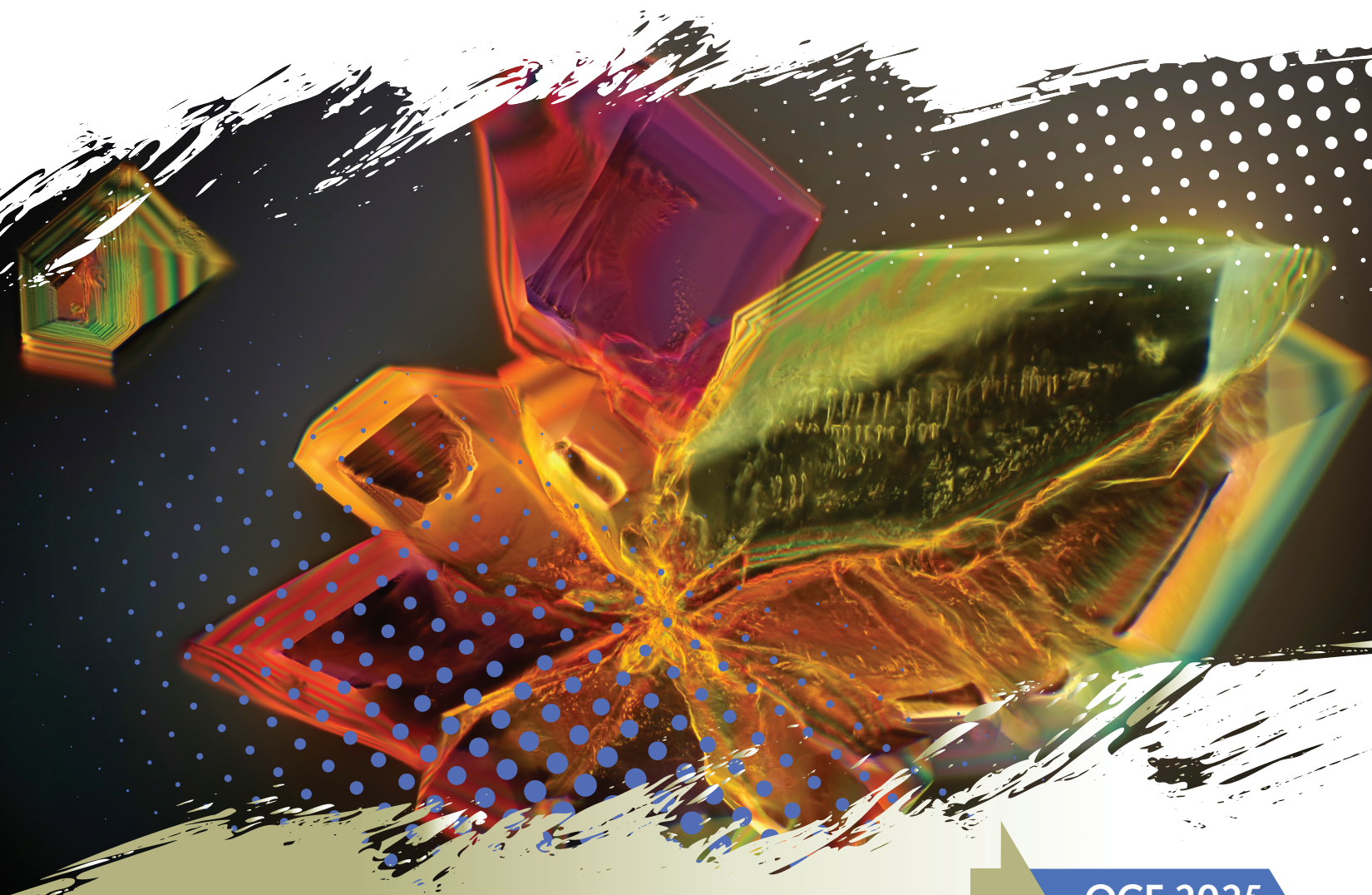


PEARSON

CHEMISTRY

QUEENSLAND

UNITS 3 & 4



Student Book

QCE 2025
Chemistry

SYLLABUS

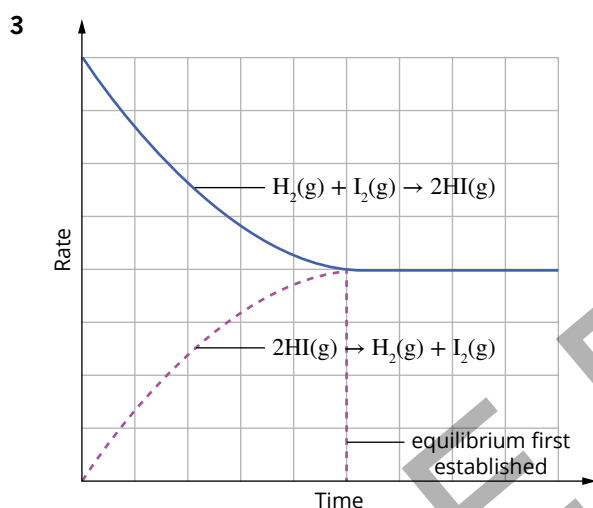
Chapter 2 Chemical equilibrium

2.1 Dynamic equilibrium

2.1 KEY QUESTIONS

- An **open** system occurs when both matter and energy are exchanged between the system and the surroundings.
 - Chemical equilibria can occur in **closed** systems.
 - In some circumstances, a reversible reaction can form a **dynamic** equilibrium.
 - The extent of reaction for chemical equilibria is **different** for different equilibria.

- false
 - false
 - true
 - false



- closed, decreases, less, reverse, increases, equal
- open; both energy and matter (carbon dioxide and water vapour) are exchanged with the surroundings
 - closed; only energy can be exchanged with the surroundings. While the can is unopened, no matter is exchanged.
 - open; both energy and matter are exchanged with the surroundings
- B and F. Equilibrium can only occur in a closed system. At the molecular level, some of the sugar in the saturated sugar solution will continue to dissolve at the same rate as some is precipitated. In the unopened bottle of sparkling mineral water, the dissolved carbon dioxide will be in equilibrium with the gaseous carbon dioxide. In all of the other situations, the reverse reaction is not occurring at the same rate as the forward reaction, because the systems are open.
- 130 kJ mol^{-1} . The activation energy is the difference between 390 kJ mol^{-1} and 260 kJ mol^{-1} , which is 130 kJ mol^{-1} .
 - Chemical equilibrium is 'dynamic' because both the forward and reverse reactions occur at the same rate. An equilibrium develops between water vapour and water when wet clothes are in a sealed bag, with water evaporating as rapidly as water vapour condenses, so the clothes remain wet.
 - When the bag is opened, water vapour escapes and the rate of evaporation exceeds the rate of condensation. The system is not in equilibrium and the clothes dry.
- 0.07 mol L^{-1}
 - 0 mol L^{-1}
 - 0.03 mol L^{-1}
 - 0.08 mol L^{-1}
 - 0.04 moles
 - The horizontal regions of the graph indicate that there is no change in the concentration of NO_2 or N_2O_4 . This is when the system is at equilibrium and both the forward and reverse reactions are occurring at the same rate.

g 6 seconds

h As the reaction proceeds, the intensity of the brown colour will increase as the concentration of NO_2 increases until equilibrium is reached. Once equilibrium is reached, the colour of the reaction mixture will remain constant.

