrogen sulfide, carbon disulfide and hydrogen is established at high temperatures, with $K = 2.1$ at 1000 K.

$$CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}$$

A 1000 K mixture contained these four gases at the following concentrations:

$[CH_4] = 0.065\ \text{mol L}^{-1}$ $[H_2S] = 0.105\ \text{mol L}^{-1}$ $[CS_2] = 0.55\ \text{mol L}^{-1}$ $[H_2] = 0.21\ \text{mol L}^{-1}$

(a) Write the equilibrium expression for the reaction. 1

$$K = \frac{[CS_2][H_2]^4}{[H_2S]^2[CH_4]}$$

(b) Explain why this mixture is not at equilibrium. Show your working. 2

When the concentrations are substituted into the equilibrium constant expression, the calculated value, reaction quotient Q, is 1.5 (not 2.1), therefore the system has not reached equilibrium.

(c) How will the concentrations of CH_4 and H_2S change as the mixture moves towards equilibrium? Explain. 2

The ratio of products to reactants in the mixture ($Q = 1.5$) is lower than $K = 2.1$. Therefore, as the mixture approaches equilibrium, the ratio of products to reactants would increase, i.e. more products are formed (CS_2 and H_2) and less reactants (CH_4 and H_2S) will be in the mixture.

(d) This reaction is endothermic. How will the value of the equilibrium constant change as temperature increases? Explain. 2

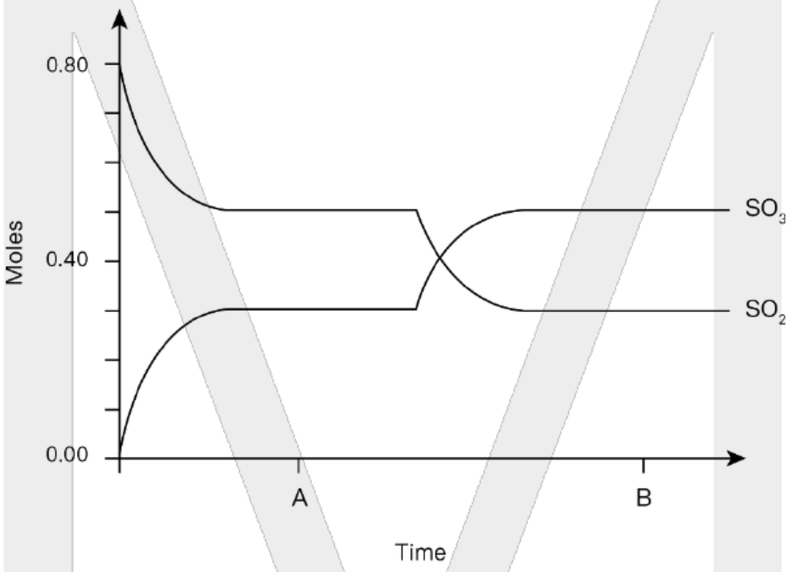
The only factor that changes the value of the equilibrium constant is temperature. Increasing the temperature would disturb the equilibrium. According to Le Chatelier's principle, the equilibrium shifts in the endothermic direction to remove heat and minimise the disturbance, increasing the concentration of the products and the value of K.

Question 13

At 25 °C, 0.80 moles of gaseous sulfur dioxide and 0.40 moles of oxygen gas were introduced into a 5.0 L reaction vessel and allowed to come to equilibrium according to the following equation:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The changes in the amounts of the sulfur-containing compounds in the container are shown below.



(a) Explain why the concentrations of the components do not change at time A and B. 2

At time A and B, the system is at equilibrium. This means that the rate of the forward and reverse reactions are the same, so each species is being produced and consumed at the same rate, resulting in constant concentrations (shown in the graph as flat, horizontal lines).

(b) Write the equilibrium constant expression for this reaction. 1

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

(c) Calculate the value for the equilibrium constant at time A. 3

Concentration (mol L^{-1})	$2SO_{2(g)}$	$O_{2(g)}$	$2SO_{3(g)}$
Initial	0.16	0.080	0.00
Change	−0.060	−0.030	+0.060
Equilibrium	0.10	0.050	0.060

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.06)^2}{(0.10)^2(0.05)} = 7.2 \text{ (2 s.f.)}$$

(d) The temperature at which the reaction was conducted was then decreased and a new equilibrium was established. Calculate the value for the equilibrium constant at time B. 3

Concentration (mol L^{-1})	$2SO_{2(g)}$	$O_{2(g)}$	$2SO_{3(g)}$
Initial	0.10	0.050	0.060
Change	−0.040	−0.020	+0.040
Equilibrium	0.060	0.030	0.10

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.10)^2}{(0.060)^2(0.030)} = 93 \text{ (2 s.f.)}$$

(e) Determine whether the forward reaction is exothermic or endothermic. Justify your answer. 3

When the temperature was decreased, the *K* value increased and the equilibrium shifted forward. According to Le Chatelier's principle, the position of equilibrium will shift in the exothermic direction to produce more heat and minimise the disturbance. Thus, the forward direction is exothermic.

(f) The pressure of the system was then increased. What effect would an increase in pressure have on the equilibrium constant? 1

An increase in pressure would have no effect on the equilibrium constant. The only condition that changes *K* is temperature.

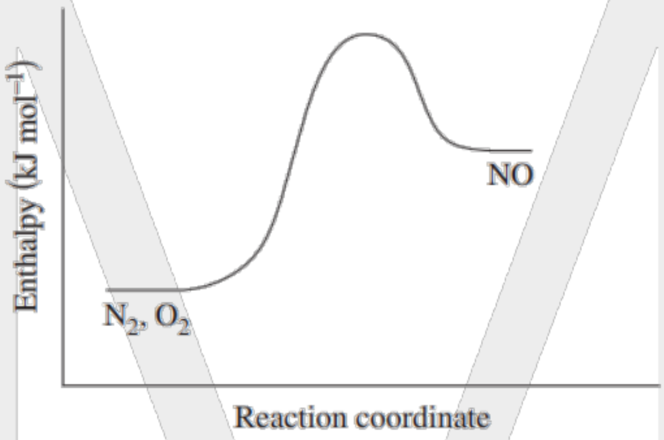
Question 14 **[2020 HSC Q26]**

Nitric oxide gas (NO) can be produced from the direct combination of nitrogen gas and oxygen gas in a reversible reaction.

(a) Write the balanced chemical equation for this reaction. **1**

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

(b) The energy profile diagram for this reaction is shown.



Explain, using collision theory, how an increase in temperature would affect the value of K_{eq} for this system. Refer to the diagram in your answer. **4**

Sample answer:

The forward reaction is endothermic. For the reaction to proceed the reacting molecules must possess the activation energy to result in successful collisions. The activation energy for the forward reaction is greater than that of the reverse, exothermic reaction. An increase in temperature will increase the average kinetic energy of all molecules, resulting in more effective collisions increasing the reaction rate for both the forward and reverse reactions. However, the added temperature will have a greater impact on the forward reaction and the rate of this reaction will be higher than that of the reverse reaction. As a result, the forward reaction is favoured. As $K = \frac{[NO]^2}{[N_2][O_2]}$, a shift to the right will result in an increase in K.

Question 15

Carbon monoxide, water vapour, carbon dioxide and hydrogen were pumped into a sealed container that was maintained at a constant temperature of 200 °C.

The following reaction occurred:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

After 30 seconds, the concentration of gases in the sealed container was found to be:

$[CO] = 0.10$ M, $[H_2O] = 0.10$ M, $[H_2] = 2.0$ M, and $[CO_2] = 2.0$ M.

The equilibrium constant at 200 °C for the above reaction is $K = 210$.

What are the relative rates of the forward reaction and the reverse reaction at 30 seconds? Explain your answer. 3

At 30 sec:

$$Q = \frac{[H_2][CO_2]}{[CO][H_2O]} = \frac{2.0 \times 2.0}{0.10 \times 0.10} = 400 \text{ (2 s.f.)}$$

Q is greater than *K*, indicating that the concentrations of products are higher than they would be at equilibrium and the concentrations of reactants are lower than their equilibrium concentrations. Thus the rate of the reverse reaction is higher than the rate of the forward reaction at 30 seconds as concentration is proportional to rate (or the reaction must shift in the reverse direction to reach equilibrium).

Question 16

The table shows the effect of temperature on the equilibrium constant (*K*) for the reaction:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Temperature (°C)	*K*
700	2.63
800	0.915
900	0.384
1000	0.184
1100	0.098

(a) Determine whether the forward reaction is endothermic or exothermic. Justify your answer. 3

K decreases with increasing temperature, which means the equilibrium is shifting in the reverse direction (to the left). According to Le Chatelier's principle, increasing the temperature shifts the equilibrium in the endothermic direction, to remove excess heat to minimise the disturbance. Hence the forward reaction is exothermic.

(b) What is the equilibrium constant for the following reaction at 900 °C? 2

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

For the original reaction:

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

For the second reaction:

$$K' = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$$

= 1 / √K (to turn *K* into *K'*, we need to flip the fraction upside down and take the square root)

= 1 / √(0.384)

= 1.61 (3 s.f.)

Question 17

A mixture of hydrogen, carbon monoxide and methanol is placed in a reaction chamber with a volume that can be adjusted. The mixture is allowed to reach equilibrium.

$$2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$$

(a) Initially, the volume of the container is 2.00 L. Account for any changes in the concentration of carbon monoxide gas when the volume of the container is instantly increased to 4.00 L. **2**

Initially, [CO] would drop as the volume of the container was suddenly increased. However, the increase in volume disturbs the equilibrium. According Le Chatelier's principle, the equilibrium will shift in the reverse direction to the side with more gaseous moles to increase pressure and minimise the disturbance. So [CO] would then start to increase again until equilibrium is re-established.

(b) The initial mixture placed in the container has 1.50 mol of hydrogen, 1.50 mol of carbon monoxide and 2.50 mol of methanol. After the volume of the container had been increased to 4.00 L and equilibrium had been re-established, the number of moles of carbon monoxide in the mixture had changed by 0.53 mol.
Calculate the equilibrium constant for this reaction. **3**

Assume that the initial position is the initial mixture in a 4 L container.

Therefore, the change in concentration of CO is 0.53 / 4 = 0.1325 M

Concentration (mol L^{-1})	$2H_2$	CO	CH_3OH
Initial	0.375	0.375	0.625
Change	+0.265	+0.1325	−0.1325
Equilibrium	0.64	0.5075	0.4925

$$K = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.4925}{(0.64)^2 \times 0.5075} = 2.4 \text{ (2 s.f.)}$$

Note: You can also fill in the ICE table using moles. You cannot fill it in with concentrations at two different volumes.

Question 18

Consider the following equilibrium expression:

$$K = \frac{[N_2][O_2]}{[NO]^2}$$

(a) Write the equation for this reaction. **1**

$2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$

(b) 0.400 moles of NO were placed in a 1.00 L vessel. The equilibrium concentration of N_2 was found to be 0.198 mol L^{-1}.

Using the equilibrium constant value, describe the position of the equilibrium. **4**

Concentration (mol L^{-1})	**$2NO_{(g)}$**	**$N_{2(g)}$**	**$O_{2(g)}$**
Initial	0.400	0.000	0.000
Change	−0.396	+0.198	+0.198
Equilibrium	0.004	0.198	0.198

$$K = \frac{[N_2][O_2]}{[NO]^2} = \frac{(0.198)^2}{(0.004)^2} = 2450 \text{ (3 s.f.)}$$

K is very large; indicating the concentrations of products is very large relative to the concentration of reactants. Thus the position of equilibrium lies to RHS.

(c) A closed 2.5 L reaction vessel containing N_2, O_2 and NO at the same temperature was analysed, and the moles of each component were found to be 0.25, 0.11 and 0.90 moles respectively. Will there be more or less NO present once the mixture reaches equilibrium? Explain. **2**

$[N_2] = 0.10$ mol L^{-1} $[O_2] = 0.044$ mol L^{-1} $[NO] = 0.36$ mol L^{-1}

$$Q = \frac{[N_2][O_2]}{[NO]^2} = \frac{0.10 \times 0.044}{(0.36)^2} = 0.034 \text{ (3 s.f.)}$$

$Q < K$, thus the forward reaction will be favoured, and NO will be decomposed. Hence there will be less NO at equilibrium.

(d) What change would result in a different value of K for this reaction? **1**

Temperature – it is the only factor which will affect the equilibrium constant.

Question 19

Calcium hydroxide dissolves in water according to the following reaction:

$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$$

(a) 3.0 g of solid calcium hydroxide was dissolved in water to form 250 mL of a saturated solution. When equilibrium had been established, the hydroxide ion concentration was measured to be 1.58×10^{-2} M. Calculate the value of *K*. 3

Concentration (mol L^{-1})	$Ca^{2+}{}_{(aq)}$	$2OH^{-}{}_{(aq)}$
Initial	0.0	0.0
Change	$+(1.58 \times 10^{-2})/2$	$+1.58 \times 10^{-2}$
Equilibrium	$(1.58 \times 10^{-2})/2$	1.58×10^{-2}

$K = [Ca^{2+}][OH^{-}]^2$

$= (1.58 \times 10^{-2}/2) \times (1.58 \times 10^{-2})^2$

$= 2.0 \times 10^{-6}$ (2 s.f.)

(b) When 100 mL of water is added to this saturated solution, the equilibrium is disturbed. How will the concentrations of Ca^{2+} and OH^{-} change as the solution moves towards equilibrium? Explain with reference to the equilibrium constant and reaction quotient. 2

When water is added, the volume is increased, thus the concentration of calcium and hydroxide ions is decreased. Thus *Q* is less than *K*, indicating that the concentrations of products are lower than they would be at equilibrium. Therefore, the equilibrium would shift right and the concentrations of Ca^{2+} and OH^{-} will increase to establish equilibrium.

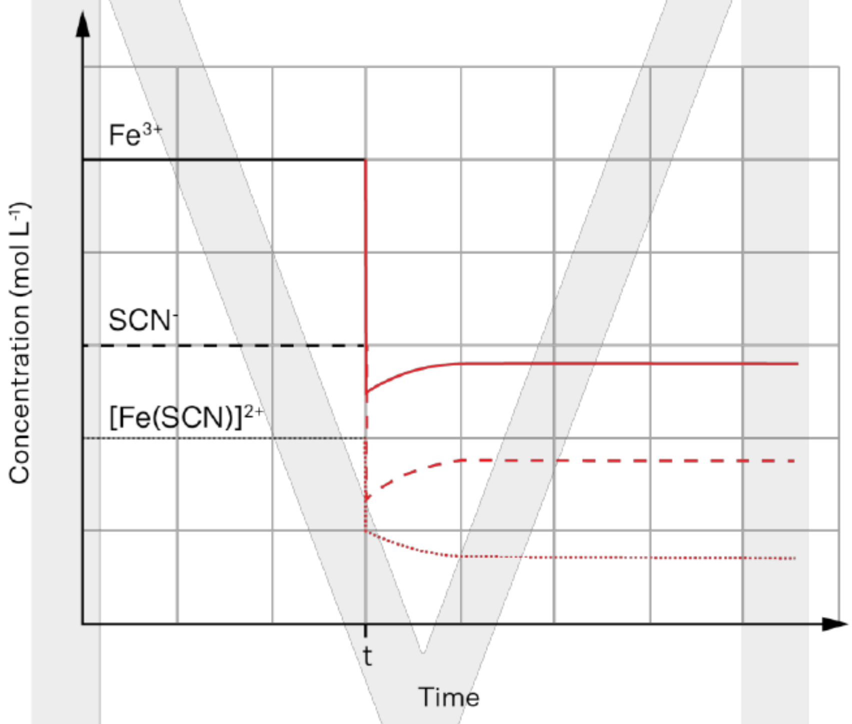
Question 20

Consider the following equilibrium reaction:

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}{}_{(aq)}$$

At time t the volume of the solution was doubled by the addition of water to the system. Sketch on the graph below to show how the concentrations would change from t until equilibrium is established again. 3

(Hint: Compare the reaction quotient and equilibrium constant to determine how the reaction will shift to establish a new equilibrium)



$$Q = \frac{\frac{1}{2}[[Fe(SCN)]^{2+}]}{\frac{1}{2}[Fe]^{3+}\,\frac{1}{2}[SCN]^{-}} = 2 \times \frac{[[Fe(SCN)]^{2+}]}{[Fe]^{3+}[SCN]^{-}} = 2\,K$$

Since $Q > K$, the equilibrium will shift left to re-establish equilibrium.

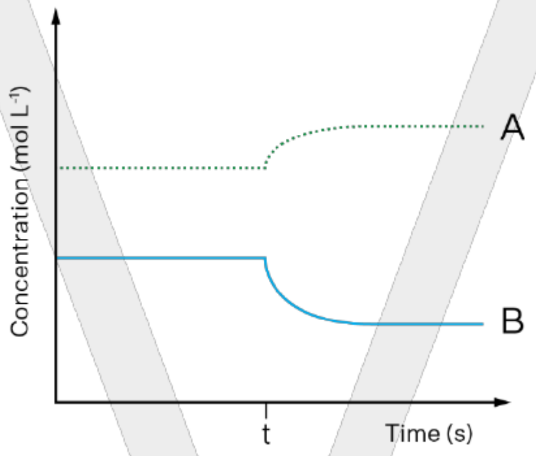
Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 21

The graph below shows the concentration of reaction species of the following reversible reaction:

$$A_{(g)} \rightleftharpoons 2B_{(g)}$$



At time t, the temperature of the system was decreased. Which correctly describes the forward reaction and the change in *K* value when a new equilibrium is reached?

(a) Exothermic and *K* increases

(b) Exothermic and *K* decreases

(c) Endothermic and *K* increases

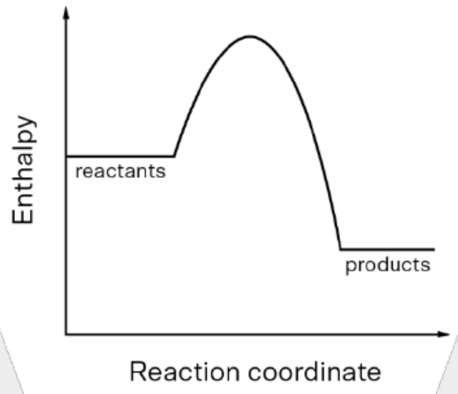
(d) Endothermic and *K* decreases

According to Le Chatelier's principle, a decrease in temperature shifts the position of equilibrium to the exothermic side to produce more heat to minimise the disturbance. Since the reaction shifted left, the reverse reaction is exothermic and the forward reaction is endothermic.

For endothermic reactions, *K* decreases with lower temperatures.

Question 22

The forward reaction of a reversible reaction is represented by the following energy profile diagram.



How will the activation energy and value of K_{eq} change if the temperature of the system is increased?

(a) Activation energy will increase and K_{eq} will increase

(b) Activation energy will increase and K_{eq} will decrease

(c) Activation energy will stay the same and K_{eq} will increase

(d) Activation energy will stay the same and K_{eq} will decrease

The activation energy of a reaction is not affected by temperature.

The forward reaction is exothermic according to the energy profile diagram. An increase in temperature shifts the equilibrium towards the endothermic direction so additional heat can be absorbed. This is the reverse direction. As a result, concentration of reactants will increase, and concentration of products will decrease.

As $K = \frac{[\text{products}]}{[\text{reactants}]}$, a shift to the left will result in a decrease in K.

Question 23

An equilibrium system is represented by the following equation:

$$Z_{(g)} \rightleftharpoons X_{(g)} + Y_{(g)}$$

If 0.50 mol of Z was introduced into a 5.00 L reaction vessel at 450 K, and 0.025 mol of X was present at equilibrium, which is the closest value for the equilibrium constant for this reaction at 450 K?

(a) $K = 2.6 \times 10^{-4}$

(b) $K = 8.3 \times 10^{-3}$

(c) $K = 120$

(d) $K = 3800$

Concentration (mol L^{-1})	$Z_{(g)}$	$X_{(g)}$	$Y_{(g)}$
Initial	0.1	0	0
Change	−0.005	+0.005	+0.005
Equilibrium	0.095	0.005	0.005

$$K = \frac{(0.005)^2}{0.095} = 2.6 \times 10^{-4}$$

Question 24

Consider the following equilibrium:

$$X_{(g)} + 2Y_{(g)} \rightleftharpoons 2Z_{(g)} \qquad K = 350$$

If 0.20 mol each of X and Y were added to a 1.0 L container and allowed to reach equilibrium, which of the following is true regarding the concentrations in the equilibrium mixture?

(a) [X] = [Y]

(b) [X] = [Y] = [Z]

(c) [X] > [Y]

(d) [X] < [Y]

The stoichiometric ratio of X and Y is 1:2, hence more of Y will be consumed as the forward reaction proceeds.

Question 25

Carbon monoxide and chlorine gases react to form phosgene. In a sealed container, this system will reach equilibrium.

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$$

At 1000 K, the equilibrium constant *K* for this reaction is 255. Which of the following correctly describes the reaction mixture at this temperature?

(a) The reaction will proceed very slowly.

(b) The equilibrium lies far to the left.

(c) The equilibrium concentrations of products and reactants are equal.

(d) The equilibrium lies far to the right.

K is very large. The larger the value of *K*, the greater the concentration of products compared to reactants, hence the further the equilibrium lies towards the right.

Question 26

Write the expression for the equilibrium constant *K* for the following equations. **4**

Equation	Equilibrium expression
$2Cl_{2(g)} + 2H_2O_{(g)} \rightleftharpoons 4HCl_{(g)} + O_{2(g)}$	$\frac{[O_2][HCl]^4}{[H_2O]^2[Cl_2]^2}$
$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$	$\frac{[Cl_2][CO]}{[COCl_2]}$
$CaCO_{3(s)} + 2HCl_{(aq)} \rightleftharpoons CO_{2(g)} + CaCl_{2(aq)} + H_2O_{(l)}$	$\frac{[CO_2][CaCl_2]}{[HCl]^2}$
$4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$	$\frac{[N_2]^2[H_2O]^6}{[O_2]^3[NH_3]^4}$

Question 27

Arrange the following reactions in order of their increasing tendency to reach completion. 1

(i) $4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$ $K = 1.0 \times 10^{228}$

(ii) $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ $K = 1.0 \times 10^{-13}$

(iii) $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ $K = 4.7 \times 10^{-4}$

(iv) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $K = 5.0 \times 10^{-31}$

(iv), (ii), (iii), (i)

Question 28

An equilibrium exists between nitrogen, hydrogen and ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

At a certain temperature, various amounts of these three gases were introduced into a 1.0 L container. When equilibrium was reached, the number of moles of ammonia had decreased by 0.080 mol, as shown by the partially completed table below.

Concentration (mol L^{-1})	N_2	H_2	NH_3
Initial	0.19	0.38	0.23
Change	+0.040	+0.12	−0.080
Equilibrium	0.23	0.50	0.15

(a) Fill in the missing data. 2

(b) Write the equilibrium constant expression for the synthesis of ammonia. 1

$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

(c) Using your answers to parts (a) and (b), calculate the value of K at this temperature. 1

$K = 0.15^2 / (0.50^3 \times 0.23)$

$= 0.78$ (2 s.f.)

Question 29

Hydrogen iodide decomposes endothermically to form hydrogen and iodine gases:

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Iodine is purple, while hydrogen iodide and hydrogen are colourless.

(a) A 1.5 L glass container was filled with 0.90 moles of hydrogen iodide gas. When equilibrium was established, there were 0.38 moles of iodine gas present in the container.

Calculate the equilibrium constant for this reaction. 3

Concentration (mol L^{-1})	$2HI_{(g)}$	$H_{2(g)}$	$I_{2(g)}$
Initial	0.60	0.00	0.00
Change	−0.50667	+0.25333	+0.25333
Equilibrium	0.09333	0.25333	0.25333

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.25333)^2}{(0.09333)^2} = 7.4 \text{ (2 s.f.)}$$

(b) The container was then cooled. Explain the change in the appearance of its contents. 2

The forward reaction is endothermic. If the container was cooled, the equilibrium is disturbed. According to Le Chatelier's priniciple, the position of equilibrium will shift to the left (in the exothermic direction) to produce more heat and minimise the disturbance. The intensity of the purple colour will therefore fade as the concentration of I_2 decreases.

Question 30

One step in the production of sulfuric acid is the formation of sulfur trioxide from sulfur dioxide and oxygen.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Initially, the concentration of sulfur dioxide was 0.090 mol L^{-1}, the concentration of oxygen was 0.070 mol L^{-1}, and there was no sulfur trioxide present in the container. After equilibrium was reached, the concentration of sulfur trioxide was 0.060 mol L^{-1}.

Calculate the equilibrium constant *K* for the reaction showing relevant working. 3

Concentration (mol L^{-1})	$2SO_{2(g)}$	$O_{2(g)}$	$2SO_{3(g)}$
Initial	0.090	0.070	0.00
Change	−0.060	−0.030	+0.060
Equilibrium	0.030	0.040	0.060

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.060)^2}{(0.030)^2(0.040)} = 100 \text{ (2 s.f.)}$$

Question 31

Nitrogen dioxide reacts to form dinitrogen tetroxide in a reversible reaction:

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \qquad \Delta H < 0$$

At 373 K, the equilibrium constant *K* for this reaction is 0.158.

At 298 K, a 2.00 L vessel initially contained 0.370 mol of NO_2. Once equilibrium had been established there was 0.0128 mol of N_2O_4 in the vessel.

(a) Explain the effect of the addition of argon gas to the 2.00 L vessel on the yield of N_2O_4 when this reaction is carried out at 298 K. **2**

The addition of argon gas has no effect on the yield of N_2O_4 because addition of an inert gas at a constant volume does not change the concentration of any species, thus the system remains at equilibrium and there will be no change in the position of the equilibrium.

(b) Calculate the equilibrium constant for this reaction at 298 K, and account for any difference from the *K* value at 373 K. **4**

Concentration (mol L^{-1})	**$2NO_{2(g)}$**	**$N_2O_{4(g)}$**
Initial	0.185	0.000
Change	−0.0128	+0.0064
Equilibrium	0.1722	0.0064

$$K = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.0064}{(0.1722)^2} = 0.216 \text{ (3 s.f.)}$$

Temperature affects the equilibrium constant, hence the value of *K* differs between the two reaction temperatures.