2.2 Factors that affect equilibrium

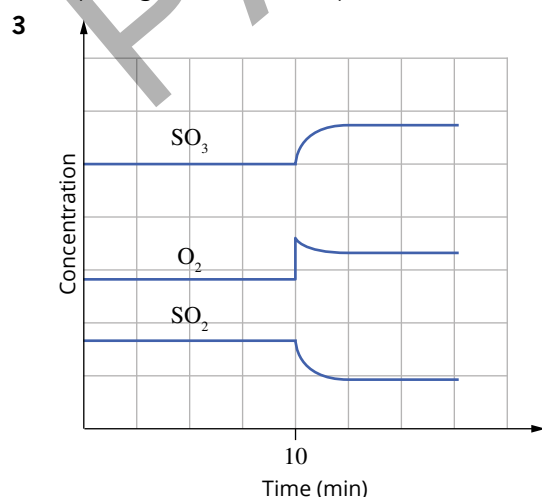
Try yourself 2.2.1

USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

Consider the following equilibrium system: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of CO gas on the equilibrium.	
Thinking	Working
Determine the initial effect of the change on the concentration of the particles.	Adding CO molecules increases the concentration (and partial pressure) of these particles.
Use collision theory to determine the initial effect on the rate of the forward (or reverse) reaction.	Collisions between CO and H_2O become more frequent, increasing the rate of the reverse reaction and reducing the concentrations (and partial pressures) of CO and H_2O molecules.
Consider how the rates of the forward and reverse reactions change as the system reaches a new equilibrium.	As more reactant molecules are formed, the rate of the forward reaction increases, until the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Predict the overall effect of the change on the position of equilibrium.	Because of the higher rate of the reverse reaction initially when the CO molecules were added, a net reverse reaction has occurred.

2.2 KEY QUESTIONS

- Le Châtelier's principle states that if an equilibrium system is subjected to a change, the position of equilibrium will shift to partially oppose the effect of the change.
- If a reactant is added to an equilibrium system, the rate of the forward reaction initially becomes **greater** than the rate of the reverse reaction. Then, as the concentration of reactants **decreases** and the concentration of products **increases**, the rate of the forward reaction **decreases** and the rate of the reverse reaction **increases** until they become equal again and a new equilibrium is formed.



- 4 a net forward reaction (shift to the right)
 b net reverse reaction (shift to the left)
 c net forward reaction (shift to the right)
- 5 a net reverse reaction (shift to the left)
 b net forward reaction (shift to the right)

2.3 Applying Le Châtelier's principle and collision theory to equilibria

Try yourself 2.3.1

USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME INCREASE

Consider the equilibrium: $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at a constant temperature.	
Thinking	Working
Determine the immediate effect of the change of volume on the pressure.	Doubling the volume will halve the pressure of all species at equilibrium.
The system will try to partially oppose the change in pressure by reducing or increasing the pressure in the system. (For a volume decrease, the system will shift in the direction of the fewest gaseous particles, and vice versa for a volume increase.) Decide how the equilibrium will respond.	There are two molecules of gas on the reactant side and one molecule of gas on the product side, so the system will shift to the left (a net reverse reaction). This increases the concentration of the reactants, including Cl_2 . (Note that the PCl_3 and Cl_2 concentrations will still be lower than they were at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

Try yourself 2.3.2

USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium: $\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \quad \Delta H = -165 \text{ kJ mol}^{-1}$ Using collision theory, explain the effect of an increase in temperature on this exothermic reaction.	
Thinking	Working
Decide what effect the temperature change has on the initial rates of reaction. Remember that, for an equilibrium system, an increase in temperature increases the proportion of molecules with the necessary energy to overcome the activation energy barrier for the endothermic reaction to a greater extent than for the exothermic reaction, and so the endothermic reaction will be favoured.	With the temperature increase, all reactant and product molecules have more energy and move faster. This reaction has a negative ΔH indicating it is an exothermic reaction. Since the reverse reaction is endothermic, its rate initially increases more than the rate of the forward reaction.
Using collision theory, consider what happens to the rates of the forward and reverse reactions.	As CH_4 and H_2O react and the concentration of products decreases, the rate of the reverse reaction will decrease. As the concentration of CO_2 and H_2 increases, the rate of the forward reaction will increase. Ultimately, the rates of the forward and reverse reactions become equal, and a new equilibrium is established.
Determine the overall effect of the change on the equilibrium.	This results in a net reverse reaction, with higher concentrations of CO_2 and H_2 and lower concentrations of CH_4 and H_2O .

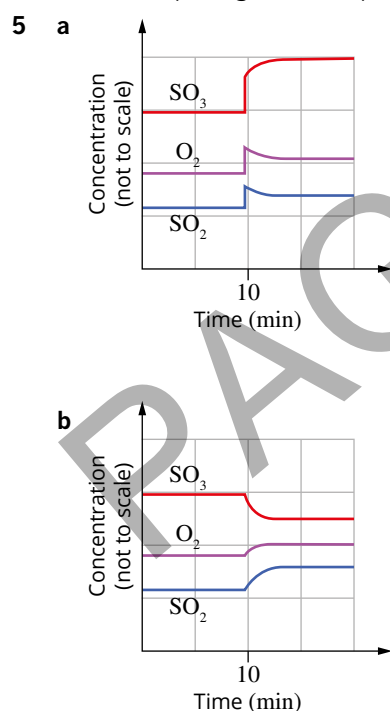
2.3 KEY QUESTIONS

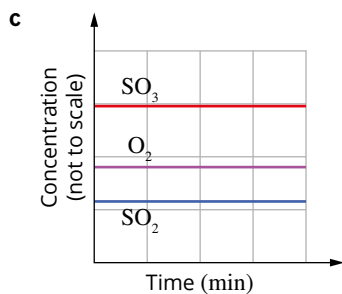
- 1 a true
 b false, since the amount of reactants increases
 c false, since the position of equilibrium shifts in the direction that produces the greater number of particles
 d true
- 2 A catalyst **lowers** the activation energy of a reaction and increases the rate of the forward and reverse reactions **equally**. The presence of a catalyst **does not** change the position of equilibrium. A catalyst **will increase** the rate at which an equilibrium is attained.

3

Change to equilibrium	Effect of change on equilibrium position
adding a reactant	shifts to the right
increasing pressure by decreasing the size of the closed container (for gases)	shifts in the direction of the least particles
adding a catalyst	no change
increasing the temperature for endothermic reactions	shifts to the right
decreasing the temperature for exothermic reactions	shifts to the right
adding water (dilution of solutions)	shifts in the direction of the most particles

- 4 Reducing the volume of the system increases the total pressure of the gas mixture. The particles will collide more frequently and the rates of both the forward and reverse reactions will increase. However, the rate of the forward reaction will increase more than the rate of the reverse reaction because there are two particles on the left side of the equation compared with one on the right. As the forward reaction proceeds, there is a decrease in the rate of the forward reaction and an increase in the rate of the reverse reaction. The rates of the forward and reverse reactions become equal again and equilibrium is re-established but, overall, there is a net forward reaction.





- 6**
- Increasing the pressure causes an increased frequency of collisions and an increased rate of both the forward and reverse reactions. However, because there are more particles on the left-hand side of the balanced equation, there will be more successful collisions in the forward direction, so a net forward reaction results.
 - A temperature increase means all reactant and product molecules have more energy and move faster. There will be more collisions and more molecules will have the necessary activation energy for reaction. An increased temperature favours an endothermic reaction because a higher proportion of molecules at the higher temperature will have the necessary energy to overcome the activation energy barrier than for the exothermic reaction. Hence, there will be a net reaction in the direction of the endothermic reaction—a net reverse reaction.
 - Adding a catalyst increases the rates of the forward and reverse reactions to the same extent. Since there is an equivalent change in the number of successful collisions in both directions, there is no net reaction.
- 7**
- net forward reaction
 - no effect
 - net forward reaction
- 8**
- An increase in volume will cause a decrease in pressure. The equilibrium system will respond by favouring the direction that increases pressure, i.e. more NO_2 will be formed in order to form a new equilibrium.
- As the volume is increased, the concentration of NO_2 will decrease, although the reaction will favour the formation of NO_2 . According to Le Châtelier's principle, the adjustment can only partially oppose the change, so the corresponding increase in concentration will not reach the initial NO_2 concentration level.
 - The mass of NO_2 will be higher. By favouring the forward reaction, the shift in equilibrium will result in a higher yield of NO_2 .
- 9**
- decrease; since the reaction is endothermic, the equilibrium will shift to the left as temperature decreases and more H_2 will be consumed
 - decrease; since the reaction is exothermic, the equilibrium will shift to the right as temperature decreases and more H_2 will be consumed

2.4 Equilibrium constants

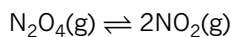
Try yourself 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

Determine the equilibrium expression for K_c for the reversible reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	
Thinking	Working
Identify the coefficients of the products and the reactants in the equation.	The product, SO_3 , has a coefficient of 2 and the reactants, SO_2 and O_2 , have coefficients of 2 and 1, respectively.
Write the expression for K_c . $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$

Try yourself 2.4.2
CALCULATING AN EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

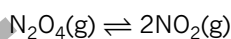


Calculate the value of the equilibrium constant, K_c , at 460°C .