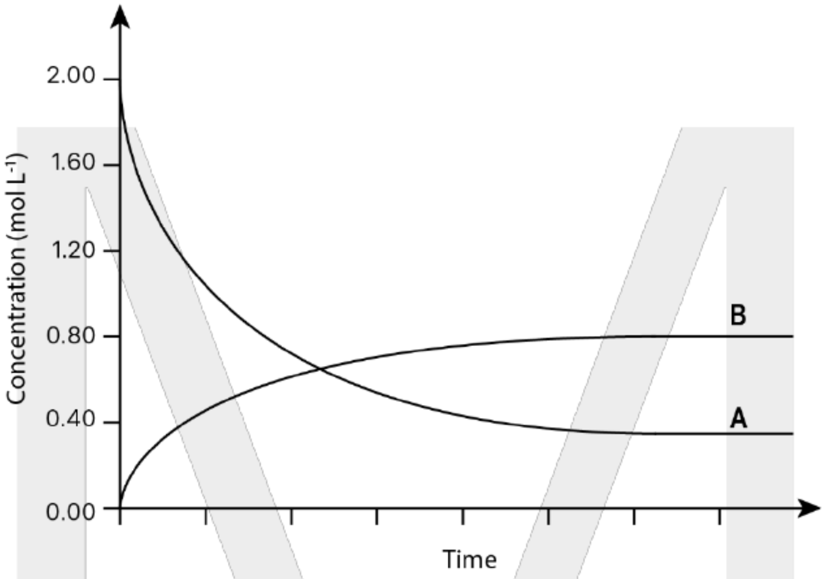
According to Le Chatelier's principle, lower temperatures will cause the equilibrium to shift in the forward exothermic direction to produce more heat and minimise the disturbance. Thus there are more products and the *K* value is larger.

Question 32

If compound A is heated, it decomposes according to the equation:

$$2A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$$

The following diagram shows the progress of the reaction.



Calculate the equilibrium constant for this reaction. 3

[C] = [B] (since A is the only reactant, and B and C are generated in a 1:1 ratio)

$$K = \frac{[B][C]}{[A]^2} = \frac{(0.80)^2}{(0.40)^2} = 4.0 \text{ (2 s.f.)}$$

Question 33

The partial decomposition of phosgene at 1250 °C is shown below.

$$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$$

(a) In one experiment, 1.00 mol of pure phosgene is placed in a 10.0 L sealed flask. When equilibrium is established at 1250 °C, 0.20 mol of phosgene remains in the flask.

(i) How many moles of CO, and of Cl_2, are in the flask at equilibrium? **3**

Concentration (mol L^{-1})	$COCl_{2(g)}$	$CO_{(g)}$	$Cl_{2(g)}$
Initial	0.100	0.000	0.000
Change	−0.0800	+0.0800	+0.0800
Equilibrium	0.0200	0.0800	0.0800

$n(CO) = n(Cl_2) = c \times V = 0.08 \times 10$

Therefore at equilibrium, 0.80 mol of each (2 s.f.)

(ii) Calculate the value for the equilibrium constant for the reaction. **2**

$$K = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{(0.0800)^2}{(0.0200)} = 0.32 \text{ (2 s.f.)}$$

(b) In another experiment, 1.00 mol of pure phosgene is placed in a 2.0 L sealed flask. Equilibrium is established at 1250 °C. How would the value of the equilibrium constant compare with the value calculated in (ii)? Explain your answer. **1**

The value of *K* only varies with temperature. As both systems reached equilibrium at the same temperature, the values of *K* will be the same.

Question 34

The following equation shows the industrially important water-gas-shift reaction:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)} \qquad \Delta H = -42 \text{ kJ mol}^{-1}$$

The equilibrium constant for this reaction at 1260 K is 0.62.

(a) Describe how *K* will change for this system if the reaction vessel is heated. 2

According to Le Chatelier's principle, the equilibrium will shift in the endothermic direction when heated in order to remove heat and minimise the disturbance. This is the reverse direction. Therefore there will be less products and more reactants, and *K* will decrease.

(b) In a reaction mixture at 1260 K:

$[H_2] = 0.35$ M, $[CO_2] = 0.25$ M, $[H_2O] = 0.55$ M and $[CO] = 0.55$ M.

Explain whether the system was at equilibrium at the time these measurements were taken. 2

$$Q = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{(0.35)(0.25)}{(0.55)^2} = 0.29 \text{ (2 s.f.)}$$

Since $Q \neq K$, the system was NOT at equilibrium.

Question 35

Natural gas (methane, CH_4) is an abundant fuel used for cooking, heating and power production. Its use in transportation is limited because it cannot be easily liquefied. There is considerable interest in finding an efficient catalyst for the following reaction, which produces methanol, a convenient liquid fuel:

$$2CH_{4(g)} + O_{2(g)} \rightleftharpoons 2CH_3OH_{(g)}$$

(a) If the equilibrium mixture is cooled, methanol liquefies. What will this do to the concentration of methane (CH_4)? **1**

Equilibrium will shift to the right, decreasing the concentration of methane.

(b) What effect will increasing the partial pressure of oxygen have on the equilibrium constant? **1**

No effect, as only temperature changes will change the value of *K*.

(c) Why is it easier to liquefy methanol than methane? **1**

Methanol has a higher boiling point as it has stronger intermolecular forces (hydrogen bonding), and hence less cooling is required for liquefaction.

Question 36

Iodine trichloride can be synthesised from the reaction of iodine gas and chlorine gas according to the following equation:

$$I_{2(g)} + 3Cl_{2(g)} \rightleftharpoons 2ICl_{3(g)}$$

Initially 0.80 mol of I_2 and 1.20 mol of Cl_2 was introduced into a 2.0 L reaction vessel and allowed to come to equilibrium at 600 K. At equilibrium there was 0.35 mol L^{-1} of $ICl_{3(g)}$.

(a) Write the equilibrium constant expression for this reaction. 1

$$K = \frac{[ICl_3]^2}{[I_2][Cl_2]^3}$$

(b) Calculate the value of K at this temperature. 3

Concentration (mol L^{-1})	$I_{2(g)}$	$3Cl_{2(g)}$	$2ICl_{3(g)}$
Initial	0.40	0.60	0.00
Change	−0.175	−0.525	+0.35
Equilibrium	0.225	0.075	0.35

$$K = \frac{(0.35)^2}{(0.225)(0.075)^3} = 1300 \text{ (2 s.f.)}$$

(c) At 350 K, the equilibrium constant K for this reaction is 3.20. Determine whether the forward reaction is exothermic or endothermic. Justify your answer. 3

K decreases with decreasing temperature, which means there are less products at lower temperatures and equilibrium shifts in the reverse direction. According to Le Chatelier's principle, decreasing the temperature shifts the equilibrium in the exothermic direction, to produce more heat to minimise the disturbance. Hence the reverse reaction is exothermic and forward reaction is endothermic.

Year 12
Chemistry
Equilibrium and Acid Reactions

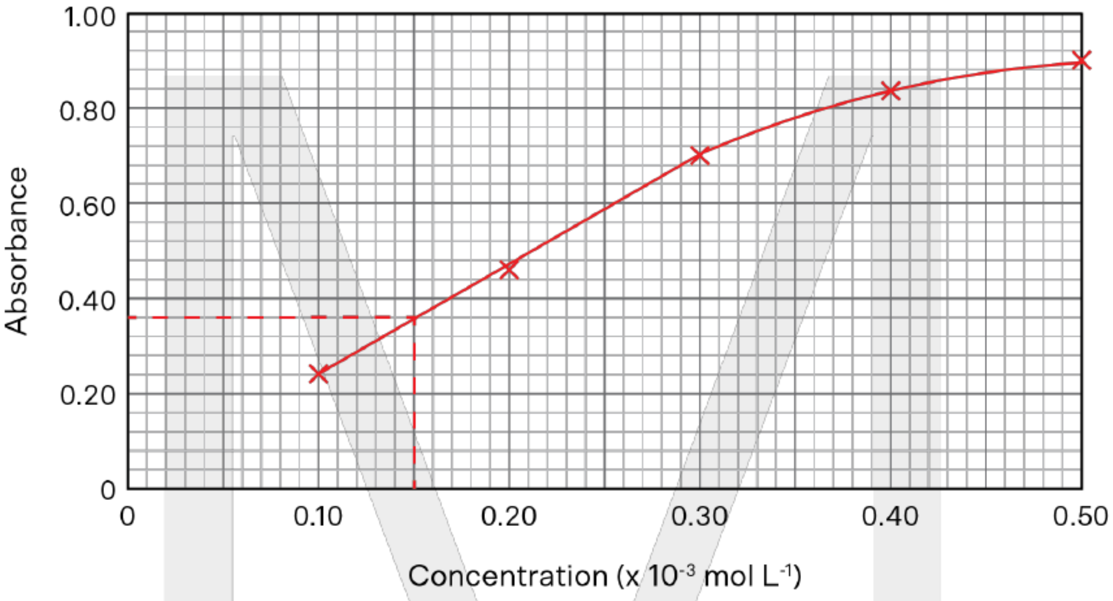
Work Book 5
Equilibrium constant 2

MATRIX
EDUCATION

Part A: Multiple choice questions

Refer to the following information for Questions 1 – 4

A student wishes to measure the concentration of cobalt(II) ions in an aqueous solution using colourimetric analysis. The absorbances of five cobalt(II) chloride standard solutions were measured and a calibration curve was constructed.



Question 1

Between which absorbances would the measured concentration be most valid and accurate?

(a) 0.00 – 0.70

(b) 0.00 – 0.90

(c) 0.24 – 0.70

(d) 0.24 – 0.90

Question 2

A solution containing an unknown concentration of Co^{2+} ions registered an absorbance of 0.36. What is the concentration of Co^{2+} ions in this solution?

(a) 0.15 mol L^{-1}

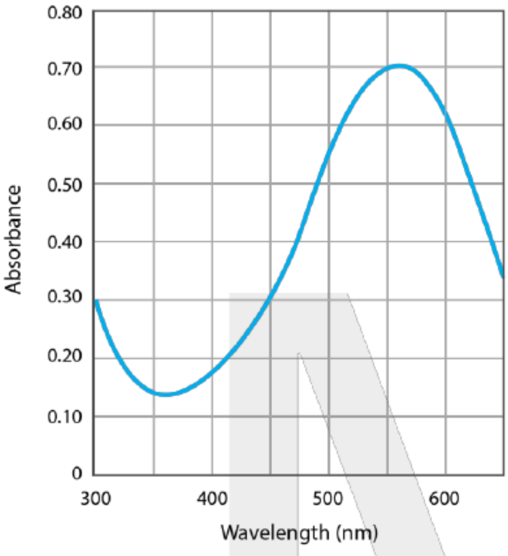
(b) 0.80 mol L^{-1}

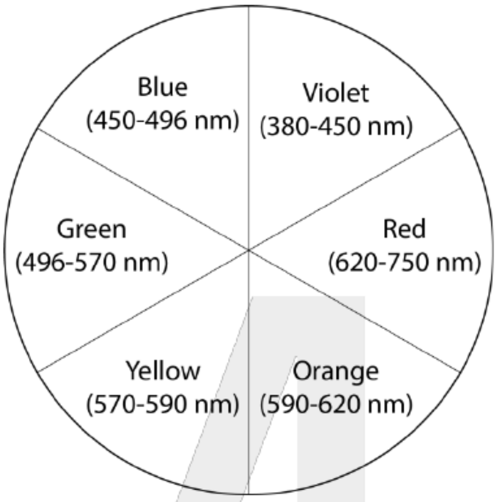
(c) 0.00015 mol L^{-1}

(d) 0.00080 mol L^{-1}

Question 3

Below is a graph of the absorbance versus wavelength for cobalt(II) chloride solution.





Which is the most appropriate colour filter to use to determine the concentration of this solution?

(a) Blue filter

(b) Green filter

(c) Red filter

(d) Orange filter

The wavelength of maximum absorbance corresponds to green. Since green light is absorbed by the sample, green wavelengths should be passed through to the sample.

Question 4

What colour would the solution appear to be?

(a) Blue

(b) Orange

(c) Pink

(d) Yellow-green

The colour perceived is the complimentary colour of the wavelength absorbed.

Question 5

Which of the following is correct regarding the Beer-Lambert Law?

(a) Beer-Lambert Law relates frequency and wavelength

(b) Beer-Lambert Law determines the volume of a sample

(c) Beer-Lambert Law relates absorbance, concentration and path length

(d) Beer-Lambert Law determines the wavelength absorbed by a sample

Question 6

The molar absorptivity for copper(II) sulfate at 635 nm is 2.81 L mol^{-1} cm^{-1}. In an experiment, the absorbance of a solution of copper(II) sulfate was measured to be 0.734 in a 1.00 cm cuvette. What was the concentration of copper(II) ions in the solution?

(a) 0.261 M

(b) 3.83 M

(c) 0.522 M

(d) 0.0485 M

$A = \varepsilon l c$

$c = 0.734/(2.81 \times 1) = 0.261$ M

Question 7

For a colourimetric measurement, 80% of the light was absorbed. The absorbance is:

(a) 0.20

(b) 0.30

(c) 0.70

(d) 0.80

$$A = \log_{10}\frac{I_o}{I} = \log_{10}\frac{100}{20} = 0.6990$$

Question 8

Which of the following is correct regarding standard solutions used for a calibration curve in a colourimetric investigation?

(a) The standard solutions used need to be very concentrated so that an accurate absorbance can be measured.
(b) Each standard solution must be prepared from scratch to avoid cross contamination.
(c) Standard solutions should be prepared by dilution from a concentrated stock solution.
(d) Only two standard solutions are required, one that is very dilute and one that is very concentrated.

Dilution of a concentrated stock solution ensures any factors affecting the absorbance reading is consistent and no new influence (such as impurities in the solution) are introduced.

Question 9

What is the purpose of the colour filter in a colourimeter?

(a) To split the light into different wavelengths
(b) To transmit the remaining light to the detector
(c) To isolate the appropriate wavelengths of light to pass to the sample
(d) To produce light for absorption

Question 10

In a colourimetry experiment, which of the following will not reduce the validity of data collected?

(a) Fingerprints on the cuvette were not wiped off
(b) The blank used was intensely coloured
(c) The sample of interest had an absorbance reading greater than 2.5
(d) The experiment was performed only once

Repetition allows the reliability to be assessed.

Question 11

Light is passed through a solution with a light path of 1.0 cm and the absorbance is recorded as 0.30. If light is passed through the same solution at the same wavelength and the light path is increased to 2.0 cm, the absorbance should be:

(a) 0.80

(b) 0.60

(c) 0.40

(d) 0.20

$A = \varepsilon l c$

Since ε and c will not change for the same solution, increasing the path length to 2 cm will result in the absorbance being doubled.

Part B: Extended response questions

Question 12

Explain how the following factors affect absorbance in a colourimetric experiment.

(a) Path length 2

The relationship between absorbance and path length is given by the Beer-Lambert Law, $A = \varepsilon lc$. As path length increases, the absorbance increases. This is because the light beam will encounter more analyte particles which will absorb more light.

(b) Analyte concentration 2

The relationship between absorbance and analyte concentration is given by the Beer-Lambert Law, $A = \varepsilon lc$. As concentration increases, the absorbance increases. This is because the light beam will encounter more analyte particles which will absorb more light.

(c) Molar absorptivity of a substance 2

The relationship between absorbance and molar absorptivity is given by the Beer-Lambert Law, $A = \varepsilon lc$. As the molar absorptivity increases, the absorbance increases. The molar absorptivity is a constant that is a measure of how strong a chemical species absorbs light at a specific wavelength. The larger the molar absorptivity, the better the substance is at absorbing light.

Question 13

A student carried out a colourimetric investigation to determine the equilibrium constant for the following reaction.

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)} \qquad \Delta H < 0$$

(a) Identify the safety precautions associated with carrying out this investigation. 2

Use safety goggles, gloves and lab coat when handling, perform experiment near water source so spills on skin can be quickly rinsed off.

(b) The student prepared some standard solutions of $Fe(NO_3)_3$ and KSCN so that a calibration curve for $[Fe(SCN)]^{2+}$ could be constructed.

(i) Explain why the use of a calibration curve to determine the concentration of $[Fe(SCN)]^{2+}$ provides a more accurate result. 2

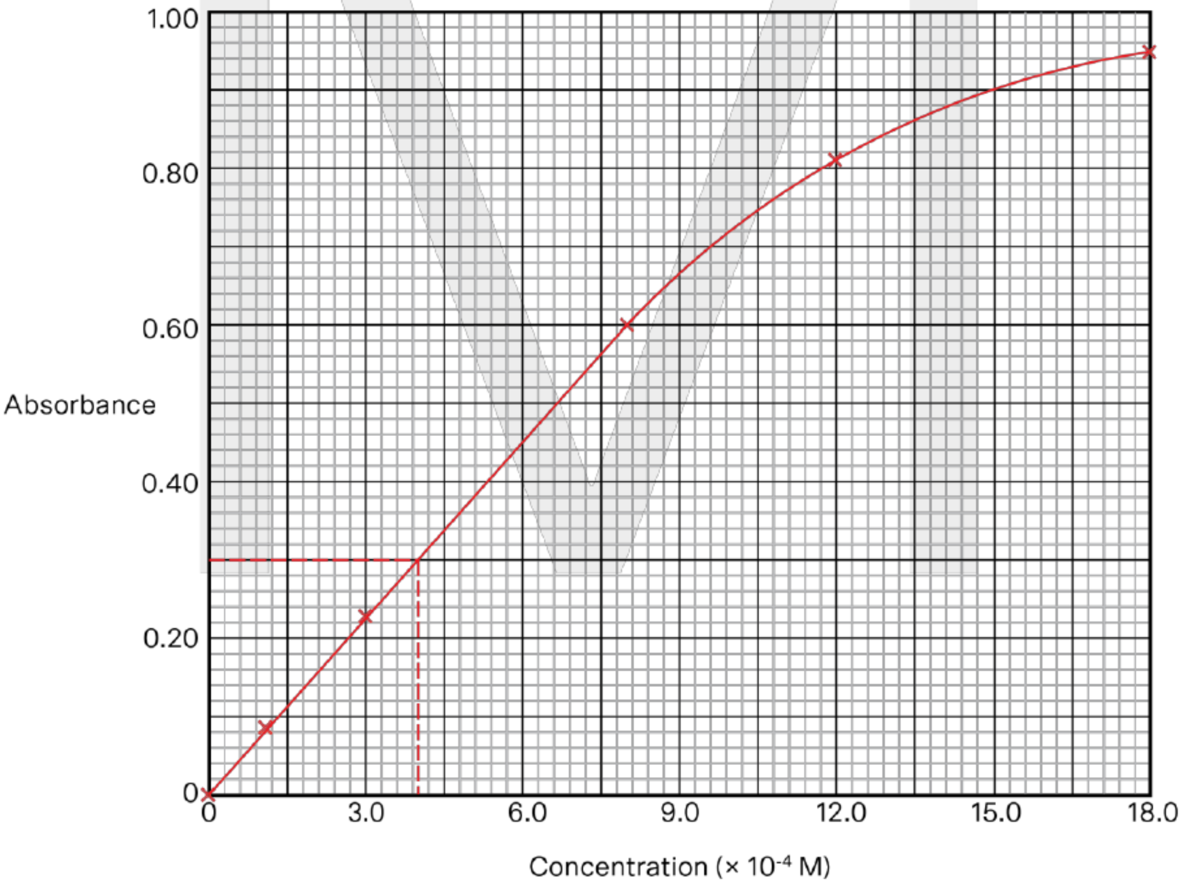
A number of factors can affect the absorbance, such as impurities in the solvent, scratches on the cuvette, stray light and instrument calibration. Measuring the absorbance of standard solutions under the same experimental conditions and then constructing a calibration curve helps to reduce any systematic errors, thus improve accuracy.

(ii) For each measurement, the student rinsed the cuvette with the standard solution to be measured immediately before use. Explain how the experimental result would be affected if the student had instead rinsed the cuvette with the distilled water immediately before use. 2

If the cuvette is rinsed with distilled water immediately before use, the solution will be further diluted by an unknown factor. This reduces the accuracy of the experimental result as the concentration measured will be less than was what was prepared.

(iii) The following absorbances were recorded for the set of standard solutions prepared by the student. Use the values from the table to construct a calibration curve. **3**

Concentration of $[Fe(SCN)]^{2+}$ (× 10^{-4} mol L^{-1})	**Absorbance**
0.0 (Blank)	0.00
1.1	0.09
3.0	0.23
8.0	0.60
12	0.81
18	0.95



(c) The student combined solutions of $Fe(NO_3)_3$ and KSCN to produce a solution in which the initial concentrations of Fe^{3+} and SCN^- were 1.5×10^{-3} M and 3.0×10^{-3} M, respectively. The absorbance of this solution was measured and found to be 0.30. Determine the equilibrium concentration of $[Fe(SCN)]^{2+}$ and calculate the value of *K*. 3

Concentration (mol L^{-1})	$Fe^{3+}_{(aq)}$	$SCN^-_{(aq)}$	$[Fe(SCN)]^{2+}_{(aq)}$
Initial	1.5×10^{-3}	3.0×10^{-3}	0
Change	-4.0×10^{-4}	-4.0×10^{-4}	$+4.0 \times 10^{-4}$
Equilibrium	1.1×10^{-3}	2.6×10^{-3}	4.0×10^{-4}

$$K = \frac{[[Fe(SCN)]^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(4.0 \times 10^{-4})}{(1.1 \times 10^{-3})(2.6 \times 10^{-3})} = 140 \text{ (2 s.f.)}$$

(d) Assess the reliability of the value of *K* obtained by this student. 2

Only one concentration was measured and the experiment was not repeated. Thus the calculated value of *K* cannot be compared with other values to conclude that the result is consistent. Therefore the value of *K* obtained by this student is not reliable.

(e) In another experiment, the student prepared the same concentrations of Fe^{3+} and SCN^- for analysis. However, the temperature of the room was 10 °C hotter. Discuss the effect this change may have on the experimental results. 2

According to Le Chatelier's principle, an increase in temperature will cause the equilibrium to shift in the endothermic direction to remove the added heat to minimise the disturbance. Since the forward reaction is exothermic, the equilibrium will shift in the reverse direction. Thus the concentration of Fe^{3+} and SCN^- increases and $[Fe(SCN)]^{2+}$ decreases. This will result in a lower absorbance value and a lower value of *K*.

Question 14

Hydrogen sulfide is a by-product of processing natural gas and refining crude oils. Elemental sulfur can be recovered from hydrogen sulfide via the following process.

$$2H_2S_{(g)} + SO_{2(g)} \rightleftharpoons 3S_{(s)} + 2H_2O_{(g)} \qquad \Delta H = -145 \text{ kJ mol}^{-1}$$

(a) Write the equilibrium constant expression for this reaction. **1**

$$K = \frac{[H_2O]^2}{[H_2S]^2[SO_2]}$$

(b) Calculate the equilibrium constant when 1.50 mol of H_2S and 1.20 mol of SO_2 react in a 3.00 L vessel at 373 K to give 0.750 mol of water vapour under equilibrium conditions. **3**

Concentration (mol L^{-1})	$2H_2S_{(g)}$	$SO_{2(g)}$	$2H_2O_{(g)}$
Initial	0.50	0.40	0.00
Change	−0.25	−0.125	+0.25
Equilibrium	0.25	0.275	0.25

$K = 0.25^2 / (0.25^2 \times 0.275)$

$= 3.636363 = 3.64$ (3 s.f.)

(c) In a second reaction conducted at the same temperature, 6.75 mol of H_2S was introduced into a reaction vessel with the same volume. When equilibrium was established, 4.50 mol of water vapour was present. Calculate the moles of SO_2 that were introduced into the second reaction. 3

Concentration (mol L^{-1})	$2H_2S_{(g)}$	$SO_{2(g)}$	$2H_2O_{(g)}$
Initial	2.25	??	0.00
Change	−1.50	−0.75	+1.50
Equilibrium	0.75	??	1.50

$K = 1.5^2 / (0.75^2 \times [SO_2]) = 3.636363$

(Same *K* as temperature is the same)

Eqm $[SO_2] = 1.5^2 / (0.75^2 \times 3.636363) = 1.10$

Initial $[SO_2] = 1.10 + 0.75 = 1.85$ M

$n(SO_2) = 1.85 \times 3 = 5.55$ mol (3 s.f.)

(d) Identify FOUR factors that would maximise the recovery of $S_{(s)}$ in this reaction. 2

Using an excess of $SO_{2(g)}$

Increasing the pressure of the system (or decreasing volume)

Decreasing the temperature

Removal of water vapour

Question 15 **[2023 HSC Q31]**

Copper(II) ions (Cu^{2+}) form a complex with lactic acid ($C_3H_6O_3$), as shown in the equation.

$$Cu^{2+}{}_{(aq)} + 2C_3H_6O_{3(aq)} \rightleftharpoons [Cu(C_3H_6O_3)_2]^{2+}{}_{(aq)}$$

This complex can be detected by measuring its absorbance at 730 nm. A series of solutions containing known concentrations of $[Cu(C_3H_6O_3)_2]^{2+}$ were prepared, and their absorbances measured.