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert the number of moles to mol L^{-1} using $c = \frac{n}{v}$.	$[\text{N}_2\text{O}_4] = \frac{n}{v}$ $= \frac{0.120}{3.00}$ $= 0.040 \text{ mol L}^{-1}$ $[\text{NO}_2] = \frac{n}{v}$ $= \frac{0.500}{3.00}$ $= 0.167 \text{ mol L}^{-1}$
State the expression for K_c .	$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
Substitute into the expression for K_c to determine the value of K_c .	$K_c = \frac{0.167^2}{0.040}$ $= 0.697$

Try yourself 2.4.3
CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium where $K_c = 0.720$ at 250°C :



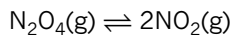
An equilibrium mixture contains 0.040 mol L^{-1} N_2O_4 at 250°C . Determine the equilibrium concentration of NO_2 in this mixture.

Thinking	Working
State the expression for K_c .	$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
Substitute the known values into the expression for K_c .	$0.720 = \frac{[\text{NO}_2]^2}{0.040}$
Rearrange the expression to make $[\text{NO}_2]$ the subject and calculate the concentration of this species.	$[\text{NO}_2] = \sqrt{0.720 \times 0.040}$ $= 0.170 \text{ mol L}^{-1}$

Try Yourself 2.4.4
PREDICTING THE DIRECTION OF A REACTION

Try yourself 2.4.5
USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetroxide (N_2O_4) at 60°C :



0.350 mol of N_2O_4 was placed in an empty 2.00 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at 60°C .

Thinking

Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled 'I' (initial), 'C' (change) and 'E' (equilibrium):

	Reactants	⇌	Products
I			
C			
E			

Enter the data provided above in the table.

When a species is consumed, the change is negative; when a species is produced, the change is positive.

Using the coefficients from the equation, calculate the moles of all species at equilibrium.

Using the volume of the vessel, calculate the equilibrium concentrations for all species at equilibrium.

Use the formula $c = \frac{n}{v}$.

State the expression for K_c and substitute the equilibrium concentrations.

Calculate the equilibrium constant, K_c .

Working

Initially, there is:

- 0.350 mol of $\text{N}_2\text{O}_4(\text{g})$
- 0.0 mol of the product $\text{NO}_2(\text{g})$.

Let x mol of N_2O_4 react and $2x$ mol of NO_2 is produced. At equilibrium, there is 0.120 mol of $\text{NO}_2(\text{g})$.

	$\text{N}_2\text{O}_4(\text{g})$	⇌	$2\text{NO}_2(\text{g})$
I	0.350 mol		0.0 mol
C	$-x$ mol		$+2x$ mol
E	$0.350 - x$ mol		$2x = 0.120$ mol

Initially, no NO_2 was present, so because 0.120 mol NO_2 has been produced at equilibrium:

$$2x = 0.120 \text{ mol}$$

$$x = 0.060 \text{ mol}$$

We can enter these values in the table:

	$\text{N}_2\text{O}_4(\text{g})$	⇌	$2\text{NO}_2(\text{g})$
I	0.350 mol		0.0 mol
C	$-x = -0.060$ mol		$+2x = 0.120$ mol
E	$0.350 - 0.060$ $= 0.290$ mol		$2x = 0.120$ mol

The volume of the vessel is 2.00 L.

$$\begin{aligned} [\text{N}_2\text{O}_4] &= \frac{n}{v} \\ &= \frac{0.290}{2.00} \\ &= 0.145 \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} [\text{NO}_2] &= \frac{n}{v} \\ &= \frac{0.120}{2.00} \\ &= 0.060 \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} K_c &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \\ &= \frac{0.060^2}{0.145} \\ &= 0.025 \end{aligned}$$

Try yourself 2.4.6
CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_c

The following equilibrium has a K_c of 4.4×10^{-8} at 200°C : $\text{X(g)} \rightleftharpoons 2\text{Y(g)}$ 0.30 mol of X was placed in an empty 2.0 L vessel at 200°C . Determine the concentration of Y at equilibrium.	
Thinking	Working
State the expression for K_c .	$K_c = \frac{[\text{Y}]^2}{[\text{X}]}$
Decide if any assumptions can be made in the calculation.	Initially, there is: <ul style="list-style-type: none"> • 0.30 mol of X(g) • 0.0 mol of the product Y(g). Since K_c is very small, we assume the amount of X at equilibrium is 0.30 mol.
Calculate the concentration of the reactant.	$[\text{X}] = \frac{n}{v}$ $= \frac{0.30}{2.0}$ $= 0.15 \text{ mol L}^{-1}$
Substitute into the expression for K_c .	$4.4 \times 10^{-8} = \frac{[\text{Y}]^2}{0.15}$
Calculate the unknown concentration, stating the assumption you made in the calculation.	$[\text{Y}]^2 = 0.15 \times 4.4 \times 10^{-8}$ $= 6.6 \times 10^{-9}$ Take the square root of both sides: $[\text{Y}] = 8.1 \times 10^{-5} \text{ mol L}^{-1}$ Since K_c is very small, the concentration of X at equilibrium was assumed to be the same as its initial concentration.

Try yourself 2.4.7
WRITING K_c EXPRESSIONS FOR HETEROGENEOUS EQUILIBRIA
Try Yourself 2.4.8
CALCULATING MOLAR SOLUBILITY FROM K_{sp} VALUES
2.4 KEY QUESTIONS

- A homogeneous system is a system in which all the species are in the same state.
 - For the general equation:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$
 the reaction quotient, Q_c , can be written as: $Q_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$
 Q_c is equal to K_c at equilibrium.
 - The equilibrium constant is the ratio of the equilibrium concentrations of the products over the equilibrium concentrations of the reactants raised to the power of their coefficients. It is given the symbol K_c and the value for the equilibrium constant changes with temperature.
- $$Q_c = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]}$$
- $$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$\text{b } K_c = \frac{[\text{N}_2]^2[\text{O}_2]}{[\text{N}_2\text{O}]^2}$$

$$\text{c } K_c = \frac{[\text{NO}_2]}{[\text{NO}][\text{O}_2]^2}$$

$$\text{d } K_c = \frac{[\text{N}_2]^2[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^3}$$

4 B. The large value of K_c ($>10^4$) indicates that the reaction favours the products.

5 The reaction quotient is $Q_c < K_c$. The reaction will shift to the right to establish equilibrium. This causes the concentration of the products to increase.

$$6 \quad Q_c = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

As $Q_c > K_c$, in order to reach equilibrium, the concentration of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ must decrease and the concentration of the reactants increase. This will occur if the reaction shifts to the left, producing more reactants.

$$7 \quad \text{a } K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$\text{b } \text{Since } \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = 100$$

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{1}{100}$$

$$= 0.01$$

$$\text{c } K_c = \frac{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}{[\text{NH}_3]}$$

d The expression in part c is equal to the square root of $\frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = 10$.

e i When an equation is reversed, the value of the equilibrium constant is the reciprocal of the original constant.

ii When the coefficients of the equation are halved, the new equilibrium constant has a value equal to the square root of the original constant.

$$8 \quad \text{a } K_c = \frac{[\text{HCl}]^2[\text{O}_2]^{\frac{1}{2}}}{[\text{H}_2\text{O}][\text{Cl}_2]}$$

$$= \sqrt{4.0 \times 10^{-4}}$$

$$= 0.020$$

$$\text{b } K_c = \frac{[\text{H}_2\text{O}][\text{Cl}_2]}{[\text{HCl}]^2[\text{O}_2]^{\frac{1}{2}}}$$

$$= \frac{1}{0.020}$$

$$= 50$$

$$9 \quad \text{a } K_c = 8.35$$

$$\text{b } K_c = 0.767$$

$$\text{c } K_c = 1.30$$

$$\text{d } K_c = 0.346$$

10 a increased

b decreased

c increased

d decreased

11 From the equation, write the expression for the equilibrium constant.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Calculate equilibrium concentrations of reactants and products.

$$[\text{NO}_2] = \frac{0.40 \text{ mol}}{2.0 \text{ L}}$$

$$= 0.20 \text{ mol L}^{-1}$$

$$[\text{N}_2\text{O}_4] = \frac{0.80 \text{ mol}}{2.0 \text{ L}}$$

$$= 0.40 \text{ mol L}^{-1}$$

Substitute equilibrium concentrations in the equilibrium expression and calculate the value of the equilibrium constant.