Concentration of $[Cu(C_3H_6O_3)_2]^{2+}$ (mol L^{-1})	Absorbance
0.000	0.00
0.010	0.13
0.020	0.28
0.030	0.43
0.040	0.57
0.050	0.72

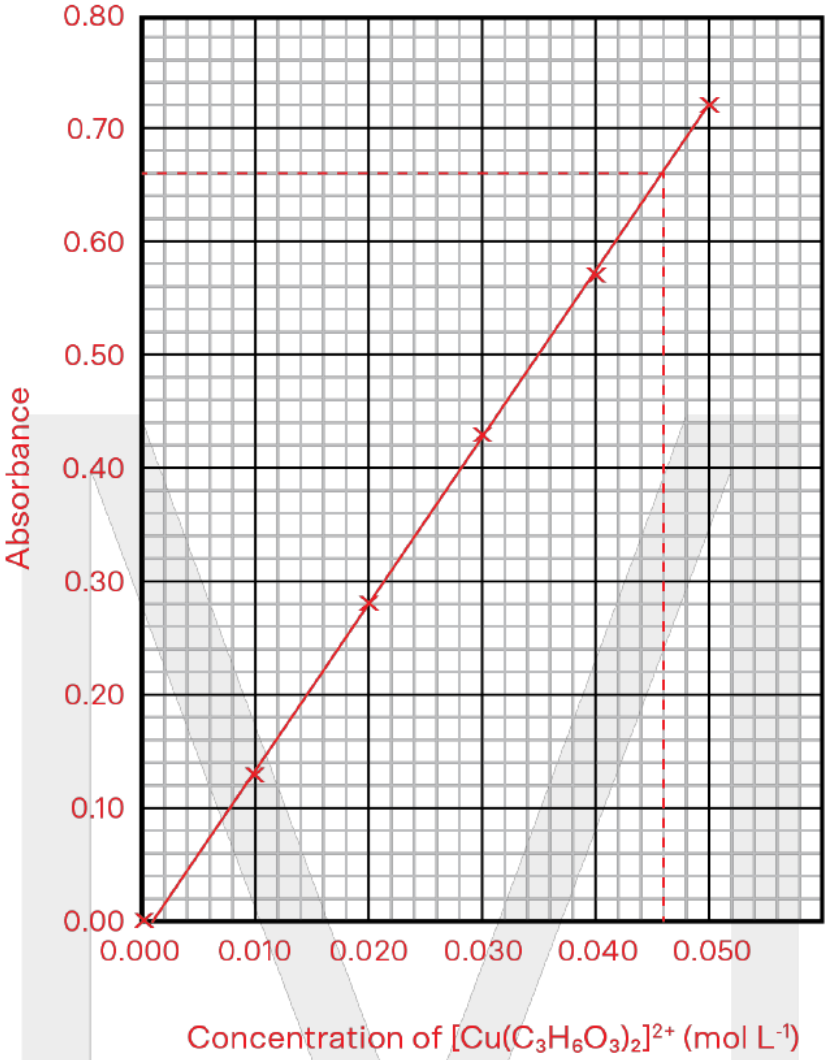
Two solutions containing Cu^{2+} and $C_3H_6O_3$ were mixed. The initial concentrations of each in the resulting solution are shown in the table.

Species	Initial concentration (mol L^{-1})
Cu^{2+}	0.056
$C_3H_6O_3$	0.111

When the solution reached equilibrium, its absorbance at 730 nm was 0.66 .

You may assume that under the conditions of this experiment, the only species present in the solution are those present in the equation above, and that $[Cu(C_3H_6O_3)_2]^{2+}$ is the only species that absorbs at 730 nm.

With the support of a line graph, calculate the equilibrium constant for the reaction. **7**



From graph:

$c([Cu(C_3H_6O_3)_2]^{2+})$ at equilibrium = 0.046 mol L^{-1}

Concentration (mol L^{-1})	**Cu^{2+}**	**$C_3H_6O_3$**	**$[Cu(C_3H_6O_3)_2]^{2+}$**
Initial	0.056	0.111	0
Change	−0.046	−0.092	+0.046
Equilibrium	0.010	0.019	0.046

$$K = \frac{[[Cu(C_3H_6O_3)_2]^{2+}]}{[Cu^{2+}][C_3H_6O_3]^2} = \frac{0.046}{0.010 \times 0.019^2} = 13000 \text{ (2 s.f.)}$$

Question 16

At 470 K, the reversible reaction of bromine gas and chlorine gas to produce bromine monochloride gas has a K value of 7.20.

$$Br_{2(g)} + Cl_{2(g)} \rightleftharpoons 2BrCl_{(g)}$$

If the reaction vessel was initially charged with 0.40 M of each reactant, calculate the concentrations of each species in the equilibrium mixture. 3

Concentration (mol L^{-1})	$Br_{2(g)}$	$Cl_{2(g)}$	$2BrCl_{(g)}$
Initial	0.40	0.40	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$0.40 - x$	$0.40 - x$	$2x$

$$K = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{(2x)^2}{(0.40 - x)^2} = 7.20$$

$$K = \frac{(2x)}{(0.40 - x)} = \sqrt{7.20}$$

$$x = \frac{0.40 \times \sqrt{7.20}}{2 + \sqrt{7.20}} = 0.2291796$$

$[Br_2]$ and $[Cl_2]$ = 0.17 M (2 s.f.) and $[BrCl]$ = 0.46 M (2 s.f.)

Question 17

Consider the following equilibrium:

$$O_{2(g)} + N_{2(g)} \rightleftharpoons 2NO_{(g)}$$

At a certain temperature, the equilibrium constant for the reaction is 3.45×10^{-3}.

(a) If 4.0 mol of nitrogen and 3.0 mol of oxygen were initially reacted to together in a 12 L flask at this temperature, calculate the final concentration of nitrogen monoxide in the equilibrium mixture. 3

Concentration (mol L^{-1})	$O_{2(g)}$	$N_{2(g)}$	$2NO_{(g)}$
Initial	0.25	0.333..	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$0.25 - x$	$0.333.. - x$	$2x$

Assuming x is small, the concentrations of reactants do not change significantly:

$$K = \frac{[NO]^2}{[O_2][N_2]} = \frac{(2x)^2}{(0.25)(0.333)} = 3.45 \times 10^{-3}$$

$$x = \sqrt{\frac{0.0002875}{4}} = 0.00847791$$

(Check assumption: 2.54% of O_2 and 3.39% of N_2, thus assumption is valid.)

[NO] = 0.017 M (2 s.f.)

If solved using quadratic equation x =0.0082335, [NO] = 0.016 M (2 s.f.)

(b) In another experiment, the same reaction was conducted at the same temperature. After 10 minutes, the concentrations of the species were:

$[N_2] = 15 \text{ mol L}^{-1}$ $[O_2] = 15 \text{ mol L}^{-1}$ $[NO] = 15 \text{ mol L}^{-1}$

Determine how the reaction will proceed as it approaches equilibrium. 3

$$Q = \frac{[NO]^2}{[O_2][N_2]} = \frac{(15)^2}{(15)(15)} = 1$$

Since $Q > K$, the concentrations of products are higher than they would be at equilibrium and the concentrations of reactants are lower than their equilibrium concentrations. Therefore, as the mixture approaches equilibrium, the ratio of products to reactants would decrease, i.e. the position of equilibrium will shift in the reverse direction.

Question 18

The Haber process for the production of ammonia is an exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Initially, 0.200 mol of ammonia were introduced into a 4.00 L container at 700 K. Given that the equilibrium concentration of hydrogen is 30 times as much as the equilibrium concentration of ammonia, calculate the equilibrium constant for this reaction at this temperature. 3

Concentration (mol L^{-1})	$N_{2(g)}$	$3H_{2(g)}$	$2NH_{3(g)}$
Initial	0	0	0.05
Change	$+x$	$+3x$	$-2x$
Equilibrium	x	$3x$	$0.05 - 2x$

Since the concentration of H_2 is 30 times the concentration of NH_3 at equilibrium:

$3x = 30 \times (0.05 - 2x)$

$3x = 1.5 - 60x$

$x = 0.0238095$

$[N_2] = 0.0238095$ M, $[H_2] = 0.0714285$ M, $[NH_3] = 0.00238095$ M

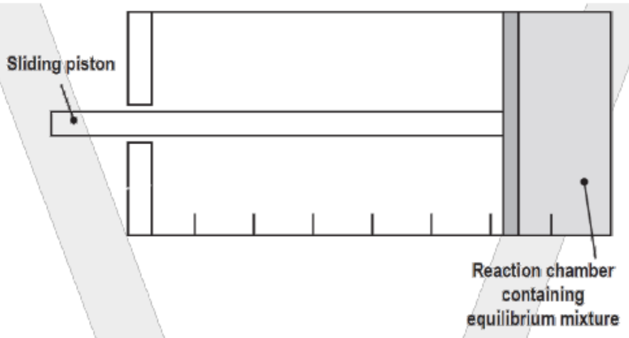
$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.00238095)^2}{(0.0714285)^3(0.0238095)} = 0.653 \text{ (3 s.f.)}$$

Question 19

Carbon monoxide gas and chlorine gas react to form phosgene ($COCl_2$) gas in a reversible reaction.

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$$

In an investigation, the reactants were introduced into a reaction chamber fitted with a sliding piston that allows the volume of the chamber to be adjusted as shown below.



(a) The original volume of the chamber is 10.0 L. Initially, 0.50 mol of chlorine gas and 0.50 mol of carbon monoxide gas were introduced. The reaction was allowed to come to equilibrium and 0.30 mol of phosgene was present in the equilibrium mixture. Calculate the equilibrium constant under these conditions. 3

Concentration (mol L^{-1})	$CO_{(g)}$	$Cl_{2(g)}$	$COCl_{2(g)}$
Initial	0.050	0.050	0
Change	−0.030	−0.030	+0.030
Equilibrium	0.020	0.020	0.030

$$K = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{(0.030)}{(0.020)^2} = 75 \text{ (2 s.f.)}$$

(b) Keeping the temperature constant, the sliding piston was then moved, halving the volume. The system was allowed to reach equilibrium. Account for any changes in the concentration of the reactants and products. 3

Initially, the concentration of reaction components increase as volume is decreased. This disturbs the equilibrium. According to Le Chatelier's principle, and the equilibrium will shift to the side with less gas moles, to decrease the pressure and minimise the disturbance. Thus the forward reaction would be favoured and the concentration of CO and Cl_2 decreases and $COCl_2$ increases until a new equilibrium is reached.

(c) Calculate the concentration of the species in the mixture after the system was allowed to re-establish equilibrium. 3

Moles before disturbance:

n(CO) and n(Cl_2) = 0.20 mol, n($COCl_2$) = 0.30 mol

Concentration with new volume (5.0 L) before new equilibrium is re-established:

c(CO) and c(Cl_2) = 0.040 mol L^{-1}, c($COCl_2$) = 0.060 mol L^{-1}

Concentration (mol L^{-1})	**$CO_{(g)}$**	**$Cl_{2(g)}$**	**$COCl_{2(g)}$**
Initial	0.040	0.040	0.060
Change	$-x$	$-x$	$+x$
Equilibrium	$0.040 - x$	$0.040 - x$	$0.060 + x$

$$K = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{(0.060 + x)}{(0.040 - x)^2} = 75 \text{ (2 s.f.)}$$

$$75x^2 - 7x + 0.06 = 0$$

Solve using quadratic equation:

x = 0.00954824

[CO] and [Cl_2] = 0.030 M (2 s.f.)

[$COCl_2$] = 0.070 M (2 s.f.)

Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 20

Which of the following is correct experimental technique for conducting a colourimetry investigation?

(a) Rinse the cuvette with distilled water immediately before adding the analyte solution.

(b) Use a new cuvette for each measurement.

(c) Rinse volumetric flasks with distilled water immediately before adding solute.

(d) Use the colourimeter as soon as possible after turning it on.

Question 21

When conducting a colourimetry investigation, which of the following steps would not be necessary?

(a) Preparation of a series of standard solutions containing the compound of interest.

(b) Plotting a calibration curve of absorbance versus concentration.

(c) Zeroing the colourimeter with a blank sample.

(d) Repeating the absorbance measurements with the other colour filters.

Question 22

To calibrate a colourimeter, a 0.250 M nickel(II) nitrate standard solution was prepared. Which of the following is correct for preparing this standard solution?

(a) 4.57 g of nickel(II) nitrate should be added to 100 mL of deionised water in a volumetric flask.

(b) 4.57 g of nickel(II) nitrate should be added to a 100 mL volumetric flask and the volume made up to the calibration mark with deionised water.

(c) 3.02 g of nickel(II) nitrate should be added to a 100 mL beaker and the volume made up to the calibration mark with deionised water.

(d) 3.02 g of nickel(II) nitrate should be added to 100 mL of deionised water in a beaker.

Standard solutions should always be prepared in a volumetric flask.

To prepare 0.250 M nickel(II) nitrate solution from 4.57 g, the **solution** needs to be 100 mL, hence water needs to be added until 100 mL is obtained.

Question 23

Nitrogen and oxygen gases react to form nitrogen monoxide:

$$O_{2(g)} + N_{2(g)} \rightleftharpoons 2NO_{(g)}$$

At 2000 K, $K = 4.2 \times 10^{-4}$. If the reaction originally only contained 15 mol L^{-1} of nitrogen monoxide, calculate the equilibrium concentration of oxygen. 3

Concentration (mol L^{-1})	$O_{2(g)}$	$N_{2(g)}$	$2NO_{(g)}$
Initial	0	0	15
Change	$+x$	$+x$	$-2x$
Equilibrium	x	x	$15 - 2x$

$$K = \frac{[NO]^2}{[O_2][N_2]} = \frac{(15 - 2x)^2}{x^2} = 4.2 \times 10^{-4}$$

$$\frac{15 - 2x}{x} = \sqrt{4.2 \times 10^{-4}}$$

$$x = \frac{15}{\sqrt{4.2 \times 10^{-4}} + 2}$$

$$x = 7.423927\ M$$

$[O_2]$ = 7.4 M (2 s.f.)

Question 24

Consider the reversible reaction:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

The decomposition of phosphorus pentachloride at 500 K has $K = 0.497$.

What are the concentrations of the species in the equilibrium mixture if 1.50 mol of phosphorus pentachloride was initially introduced into the 5.00 L reaction vessel? 3

Concentration (mol L^{-1})	$PCl_{5(g)}$	$PCl_{3(g)}$	$Cl_{2(g)}$
Initial	0.300	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.300 - x$	x	x

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)^2}{(0.300 - x)} = 0.497$$

$$x^2 + 0.497x - 0.1491 = 0$$

Solve using quadratic equation:

$x = 0.21069$

$[PCl_3]$ and $[Cl_2]$ = 0.211 M (3 s.f.)

$[PCl_5]$ = 0.0893 M (3 s.f.)

Question 25

The reaction of hydrogen and iodine gases to form hydrogen iodide gas at 730 K has the equilibrium constant 490.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K = 490$$

If the initial concentration of hydrogen was 0.500 mol L^{-1} and 85.0% of the hydrogen was converted to hydrogen iodide at equilibrium, what was the initial concentration of iodine added to the reaction flask? 3

15% of $H_{2(g)}$ left at equilibrium: 0.075 mol L^{-1}

Concentration (mol L^{-1})	$H_{2(g)}$	$I_{2(g)}$	$2HI_{(g)}$
Initial	0.500	x	0
Change	− 0.425	− 0.425	+0.850
Equilibrium	0.075	$x - 0.425$	0.850

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.850^2}{0.075 \times (x - 0.425)} = 490$$

x =0.44465986 M

$[I_2]_{initial}$ = 0.445 M (3 s.f.)

Question 26

A colourimeter was used to determine the equilibrium constant for the following reaction:

$$[Ni(H_2O)_6]^{2+}{}_{(aq)} + 6NH_{3(aq)} \rightleftharpoons [Ni(NH_3)_6]^{2+}{}_{(aq)} + 6H_2O_{(l)}$$

The formation of the nickel-ammonia complex gives a highly blue coloured solution. A blank sample in addition to five standard solutions of $[Ni(NH_3)_6]^{2+}$ were prepared and their absorbances were measured. The data are in the table below.

Test Tube	Concentration of $[Ni(NH_3)_6]^{2+}$ ($\times 10^{-4}$ mol L^{-1})	Absorbance
Blank	0.0	0.00
A	1.1	0.15
B	3.2	0.32
C	5.0	0.44
D		0.57
E	9.0	0.73

(a) Determine the concentration of $[Ni(NH_3)_6]^{2+}$ in test tube D if 3.0 mL of 1.5 M NH_3 solution was mixed with 1.5 mL of 0.0048 M $[Ni(H_2O)_6]^{2+}$ solution and the solution was made up to a final volume of 10 mL with distilled water. 2

$n(NH_3) = 1.5 \times 0.003 = 0.0045$ mol

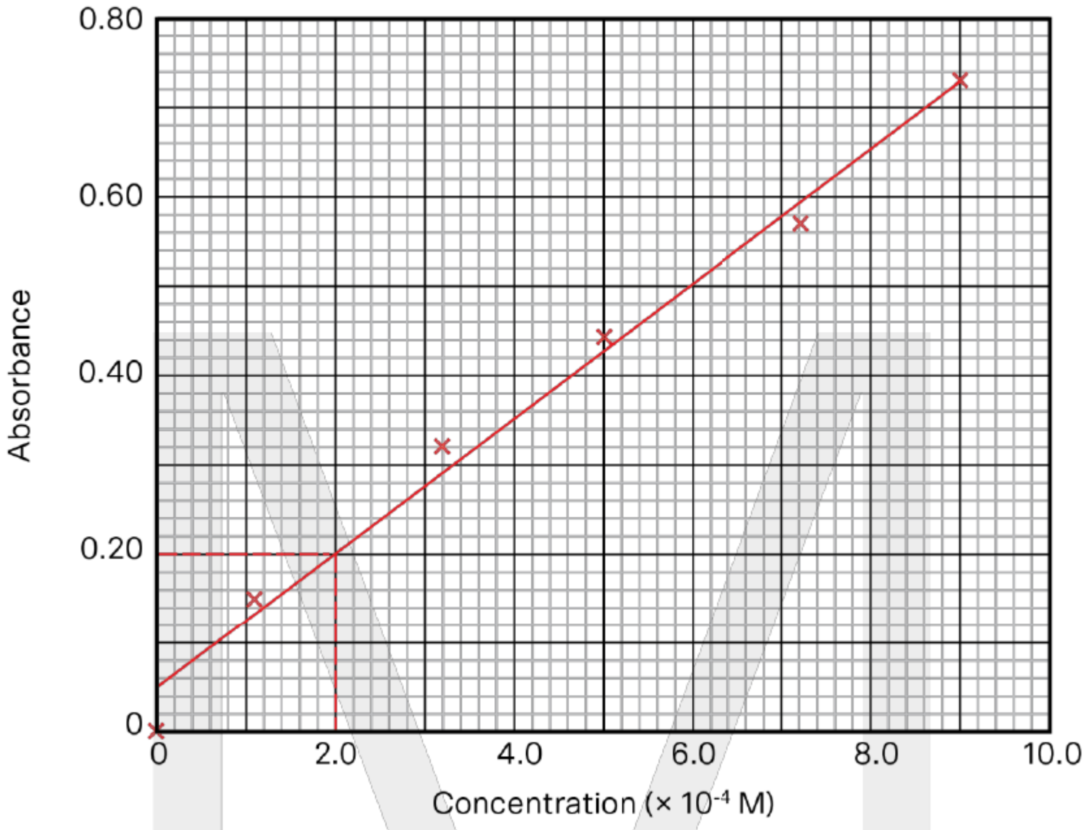
$n([Ni(H_2O)_6]^{2+}) = 0.0048 \times 0.0015 = 7.2 \times 10^{-6}$ mol

Ammonia is used in a large excess. Hence assuming reaction goes to completion:

$n([Ni(NH_3)_6]^{2+}) = n([Ni(H_2O)_6]^{2+}) = 7.2 \times 10^{-6}$ mol

$c([Ni(NH_3)_6]^{2+}) = 7.2 \times 10^{-6} / 0.010 = 7.2 \times 10^{-4}$ mol L^{-1}

(b) Plot a calibration curve in the space below. 3



(c) If a sample that initially contained 4.5×10^{-4} M of $[Ni(H_2O)_6]^{2+}$ and 1.4×10^{-3} M of NH_3 had an absorbance of 0.20, determine the equilibrium concentration of $[Ni(NH_3)_6]^{2+}$ and calculate the value of *K*. 3

Concentration (mol L^{-1})	**$[Ni(H_2O)_6]^{2+}$**	**$6NH_3$**	**$[Ni(NH_3)_6]^{2+}$**
Initial	4.5×10^{-4}	1.4×10^{-3}	0
Change	-2.0×10^{-4}	-1.2×10^{-3}	$+2.0 \times 10^{-4}$
Equilibrium	2.5×10^{-4}	2.0×10^{-4}	2.0×10^{-4}

$$K = \frac{[[Ni(NH_3)_6]^{2+}]}{[[Ni(H_2O)_6]^{2+}][NH_3]^6} = \frac{(2.0 \times 10^{-4})}{(2.0 \times 10^{-4})^6(2.5 \times 10^{-4})} = 1.3 \times 10^{22} \text{ (2 s.f.)}$$

Question 27

Consider the following equilibrium:

$$A_{(aq)} + B_{(aq)} \rightleftharpoons C_{(aq)} \qquad K = 0.85$$

Initially only sample C was introduced into a volume of water and its original concentration was 0.45 M. Assuming the initial concentration of A and B was zero, determine the concentration of C once equilibrium is established. 3

Concentration (mol L^{-1})	$A_{(aq)}$	$B_{(aq)}$	$C_{(aq)}$
Initial	0	0	0.45
Change	$+x$	$+x$	$-x$
Equilibrium	x	x	$0.45-x$

$$K = \frac{[C]}{[A][B]} = \frac{0.45-x}{x^2} = 0.85$$

$$0.85x^2 + x - 0.45 = 0$$

Solve using quadratic equation:

x =0.34741

[C] = 0.10 M (2 s.f.)

Question 28

Ammonia undergoes hydrolysis according to the following equation:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K = 1.8 \times 10^{-5}$$

If the original solution only contained 3.20 M NH_3, calculate the concentration of each species at equilibrium. 3

Concentration (mol L^{-1})	$NH_{3(aq)}$	$NH_4^+{}_{(aq)}$	$OH^-{}_{(aq)}$
Initial	3.20	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$3.20 - x$	x	x

Assuming that x is small compared to initial $[NH_3]$, $3.20 - x \approx 3.20$

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{(3.2)} = 1.8 \times 10^{-5}$$

$$x = \sqrt{1.8 \times 10^{-5} \times 3.2} = 0.007589466$$

(Check assumption: 0.23% of NH_3, thus assumption is valid.

$[NH_3] = 3.2$ M (2 s.f.)

$[NH_4^+]$ and $[OH^-] = 0.0076$ M (2 s.f.)

If solved using quadratic equation $x = 0.0075805$

Question 29

Consider the reversible reaction

$$2X_{(g)} \rightleftharpoons X_{2(g)} \qquad K = 235$$

If the initial concentration of X is 0.80 M, calculate the equilibrium concentration of $X_{2(g)}$. 3

Concentration (mol L^{-1})	$2X_{(g)}$	$X_{2(g)}$
Initial	0.80	0
Change	$-2x$	$+x$
Equilibrium	$0.80 - 2x$	x

$$K = \frac{[X_2]}{[X]^2} = \frac{x}{(0.80 - 2x)^2} = 235$$

$$940x^2 - 753x + 150.4 = 0$$

Solve using quadratic equation:

$$x = 0.3798966333$$

[X] = 0.040 M (2 s.f.)

$[X_2]$ = 0.38 M (2 s.f.)

Question 30

A group of students performed an experiment using colourimetry to determine the equilibrium constant for the reaction:

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons [Fe(SCN)]^{2+}_{(aq)}$$

The students combined solutions of $Fe(NO_3)_3$ and NaSCN to produce this equilibrium solution.

(a) The absorbance of the solution was measured in a colourimeter using a 1.00 cm cuvette and was found to be 0.0931. Calculate the equilibrium concentration of $[Fe(SCN)]^{2+}$ if the literature value for the molar absorptivity of $[Fe(SCN)]^{2+}$ is 4.70×10^3 L mol^{-1} cm^{-1}. 2

$A = \varepsilon l c$

$c = 0.0931 / (4.7 \times 10^3 \times 1.0) = 1.98 \times 10^{-5}$ M (3 s.f.)

(b) The initial concentrations of Fe^{3+} and SCN^- prepared were 9.34×10^{-4} mol L^{-1} and 1.70×10^{-4} mol L^{-1}, respectively. Calculate the value of the equilibrium constant. 3

Concentration (mol L^{-1})	$Fe^{3+}_{(aq)}$	$SCN^{-}_{(aq)}$	$[Fe(SCN)]^{2+}_{(aq)}$
Initial	9.34×10^{-4}	1.7×10^{-4}	0
Change	-1.98×10^{-5}	-1.98×10^{-5}	$+1.98 \times 10^{-5}$
Equilibrium	9.142×10^{-4}	1.502×10^{-4}	1.98×10^{-5}

$$K = \frac{[[Fe(SCN)]^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(1.98 \times 10^{-5})}{(9.142 \times 10^{-4})(1.502 \times 10^{-4})} = 144 \text{ (3 s.f.)}$$

(c) Explain why the students should have used of a calibration curve to determine the concentration of $[Fe(SCN)]^{2+}$ instead of calculating the concentration using the molar absorptivity. 2

A number of factors can affect the absorbance, such as impurities in the solvent, scratches on the cuvette, stray light and instrument calibration. Measuring the absorbance of standard solutions under the same experimental conditions and then constructing a calibration curve helps to reduce any systematic errors, thus improve accuracy.

Question 31

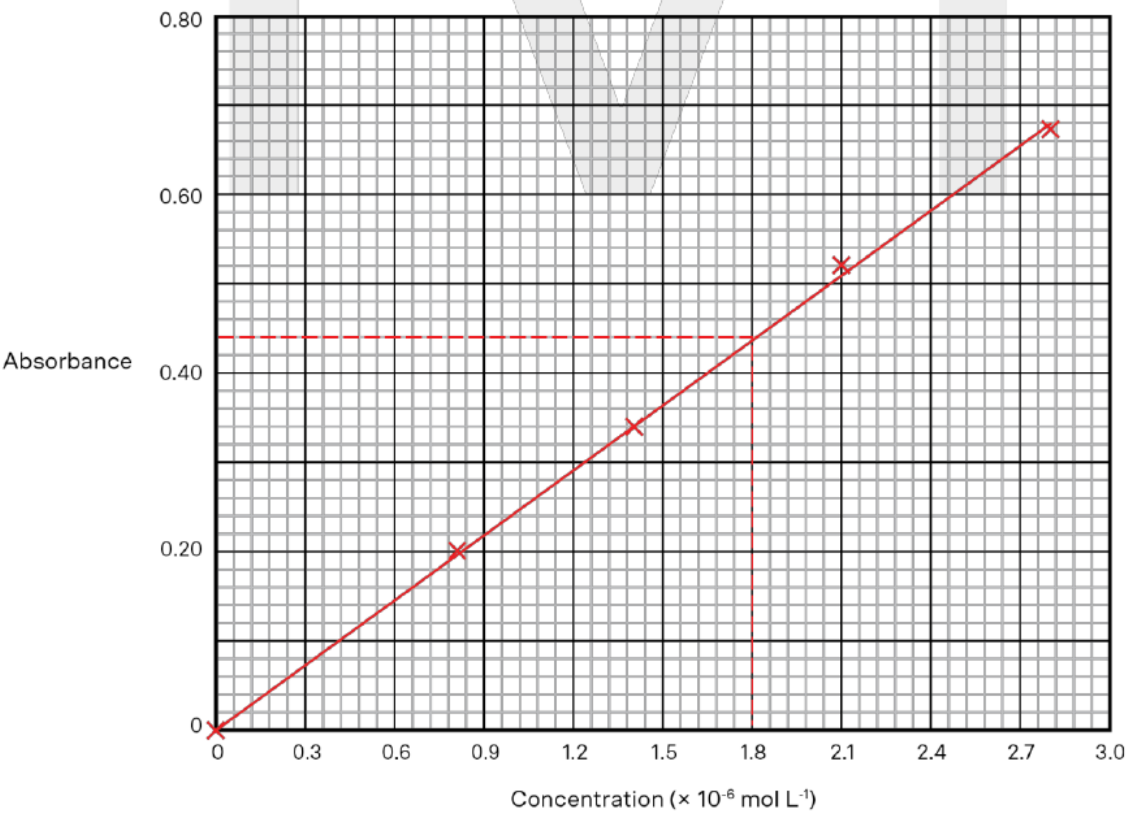
Bromothymol blue (HBB) is a commonly used acid-base indicator that forms the following equilibrium in aqueous solution:

$$\underset{\text{(Yellow)}}{HBB_{(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{(Blue)}}{BB^-_{(aq)}}$$

To determine the equilibrium constant *K* for this equilibrium, a colourimetric investigation was carried out.

(a) A blank sample in addition to four standard solutions were prepared and their absorbances were measured. Plot a calibration curve using the data in the table below. 3

Concentration of BB^- ($\times 10^{-6}$ mol L^{-1})	Absorbance
0.0 (Blank)	0.00
0.8	0.20
1.4	0.34
2.1	0.52
2.8	0.67



(b) A sample was then prepared by dissolving 26.8 mg of bromothymol blue into distilled water to make the final volume made up to 1.0 L. The solution was allowed to equilibrate and the absorbance was measured to be 0.44.

Determine the equilibrium concentration of [BB^-] and calculate the value of K.

The molar mass of bromothymol blue is 624.39 g mol^{-1}. 3

n(HBB) = 0.0268 / 624.39 = 4.292189×10^{-5} mol

c(HBB) initially = 4.292189×10^{-5} / 1.0 = 4.292189×10^{-5} mol L^{-1}

From graph:

c(BB^-) at equilibrium = 1.8×10^{-6} mol L^{-1}

Concentration (mol L^{-1})	HBB	H^+	BB^-
Initial	4.292189×10^{-5}	0	0
Change	-1.8×10^{-6}	$+1.8 \times 10^{-6}$	$+1.8 \times 10^{-6}$
Equilibrium	4.112189×10^{-5}	1.8×10^{-6}	1.8×10^{-6}

$$K = \frac{[H^+][BB^-]}{[HBB]} = \frac{(1.8 \times 10^{-6})^2}{(4.112189 \times 10^{-5})} = 7.9 \times 10^{-8} \text{ (2 s.f.)}$$

Question 32

2.00 moles of hydrogen gas and 7.00 moles of fluorine gas are mixed in a 3.00 L container, and react to form hydrogen fluoride.

$$H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$$

The equilibrium constant for this reaction is 1.15×10^2 at 298 K. Calculate the pressure inside the flask at equilibrium. 2

Total moles of gas = 9.00 mol

$$P = \frac{nRT}{V} = \frac{9.00 \times 8.314 \times 298}{3.00} = 7420 \text{ kPa (3s.f.)}$$

Note: Since there are two moles of gas on both sides, there's no change in pressure when the system reaches equilibrium. Hence the pressure at equilibrium remains as 7420 kPa.

Year 12
Chemistry
Equilibrium and Acid Reactions

Work Book 6
Solubility equilibria 1

MATRIX
EDUCATION

Part A: Multiple choice questions

Question 1

Based on the K_{sp} values, which correctly lists the compounds in order of increasing solubility?

(a) AgBr, $BaSO_4$, $CaCO_3$, $FePO_4$

(b) $BaSO_4$, $CaCO_3$, $FePO_4$, AgBr

(c) $CaCO_3$, $BaSO_4$, AgBr, $FePO_4$

(d) $FePO_4$, AgBr, $BaSO_4$, $CaCO_3$

For salts that produce the same total number of ions, the K_{sp} values can be directly compared. The larger the K_{sp} value, the greater the extent of dissolution and hence the greater the solubility.

Question 2

The solubility product for aluminium phosphate is given by:

(a) $[Al^{3+}]^3\,[PO_4^{3-}]^3$

(b) $3[Al^{3+}]\,3[PO_4^{3-}]$

(c) $[Al^{3+}]\,[PO_4^{3-}]$

(d) $[Al_3]\,[(PO_4)_3]$

$AlPO_{4(s)} \rightleftharpoons Al^{3+}_{(aq)} + PO_4^{3-}{}_{(aq)}$ $\qquad K_{sp} = [Al^{3+}][PO_4^{3-}]$

Question 3

A saturated solution containing a compound with a large K_{sp} value will be predicted to have:

(a) low solubility

(b) high conductivity

(c) high entropy

(d) low enthalpy

The larger the K_{sp} value, the greater the extent of dissolution and hence the greater the number of ions in solution. The more ions, the more conductive the solution.

Question 4

A sample of ammonium nitrate is added to water, and stirred to form a solution. The temperature of the solution changes from 24.1 °C to 21.5 °C. What are the signs of ΔH and ΔS?

	ΔH	ΔS
(a)	Positive	Positive
(b)	Positive	Negative
(c)	Negative	Positive
(d)	Negative	Negative

The temperature decreases so the dissolution must be endothermic, hence $\Delta H > 0$.

The fact that it dissolves means $\Delta G < 0$ at 24.1 °C, so ΔS must not be negative (dissolution also usually means $\Delta S > 0$).

Question 5 [2019 HSC Q3]

Which of the following metal carbonates has the highest molar solubility?

(a) Calcium carbonate

(b) Copper(II) carbonate

(c) Iron(II) carbonate

(d) Lead(II) carbonate

For salts that produce the same total number of ions, the K_{sp} values can be directly compared. The larger the K_{sp} value, the greater the extent of dissolution and hence the greater the solubility.

Question 6

How would the concentration of $CO_3^{2-}{}_{(aq)}$ ions in equilibrium with $Na_2CO_{3(s)}$ be affected if the concentration of $Na^+{}_{(aq)}$ ions were halved?

(a) No change

(b) Decreased by a factor of 2

(c) Increased by a factor of 2

(d) Increased by a factor of 4

$Na_2CO_{3(s)} \rightleftharpoons 2Na^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Na^+]^2[CO_3^{2-}]$

Let the concentration of the dissolved ionic compound be x. Thus $[Na^+] = 2x$ and $[CO_3^{2-}] = x$. Thus $K_{sp} = (2x)^2(x) = 4x^3$.

Since K_{sp} value must remain the same, if $[Na^+] = x$, $[CO_3^{2-}]$ must be $4x$.

Question 7

The K_{sp} value for silver chloride is 2.0×10^{-10}. Which of the following statements is correct?

(a) AgCl is very soluble in water as its K_{sp} value is large

(b) AgCl is not very soluble in water as its K_{sp} value is large

(c) AgCl is very soluble in water as its K_{sp} value is small

(d) AgCl is not very soluble in water as its K_{sp} value is small

The smaller the K_{sp} value, the lower the extent of dissolution and hence the lower the solubility.

Question 8

What occurs when the solubility of an ionic compound increases?

	Conductivity	K_{sp}
(a)	Increases	Increases
(b)	Increases	Decreases
(c)	Decreases	Increases
(d)	Decreases	Decreases

The greater the extent of dissolution, the greater the number of ions in solution. The more ions, the more conductive the solution and the larger the K_{sp}.

Question 9

The K_{sp} of magnesium phosphate:

(a) changes with temperature

(b) changes with volume

(c) changes with concentration

(d) changes with pressure

Only temperature changes the value of *K*.

Question 10

The concentration of azide ions in a saturated solution of lead(II) azide $Pb(N_3)_2$ is 1.71×10^{-3} M. What is the K_{sp} of lead(II) azide?

(a) 1.17×10^{-5}

(b) 2.92×10^{-6}

(c) 2.00×10^{-8}

(d) 2.50×10^{-9}

$$Pb(N_3)_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2N_3^-{}_{(aq)}$$

$[N_3^-] = 1.71 \times 10^{-3}$ M, $[Pb^{2+}] = 8.55 \times 10^{-4}$ M

$K_{sp} = [Pb^{2+}][N_3^-]^2 = (8.55 \times 10^{-4})(1.71 \times 10^{-3})^2 = 2.50 \times 10^{-9}$

Question 11

0.20 mol of sodium chloride dissolves in water to make 3.5 L of aqueous solution with a density of 1.05 g mL^{-1}. What is the concentration of NaCl in the solution?

(a) 0.32% w/w

(b) 32 ppm

(c) 3.3% w/w

(d) 33 ppm

Convert units to mass

m(NaCl) = n × MM = 0.20 × (22.99 + 35.45) = 11.688 g

m(solution) = V × d = 3500 × 1.05 = 3675 g

%w/w = (solute / solution) × 100 = (11.688 / 3675) × 100 = 0.32%

Part B: Extended response questions

Question 12

Describe the processes occurring when solid sodium sulfate dissolves exothermically in water in terms of:

(a) Intramolecular and intermolecular forces 2

Ionic bonds in sodium sulfate and hydrogen bonds in water break as the ions begin to dissolve. Ion-dipole forces form between individual ions and water, arranging the water molecules into solvation layers around the ions.

(b) Entropy 2

The entropy of the solute increases as sodium sulfate dissolves because the dissociated ions are more dispersed. The entropy of the solvent decreases due to the formation of an organised solvation sphere of water molecules around the solute.

(c) Enthalpy 1

Since the dissolution of sodium sulfate in water is exothermic, the enthalpy decreases as sodium sulfate dissolves.

Question 13

Write **dissociation equations** for the following ionic substances and the corresponding solubility product. 6

(a) $KCl_{(s)} \rightleftharpoons K^{+}_{(aq)} + Cl^{-}_{(aq)}$ $K_{sp} = [K^{+}][Cl^{-}]$

(b) $Mg(NO_3)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2NO_3^{-}{}_{(aq)}$ $K_{sp} = [Mg^{2+}][NO_3^{-}]^2$

(c) $RbOH_{(s)} \rightleftharpoons Rb^{+}_{(aq)} + OH^{-}_{(aq)}$ $K_{sp} = [Rb^{+}][OH^{-}]$

(d) $Li_2SO_{4(s)} \rightleftharpoons 2Li^{+}_{(aq)} + SO_4^{2-}{}_{(aq)}$ $K_{sp} = [Li^{+}]^2[SO_4^{2-}]$

(e) $Na_2CO_{3(s)} \rightleftharpoons 2Na^{+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Na^{+}]^2[CO_3^{2-}]$

(f) $(NH_4)_3PO_{4(s)} \rightleftharpoons 3NH_4^{+}{}_{(aq)} + PO_4^{3-}{}_{(aq)}$ $K_{sp} = [NH_4^{+}]^3[PO_4^{3-}]$

Question 14

A 2.0 g sample of lead(II) chloride containing radioactive lead-209 was added to beaker containing a saturated solution of non-radioactive lead(II) chloride.

(a) Write a balanced chemical equation for the reaction occurring in the beaker. 1

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

(b) Explain, with reference to dynamic equilibrium, how the radioactive lead(II) ions would be distributed after several hours. 2

A dynamic equilibrium exists in a saturated solution where the rate of the forward dissolution reaction is equal to the rate of the reverse precipitation reaction. Since the forward and reverse reactions continue to occur, the radioactive ions will be distributed in both the solution (as dissolution occurs) and in the solid (as precipitation occurs).

(c) Explain how the equilibrium will shift when the following substances are added to the saturated solution above:

(i) Solid lead(II) chloride 2

The addition of solid lead(II) chloride does not shift the equilibrium. The equilibrium constant is dependent on the concentration of the lead(II) ions and chloride ions only.

(ii) Water 2

Addition of water increases the volume, hence decreases the concentration of ions disturbing equilibrium. According to Le Chatelier's principle, equilibrium shifts right to produce more ions and increase their concentration to minimise the disturbance.

Question 15

The solubility product constants at 25 °C for two ionic compounds are given below.

Salt	K_{sp} at 25 °C
Cobalt(II) carbonate	1.4×10^{-13}
Cobalt(II) hydroxide	1.6×10^{-15}

(a) Explain what is meant by "solubility product constant". **1**

Solubility constant (K_{sp}) describes the equilibrium between a solid and its ions in solution (measures the extent of dissolution).

(b) Explain what is meant by "solubility". **1**

The solubility of a compound is the maximum amount of solute that can dissolve in a specific volume of solvent at a certain temperature.

(c) Which of the salts is more soluble at 25 °C? Explain your answer and show working **5**

$CoCO_{3(s)} \rightleftharpoons Co^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)}$ $K_{sp} = [Co^{2+}][CO_3{}^{2-}] = 1.4 \times 10^{-13}$

Let moles of $CoCO_3$ in 1 L = x, thus $[Co^{2+}] = [CO_3{}^{2-}] = x$

$K_{sp} = x^2 = 1.4 \times 10^{-13}$

$x = 3.7 \times 10^{-7}$

Solubility of $CoCO_3 = 3.7 \times 10^{-7}$ mol/L

$Co(OH)_{2(s)} \rightleftharpoons Co^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp} = [Co^{2+}][OH^-]^2 = 1.6 \times 10^{-15}$

Let moles of $Co(OH)_2$ in 1 L = x, thus $[Co^{2+}] = x$, $[OH^-] = 2x$

$K_{sp} = (x)(2x)^2 = 1.6 \times 10^{-15}$

$x = 7.4 \times 10^{-6}$

Solubility of $Co(OH)_2 = 7.4 \times 10^{-6}$ mol/L

Since a greater number of moles of cobalt hydroxide can dissolve in one litre of solution, it is more soluble.

Question 16

(a) Distinguish between a saturated and unsaturated solution. 2

A saturated solution contains the maximum amount of solute that will dissolve at a particular temperature. An unsaturated solution contains less than the maximum amount of solute that can be dissolved at a particular temperature.

(b) Water is added to 0.46 g of calcium hydroxide to make 2.25 L of solution at 25 °C. Will the solution be in dynamic equilibrium? Explain your answer. 4

$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$ $K_{sp} = [Ca^{2+}][OH^{-}]^2 = 5.02 \times 10^{-6}$

Let moles of $Ca(OH)_2$ in 1 L = x, thus $[Ca^{2+}] = x$, $[OH^{-}] = 2x$

$K_{sp} = (x)(2x)^2 = 5.02 \times 10^{-6}$, thus $x = 0.0107865$

Solubility of $Ca(OH)_2$ = 0.0107865 mol/L

= (0.0107865 × (40.08+32.00+2.016)) g/L = 0.799 g/L

Therefore 1.798 g can dissolve in 2.25 L.

Since the solution contains less than the maximum amount of solute that can be dissolved, it is not saturated and so it is not in dynamic equilibrium.

(c) Calculate the maximum mass, in mg, of nickel(II) carbonate ($K_{sp} = 6.6 \times 10^{-9}$) that would dissolve in 500 mL of aqueous solution. 3

$NiCO_{3(s)} \rightleftharpoons Ni^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}$ $K_{sp} = [Ni^{2+}][CO_3{}^{2-}] = 6.6 \times 10^{-9}$

Let moles of $NiCO_3$ in 1 L = x, thus $[Ni^{2+}] = x$, $[CO_3{}^{2-}] = x$

$K_{sp} = x^2 = 6.6 \times 10^{-9}$, thus $x = 8.124038 \times 10^{-5}$

Solubility of $NiCO_3$ = 8.1240×10^{-5} mol/L

In g/L: $(8.1240 \times 10^{-5} \times (58.69 + 12.01 + 16 \times 3)) = 9.64323 \times 10^{-3}$ g/L

In 500 mL, $9.64323 \times 10^{-3} \times 0.5 = 0.00482$ g = 4.8 mg can dissolve.

Question 17

The K_{sp} of aluminium hydroxide at 25 °C is 1.8×10^{-5}.

(a) Calculate the concentration of a saturated solution of aluminium hydroxide in moles per litre. **2**

$Al(OH)_{3(s)} \rightleftharpoons Al^{3+}{}_{(aq)} + 3OH^{-}{}_{(aq)}$ $K_{sp} = [Al^{3+}][OH^{-}]^3 = 1.8 \times 10^{-5}$

Let moles of $Al(OH)_3$ in 1 L = x, thus $[Al^{3+}] = x$, $[OH^-] = 3x$

$K_{sp} = (x)(3x)^3 = 27x^4 = 1.8 \times 10^{-5}$

$x = 0.02857$

$[Al(OH)_{3(aq)}] = 0.029$ mol L^{-1} (2 s.f.)

(b) Calculate the concentration of a saturated solution of aluminium hydroxide as % w/w (solution density = 1.00 g mL^{-1}). **1**

$[Al(OH)_{3(aq)}] = 0.02857...$ mol L^{-1}

$m(Al(OH)_{3(aq)}) = 0.02857... \times (26.98 + 16 \times 3 + 1.008 \times 3) = 2.2289178$ g

m(solution) = 1000 g

%w/w = (2.2289178/1000) × 100 = 0.22% w/w (2 s.f.)

(c) Calculate the concentration of a saturated solution of aluminium hydroxide in ppm. **1**

Concentration of $Al(OH)_{3(aq)}$ = 2.2289178 g L^{-1}

= 2.2289178×10^3 mg L^{-1}

= 2200 ppm (2 s.f.)

(d) If 5.4 g of aluminium hydroxide is mixed with water to make 750 mL of solution, what mass of aluminium hydroxide remains undissolved? **1**

Maximum mass of $Al(OH)_3$ that dissolves in 750 mL (750 g):

0.22289% × 750 = 1.671688 g

Thus mass of $Al(OH)_3$ that will be undissolved = 5.4 − 1.671688 = 3.7 g (2 s.f.)

Question 18

(a) The solubility of lead(II) iodide is 4.19×10^{-3} mol L^{-1} at 60 °C. Calculate its solubility product at this temperature. **2**

$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$

$[Pb^{2+}] = 4.19 \times 10^{-3}$ M, $[I^{-}] = 8.38 \times 10^{-3}$ M

$K_{sp} = [Pb^{2+}][I^{-}]^2 = (4.19 \times 10^{-3})(8.38 \times 10^{-3})^2 = 2.94 \times 10^{-7}$ (2 s.f.)

(b) The solubility of calcium oxalate CaC_2O_4 is 6.7×10^{-4} g per 100 mL at 20 °C. Calculate its solubility product at this temperature. **3**

Solubility of $CaC_2O_4 = 6.7 \times 10^{-3}$ g/L

$= (6.7 \times 10^{-3} / (40.08 + 12.01 \times 2 + 16 \times 4))$ mol/L $= 5.2302888 \times 10^{-5}$ mol/L

$CaC_2O_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + C_2O_4{}^{2-}_{(aq)}$

$[Ca^{2+}]$ and $[C_2O_4{}^{2-}] = 5.2302888 \times 10^{-5}$ mol/L

$K_{sp} = [Ca^{2+}][C_2O_4{}^{2-}] = (5.2302888 \times 10^{-5})^2 = 2.7 \times 10^{-9}$ (2 s.f.)

(c) When 2.00 g of aluminium fluoride was mixed with water to make 100 mL of solution at 40 °C, 1.09 g of aluminium fluoride remained undissolved. Calculate its solubility product at this temperature. **3**

Solubility of $AlF_3 = 9.1$ g/L

$= (9.1 / (26.98 + 19.00 \times 3))$ mol/L $= 0.108359$ mol/L

$AlF_{3(s)} \rightleftharpoons Al^{3+}_{(aq)} + 3F^{-}_{(aq)}$

$[Al^{3+}] = 0.108359$ mol/L and $[F^{-}] = 0.325077$ mol/L

$K_{sp} = [Al^{3+}][F^{-}]^3 = 0.108359 \times (0.325077)^3 = 3.72 \times 10^{-3}$ (3 s.f.)

Question 19

The following enthalpy and entropy data apply to sodium chloride and calcium chloride dissolving in water at 25 °C.

	Sodium chloride	Calcium chloride
$\Delta H_{sol}^{\ominus}$ (kJ mol^{-1})	+3.87	−82.9
$\Delta S_{sol}^{\ominus}$ (J K^{-1} mol^{-1})	+43.3	−44.7

(a) Explain the difference in the enthalpy changes of the two salts. **3**

The ΔH_{sol} results from the energy difference between the energy required to break cohesive forces and the energy produced when adhesives forces form.

Since ΔH of sodium chloride is positive, the energy required to break the cohesive forces is greater than the energy released when adhesive forces form. Hence, the ionic bonds between sodium and chloride ions and the hydrogen bonding within the water are stronger than the ion-dipole forces formed.

Since ΔH of calcium chloride is negative, the ion-dipole forces formed are stronger than the ionic bonds between calcium and chloride ions and the hydrogen bonding within the water.

(b) Determine whether the salts above are soluble or insoluble in water at 25°C. Explain your answer with reference to the relative enthalpy and entropy contributions. **4**

$\Delta G_{sol}^{\ominus}(NaCl) = 3.87 - 298.15 \times 0.0433 = -9.04$ kJ mol^{-1}

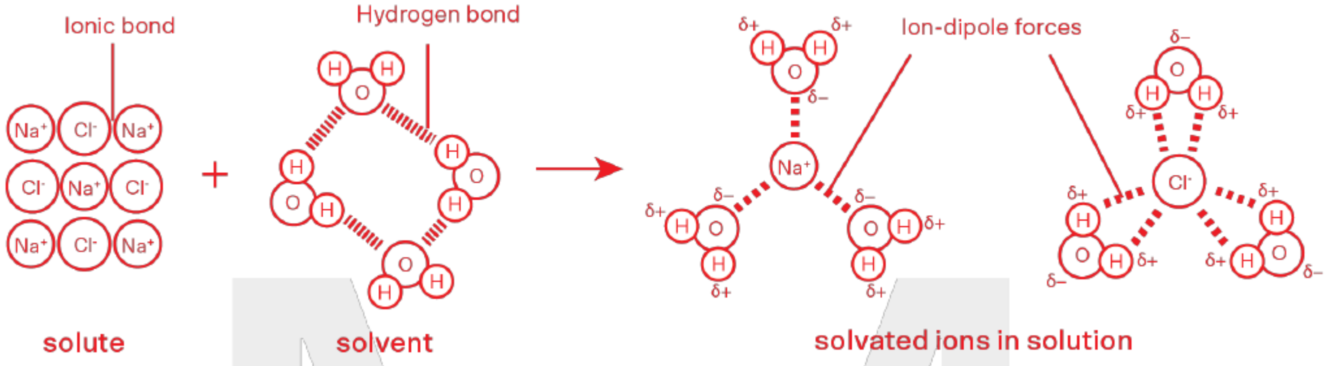
$\Delta G_{sol}^{\ominus}(CaCl_2) = -82.9 - 298.15 \times -0.0447 = -69.6$ kJ mol^{-1}

Both salts have a negative free energy change at 25°C, hence are soluble in water.

Sodium chloride has a positive ΔH; which has a positive contribution to ΔG, but a positive ΔS, which results in a negative contribution to ΔG. Since the $-T\Delta S$ contribution is greater than the positive ΔH, $\Delta G < 0$.

Calcium chloride has a negative ΔS; which results positive $-T\Delta S$ contribution to ΔG. However, the significantly negative ΔH is greater than the $-T\Delta S$ contribution, resulting in a negative ΔG.

(c) Draw a labelled diagram to show the changes that occur in bonding when sodium chloride dissolves in water. 3



Question 20

23.0 mg of iron(II) carbonate is added to water to make 0.95 L of solution at 25 °C.

(a) What percentage of the iron(II) ions in the mixture is dissolved? 3

$FeCO_{3(s)} \rightleftharpoons Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

$K_{sp} = [Fe^{2+}][CO_3^{2-}] = 3.13 \times 10^{-11}$

$K_{sp} = x^2 = 3.13 \times 10^{-11}$

$x = 5.59 \times 10^{-6}$

Solubility of $FeCO_3 = 5.59 \times 10^{-6}$ mol $L^{-1} = 6.48 \times 10^{-4}$ g/L

Solubility of $FeCO_3$ in 0.95 L $= 6.16 \times 10^{-4}$ g = 0.616 mg

% dissolved: 0.616 / 23 × 100 = 2.7% (2 s.f.)

(b) How much additional water is required to dissolve all of the iron(II) carbonate? 1

Volume of solution required to dissolve 23 mg of $FeCO_3$

$= 0.023 / 6.48 \times 10^{-4} = 35.483148$ L

Thus additional volume = 35.483148 L − 0.95 L = 34.533 L = 35 L (2 s.f.)

Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 21

Ionic compounds dissolve in water because water molecules:

(a) are covalently bonded

(b) are uncharged

(c) are polar

(d) are charged

Polarity in water allows the formation of strong ion-dipole forces between the water molecules and the ions in the ionic compound. The strong adhesive forces disrupt the ionic bonds between the ions, allowing the ions to dissociate and be dissolved.

Question 22

Match the indicated measures of concentration with the appropriate substances.

	% v/v	% w/v	ppm	$mol\ L^{-1}$
(a)	Alcohol in wine	$\text{Vinegar}_{(aq)}$	Selenium in soil	$HCl_{(aq)}$
(b)	$\text{Vinegar}_{(aq)}$	$HCl_{(aq)}$	Alcohol in wine	Selenium in soil
(c)	$HCl_{(aq)}$	Selenium in soil	$\text{Vinegar}_{(aq)}$	Alcohol in wine
(d)	Alcohol in wine	$HCl_{(aq)}$	Selenium in soil	$\text{Vinegar}_{(aq)}$

Question 23

Which one of the following salts has the highest solubility?

	Salt	Solubility at 25 °C
(a)	A	14 g per 55 mL of water
(b)	B	20 g per 75 mL of water
(c)	C	10 g per 30 mL of water
(d)	D	18 g per 60 mL of water

(a): 14 g/55 mL = 0.25 g/mL

(b): 20 g/75 mL = 0.26 g/mL

(c): 10 g/30 mL = 0.33 g/mL

(d): 18 g/60 mL = 0.30 g/mL

Question 24 [2019 HSC Q11]

A saturated solution of barium carbonate was stored in a flask. Solid barium carbonate containing radioactive carbon-14 was added to the solution. The mixture was allowed to stand for several days and was then filtered.

Radioactivity could reasonably be expected to be found in

(a) the filtrate only.

(b) the residue only.

(c) both residue and filtrate.

(d) neither residue nor filtrate.

A dynamic equilibrium exists in a saturated solution where the rate of the forward dissolution reaction is equal to the rate of the reverse precipitation reaction. Since the forward and reverse reactions continue to occur, the radioactive carbon-14 in the carbonate ions will be distributed in both the filtrate (as dissolution occurs) and in the residue (as precipitation occurs).

Question 25

Define the following terms:

(a) Ionic bonding **1**

An electrostatic attraction between a cation and an anion.

(b) Covalent bonding **1**

A chemical bond formed via shared pair(s) of electrons.

(c) Hydrogen bonding **1**

A strong electrostatic attraction between a lone pair on a highly electronegative atom (N, O or F) and a hydrogen atom covalently bonded to a highly electronegative atom (N, O or F).

(d) Dispersion force **1**

Electrostatic attractions between fluctuating dipoles.

(e) Ion-dipole force **1**

Electrostatic intermolecular attraction between a permanent dipole and an ion.

Question 26

Compare the dissolution of glucose $C_6H_{12}O_{6(s)}$ and sodium chloride in water, in terms of bonding. **4**

Glucose is a covalent molecular compound. When it dissolves, cohesive hydrogen bonds in glucose and in water break, and adhesive hydrogen bonds form between glucose and water causing solvation.

Sodium chloride is an ionic compound. When it dissolves, ionic bonds between sodium and chloride ions break, and hydrogen bonds in water break. Adhesive ion-dipole forces form between the ions and water molecules.

Question 27

Explain how the equilibrium shifts when the following are added to a saturated solution of sodium sulfate.

(a) Solid sodium sulfate 2

The addition of solid sodium sulfate does not change the concentrations of sodium and sulfate ions, hence $Q = K_{sp}$, and equilibrium is not disturbed. Thus, equilibrium does not shift when solid sodium sulfate is added.

(b) Water 2

Addition of water increases the volume, hence decreases the concentration of ions and disturbs equilibrium. According to Le Chatelier's principle, equilibrium shifts right to produce more ions and increase their concentration to minimise the disturbance.

Question 28 **[HSC Sample Q16]**

A 100 mL saturated solution of calcium hydroxide at 25°C contains 0.173 g of calcium hydroxide.

(a) Calculate the solubility product (K_{sp}) of this salt at 25°C. 3

$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$ $K_{sp} = [Ca^{2+}][OH^{-}]^2$

Concentration of $Ca(OH)_2$ = 0.173 g/100 mL

n = m/M = 0.173/74.093 = 0.00233 moles in 100 mL

Concentration in mol L^{-1} = 0.0233 mol L^{-1}

Concentration of Ca^{2+} = 0.0233 mol L^{-1} and concentration of OH^{-} = 0.0466 mol L^{-1}

$K_{sp} = 0.0233 \times (0.0466)^2 = 5.06 \times 10^{-5}$

(b) Explain why the undissolved solid is not included in the expression for the solubility product constant. 1

The amount of undissolved solid is not included in the K_{sp} expression because it remains constant. There is no change in concentration.

Question 29

(a) Define solubility. **1**

The solubility of a compound is the maximum amount of solute that can dissolve in a specific volume of solvent at a certain temperature.

(b) Outline the relationships between solubility and K_{sp}. **1**

K_{sp} describes the equilibrium between a solid and its ions in solution, thus it measures the extent of dissolution. The larger the value of K_{sp}, the greater the extent of dissolution, thus the more soluble the compound is.

(c) The K_{sp} of thallium(I) chloride is 1.9×10^{-4} and the K_{sp} of silver carbonate is 8.5×10^{-12} at 25 °C. Compare the solubility of the two salts. **4**

$TlCl_{(s)} \rightleftharpoons Tl^{+}_{(aq)} + Cl^{-}_{(aq)}$ $\quad K_{sp} = [Tl^{+}][Cl^{-}] = 1.9 \times 10^{-4}$

Let moles of TlCl in 1 L = x, thus $[Tl^{+}] = [Cl^{-}] = x$

$K_{sp} = x^2 = 1.9 \times 10^{-4}$ $\quad x = 1.3784 \times 10^{-2}$

Solubility of TlCl = 1.4×10^{-2} mol/L

$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $\quad K_{sp} = [Ag^{+}]^2[CO_3^{2-}] = 8.5 \times 10^{-12}$

Let moles of Ag_2CO_3 in 1 L = x, thus $[Ag^{+}] = 2x$, $[CO_3^{2-}] = x$

$K_{sp} = (2x)^2(x) = 8.5 \times 10^{-12}$ $\quad x = 1.28564 \times 10^{-4}$

Solubility of Ag_2CO_3 = 1.3×10^{-4} mol/L

Since a greater number of moles of thallium(I) chloride can dissolve in one litre of solution, it is more soluble.

(d) Describe the processes occurring when a solid ionic compound dissolves in water in terms of intramolecular and intermolecular forces. **2**

When a solid ionic compound is added to water, the ions at the surface of the crystal become surrounded by water molecules. The ions dissociate from the crystal when the ion-dipole forces between the ions and water become stronger than the ionic bonds between the ions and the hydrogen bonding between water molecules. As the ions are dissociated from the crystal, they become solvated by water molecules and remain dissolved.

Question 30

(a) A saturated solution of lithium carbonate in pure water at 40 °C contains 1.17 g of solute per 100.0 mL of solution. Calculate the solubility product constant of lithium carbonate at this temperature. 3

Solubility of Li_2CO_3 = 1.17 g/0.100 L = 11.7 g/L

= (11.7/(6.941 × 2 +12.01 +16.00 × 3)) mol/L = 0.158339 mol/L

$Li_2CO_{3(s)} \rightleftharpoons 2Li^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

$[Li^+]$ = 0.316678 mol/L and $[CO_3^{2-}]$ = 0.158339 mol/L

$K_{sp} = [Li^+]^2[CO_3^{2-}] = (0.316678)^2 \times 0.158339 = 0.0159$ (3 s.f.)

(b) The K_{sp} of lithium carbonate is 2.90×10^{-2} at 10 °C.

(i) What conclusion can be drawn about the solubility of lithium carbonate in water as temperature decreases? Explain your answer. 2

The solubility of lithium carbonate in water increases as temperature decreases. The K_{sp} value is larger at a lower temperature. Thus, the equilibrium is more shifted forward, meaning a greater extent of dissolution and hence greater solubility.

(ii) What mass of lithium carbonate is required to make 100 mL of saturated solution at 10 °C? 3

$Li_2CO_{3(s)} \rightleftharpoons 2Li^+_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Li^+]^2[CO_3^{2-}] = 2.90 \times 10^{-2}$

Let moles of Li_2CO_3 in 1 L = x, thus $[Li^+] = 2x$, $[CO_3^{2-}] = x$

$K_{sp} = (2x)^2\ x = 4x^3 = 2.9 \times 10^{-2}$, thus $x = 0.19354...$

Solubility of Li_2CO_3 = 0.19354...mol/L

In g/L: (0.19354...× (6.941 × 2 + 12.01 + 16 × 3)) = 14.301... g/L

In 100 mL, 14.301... × 0.1 = 1.43 g can dissolve (3 s.f.).

Question 31

Calculate the molar solubility of silver sulfide, given the K_{sp} is 8.00×10^{-51} at 25 °C. 2

$Ag_2S_{(s)} \rightleftharpoons 2Ag^+_{(aq)} + S^{2-}_{(aq)}$ $K_{sp} = [Ag^+]^2[S^{2-}] = 8.00 \times 10^{-51}$

Let moles of Ag_2S in 1 L = x, thus $[Ag^+] = 2x$, $[S^{2-}] = x$

$K_{sp} = (2x)^2(x) = 8.00 \times 10^{-51}$

$x = 1.2599 \times 10^{-17}$

Solubility of $Ag_2S = 1.26 \times 10^{-17}$ mol/L (3 s.f.)

Question 32

Calculate the concentration of hydroxide ions, in grams per litre, in a saturated solution of zinc hydroxide. The K_{sp} of zinc hydroxide is 3.0×10^{-17}. 3

$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp} = [Zn^{2+}][OH^-]^2 = 3.0 \times 10^{-17}$

Let moles of $Zn(OH)_2$ in 1 L = x, thus $[Zn^{2+}] = x$, $[OH^-] = 2x$

$K_{sp} = (x)(2x)^2 = 3.0 \times 10^{-17}$

$x = 1.9574 \times 10^{-6}$

$[OH^-] = 2 \times 1.9574 \times 10^{-6} = 3.9148 \times 10^{-6}$ mol/L

$= (3.9148 \times 10^{-6} \times (16.00 + 1.008))$ g/L

$= 6.7 \times 10^{-5}$ g/L (2 s.f.)

Question 33

The following enthalpy and entropy data apply to the dissolution of silver iodide in water at 25 °C.

$\Delta H_{sol}^{\ominus}$ (kJ mol^{-1})	$\Delta S_{sol}^{\ominus}$ (J K^{-1} mol^{-1})
112.2	68.5

(a) Account for the sign of the enthalpy change. 2

The ionic bonds between silver and iodide ions and the hydrogen bonding within the water are stronger than the ion-dipole forces formed between the ions and water, thus the energy required to break the cohesive forces is greater than the energy released when adhesive forces form. Hence ΔH_{sol} of silver iodide is positive.

(b) Account for the sign of the entropy change. 2

The entropy of the silver iodide increases as it dissolves because the dissociated ions are more dispersed. The entropy of the water decreases due to the formation of an organised solvation sphere of water molecules around the solute. Since the entropy increase of the solute is greater than the entropy decrease of the solvent, the overall entropy increases.

(c) Determine whether silver iodide is soluble or insoluble in water at 25°C. Explain your answer with reference to the relative enthalpy and entropy contributions and the resultant $\Delta G^{\ominus}$. 3

$\Delta G_{sol}^{\ominus}(AgI) = 112.2 - 298.15 \times 0.0685 = 91.8$ kJ mol^{-1}

Silver iodide has a positive free energy change at 25°C, hence is insoluble in water.

Silver iodide has a positive ΔH; which has a positive contribution to ΔG, but a positive ΔS, which results in a negative contribution to ΔG. However, since the $-T\Delta S$ contribution is smaller than the positive ΔH, $\Delta G > 0$.

(d) The K_{sp} of silver iodide is 8.52×10^{-17} at 25 °C. What can you conclude about the solubility of silver iodide and its equilibrium position from this value? Explain your answer. 2

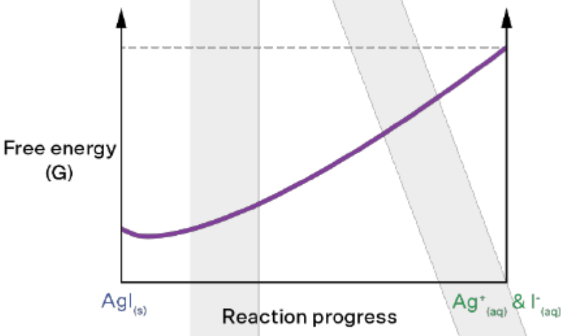
K_{sp} describes the equilibrium between a solid and its ions in solution.

$AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$ $K_{sp} = [Ag^+][I^-] = 8.52 \times 10^{-17}$

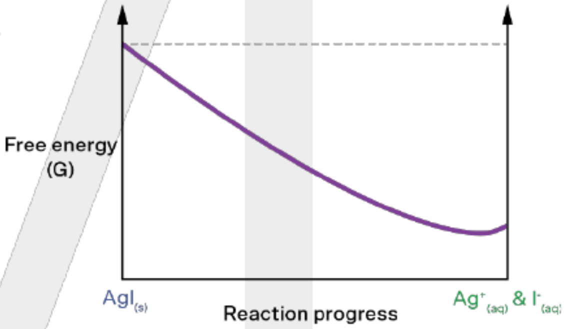
Since the K_{sp} value is very small, the concentration of ions in the saturated (equilibrium) solution is very small, thus the extent of dissolution is very small. Hence silver iodide is not very soluble in water at 25 °C and the equilibrium position lies very far to the left (favours reactants).

(e) Which of the following free energy curves below shows the variation in Gibbs free energy for the dissolution of silver iodide in water at 25 °C?

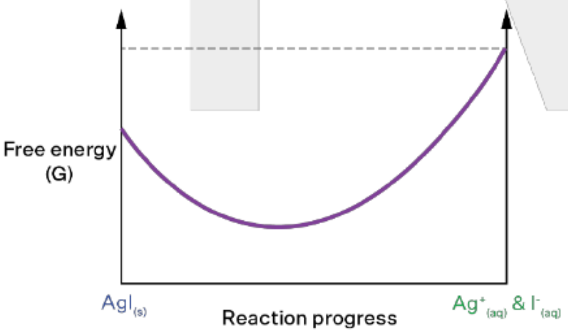
(i)



(ii)



(iii)



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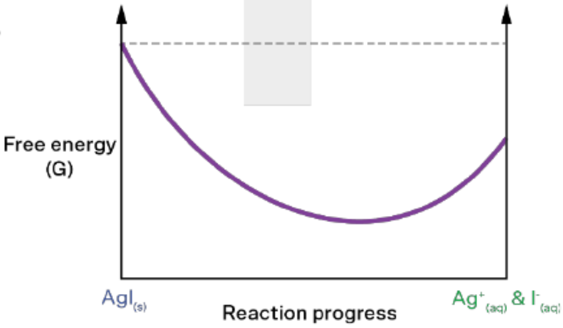


Year 12
Chemistry
Equilibrium and Acid Reactions

Work Book 7
Solubility equilibria 2

MATRIX
EDUCATION

Part A: Multiple choice questions

Question 1

In which of the following solutions would barium sulfate be most soluble?

(a) Potassium sulfate

(b) Barium chloride

(c) Copper nitrate

(d) Aluminium sulfate

There is no common ion in copper nitrate.

Question 2

In which of the following solutions would silver chloride be least soluble?

(a) 0.50 M sodium chloride

(b) 0.5 M calcium chloride

(c) 0.5 M silver nitrate

(d) 0.25 M aluminium chloride

0.50 M sodium chloride dissolves to give 0.50 M chloride ions.

0.50 M calcium chloride dissolves to give 1.0 M chloride ions.

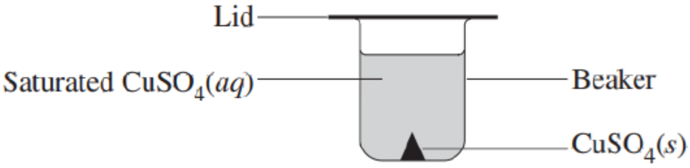
0.50 M silver nitrate dissolves to give 0.50 M silver ions.

0.25 M aluminium chloride dissolves to give 0.75 M chloride ions.

The greater the concentration of the common ion, the lower the solubility of silver chloride.

Question 3 **[2020 HSC Q17]**

The following apparatus was set up in a temperature-controlled laboratory.



Excess solid sodium hydroxide is added to the beaker.

Which row of the table correctly identifies the change in the $CuSO_{4(s)}$ mass and the colour of the solution after several days?

	Solid $CuSO_4$ mass	Colour of solution
(a)	No change	No change
(b)	No change	Blue colour fades
(c)	Decreases	Blue colour intensifies
(d)	Decreases	Blue colour fades

The following equilibrium occurs in the saturated solution of copper(II) sulfate :

$CuSO_{4(s)} \rightleftharpoons Cu^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Addition of sodium hydroxide results in the precipitation of $Cu(OH)_{2(s)}$, which reduces the concentration of $Cu^{2+}_{(aq)}$ and disturbs the equilibrium. As a result, more $CuSO_{4(s)}$ will dissolve to minimise the disturbance (Le Chatelier's Principle).

Since some Cu^{2+} ions are removed through precipitation, its concentration is lower and hence its characteristic the blue colour will fade.

Question 4

To produce a precipitate of silver chloride, which of the following solutions need to be mixed together?

(a) Silver and chlorine

(b) Silver and sodium chloride

(c) Silver nitrate and lead(II) chloride

(d) Silver nitrate and magnesium chloride

A precipitate forms from the reaction of two solutions. Lead(II) chloride has poor solubility, thus would not give appreciable amounts of chloride ions required for precipitation.

Question 5

A solution of sodium sulfate was mixed with an aqueous solution containing 0.100 mol L^{-1} lead(II) nitrate and 0.300 mol L^{-1} barium nitrate at 25 °C. Which ionic compound would precipitate first?

(a) Barium sulfate

(b) Lead sulfate

(c) Sodium nitrate

(d) Lead nitrate

Barium sulfate has a lower K_{sp} than lead(II) sulfate, thus is less soluble and will precipitate first.

Question 6

Adding which of the following species as a solid to a saturated solution of sodium phosphate would affect the solubility of sodium phosphate the least?

(a) Sodium acetate

(b) Lithium phosphate

(c) Lead(II) phosphate

(d) Sodium hydroxide

Lead(II) phosphate has the lowest solubility, thus would cause the smallest change in concentration of the common ion (PO_4^{3-}). Therefore, it will cause the smallest shift in the equilibrium.

Question 7

If equal volumes of 2×10^{-9} mol L^{-1} solutions of silver nitrate and sodium iodide are mixed at 25 °C, what will occur?

(a) Silver nitrate will precipitate

(b) Silver iodide will precipitate

(c) Sodium iodide will precipitate

(d) No precipitate will form

Equal volumes means concentrations will be halved, $[AgNO_3] = [NaI] = 1 \times 10^{-9}$ M

Precipitate that could be formed is silver iodide.

$AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$ $K_{sp} = [Ag^+][I^-] = 8.52 \times 10^{-17}$

$[Ag^+] = 1 \times 10^{-9}$ M, $[I^-] = 1 \times 10^{-9}$ M

$Q = (1 \times 10^{-9})^2 = 1 \times 10^{-18} < K_{sp}$, therefore no precipitate forms

Question 8 [2019 HSC Q17]

A student makes a solution with a final volume of 200 mL by mixing 100 mL of 0.0500 mol L^{-1} barium nitrate solution with 100 mL of 0.100 mol L^{-1} sodium hydroxide solution.

Which row of the table correctly identifies if a precipitate will form under these conditions and the reason?

	Will a precipitate form?	Reason
(a)	Yes	$Q > K_{sp}$
(b)	Yes	$Q < K_{sp}$
(c)	No	$Q > K_{sp}$
(d)	No	$Q < K_{sp}$

Precipitate that could be formed is barium hydroxide.

$Ba(OH)_{2(s)} \rightleftharpoons Ba^{2+}_{(aq)} + 2OH^{-}_{(aq)}$ $K_{sp} = [Ba^{2+}][OH^{-}]^2 = 2.55 \times 10^{-4}$

Equal volumes of barium nitrate and sodium hydroxide means concentrations will be halved.

$[Ba^{2+}] = 0.025$ mol L^{-1} and $[OH^{-}] = 0.05$ mol L^{-1}

$Q = (0.025)(0.05)^2 = 6.25 \times 10^{-5}$

Since $Q < K_{sp}$, no precipitate will form.

Question 9

Which of the following pairs of solutions would form a precipitate when mixed?

	Calcium nitrate	Sodium sulfate
(a)	50.0 mL of 0.0046 M	50.0 mL of 0.030 M
(b)	20.0 mL of 0.25 M	35.0 mL of 7.0×10^{-4} M
(c)	1.0 mL of 0.0027 M	1.0 mL of 0.065 M
(d)	3.0 mL of 0.18 M	1.5 mL of 4.0×10^{-3} M

$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$ $K_{sp} = [Ca^{2+}][SO_4^{2-}] = 4.93\times10^{-5}$

(a): $Q = 0.0023 \times 0.015 = 3.45 \times 10^{-5}$

(b): $Q = 0.0909090 \times 0.000445 = 4.05 \times 10^{-5}$

(c): $Q = 0.00135 \times 0.0325 = 4.39 \times 10^{-6}$

(d): $Q = 0.12 \times 0.001333 = 1.60 \times 10^{-4}$

Precipitation occurs when $Q > K_{sp}$

Part B: Extended response questions

Question 10

Write full formula equations and net ionic equations for any precipitation reactions that can occur when the following solutions are mixed together. If there is no reaction, state “no reaction”. 6

(a) Zinc chloride and sodium carbonate

$\mathrm{ZnCl_{2(aq)} + Na_2CO_{3(aq)} \rightarrow ZnCO_{3(s)} + 2NaCl_{(aq)}}$

$\mathrm{Zn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow ZnCO_{3(s)}}$

(b) Lithium hydroxide and aluminium nitrate

$\mathrm{3LiOH_{(aq)} + Al(NO_3)_{3(aq)} \rightarrow Al(OH)_{3(s)} + 3LiNO_{3(aq)}}$

$\mathrm{3OH^{-}{}_{(aq)} + Al^{3+}_{(aq)} \rightarrow Al(OH)_{3(s)}}$

(c) Silver nitrate and barium chloride

$\mathrm{2AgNO_{3(aq)} + BaCl_{2(aq)} \rightarrow 2AgCl_{(s)} + Ba(NO_3)_{2(aq)}}$

$\mathrm{Ag^{+}_{(aq)} + Cl^{-}{}_{(aq)} \rightarrow AgCl_{(s)}}$

(d) Lead(II) nitrate and calcium bromide

$\mathrm{Pb(NO_3)_{2(aq)} + CaBr_{2(aq)} \rightarrow PbBr_{2(s)} + Ca(NO_3)_{2(aq)}}$

$\mathrm{Pb^{2+}_{(aq)} + 2Br^{-}{}_{(aq)} \rightarrow PbBr_{2(s)}}$

(e) Potassium carbonate and iron(II) nitrate

$\mathrm{K_2CO_{3(aq)} + Fe(NO_3)_{2(aq)} \rightarrow FeCO_{3(s)} + 2KNO_{3(aq)}}$

$\mathrm{CO_3^{2-}{}_{(aq)} + Fe^{2+}_{(aq)} \rightarrow FeCO_{3(s)}}$

(f) Rubidium sulfate and barium chloride

$\mathrm{Rb_2SO_{4(aq)} + BaCl_{2(aq)} \rightarrow BaSO_{4(s)} + 2RbCl_{(aq)}}$

$\mathrm{SO_4^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} \rightarrow BaSO_{4(s)}}$

Question 11

Equal volumes of 2.0×10^{-3} M magnesium chloride and sodium phosphate solutions were mixed at 25 °C.

(a) Write an equation for the precipitation reaction that occurs. 1

$3MgCl_{2(aq)} + 2Na_3PO_{4(aq)} \rightarrow Mg_3(PO_4)_{2(s)} + 6NaCl_{(aq)}$

(b) Using a calculation, explain why a precipitate will form at this temperature. Refer to reaction quotient (*Q*) and solubility product (K_{sp}) in your answer. 3

$Mg_3(PO_4)_{2(s)} \rightleftharpoons 3Mg^{2+}{}_{(aq)} + 2PO_4{}^{3-}{}_{(aq)}$ $K_{sp} = [Mg^{2+}]^3[PO_4{}^{3-}]^2 = 1.04 \times 10^{-24}$

Equal volumes of $MgCl_2$ and Na_3PO_4 means concentrations will be halved:

Let the volume of each solution be V L.

$n(Mg^{2+}) = n(MgCl_2) = (2.0 \times 10^{-3}) \times V$ mol

Final $[Mg^{2+}] = ((2.0 \times 10^{-3}) \times V) / 2V = 1.0 \times 10^{-3}$ M

Same calculation for $[PO_4{}^{3-}]$. Thus, $[PO_4{}^{3-}] = 1.0 \times 10^{-3}$ M

$Q = (1.0 \times 10^{-3})^5 = 1.0 \times 10^{-15}$

Since $Q > K_{sp}$, a precipitate will form. Since the concentration of dissolved ions exceeds the amount that would be present at equilibrium, the reaction must shift in the reverse direction to decrease dissolved ions to reach equilibrium.

Question 12

Lithium carbonate is an inorganic compound used in the treatment of mood disorders.

(a) Write a balanced chemical equation for the dissolution of lithium carbonate, and the corresponding expression for K_{sp}. 2

$Li_2CO_{3(s)} \rightleftharpoons 2Li^+_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Li^+]^2[CO_3^{2-}]$

(b) Calculate its K_{sp} at 25 °C if its solubility is 1.25 g per 100 mL. 3

$n(Li_2CO_3) = 1.25/(6.941 \times 2 + 12.01 + 16.00 \times 3) = 0.01691658$ mol

Solubility = 0.0169 mol/0.1 L = 0.169 mol/L

$[Li^+] = 0.338$ M and $[CO_3^{2-}] = 0.169$ M

$K_{sp} = (0.338)^2(0.169) = 1.94 \times 10^{-2}$ (3 s.f.)

(c) 5.0 mL of saturated lithium carbonate solution was diluted to 250.0 mL. 20.0 mL of the diluted solution was mixed with 40.0 mL of 0.042 M barium nitrate. Will a precipitate form? Show working. 3

Precipitate that could be formed is barium carbonate.

$BaCO_{3(s)} \rightleftharpoons Ba^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Ba^{2+}][CO_3^{2-}] = 2.58 \times 10^{-9}$

Diluted $[CO_3^{2-}] = c_1V_1/V_2 = (0.169 \times 0.005)/0.250 = 0.003383$ M

$n(CO_3^{2-}) = c \times V = 0.003383 \times 0.020 = 6.7666 \times 10^{-5}$ mol

$[CO_3^{2-}]$ in reaction $= (6.7666 \times 10^{-5})/0.060 = 1.12777 \times 10^{-3}$ mol L^{-1}

$n(Ba^{2+}) = 0.042 \times 0.04 = 0.00168$ mol

$[Ba^{2+}]$ in reaction $= 0.00168/0.060 = 0.028$ mol L^{-1}

$Q = (1.12777 \times 10^{-3})(0.028) = 3.2 \times 10^{-5}$ (2 s.f.)

Since $Q > K_{sp}$, a precipitate will form.

Question 13

The K_{sp} of copper(II) chromate $CuCrO_4$ at 25 °C is 3.6×10^{-6}.

(a) State what is meant by the common ion effect. **1**

In a saturated solution, addition of an aqueous ion will lower the solubility of any ionic compound containing that ion.

(b) Write an equation for the dissolution of copper(II) chromate and the expression for its solubility product. **1**

$CuCrO_{4(s)} \rightleftharpoons Cu^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$ $K_{sp} = [Cu^{2+}][CrO_4^{2-}]$

(c) Calculate the solubility of copper(II) chromate in pure water at 25 °C in grams per litre. **2**

Let moles of $CuCrO_4$ in 1 L = x, thus $[Cu^{2+}] = [CrO_4^{2-}] = x$

$K_{sp} = x^2 = 3.6 \times 10^{-6}$ $\therefore x = 0.001897$

Solubility of $CuCrO_4$ = 0.001897 mol L^{-1} = 0.34 g/L (2 s.f.)

(d) Calculate the solubility of copper(II) chromate in 0.20 M copper(II) nitrate at 25 °C in grams per litre. **3**

Concentration (mol L^{-1})	$CuCrO_{4(s)}$	$\rightleftharpoons$	$Cu^{2+}_{(aq)}$	+	$CrO_4^{2-}{}_{(aq)}$
Initial	-		0.20		0
Change	-		$+x$		$+x$
Equilibrium	-		$0.20 + x$		x

Assuming the $[Cu^{2+}]$ does not change very much since K_{sp} is very small:

$K_{sp} = 0.2x = 3.6 \times 10^{-6}$

$\therefore x = 1.8 \times 10^{-5}$ (Check assumption: $(1.8 \times 10^{-5} / 0.20) \times 100 = 0.009\%$, so assumption is valid)

Thus solubility of $CuCrO_4$ is 1.8×10^{-5} mol/L = 3.2×10^{-3} g/L (2 s.f.)

(e) Explain the difference in the solubility of copper(II) chromate in copper(II) nitrate compared to pure water, with reference to Le Chatelier's principle. 3

Dissolution of copper(II) chromate in a saturated solution exist in equilibrium:

$$CuCrO_{4(s)} \rightleftharpoons Cu^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

The presence of Cu^{2+} ions in copper nitrate would decrease the solubility of copper(II) chromate. As there is a higher concentration of the Cu^{2+} ions in the solution, equilibrium is disturbed. According to Le Chatelier's principle, the equilibrium will shift left to remove the copper ions to minimise the disturbance. Hence more solid copper(II) chromate forms, resulting in decreased solubility of copper(II) chromate.

(f) What is the percentage decrease in the solubility of copper(II) chromate when it is dissolved in 0.20 M copper(II) nitrate instead of distilled water? 1

% decrease in solubility = $(0.34 - 3.2 \times 10^{-3})/0.34 \times 100 = 99\%$ (2 s.f.)

Question 14

4.0 g each of barium nitrate and potassium carbonate powder are added to water to make 1.0 L of solution. A precipitate formed.

(a) Write a balanced chemical equation to show the formation of the precipitate. **1**

$Ba(NO_3)_{2(aq)} + K_2CO_{3(aq)} \rightarrow BaCO_{3(s)} + 2KNO_{3(aq)}$

(b) Assuming that the precipitate is completely insoluble, use a limiting reactant calculation to determine the concentration of each ion in solution. **3**

$n(Ba(NO_3)_2) = 4 / (137.3 + 14.01 \times 2 + 16 \times 6) = 0.015306$ mol

$n(K_2CO_3) = 4 / (39.10 \times 2 + 12.01 + 16 \times 3) = 0.028941$ mol

Barium nitrate is limiting reactant.

$n(Ba^{2+}) = 0$, therefore $[Ba^{2+}] = 0.0$ M (2 s.f.)

$n(CO_3^{2-})_{excess} = 0.028941 - 0.015306 = 0.0136345$ mol

Since volume = 1 L, $[CO_3^{2-}] = 0.014$ M (2 s.f.)

$n(NO_3^-) = 2 \times 0.015306$ mol $= 0.030613$ mol

$n(K^+) = 2 \times 0.028941$ mol $= 0.0578829$ mol

Since volume = 1 L, $[NO_3^-] = 0.031$ M and $[K^+] = 0.058$ M (2 s.f.)

(c) However, barium carbonate is slightly soluble. Using your answer from (b), perform a common ion calculation to determine the actual concentration of each ion in solution. 3

Let x be moles of $BaCO_3$ that can dissolve in 1 L of solution with excess CO_3^{2-}, thus $[Ba^{2+}] = x$ mol L^{-1}

Concentration (mol L^{-1})	$BaCO_{3(s)}$	$\rightleftharpoons$	$Ba^{2+}_{(aq)}$	+	$CO_3^{2-}{}_{(aq)}$
Initial			0		0.0136345
Change			$+x$		$+x$
Equilibrium			x		$0.0136345 + x$

Assuming that x is small compared to initial $[CO_3^{2-}]$, $0.0136345 + x \approx 0.0136345$

$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 2.58 \times 10^{-9}$

$x(0.0136345) = 2.58 \times 10^{-9}$

$x = 1.8922 \times 10^{-7}$

(Check assumption: $(1.8922 \times 10^{-7} / 0.0136345) \times 100 < 5\%$)

$[Ba^{2+}] = 1.9 \times 10^{-7}$ M (2 s.f.)

$[CO_3^{2-}] = 0.014$ M (2 s.f.)

Since NO_3^- and K^+ are spectator ions, concentrations are the same.

$[NO_3^-] = 0.031$ M and $[K^+] = 0.058$ M (2 s.f.)

Question 15

The solubility of lanthanum(III) iodate $La(IO_3)_3$ in a 0.55 mol L^{-1} potassium iodate solution is 2.99×10^{-8} g L^{-1} at 25 °C. Calculate the K_{sp} for $La(IO_3)_3$. 3

Solubility of $La(IO_3)_3 = 2.99 \times 10^{-8}$ g/L

$= (2.99 \times 10^{-8} / (138.9 + 126.9 \times 3 + 16 \times 9))$ mol/L $= 4.5057 \times 10^{-11}$ mol/L

Concentration (mol L^{-1})	$La(IO_3)_{3(s)}$	$\rightleftharpoons$	$La^{3+}_{(aq)}$	+	$3IO_3^-{}_{(aq)}$
Initial	-		0		0.55
Change	-		$+ 4.5057 \times 10^{-11}$		$+ 1.35171 \times 10^{-10}$
Equilibrium	-		4.5057×10^{-11}		$0.55 + 1.35171 \times 10^{-10}$

$K_{sp} = [La^{2+}][IO_3^-]^3 = (4.5057 \times 10^{-11})(0.55 + 1.35171 \times 10^{-10})^3 = 7.5 \times 10^{-12}$ (2 s.f.)

Question 16

When 70.5 mL of 0.955 mol L^{-1} lead nitrate solution was mixed with 90.0 mL of 1.50 mol L^{-1} sodium fluoride solution, a precipitate of lead(II) fluoride was obtained. The mass of the dried precipitate was 16.45 g.

Calculate the K_{sp} of lead(II) fluoride. 5

$n(PbF_2)$ precipitate = 16.45 g ÷ 245.2 g mol^{-1} = 0.067088 mol

$n(Pb^{2+})$ in initial solution = 0.955 mol L^{-1} × 0.0705 L = 0.0673275 mol

$n(Pb^{2+})$ at equilibrium = 0.0673275 mol − 0.067088 mol = 2.394086×10^{-4} mol

$[Pb^{2+}]$ at equilibrium = 2.394086×10^{-4} mol ÷ 0.1605 L = 1.49164×10^{-3} mol L^{-1}

$n(F^-)$ in initial solution = 1.50 mol L^{-1} × 0.0900 L = 0.135 mol

$n(F^-)$ at equilibrium = 0.135 mol − (2 × 0.067088 mol) = 8.23817×10^{-4} mol

$[F^-]$ at equilibrium = 8.23817×10^{-4} mol ÷ 0.1605 L = 5.132818×10^{-3} mol L^{-1}

$K_{sp} = [Pb^{2+}][F^-]^2 = (1.49164 \times 10^{-3}) \times (5.132818 \times 10^{-3})^2 = 3.93 \times 10^{-8}$ (3 s.f.)

Question 17

(a) The K_{sp} of iron(II) fluoride is 2.36×10^{-6} at 25 °C. What is the concentration, in mol L^{-1}, of Fe^{2+} ions in a saturated solution of iron(II) fluoride at this temperature? 2

$FeF_{2(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2F^{-}_{(aq)}$ $K_{sp} = [Fe^{2+}][F^{-}]^2 = 2.36 \times 10^{-6}$

Let moles of FeF_2 in 1 L = x, thus $[Fe^{2+}] = x$, $[F^{-}] = 2x$

$K_{sp} = (x)(2x)^2 = 2.36 \times 10^{-6}$ $\therefore x = 8.3872 \times 10^{-3}$

$[Fe^{2+}] = 8.39 \times 10^{-3}$ mol/L (3 s.f.)

(b) How many grams of iron(II) fluoride would dissolve in water to make 500 mL of saturated aqueous solution? 2

$[FeF_2] = 8.39 \times 10^{-3}$ mol/L = $(8.39 \times 10^{-3} \times (55.85 + 19.00 \times 2))$ g /L = 0.787139 g/L

Thus in 500 mL, 0.394 g can dissolve.

(c) How many grams of iron(II) fluoride would dissolve in 500 mL of 1.50 M sodium fluoride solution? 3

Let $[Fe^{2+}] = x$ mol L^{-1}

Concentration (mol L^{-1})	$FeF_{2(s)}$	$\rightleftharpoons$	$Fe^{2+}_{(aq)}$	+	$2F^{-}_{(aq)}$
Initial	-		0		1.50
Change	-		$+x$		$+2x$
Equilibrium	-		x		$1.50 + 2x$

Assuming that x is small compared to initial $[F^{-}]$, $1.50 + 2x \approx 1.50$

$K_{sp} = [Fe^{2+}][F^{-}]^2 = x(1.50)^2 = 2.36 \times 10^{-6}$

$\therefore x = 1.05 \times 10^{-6}$ (Check assumption: $((1.05 \times 10^{-6} \times 2) / 1.50) \times 100 < 5\%$)

Solubility of FeF_2 in 1.50 M NaF = 1.05×10^{-6} mol L^{-1} = 9.84×10^{-5} g L^{-1}

Thus in 500 mL, 4.92×10^{-5} g can dissolve.

(d) Explain why the answers to (b) and (c) differ, with reference to the microscopic processes occurring within the solutions. 2

Sodium fluoride dissolves to form sodium and fluoride ions (common ion). As there is a higher concentration of the fluoride ions, there are more collisions. Hence, the rate of the reverse reaction increases relative to the forward reaction and equilibrium shifts left to produce more solid iron(II) fluoride: $FeF_{2(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2F^{-}_{(aq)}$

Question 18

Lead is a contaminant in water that can cause poisoning.

(a) What concentration (in mol L^{-1}) of bromide ions would be required to reduce the concentration of lead ions in an aqueous solution to 15 ppb? 3

Concentration of lead ions: 15 µg/kg = 1.5×10^{-5} g/L = 7.239×10^{-8} mol/L

$PbBr_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Br^{-}_{(aq)}$ $K_{sp} = [Pb^{2+}][Br^{-}]^2 = 6.60 \times 10^{-6}$

Let $[Br^{-}] = x$,

$K_{sp} = (7.239 \times 10^{-8})(x^2) = 6.60 \times 10^{-6}$

$x = 9.548193546$

$[Br^{-}] = 9.5$ mol/L (2 s.f.)

(b) 2000 L of water contains lead ions at a concentration of 200 ppb. What mass of solid potassium bromide must be added to reduce this to 15 ppb? 2

$[Br^{-}] = 9.5$ mol/L is required for lead ion concentration to be 15 ppb

For 2000 L:

$n(Br^{-})$ required = $9.548193546 \times 2000 = 19096$ mol = n(KBr)

m(KBr) = $19096 \times (39.10+79.90)$ = 2.3 tonnes (2 s.f.)

Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 19

In which of the following solutions would lead(II) phosphate be least soluble?

(a) 0.10 M lead(II) nitrate

(b) 0.10 M sodium phosphate

(c) 0.10 M nitric acid

(d) Distilled water

$Pb_3(PO_4)_{2(s)} \rightleftharpoons 3Pb^{2+}_{(aq)} + 2PO_4{}^{3-}_{(aq)}$ $K_{sp} = [Pb^{2+}]^3[PO_4{}^{3-}]^2 = 8.0 \times 10^{-43}$

Let x be moles of $Pb_3(PO_4)_2$ that dissolves in 1 L

(a): 0.10 M lead(II) nitrate dissolves to give 0.10 M Pb^{2+} ions

$(0.10)^3(2x)^2 = 8.0 \times 10^{-43}$

$x = 1.41 \times 10^{-20}$

(b): 0.10 M sodium phosphate dissolves to give 0.10 M $PO_4{}^{3-}$ ions.

$(3x)^3(0.10)^2 = 8.0 \times 10^{-43}$

$x = 1.44 \times 10^{-14}$

No common ion in (c) and (d)

Question 20

12.5 mL of 0.025 M copper(II) sulfate and 24.0 mL of 0.015 M sodium carbonate are mixed together at 25 °C.

Which row of the table correctly identifies if a precipitate will form under these conditions and the reason?

	Will a precipitate form?	Reason
(a)	Yes	$Q > K_{sp}$
(b)	Yes	$Q < K_{sp}$
(c)	No	$Q > K_{sp}$
(d)	No	$Q < K_{sp}$

Precipitate that could be formed is copper carbonate.

$CuCO_{3(s)} \rightleftharpoons Cu^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}$ $K_{sp} = [Cu^{2+}][CO_3{}^{2-}] = 1.4 \times 10^{-10}$

$n(Cu^{2+}) = 0.025 \times 0.0125 = 3.125 \times 10^{-4}$ mol

$[Cu^{2+}] = 3.125 \times 10^{-4} / 0.0365 = 8.56164 \times 10^{-3}$ mol L^{-1}

$n(CO_3{}^{2-}) = 0.015 \times 0.024 = 3.6 \times 10^{-4}$ mol

$[CO_3{}^{2-}] = 3.6 \times 10^{-4} / 0.0365 = 9.86301 \times 10^{-3}$ mol L^{-1}

$Q = (8.56164 \times 10^{-3})(9.86301 \times 10^{-3}) = 8.4 \times 10^{-5} > K_{sp}$ therefore precipitate forms

Question 21

1.00 mL volumes of 0.05 mol L^{-1} sodium carbonate solutions were added to 100 mL samples of 6×10^{-4} mol L^{-1} Mg^{2+} ions, 8×10^{-4} mol L^{-1} Ca^{2+} ions and 4×10^{-4} mol L^{-1} Pb^{2+} ions. Which ionic compounds would precipitate?

(a) $MgCO_3$ and $CaCO_3$

(b) $MgCO_3$ and $PbCO_3$

(c) $CaCO_3$ and $PbCO_3$

(d) $MgCO_3$, $CaCO_3$ and $PbCO_3$

$[CO_3^{2-}] = 4.950495 \times 10^{-4}$ M

$[Mg^{2+}] = 5.940594 \times 10^{-4}$ M, $Q = 2.94 \times 10^{-7} < K_{sp}$ $(MgCO_3)$

$[Ca^{2+}] = 7.920792 \times 10^{-4}$ M, $Q = 3.92 \times 10^{-7} > K_{sp}$ $(CaCO_3)$

$[Pb^{2+}] = 3.960396 \times 10^{-4}$ M, $Q = 1.96 \times 10^{-7} > K_{sp}$ $(PbCO_3)$

Question 22

Complete the full formula equation and write net ionic equations for the following reactions.

(a) $FeSO_{4(aq)} + Li_2CO_{3(aq)} \rightarrow FeCO_{3(s)} + Li_2SO_{4(aq)}$ 2

$Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_{3(s)}$

(b) $3Cu(NO_3)_{2(aq)} + 2Na_3PO_{4(aq)} \rightarrow Cu_3(PO_4)_{2(s)} + 6NaNO_{3(aq)}$ 2

$3Cu^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)} \rightarrow Cu_3(PO_4)_{2(s)}$

(c) $BaCl_{2(aq)} + Pb(NO_3)_{2(aq)} \rightarrow PbCl_{2(s)} + Ba(NO_3)_{2(aq)}$ 2

$Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightarrow PbCl_{2(s)}$

Question 23

Sodium chloride dissolves to give Na^+ and Cl^- ions. If solid sodium chloride is added to a saturated solution of lead(II) chloride, what would be the effect on the solubility of lead chloride? Explain your answer with reference to Le Chatelier's principle. 3

Dissolution of lead(II) chloride in a saturated solution exist in equilibrium:

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Sodium chloride dissolves to form Na^+ ions and Cl^- ions. As there is a higher concentration of the Cl^- ions in the solution, equilibrium is disturbed. According to Le Chatelier's principle, the equilibrium will shift to the left to remove the chloride ions to minimise the disturbance. Hence there is more solid lead(II) chloride formed, resulting in decreased solubility of lead(II) chloride.

Question 24

Soaps like sodium palmitate are ionic compounds. In the manufacture of soap, salt is added to an aqueous solution of soap to precipitate the soap so it can be collected via filtration, in a process called "salting out".

Explain how "salting out" works with reference to equilibrium and collision theory. 3

The sodium ion from the salt (sodium chloride) is a common ion to the sodium ions in the aqueous solution of sodium palmitate. In a saturated solution, solid and aqueous sodium palmitate exists in equilibrium. The addition of sodium ions (from salt) results in an increase in the concentration of sodium ions in the solution, causing the rate of precipitation to be faster than the rate of dissolution as there would be a greater frequency of collisions between the ions in solution. This results in more soap precipitating out of solution than dissolving.

Question 25

A solution of lead(II) nitrate was mixed with sodium iodide solution to produce 500 mL of solution. If the final concentration of sodium iodide was 0.010 mol L^{-1}, calculate the minimum concentration in mol L^{-1} of lead ions in the final solution that is needed to cause precipitation. 2

$PbI_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$ $K_{sp} = [Pb^{2+}][I^{-}]^2 = 9.8 \times 10^{-9}$

$[I^{-}] = 0.010 \text{ mol L}^{-1}$

$[Pb^{2+}] \times (0.010)^2 = 9.8 \times 10^{-9}$

$[Pb^{2+}] = 9.8 \times 10^{-5} \text{ mol L}^{-1}$

Question 26

(a) Explain what is meant by the “common ion effect.” 1

The solubility of a salt is reduced by the presence of one of its constituent ions (the common ion) already in the solution.

(b) Magnesium hydroxide is sparingly soluble in water. Write a balanced chemical equation for the dissolution of magnesium hydroxide, and the corresponding expression for K_{sp} 2

$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)}$ $K_{sp} = [Mg^{2+}][OH^{-}]^2$

(c) Determine the mass of magnesium hydroxide that will remain undissolved at 25 °C when 0.0343 g of magnesium hydroxide is added to water to make a 375 mL solution. 3

Let moles of $Mg(OH)_{2(s)}$ in 1 L = x, thus $[Mg^{2+}] = x$, $[OH^{-}] = 2x$

$K_{sp} = (x)(2x)^2 = 5.61 \times 10^{-12}$ $\therefore x = 1.11935 \times 10^{-4}$

Solubility of $Mg(OH)_2$ = 1.11935×10^{-4} mol/L = 6.5287×10^{-3} g/L

Thus 2.4482×10^{-3} g can dissolve in 375 mL.

Undissolved solid = $0.0343 - 2.4482 \times 10^{-3} = 0.0319$ g (3 s.f.)

(d) What extra mass of magnesium hydroxide will precipitate when 0.0200 g of sodium hydroxide is added to the solution in (c)? **4**

$n(OH^-) = 0.0200 / (232.99 + 1.008 + 16.00) = 5.000 \times 10^{-4}$ mol

$[OH^-] = 5.000 \times 10^{-4}/0.0375 = 1.333 \times 10^{-3}$ mol/L

Let x be moles of $Mg(OH)_2$ that can dissolve in 1 L of NaOH, thus $[Mg^{2+}] = x$ mol L^{-1}

Concentration (mol L^{-1})	$Mg(OH)_{2(s)}$	$\rightleftharpoons$	$Mg^{2+}_{(aq)}$	+	$2OH^-_{(aq)}$
Initial	-		0		1.333×10^{-3}
Change	-		$+x$		$+2x$
Equilibrium	-		x		$1.333 \times 10^{-3} + 2x$

Assuming that x is small compared to initial $[OH^-]$, $1.333 \times 10^{-3} + 2x \approx 1.333 \times 10^{-3}$

$x(1.333 \times 10^{-3})^2 = 5.61 \times 10^{-12}$

$x = 3.1553 \times 10^{-6}$ (Check assumption: $((3.1553 \times 10^{-6} \times 2) / 1.333 \times 10^{-3}) \times 100 < 5\%$)

Solubility of $Mg(OH)_2$ in NaOH = 3.1553×10^{-6} mol L^{-1}

Difference in solubility = $1.11935 \times 10^{-4} - 3.1553 \times 10^{-6} = 1.0878 \times 10^{-4}$ mol/L = 6.34×10^{-3} g/L

Thus 2.38×10^{-3} g more will be undissolved in 375 mL.

Question 27 **[2023 HSC Q34]**

When 125 mL of a magnesium nitrate solution is mixed with 175 mL of a 1.50 mol L^{-1} sodium fluoride solution, 0.6231 g of magnesium fluoride (MM = 62.31 g mol^{-1}) precipitates. The K_{sp} of magnesium fluoride is 5.16×10^{-11}.

Calculate the equilibrium concentration of magnesium ions in this solution. 5

$MgF_{2(s)} \rightleftharpoons Mg^{2+}{}_{(aq)} + 2F^{-}{}_{(aq)}$ $K_{sp} = [Mg^{2+}][F^{-}]^2 = 5.16 \times 10^{-11}$

$n(NaF) = 1.50 \times 0.175 = 0.2625$ mol $= n(F^{-})$total

$n(MgF_2) = 0.6231/62.31 = 0.01$ mol

$n(F^{-})$used = 0.02 mol

$n(F^{-})$remaining = 0.2625 − 0.02 = 0.2425 mol

$[F^{-}] = 0.2425 / (0.125 + 0.175) = 0.808333$ mol L^{-1}

$[Mg^{2+}] = K_{sp} / [F^{-}]^2 = (5.16 \times 10^{-11}) / (0.808333)^2 = 7.90 \times 10^{-11}$ mol L^{-1} (3 s.f.)

Question 28

The solubility of mercury(II) bromide in water is 0.56 g per 100 mL at 20 °C. Calculate how many grams of mercury(II) bromide would dissolve in 45 mL of 2.0 mol L^{-1} lithium bromide solution. **4**

Solubility of $HgBr_2$ = 5.6 g/L = (5.6/(200.6 + 79.90 × 2)) mol/L = 0.015538 mol/L

$HgBr_{2(s)} \rightleftharpoons Hg^{2+}_{(aq)} + 2Br^{-}_{(aq)}$

$[Hg^{2+}]$ = 0.015538 M and $[Br^{-}]$ = 0.031076 M

$K_{sp} = [Hg^{2+}][Br^{-}]^2 = (0.015538)(0.031076)^2 = 1.5006 \times 10^{-5}$

Let x be moles of $HgBr_2$ that dissolves in 1 L of LiBr, thus $[Hg^{2+}] = x$ mol L^{-1}

Concentration (mol L^{-1})	$HgBr_{2(s)}$	$\rightleftharpoons$	$Hg^{2+}_{(aq)}$	+	$2Br^{-}_{(aq)}$
Initial	-		0		2.0
Change	-		$+x$		$+2x$
Equilibrium	-		x		$2.0 + 2x$

Assuming that x is small compared to initial $[Br^{-}]$, $2.0 + 2x \approx 2.0$

$x(2.0)^2 = 1.5006 \times 10^{-5}$

$\therefore x = 3.7515 \times 10^{-6}$ (Check assumption: $((3.7515 \times 10^{-6} \times 2) / 2.0) \times 100 < 5\%$)

Solubility of $HgBr^2$ in 2.0 M LiBr = 3.7515×10^{-6} mol L^{-1} = 1.352055×10^{-4} g L^{-1}

Thus in 45 mL, 6.1×10^{-5} g can dissolve.

Question 29

4.35 g calcium chloride and 5.50 g of lead(II) nitrate was added to deionised water at 25 °C to make 0.600 L of solution.

(a) Using a calculation, show that a precipitate will form at this temperature. 3

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$ $K_{sp} = [Pb^{2+}][Cl^{-}]^2 = 1.70 \times 10^{-5}$

$n(Pb^{2+}) = 5.50/(207.2 + 14.01 \times 2 + 16 \times 6) = 0.016605$ mol

$[Pb^{2+}] = 0.016605/0.6 = 0.027675$ mol L^{-1}

$n(Cl^{-}) = 2 \times n(CaCl_2) = 2 \times (4.35/(40.08 + 35.45 \times 2)) = 0.07839$ mol

$[Cl^{-}] = 0.07839 / 0.6 = 0.130654$ mol L^{-1}

$Q = (0.027675)(0.130654)^2 = 4.72 \times 10^{-4}$

Since $Q > K_{sp}$, a precipitate will form.

(b) Determine the mass of precipitate formed at this temperature. 4

$[Cl^{-}]$excess = $0.130654 - (0.027675 \times 2) = 0.0753032$ mol L^{-1}

Let x be moles of $PbCl_2$ that dissolves in 1 L

Concentration (mol L^{-1})	$PbCl_{2(s)}$	$\rightleftharpoons$	$Pb^{2+}{}_{(aq)}$	+	$2Cl^{-}{}_{(aq)}$
Initial	-		0		0.0753032
Change	-		$+x$		$+2x$
Equilibrium	-		x		$0.0753032 + 2x$

Assuming that x is small compared to initial $[Cl^{-}]$, $0.0753032 + 2x \approx 0.0753032$

$x(0.0753032)^2 = 1.70 \times 10^{-5}$ $\therefore x = 2.999793 \times 10^{-3}$

$n(PbCl_2)$ dissolving in 0.600 L = $2.999793 \times 10^{-3} \times 0.600 = 1.798758 \times 10^{-3}$ mol

Theoretical maximum $n(PbCl_2))$ precipitated = 0.016605 mol

Actual $n(PbCl_2)$ precipitated = $0.016605 - 1.798758 \times 10^{-3} = 0.0148065$ mol

$m(PbCl_2) = 0.0148065 \times (207.2 + 35.45 \times 2) = 4.11769$ g = 4.12 g (3 s.f.)

(c) Explain, with reference to reaction quotient (Q) and solubility product (K_{sp}), how the equilibrium shifts when the following are added to the solution above:

(i) Solid potassium chloride 2

The following equilibrium exists in solution: $PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

Solid potassium carbonate dissolves to form potassium and chloride ion (a common ion). As there is a higher concentration of the chloride ions in the solution, $Q > K_{sp}$ and equilibrium is disturbed. To re-establish equilibrium, the concentration of the ions need to decrease, hence the equilibrium will shift to the left.

(ii) Solid lead chloride 2

Adding solid lead chloride doesn't change the concentrations of lead and chloride ions as the solution is saturated. $Q = K_{sp}$ so the system remains at equilibrium and does not shift.

(iii) Water 2

Addition of water increases the volume, hence decreases the concentration of ions. $Q < K_{sp}$, so the equilibrium shifts right to produce more ions and increase their concentration to re-establish equilibrium.

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Chemistry
Equilibrium and Acid Reactions

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MATRIX
EDUCATION

Part A: Multiple choice questions

Question 1

Which of the following statements is NOT always true regarding a saturated solution containing some undissolved solid solute?

(a) No further solute will dissolve

(b) The rate of formation of the solute crystals is the same as the rate of dissociation of the solute crystals

(c) Cooling of the solution will cause precipitation

(d) The amount of solid will vary with temperature

Solubility can increase or decrease as temperature decreases depending on the salt.

Question 2

How would the concentration of Ca^{2+} ions in equilibrium with $Ca(OH)_{2(s)}$ be affected if the concentration of OH^- ions were doubled?

(a) Decrease by a factor of 2

(b) Decrease by a factor of 4

(c) Decrease by a factor of 16

(d) No change

$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp} = [Ca^{2+}][OH^-]^2$

Let the concentration of the dissolved ionic compound be x. Thus $[Ca^{2+}] = x$ and $[OH^-] = 2x$. Thus $K_{sp} = (x)(2x)^2 = 4x^3$. Since K_{sp} value must remain the same, if $[OH^-] = 4x$, $[Ca^{2+}]$ is ¼ x.

Question 3

What volume of water is required to dissolve 8.5 kg of magnesium hydroxide at 25 °C?

(a) 8.7×10^7 L

(b) 7.6×10^7 L

(c) 1.3×10^6 L

(d) 6.2×10^7 L

$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp} = [Mg^{2+}][OH^-]^2 = 5.61 \times 10^{-12}$

Let moles of $Mg(OH)_2$ in 1 L = x, thus $[Mg^{2+}] = x$, $[OH^-] = 2x$

$K_{sp} = (x)(2x)^2 = 5.61 \times 10^{-12}$

$x = 1.119 \times 10^{-4}$

Solubility of $Mg(OH)_2 = 1.119 \times 10^{-4}$ mol/L

$= (1.119 \times 10^{-4} \times (24.31 + 16 + 1.008))$ g/L $= 6.5287 \times 10^{-3}$ g/L $= 6.5287 \times 10^{-6}$ kg/L

To dissolve 8.5 kg: $8.5/(6.5287 \times 10^{-6}) = 1301934$ L

Question 4

A saturated solution of magnesium fluoride has a concentration of 130 ppm at 25 °C. What is its K_{sp}?

(a) 3.6×10^{-8}
(b) 4.4×10^{-6}
(c) 9.1×10^{-9}
(d) 8.7×10^{-6}

$MgF_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2F^-_{(aq)}$ $K_{sp} = [Mg^{2+}][F^-]^2$

Concentration of MgF_2 = 130 mg/kg = 0.130 g/L = 0.0020863 mol/L
$[Mg^{2+}] = 0.0020863$ M, $[F^-] = 0.00417268$ M
$K_{sp} = 0.0020863 \times (0.00417268)^2 = 3.6 \times 10^{-8}$

Question 5

What is the solubility of silver iodide at 25 °C?

(a) 9.23 mg per L
(b) 2.17 ppb
(c) 2.17 mg per mL
(d) 9.23% w/w

$AgI_{(s)} \rightleftharpoons Ag^+_{(aq)} + I^-_{(aq)}$ $K_{sp} = [Ag^+][I^-] = 8.52 \times 10^{-17}$

Let $[Ag^+]$ and $[I^-] = x$
$K_{sp} = x^2 = 8.52 \times 10^{-17}$
Therefore, $[Ag^+]$ and $[I^-] = 9.23 \times 10^{-9}$ mol L^{-1}
$[AgI] = [Ag^+] = 9.23 \times 10^{-9}$ mol L^{-1} $= 2.17 \times 10^{-6}$ g L^{-1} $= 2.17$ μg L^{-1}

Question 6

Which one of the following salts has the highest water solubility at 25 °C?

(a) Lead(II) iodide

(b) Barium sulfate

(c) Silver carbonate

(d) Magnesium phosphate

(a) $K_{sp} = [Pb^{2+}][I^-]^2 = 9.8 \times 10^{-9}$, $[PbI_2] = 1.3 \times 10^{-3}$ mol L^{-1}

(b) $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$, $[BaSO_4] = 1.0 \times 10^{-5}$ mol L^{-1}

(c) $K_{sp} = [Ag^+]^2[CO_3^{2-}] = 8.46 \times 10^{-12}$, $[Ag_2CO_3] = 1.3 \times 10^{-4}$ mol L^{-1}

(d) $K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2 = 1.04 \times 10^{-24}$, $[Mg_3(PO_4)_2] = 6.3 \times 10^{-6}$ mol L^{-1}

Question 7

In which of the following solutions does calcium sulfate have the highest solubility?

(a) 0.0230 mol L^{-1} calcium chloride

(b) 0.0105 mol L^{-1} sodium sulfate

(c) 0.0110 mol L^{-1} magnesium sulfate

(d) 0.0245 mol L^{-1} calcium nitrate

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 4.93 \times 10^{-5}$

Let moles of $CaSO_4$ in 1 L = x

(a) $K_{sp} = 0.023x = 4.93 \times 10^{-5}$, $x = 2.1 \times 10^{-3}$ mol L^{-1}

(b) $K_{sp} = x0.0105 = 4.93 \times 10^{-5}$, $x = 4.7 \times 10^{-3}$ mol L^{-1}

(c) $K_{sp} = x0.0110 = 4.93 \times 10^{-5}$, $x = 4.5 \times 10^{-3}$ mol L^{-1}

(d) $K_{sp} = 0.0245x = 4.93 \times 10^{-5}$, $x = 2.0 \times 10^{-3}$ mol L^{-1}

Question 8

Aboriginal people had developed methods of removing toxins in cycad seeds to allow for consumption. Which of the following is an example of the use of solution equilibria to remove toxins?

(a) Fermentation

(b) Crushing

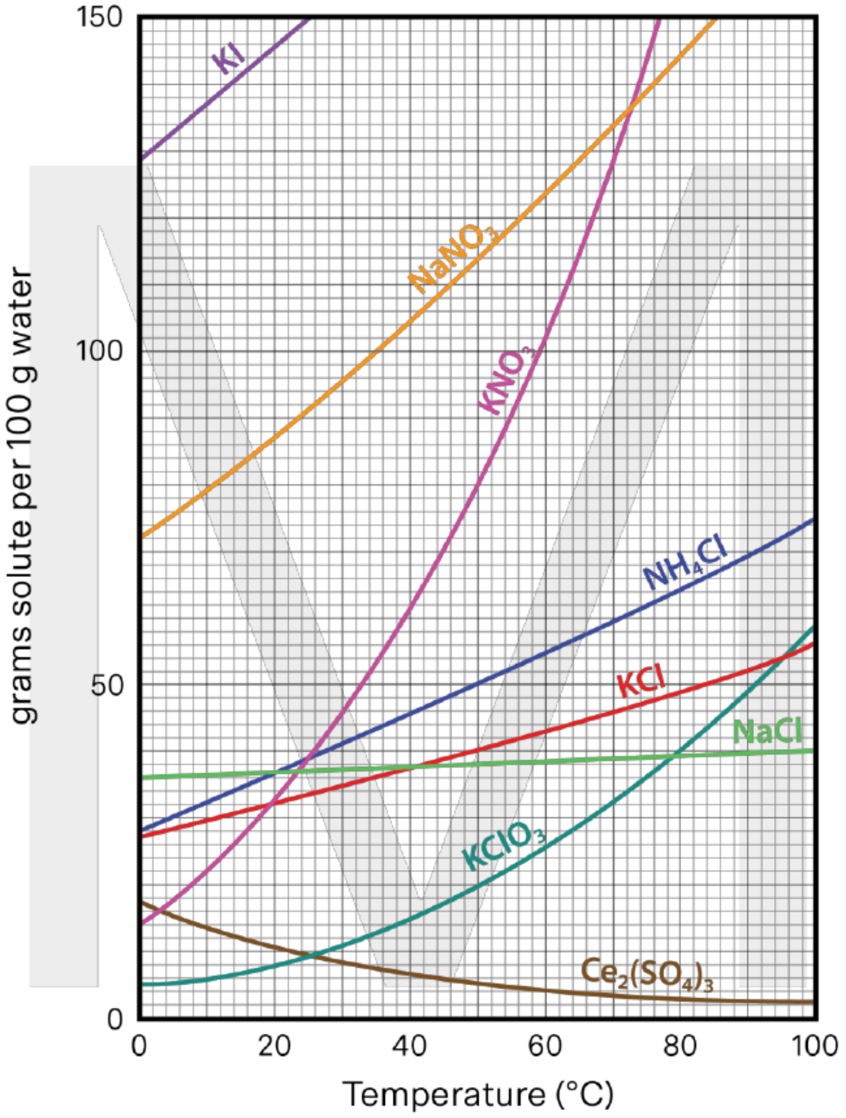
(c) Roasting

(d) Leaching

Part B: Extended response questions

Question 9

Use the solubility curves below to answer the following questions.



(a) What is the concentration of a saturated solution of $KClO_3$ at 50 °C? Express your answer in %w/w. 2

Solubility at 50 °C: 20 g of $KClO_3$ /100 g of water

m($KClO_3$) = 20 g, m(solution) = 120 g

%w/w = (20/120) × 100 = 17% w/w (2 s.f.)

(b) Given that the density of saturated $KClO_3$ at 50 °C is 1.1 g mL^{-1}, calculate the K_{sp} of $KClO_3$ at this temperature. 3

$m(KClO_3) = 20$ g, $m(\text{solution}) = 120$ g

$n(KClO_3) = 20 / (39.10 + 35.45 + 16 \times 3) = 0.1631986944$ mol

$V(KClO_3) = 120 / 1.1 = 109.09$ mL $= 0.10909$ L

$[KClO_3] = 0.1631986944 / 0.10909 = 1.495988$ mol L^{-1}

$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO_3^-{}_{(aq)}$

$[K^+] = [ClO_3^-] = 1.495988$ mol L^{-1}

$K_{sp} = [K^+][ClO_3^-] = (1.495988)^2 = 2.2$ (2 s.f.)

(c) 15.0 g of $KClO_3$ was added to 150 mL of saturated $KClO_3$ at 50 °C. The solution was then heated. At what temperature would all of the $KClO_3$ dissolve? 3

Mass of saturated solution = $150 \times 1.1 = 165$ g

Solubility at 50 °C: 20 g of $KClO_3$ /100 g of water

= 20 g $KClO_3$ /120 g of solution = 27.5 g $KClO_3$ /165 g of solution

Mass of water to dissolve 27.5 g of $KClO_3$ = 165 − 27.3 = 137.5 g

Total $KClO_3$ = 27.5 + 15 = 42.5 g

Thus total $KClO_3$ in water = 42.5 g / 137.5 g of water = 30.909 g / 100 g of water

From the graph, ~31 g of $KClO_3$ will dissolve in 100 g of water at 68 °C.

(d) A saturated solution containing 200 g of water was cooled from 50 °C to 20 °C. 94 g of solid solute crystallised from solution. What is the identity of the solute? Explain your answer. 2

Difference: 47 g of solute / 100 g of water

The solute is KNO_3. The solubility of KNO_3 at 50 °C is 80 g /100 g of water and the solubility at 20 °C is 33 g /100 g of water. This means 47 g of solute will crystallise from 100 g of water when cooled from 50 °C to 20 °C. This corresponds to 94 g of solute crystallising from 200 g of water.

(e) A solution of saturated KCl at 20 °C containing 30 g of water was reacted with excess silver nitrate solution. What mass of precipitate formed? Include a balanced chemical equation in your answer. 3

$KCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + KNO_{3(aq)}$

Solubility at 20 °C: 32 g of KCl /100 g of water = 9.6 g KCl /30 g of water

n(KCl) = 9.6/(39.1 + 35.45) = 0.1287726 mol

n(AgCl) = n(KCl) = 0.1287726 mol

m(AgCl) = 0.1287726 × (107.9 + 35.45) = 18 g (2 s.f.)

Question 10

A 1.00 litre sample of ground water was analysed and found to contain equal moles of dissolved silver carbonate and lead(II) carbonate. If water was allowed to evaporate, which ionic compound will precipitate first? Support your answer with calculations. 4

$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Ag^+]^2[CO_3^{2-}] = 8.46 \times 10^{-12}$

Let moles of Ag_2CO_3 in 1 L = x, thus $[Ag^+] = 2x$ and $[CO_3^{2-}] = x$

$K_{sp} = (2x)^2\, x = 8.46 \times 10^{-12}$

$x = 1.2836 \times 10^{-4}$

Solubility of Ag_2CO_3 = 1.28×10^{-4} mol/L

$PbCO_{3(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = [Pb^{2+}][CO_3^{2-}] = 7.40 \times 10^{-14}$

Let moles of $PbCO_3$ in 1 L = x, thus $[Pb^{2+}] = [CO_3^{2-}] = x$

$K_{sp} = x^2 = 7.4 \times 10^{-14}$

$x = 2.72029 \times 10^{-7}$

Solubility of $PbCO_3$ = 2.72×10^{-7} mol/L

As $PbCO_3$ has a lower solubility than Ag_2CO_3, $PbCO_3$ will precipitate first.

Question 11

(a) A saturated solution of lead(II) fluoride in pure water at 20 °C contains 0.0671 g of solute per 100.0 mL of solution. Calculate the value of K_{sp} for this compound at this temperature. **3**

Solubility of PbF_2 = 0.671 g/L

= (0.671 / (207.2 + 19.00 × 2)) mol/L= 2.7365×10^{-3} mol/L

$PbF_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2F^{-}_{(aq)}$

$[Pb^{2+}] = 2.7365 \times 10^{-3}$ mol/L and $[F^-] = 5.473 \times 10^{-3}$ mol/L

$K_{sp} = [Pb^{2+}][F^-]^2 = (2.7365 \times 10^{-3})(5.473 \times 10^{-3})^2 = 8.20 \times 10^{-8}$ (3 s.f.)

(b) Will lead(II) fluoride precipitate if solutions of 25.0 mL of 2.30×10^{-5} mol L^{-1} KF and 40.5 mL of 1.25×10^{-5} mol L^{-1} $Pb(NO_3)_2$ are mixed together at 20 °C? Show working. **3**

$PbF_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2F^{-}_{(aq)}$ $K_{sp} = [Pb^{2+}][F^-]^2 = 8.20 \times 10^{-8}$

$[F^-]_{final} = (2.30 \times 10^{-5} \times 0.025) / 0.0655 = 8.7786 \times 10^{-6}$ mol L^{-1}

$[Pb^{2+}]_{final} = (1.25 \times 10^{-5} \times 0.0405) / 0.0655 = 7.7290 \times 10^{-6}$ mol L^{-1}

$Q = (7.7290 \times 10^{-6})(8.7786 \times 10^{-6})^2 = 5.96 \times 10^{-16}$ (3 s.f.)

Since $Q < K_{sp}$, no precipitate will form.

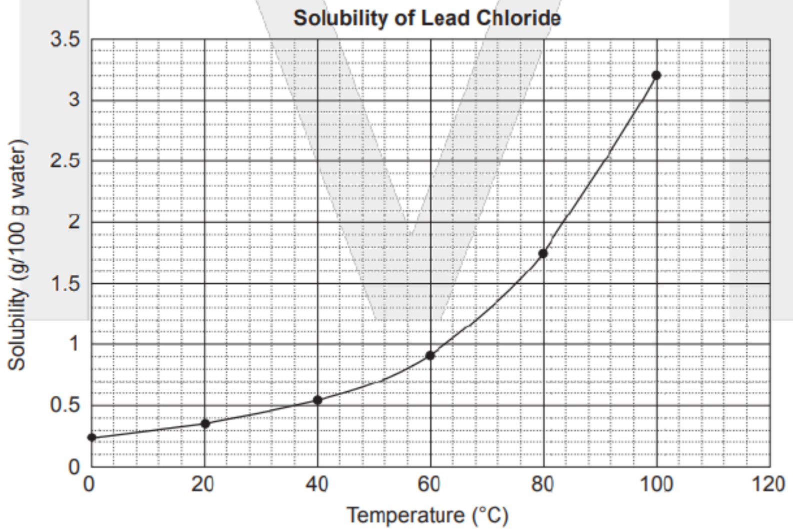
Question 12 **[HSC Sample Q17]**

The information in the table shows how the solubility of lead chloride is affected by temperature.

Temperature (°C)	Solubility (g/100g water)
0	0.25
20	0.35
40	0.55
60	0.90
80	1.75
100	3.20

Using a graph, calculate the solubility product (K_{sp}) of the dissolution of lead chloride at 50 °C. Include a fully labelled graph and a relevant chemical equation in your answer. 6

Modified NESA sample answer



$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

At 50°C, solubility is 0.7 g/100 mL, so it is 7 g/L.

Convert this to mol L^{-1}: $n = 7 / 278.1 = 0.0252$ $\therefore 0.0252 \text{ mol L}^{-1}$

$K_{sp} = x \times (2x)^2 = 4x^3 = 4(0.0252)^3 = 6 \times 10^{-5}$

Question 13

The solubility of cadmium(II) fluoride in water is 4.0 g per 100 mL at 20 °C. Calculate how many grams of cadmium(II) fluoride would dissolve in 100 mL of 2.0 mol L^{-1} lithium fluoride solution. **4**

Solubility of CdF_2 = 40 g/L = (40/(112.4 + 19.00 × 2)) mol/L = 0.265957 mol/L

$CdF_{2(s)} \rightleftharpoons Cd^{2+}_{(aq)} + 2F^-_{(aq)}$

$[Cd^{2+}]$ = 0.265957 M and $[F^-]$ = 0.531914 M

$K_{sp} = [Cd^{2+}][F^-]^2 = (0.265957)(0.531914)^2 = 0.075248$

Let $[Cd^{2+}] = x$ mol L^{-1}

Concentration (mol L^{-1})	$CdF_{2(s)}$	$\rightleftharpoons$	$Cd^{2+}_{(aq)}$	+	$2F^-_{(aq)}$
Initial	-		0		2.0
Change	-		$+x$		$+2x$
Equilibrium	-		x		$2.0 + 2x$

Assuming that x is small compared to initial $[F^-]$, $2.0 + 2x \approx 2.0$

$x(2.0)^2 = 0.075248$

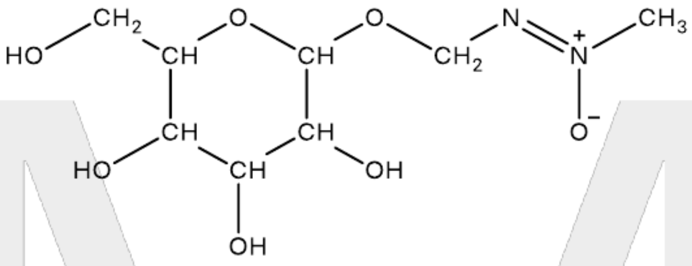
$x = 0.018812$ (Check assumption: ((0.018812 × 2) / 2.0) × 100 = 1.88%, thus valid)

Solubility of CdF_2 in 2.0 M LiF = 0.018812 mol L^{-1} = 2.82933 g L^{-1}

Thus in 100 mL, 0.28 g (2 s.f.) can dissolve.

Question 14

The seeds of cycads have been traditionally used as a food source for Aboriginal and Torres Strait Islander People despite their toxic qualities.
Cycasin is one of several toxins found in cycad plants. It is a carcinogenic and neurotoxic compound.



Cycasin

With reference to the structure of cycasin and its solubility equilibria, discuss the effectiveness of leaching as a method to remove this toxin from cycad seeds. **4**

Cycasin bears multiple hydroxyl (OH) groups that make it a polar molecule capable of forming many strong adhesive hydrogen bonds with water. This allows it to effectively disrupt the cohesive hydrogen bonds within water molecules and within cycasin, and hence allowing it to be water soluble. This means this toxin can be effectively removed from cycad seeds through leaching.

The solid cycasin and aqueous cycasin exist in dynamic equilibrium inside the seeds.

$\text{cycasin}_{(s)} \rightleftharpoons \text{cycasin}_{(aq)}$

When the seeds are soaked in water, the concentration of the aqueous cycasin is decreased, disturbing the equilibrium. According to Le Chatelier's principle, the equilibrium shifts in the direction to produce more aqueous cycasin to minimise the disturbance. As a result, solid cycasin will be converted to aqueous cycasin that can be washed away.

Question 15

Determine the molar solubility of calcium hydroxide in 0.200 mol L⁻¹ potassium hydroxide solution. 3

$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}$ $K_{sp} = [Ca^{2+}][OH^{-}]^2 = 5.02 \times 10^{-6}$

Let $[Ca^{2+}] = x$ mol L⁻¹

Concentration (mol L⁻¹)	$Ca(OH)_{2(s)}$	$\rightleftharpoons$	$Ca^{2+}_{(aq)}$	+	$2OH^{-}_{(aq)}$
Initial	-		0		0.200
Change	-		$+x$		$+2x$
Equilibrium	-		x		$0.200 + 2x$

Assuming that x is small compared to initial [OH⁻], $0.200 + 2x \approx 0.200$

$x(0.200)^2 = 5.02 \times 10^{-6}$

$x = 1.255 \times 10^{-4}$ (Check assumption: $((1.255 \times 10^{-4} \times 2) / 2.0) \times 100 = 0.13\%$, thus valid)

Solubility of $Ca(OH)_2$ in 0.2 M KOH = 1.26×10^{-4} mol L⁻¹ (3 s.f.)

Question 16

Calculate the minimum concentration, in mol L^{-1}, of sodium sulfate solution required to reduce the solubility of barium sulfate to 2.15×10^{-7} mol L^{-1} at 25 °C. 3

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$ $K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = 1.08 \times 10^{-10}$

Let $[Na_2SO_4] = x$ mol L^{-1}

Concentration (mol L^{-1})	$BaSO_{4(s)}$	$\rightleftharpoons$	$Ba^{2+}_{(aq)}$	+	$SO_4{}^{2-}_{(aq)}$
Initial	-		0		x
Change	-		$+ 2.15 \times 10^{-7}$		$+ 2.15 \times 10^{-7}$
Equilibrium	-		2.15×10^{-7}		$x + 2.15 \times 10^{-7}$

$K_{sp} = (2.15 \times 10^{-7})(x + 2.15 \times 10^{-7}) = 1.08 \times 10^{-10}$

$x = 5.0211 \times 10^{-4}$

$[Na_2SO_4] = 5.02 \times 10^{-4}$ mol/L

Question 17

3.0 g of calcium sulfate was mixed with distilled water to form 200 mL of saturated solution.

(a) Write an equation for the equilibrium present in this solution. 1

$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$

(b) What mass of solid would remain undissolved once equilibrium has been established? 3

$K_{sp} = [Ca^{2+}][SO_4{}^{2-}] = 4.93 \times 10^{-5}$

$K_{sp} = x^2 = 4.93 \times 10^{-5}$

$x = 0.00702$

Solubility of $CaSO_4$ = 0.00702 mol L^{-1} = 0.956 g/L

Solubility of $CaSO_4$ in 0.200 L = 0.191 g

Undissolved solid: 3.0 – 0.191 = 2.8 g (2 s.f.)

(c) The solution was diluted to 1.20 L. What additional mass of calcium sulfate would dissolve? 2

Solubility of $CaSO_4$ in 1.200 L = 1.15 g

Already dissolved = 0.191 g

Therefore an additional 1.15 – 0.191 = 0.96 g (2 s.f.) of $CaSO_4$ will dissolve.

(d) If a concentrated solution of calcium nitrate was added to this solution, what would occur? Explain in terms of collision theory. 3

Since the solution is saturated, the solid and aqueous calcium sulfate would exist in equilibrium. If more calcium nitrate is added to the solution, the concentration of calcium ions increases, causing the reverse rate of reaction to be faster than the forward rate of reaction as there would be a greater frequency of collisions between the ions in solution. This results in more calcium nitrate crystallising than dissolving, hence solubility is decreased. It is an example of the common ion effect.

(e) Evaluate the statement: “In a saturated ionic solution, ionic bonds are broken but there is no change in the mass of solid dissolved.” 2

This statement is accurate. Ionic bonds are broken as the dissolution reaction occurs. However, in a saturated ionic solution, the solid and aqueous ionic compounds exist in dynamic equilibrium. Thus, the reverse crystallisation reaction occurs at the same rate as the forward dissolution reaction. Consequently, there are no macroscopic changes occurring, thus no change in mass of solid dissolved.

Question 18

Determine if a precipitate would form when 346 mL of 2.37 ppb iron(II) chloride solution and 280 mL of 10.8 ppm potassium hydroxide solution are mixed at 25 °C. 3

Precipitate that could be formed is iron(II) hydroxide.

$Fe(OH)_{2(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp} = [Fe^{2+}][OH^-]^2 = 4.87 \times 10^{-17}$

Solubility of $FeCl_2$ = 2.37 ppb

$= (2.37 \times 10^{-6} / (55.85 + 35.45 \times 2))$ mol/L $= 1.8698 \times 10^{-8}$ mol L^{-1}

Solubility of KOH = 10.8 ppm

$= (10.8 \times 10^{-3} / (39.10 + 16.00 + 1.008))$ mol/L $= 1.9248 \times 10^{-4}$ mol L^{-1}

$[Fe^{2+}]_{final} = (1.8698 \times 10^{-8} \times 0.346) / 0.626 = 1.03348 \times 10^{-8}$ mol L^{-1}

$[OH^-]_{final} = (1.9248 \times 10^{-4} \times 0.280) / 0.626 = 8.60959 \times 10^{-5}$ mol L^{-1}

$Q = (1.03348 \times 10^{-8})(8.60959 \times 10^{-5})^2 = 7.66 \times 10^{-17}$ (3 s.f.)

Since $Q > K_{sp}$, a precipitate will form.

Part C: Additional practice questions

The questions in this part are intended to be used for revision purposes. However, from time to time your teacher may prescribe some of these questions for homework.

Question 19

A saturated solution of a salt has a concentration of 5.8×10^{-5} M. What is the salt?

(a) Copper (II) carbonate

(b) Iron(II) carbonate

(c) Barium carbonate

(d) Calcium carbonate

(a) $K_{sp} = [Cu^{2+}][CO_3^{2-}] = 1.4 \times 10^{-10}$, $[Cu^{2+}] = [CO_3^{2-}] = 1.2 \times 10^{-5}$

(b) $K_{sp} = [Fe^{2+}][CO_3^{2-}] = 3.13 \times 10^{-11}$, $[Fe^{2+}] = [CO_3^{2-}] = 5.6 \times 10^{-6}$

(c) $K_{sp} = [Ba^{2+}][CO_3^{2-}] = 2.58 \times 10^{-9}$, $[Ba^{2+}] = [CO_3^{2-}] = 5.1 \times 10^{-5}$

(d) $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 3.36 \times 10^{-9}$, $[Ca^{2+}] = [CO_3^{2-}] = 5.8 \times 10^{-5}$

Question 20

What is the concentration of hydroxide ions in a saturated solution of iron(II) hydroxide at 25 °C?

(a) 2.1×10^{-4} g L^{-1}

(b) 2.3×10^{-6} g L^{-1}

(c) 7.8×10^{-5} g L^{-1}

(d) 1.6×10^{-4} g L^{-1}

$Fe(OH)_{2(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2OH^-_{(aq)}$ $K_{sp} = [Fe^{2+}][OH^-]^2 = 4.87 \times 10^{-17}$

Let moles of $Fe(OH)_2$ in 1 L = x, thus $[Fe^{2+}] = x$, $[OH^-] = 2x$

$Ksp = (x)(2x)^2 = 4.87 \times 10^{-17}$

$x = 2.300 \times 10^{-6}$

$[OH^-] = 4.6010 \times 10^{-6}$ mol/L = $(4.6010 \times 10^{-6} \times (16 + 1.008))$ g/L

Question 21

The mass of chloride ions in 75 L of 95 ppm calcium chloride solution is:

(a) 7.1 g

(b) 4.6 g

(c) 3.3 g

(d) 9.1 g

95 ppm = 95 mg/kg = 0.095 g/L

$c(CaCl_2) = 0.095 / (40.08 + 35.45 \times 2) = 8.56 \times 10^{-4}$ M

$n(Cl^-)$ in 75 L = $8.56 \times 10^{-4} \times 2 \times 75 = 0.1284$ mol

$m(Cl^-) = 0.1284 \times 35.45 = 4.55$ g

Question 22

The molar solubilities of the following compounds at a certain temperature are listed below. Which of the following K_{sp} values is not correctly calculated?

	Compound	Molar solubility	K_{sp}
(a)	Lead(II) fluoride	1.9×10^{-3}	2.7×10^{-8}
(b)	Lithium phosphate	3.3×10^{-3}	1.2×10^{-10}
(c)	Cadmium(II) carbonate	2.3×10^{-6}	5.3×10^{-12}
(d)	Cobalt(II) sulfide	2.2×10^{-11}	5.0×10^{-22}

$$Li_3PO_{4(s)} \rightleftharpoons 3Li^+_{(aq)} + PO_4{}^{3-}{}_{(aq)}$$

$[Li^+] = 3 \times 3.3 \times 10^{-3} = 9.9 \times 10^{-3}$ M and $[PO_4{}^{3-}] = 3.3 \times 10^{-3}$ M

$K_{sp} = [Li^+]^3[PO_4{}^{3-}] = 3.2 \times 10^{-9}$

Question 23

Determine the solubility product constant K_{sp} for lithium phosphate if 955 mg of solid lithium phosphate can dissolve in water to make a 2.50 L saturated solution of lithium phosphate at 25°C. 3

Solubility of Li_3PO_4 = 0.955 g/2.5 L = 0.382 g/L

= (0.382/(6.941 × 3 + 30.97 + 16 × 4)) mol/L = 3.29899×10^{-3} mol/L

$Li_3PO_{4(s)} \rightleftharpoons 3Li^+_{(aq)} + PO_4^{3-}{}_{(aq)}$

$[Li^+] = 9.89697 \times 10^{-3}$ mol/L and $[PO_4^{3-}] = 3.29899 \times 10^{-3}$ mol/L

$K_{sp} = [Li^+]^3[PO_4^{3-}] = (9.89697 \times 10^{-3})^3(3.29899 \times 10^{-3}) = 3.20 \times 10^{-9}$ (2 s.f.)

Question 24

The K_{sp} of potassium chloride at 25°C is 21.7. Determine the mass of potassium chloride required to make a 300 mL saturated solution in water. 3

$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$ $K_{sp} = [K^+][Cl^-] = 21.7$

Let moles of KCl in 1 L = x, thus $[K^+] = x$, $[Cl^-] = x$

$K_{sp} = x^2 = 21.7$, thus $x = 4.6583$

Solubility of KCl = 4.6583 mol/L = (4.6583 × (39.10 + 35.35)) g/L = 347 g/L

In 300 mL: 347 × 0.3 = 104 g (3 s.f.)

Question 25

Determine the solubility of lead(II) sulfate at 25°C in:

(a) Pure water **2**

$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)}$ $K_{sp} = [Pb^{2+}][SO_4^{2-}] = 2.53 \times 10^{-8}$

Let moles of $PbSO_4$ in 1 L = x, thus $[Pb^{2+}]$ and $[SO_4^{2-}] = x$

$K_{sp} = x^2 = 2.53 \times 10^{-8}$ $\therefore x = 1.590597 \times 10^{-4}$

Solubility = 1.59×10^{-4} mol/L (3 s.f.)

(b) 0.0500 M lead(II) nitrate **3**

Let x be moles of $PbSO_4$ that can dissolve in 1 L

Concentration (mol L^{-1})	$PbSO_{4(s)}$	$\rightleftharpoons$	$Pb^{2+}_{(aq)}$	+	$SO_4^{2-}_{(aq)}$
Initial			0.0500		0
Change			$+ x$		$+ x$
Equilibrium			$0.0500 + x$		x

Assuming x is small compared to initial $[Pb^{2+}]$, $0.0500 + x \approx 0.0500$

$0.0500x = 2.53 \times 10^{-8}$

$x = 5.06 \times 10^{-7}$ (Check assumption: $(5.06 \times 10^{-7}/ 0.0500) \times 100 < 5\%$)

Solubility = 5.06×10^{-7} mol/L (3 s.f.)

(c) 0.0500 M potassium sulfate **1**

Concentration of sulfate ion (common ion) is 0.0500 M, same as previous calculation.

Solubility = 5.06×10^{-7} mol/L (3 s.f.)

Question 26

A 100 mL solution contains of 0.150 mmol L^{-1} of chloride ions and 0.100 mmol L^{-1} of bromide ions.

(a) If silver ions were slowly added to the solution at 25 °C, which precipitate would form first? Explain your answer. 2

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$ $K_{sp} = [Ag^+][Cl^-] = 1.77 \times 10^{-10}$

$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$ $K_{sp} = [Ag^+][Br^-] = 5.35 \times 10^{-13}$

Silver bromide is less soluble compared to silver chloride, thus would precipitate first.

(b) If 1.00 mL of 0.0500 mmol L^{-1} solution of silver was added to the solution:

(i) Will both silver chloride and silver bromide precipitate from solution? Show working. 3

$[Ag^+]_{final} = (0.0500 \times 10^{-3} \times 0.001) / 0.101 = 4.9505 \times 10^{-7}$ mol L^{-1}

$[Cl^-]_{final} = (0.150 \times 10^{-3} \times 0.100) / 0.101 = 1.4851 \times 10^{-4}$ mol L^{-1}

$[Br^-]_{final} = (0.100 \times 10^{-3} \times 0.100) / 0.101 = 9.90099 \times 10^{-5}$ mol L^{-1}

AgCl precipitate: $Q = (4.9505 \times 10^{-7})(1.4851 \times 10^{-4}) = 7.35 \times 10^{-11}$ (3 s.f.) $< K_{sp}$

AgBr precipitate: $Q = (4.9505 \times 10^{-7})(9.90099 \times 10^{-5}) = 4.90 \times 10^{-11}$ (3 s.f.) $> K_{sp}$

Thus no AgCl precipitate will form and AgBr precipitate will form.

(ii) What will the concentration, in mol L^{-1}, of the chloride and bromide ions be in solution? 4

Since no chloride ions precipitate:

$[Cl^-]_{final} = (0.150 \times 10^{-3} \times 0.100) / 0.101 = 1.49 \times 10^{-4}$ mol L^{-1} (3 s.f.)

Assuming the AgBr precipitate is completely insoluble:

Ag^+ is limiting reactant:

$[Br^-]_{excess} = 9.90099 \times 10^{-5} - 4.9505 \times 10^{-7} = 9.851485 \times 10^{-5}$ mol L^{-1}

However, some AgBr will dissolve. Let $[Ag^+] = x$ mol L^{-1}

Concentration (mol L^{-1})	$AgBr_{(s)}$	$\rightleftharpoons$	$Ag^+_{(aq)}$	+	$Br^-_{(aq)}$
Initial			0		9.851485×10^{-5}
Change			$+x$		$+x$
Equilibrium			x		$9.851485 \times 10^{-5} + x$

Assuming x is small compared to initial $[Br^-]$, $9.851485 \times 10^{-5} + x \approx 9.851485 \times 10^{-5}$

$K_{sp} = [Ag^+][Br^-] = 5.35 \times 10^{-13}$

$x(9.851485 \times 10^{-5}) = 5.35 \times 10^{-13}$

$x = 5.43065 \times 10^{-9}$ (Check assumption: $(5.43065 \times 10^{-9} / 9.851485 \times 10^{-5}) \times 100 < 5\%$)

$[Br^-] = 9.851485 \times 10^{-5} + 5.43065 \times 10^{-9} = 9.85 \times 10^{-5}$ (2 s.f.)

Question 27

(a) Calculate the concentration of a saturated solution of silver sulfate at 25 °C in moles per litre. 2

$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$ $K_{sp} = [Ag^+]^2[SO_4^{2-}] = 1.20 \times 10^{-5}$

Let moles of Ag_2SO_4 in 1 L = x, thus $[Ag^+] = 2x$, $[SO_4^{2-}] = x$

$K_{sp} = (2x)^2(x) = 1.20 \times 10^{-5}$

$[Ag_2SO_4] = x = 0.0144$ mol/L (3 s.f.)

(b) Calculate the concentration of a saturated solution of silver sulfate at 25 °C as % w/w (solution density = 0.546 g mL^{-1}) 2

$[Ag_2SO_4] = 0.014422$ mol/L

m(Ag_2SO_4) = 0.014422 × (107.9 × 2 + 32.07 + 16 × 4) = 4.4979437 g

m(solution) = 0.546 × 1000 = 0.546 g

% w/w = 4.4979437 / 0.546 × 100 = 0.824% w/w (3 s.f.)

(c) Calculate the solubility of silver sulfate in g per 100 mL of water at 25 °C. 2

Concentration: 0.824 g / 100 g of solution

Mass of solvent = 100 − 0.824 = 99.176 g = 99.176 mL of water

Solubility = 0.824 g / 99.176 mL × 100 = 0.831 g / 100 mL (3 s.f.)

(d) 23.0 mg of silver sulfate is added to 0.950 mL of water at 25 °C. How much additional water is required to dissolve all of the silver sulfate? 2

Solubility = 0.831 g / 100 mL

Volume required for 23 mg: 0.023 × 0.831/100 = 2.7689 mL

Additional volume = 2.7689 − 0.950 = 1.82 mL (3 s.f.)

Question 28

540 mL of 2.00×10^{-4} mol L^{-1} sodium sulfate solution was placed in a beaker. In order to just start precipitation of barium sulfate, 350 mL of 1.30×10^{-4} mol L^{-1} of barium chloride was required.

(a) What is the K_{sp} value for barium sulfate at the temperature this reaction was conducted? 3

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$ $K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$

$[Ba^{2+}]_{final} = (1.30 \times 10^{-4} \times 0.350) / 0.890 = 5.112 \times 10^{-5}$ mol L^{-1}

$[SO_4{}^{2-}]_{final} = (2.00 \times 10^{-4} \times 0.540) / 0.890 = 1.213 \times 10^{-4}$ mol L^{-1}

$K_{sp} = (5.112 \times 10^{-5})(1.213 \times 10^{-4}) = 6.20 \times 10^{-9}$ (3 s.f.)

(b) The solubility of barium sulfate increases with increasing temperatures. Was the precipitation reaction conducted at a higher or lower temperature than 25 °C? Justify your answer. 2

At 25 °C: $K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = 1.08 \times 10^{-10}$

The K_{sp} at the temperature the reaction was conducted is greater than the K_{sp} at 25 °C. A larger K_{sp} indicates more ions were present in the saturated solution, and thus the extent of dissolution is greater. Since the solubility of barium sulfate increases with increasing temperatures, the temperature the reaction was performed is greater than 25 °C.

Question 29

The K_{sp} of silver chromate Ag_2CrO_4 at 25 °C is 1.12×10^{-12}.

(a) Write dissociation equation for silver chromate and the corresponding solubility product. **1**

$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$ $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

(b) Calculate the concentration, in mol L⁻¹, of chromate ions in a saturated solution of silver chromate at 25 °C. **2**

Let moles of Ag_2CrO_4 in 1 L = x, thus $[Ag^+] = 2x$, $[CrO_4^{2-}] = x$

$K_{sp} = (2x)^2(x) = 4x^3 = 1.12 \times 10^{-12}$

$x = 6.5421 \times 10^{-5}$

$[CrO_4^{2-}] = 6.54 \times 10^{-5}$ mol/L (3 s.f.)

(c) A 0.100 mol sample of solid silver nitrate was added to a 2.00 L saturated solution of silver chromate at 25 °C.

(i) What would happen to the concentration of chromate ions? Explain in terms of Le Chatelier's principle. **2**

Silver nitrate dissolves to form silver ions and nitrate ions. As there is a higher concentration of the silver ions in the solution, equilibrium is disturbed. According to Le Chatelier's principle, the equilibrium will shift to the left to remove the silver ions to minimise the disturbance. Hence the concentration of chromate ions will decrease.

(ii) Assuming there is no volume change, calculate the concentration, in mol L⁻¹, of chromate ions in this solution. **3**

Let moles of Ag_2CrO_4 in 1 L = x, thus $[Ag^+] = 2x$, $[CrO_4^{2-}] = x$

Concentration (mol L⁻¹)	$Ag_2CrO_{4(s)}$	$\rightleftharpoons$	$2Ag^+_{(aq)}$	+	$CrO_4^{2-}{}_{(aq)}$
Initial	-		0.05		0
Change	-		$+2x$		$+x$
Equilibrium	-		$0.05 + 2x$		x

Assuming x is small compared to initial $[Ag^+]$, $0.05 + 2x \approx 0.05$

$x(0.05)^2 = 1.12 \times 10^{-12}$

$x = 4.48 \times 10^{-10}$ (Check assumption: $((4.48 \times 10^{-10} \times 2) / 0.05) \times 100 < 5\%$, thus valid)

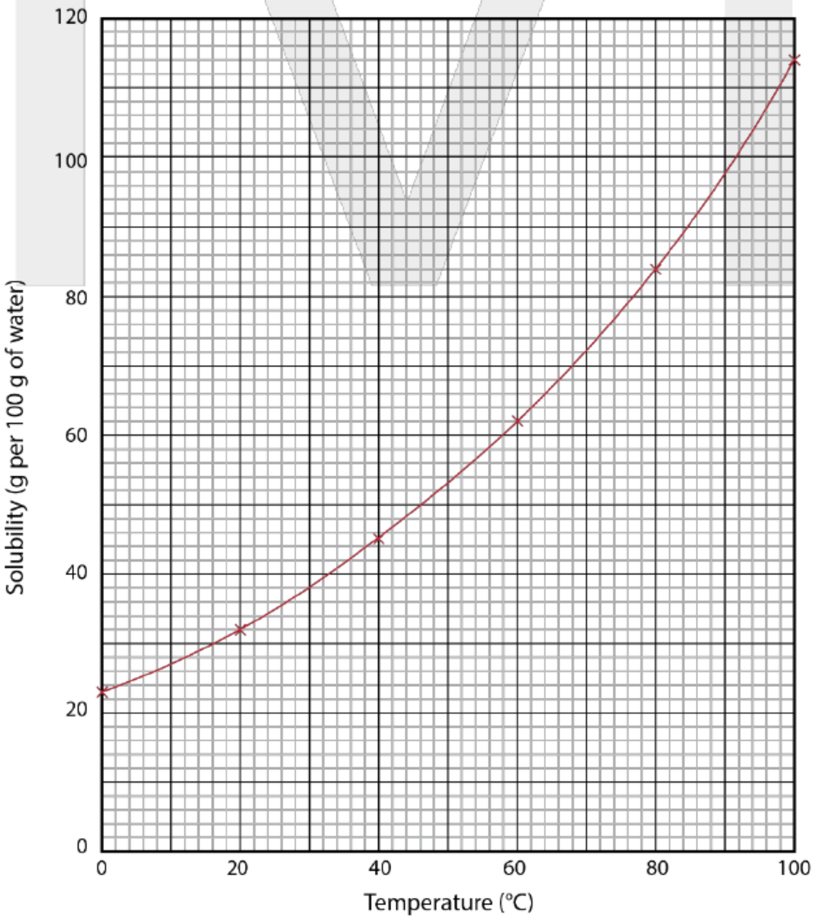
$[CrO_4^{2-}] = 4.48 \times 10^{-10}$ mol/L (3 s.f.)

Question 30

The table below shows how the solubility of copper(II) sulfate is affected by temperature.

Temperature (°C)	Solubility (g/100g water)
0	23
20	32
40	45
60	62
80	84
100	114

(a) Plot a solubility curve for copper(II) sulfate on the graph below. 3



(b) What is the maximum mass of copper(II) sulfate that will dissolve in 50 g of water at 30 °C? 2

Solubility at 30 °C: 38 g of $CuSO_4$ /100 g of water

Therefore in 19 g of $CuSO_4$ can dissolve in 50 g of water

(c) What is the concentration of a saturated solution of copper(II) sulfate at 55 °C in %w/w? 2

Solubility at 55 °C: 57 g of $CuSO_4$ /100 g of water

%w/w = (57/ 157) × 100 = 36% w/w

(d) Calculate the mass of copper(II) sulfate that will precipitate out of solution if a saturated solution of copper(II) sulfate containing 300 g of water is cooled from 75 °C to 20 °C. 3

Solubility at 75 °C: 78 g per 100 g water, 234 g per 300 g water

Solubility at 20 °C: 32 g per 100 g water, 96 g per 300 g water

Difference = 234 − 96 = 138 g = 140 g (2 s.f.)

(e) If 25 g of copper(II) sulfate is dissolved in 55 g of water at 60 °C and then the solution was allowed to cool, at what temperature would a precipitate first appear? 2

25 g in 55 g water = 45.45 g per 100 g water

From the graph: 40.5 °C = 41 °C (2 s.f.)

(f) If 65 g of copper(II) sulfate was added to 120 g of water, what is the minimum temperature that the solution needs to be for all the solid to be completely dissolved? 2

65 g in 120 g water = 54.2 g per 100 g water

From the graph: 51 °C

Question 31

(a) Explain how solubility equilibria are used by Aboriginal and Torres Strait Islander peoples when removing toxins from cycad fruit. 2

Toxins in the cycad fruit are water soluble. The solid toxin and aqueous toxin exist in equilibrium inside the fruit. When the fruit is soaked in water, the concentration of the aqueous toxin is decreased, disturbing the equilibrium. According to Le Chatelier's principle, the equilibrium shifts in the direction to produce more aqueous toxin to minimise the disturbance. As a result, solid toxins are converted to aqueous toxins that can be washed away.

(b) Identify another method used by Aboriginal and Torres Strait Islander peoples to remove toxins from cycad fruit. 1

Cooking or fermentation

2023 HIGHER SCHOOL CERTIFICATE EXAMINATION

Chemistry

FORMULAE SHEET

$n = \frac{m}{MM}$ $c = \frac{n}{V}$ $PV = nRT$

$q = mc\Delta T$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\text{pH} = -\log_{10}[\text{H}^+]$

$pK_a = -\log_{10}[K_a]$ $A = \varepsilon lc = \log_{10}\frac{I_o}{I}$

Avogadro constant, N_A	6.022×10^{23} mol^{-1}
Volume of 1 mole ideal gas: at 100 kPa and	
at 0°C (273.15 K)	22.71 L
at 25°C (298.15 K)	24.79 L
Gas constant	8.314 J mol^{-1} K^{-1}
Ionisation constant for water at 25°C (298.15 K), K_w	1.0×10^{-14}
Specific heat capacity of water	4.18×10^3 J kg^{-1} K^{-1}

DATA SHEET

Solubility constants at 25°C

Compound	K_{sp}	*Compound*	K_{sp}
Barium carbonate	2.58×10^{-9}	Lead(II) bromide	6.60×10^{-6}
Barium hydroxide	2.55×10^{-4}	Lead(II) chloride	1.70×10^{-5}
Barium phosphate	1.3×10^{-29}	Lead(II) iodide	9.8×10^{-9}
Barium sulfate	1.08×10^{-10}	Lead(II) carbonate	7.40×10^{-14}
Calcium carbonate	3.36×10^{-9}	Lead(II) hydroxide	1.43×10^{-15}
Calcium hydroxide	5.02×10^{-6}	Lead(II) phosphate	8.0×10^{-43}
Calcium phosphate	2.07×10^{-29}	Lead(II) sulfate	2.53×10^{-8}
Calcium sulfate	4.93×10^{-5}	Magnesium carbonate	6.82×10^{-6}
Copper(II) carbonate	1.4×10^{-10}	Magnesium hydroxide	5.61×10^{-12}
Copper(II) hydroxide	2.2×10^{-20}	Magnesium phosphate	1.04×10^{-24}
Copper(II) phosphate	1.40×10^{-37}	Silver bromide	5.35×10^{-13}
Iron(II) carbonate	3.13×10^{-11}	Silver chloride	1.77×10^{-10}
Iron(II) hydroxide	4.87×10^{-17}	Silver carbonate	8.46×10^{-12}
Iron(III) hydroxide	2.79×10^{-39}	Silver hydroxide	2.0×10^{-8}
Iron(III) phosphate	9.91×10^{-16}	Silver iodide	8.52×10^{-17}
		Silver phosphate	8.89×10^{-17}
		Silver sulfate	1.20×10^{-5}

Some standard potentials

$K^+ + e^-$	$\rightleftharpoons$	$K(s)$	–2.94 V
$Ba^{2+} + 2e^-$	$\rightleftharpoons$	$Ba(s)$	–2.91 V
$Ca^{2+} + 2e^-$	$\rightleftharpoons$	$Ca(s)$	–2.87 V
$Na^+ + e^-$	$\rightleftharpoons$	$Na(s)$	–2.71 V
$Mg^{2+} + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.36 V
$Al^{3+} + 3e^-$	$\rightleftharpoons$	$Al(s)$	–1.68 V
$Mn^{2+} + 2e^-$	$\rightleftharpoons$	$Mn(s)$	–1.18 V
$H_2O + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g) + OH^-$	–0.83 V
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	$Zn(s)$	–0.76 V
$Fe^{2+} + 2e^-$	$\rightleftharpoons$	$Fe(s)$	–0.44 V
$Ni^{2+} + 2e^-$	$\rightleftharpoons$	$Ni(s)$	–0.24 V
$Sn^{2+} + 2e^-$	$\rightleftharpoons$	$Sn(s)$	–0.14 V
$Pb^{2+} + 2e^-$	$\rightleftharpoons$	$Pb(s)$	–0.13 V
$H^+ + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00 V
$SO_4^{2-} + 4H^+ + 2e^-$	$\rightleftharpoons$	$SO_2(aq) + 2H_2O$	0.16 V
$Cu^{2+} + 2e^-$	$\rightleftharpoons$	$Cu(s)$	0.34 V
$\frac{1}{2}O_2(g) + H_2O + 2e^-$	$\rightleftharpoons$	$2OH^-$	0.40 V
$Cu^+ + e^-$	$\rightleftharpoons$	$Cu(s)$	0.52 V
$\frac{1}{2}I_2(s) + e^-$	$\rightleftharpoons$	I^-	0.54 V
$\frac{1}{2}I_2(aq) + e^-$	$\rightleftharpoons$	I^-	0.62 V
$Fe^{3+} + e^-$	$\rightleftharpoons$	Fe^{2+}	0.77 V
$Ag^+ + e^-$	$\rightleftharpoons$	$Ag(s)$	0.80 V
$\frac{1}{2}Br_2(l) + e^-$	$\rightleftharpoons$	Br^-	1.08 V
$\frac{1}{2}Br_2(aq) + e^-$	$\rightleftharpoons$	Br^-	1.10 V
$\frac{1}{2}O_2(g) + 2H^+ + 2e^-$	$\rightleftharpoons$	H_2O	1.23 V
$\frac{1}{2}Cl_2(g) + e^-$	$\rightleftharpoons$	Cl^-	1.36 V
$\frac{1}{2}Cr_2O_7^{2-} + 7H^+ + 3e^-$	$\rightleftharpoons$	$Cr^{3+} + \frac{7}{2}H_2O$	1.36 V
$\frac{1}{2}Cl_2(aq) + e^-$	$\rightleftharpoons$	Cl^-	1.40 V
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	1.51 V
$\frac{1}{2}F_2(g) + e^-$	$\rightleftharpoons$	F^-	2.89 V

Aylward and Findlay, *SI Chemical Data* (5th Edition) is the principal source of data for the standard potentials. Some data may have been modified for examination purposes.