$$K_c = \frac{0.20^2}{0.40}$$

$$= 0.10$$

$$12 \quad K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$$

$$= \frac{0.280}{2.4 \times 10^{-2} \times 0.108}$$

$$= 1.1 \times 10^2$$

$$13 \quad K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$= \frac{15.50^2}{0.0542^2 \times [\text{O}_2]}$$

$$= 6.44 \times 10^5$$

$$[\text{O}_2] = \frac{15.50^2}{0.0542^2 \times (6.44 \times 10^5)}$$

$$= 0.127 \text{ mol L}^{-1}$$

14

	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$
I	4.45		5.50		0
C	$-x = -0.350$		$-x = -0.350$		$+x = 0.350$
E	$4.45 - x$ $= 4.45 - 0.350$ $= 4.10$		$5.50 - x$ $= 5.50 - 0.350$ $= 5.15$		$x = 0.350$

volume of vessel = 2.00 L

$$[\text{PCl}_3] = \frac{4.10}{2.00} = 2.05 \text{ mol L}^{-1}$$

$$[\text{Cl}_2] = \frac{5.15}{2.00} = 2.58 \text{ mol L}^{-1}$$

$$[\text{PCl}_5] = \frac{0.350}{2.00} = 0.180 \text{ mol L}^{-1}$$

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

$$= \frac{0.180}{2.05 \times 2.58}$$

$$= 0.034$$

15

	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightleftharpoons	$2\text{NH}_3(\text{g})$
I	5.89		8.23		0
C	$-x = -0.240$		$-3x = -0.720$		$+2x = 0.480$
E	$5.89 - x$ $= 5.89 - 0.240$ $= 5.65$		$8.23 - 3x$ $= 8.23 - 0.720$ $= 7.51$		$2x = 0.480$

volume of vessel = 5.00 L

$$[\text{N}_2] = \frac{5.65}{5.00} = 1.13 \text{ mol L}^{-1}$$

$$[\text{H}_2] = \frac{7.51}{5.00} = 1.50 \text{ mol L}^{-1}$$

$$[\text{NH}_3] = \frac{0.480}{5.00} = 0.096 \text{ mol L}^{-1}$$

$$\begin{aligned} K_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\ &= \frac{0.096^2}{1.13 \times 1.50^3} \\ &= 2.41 \times 10^{-3} \end{aligned}$$

16 a From the equation, write the expression for the equilibrium constant.

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

Calculate equilibrium concentrations of reactants.

$$[\text{H}_2] = \frac{0.220 \text{ mol}}{2.00 \text{ L}} = 0.110 \text{ mol L}^{-1}$$

$$[\text{I}_2] = \frac{0.110 \text{ mol}}{2.00 \text{ L}} = 0.055 \text{ mol L}^{-1}$$

Substitute equilibrium concentrations in the equilibrium expression and calculate the concentration of HI.

$$48.8 = \frac{0.110 \times 0.055}{[\text{HI}]^2}$$

$$[\text{HI}]^2 = \frac{0.110 \times 0.055}{48.8}$$

$$\begin{aligned} [\text{HI}] &= \sqrt{\frac{0.110 \times 0.055}{48.8}} \\ &= 0.01113 \text{ mol L}^{-1} \\ &= 0.011 \text{ mol L}^{-1} \end{aligned}$$

b

	2HI(g)	\rightleftharpoons	H ₂ (g)	+	I ₂ (g)
I	4.00		0		0
C	-2x = -0.880 (so x = 0.440)		+x = 0.440		+x = 0.440
E	4.00 - 2x = 4.00 - 0.880 = 3.12 [HI] = $\frac{3.12 \text{ mol}}{2.00 \text{ L}}$ = 1.56 mol L ⁻¹		x = 0.440 [H ₂] = $\frac{0.440 \text{ mol}}{2.00 \text{ L}}$ = 0.220 mol L ⁻¹		x = 0.440 [I ₂] = $\frac{0.440 \text{ mol}}{2.00 \text{ L}}$ = 0.220 mol L ⁻¹

$$\begin{aligned} K_c &= \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \\ &= \frac{0.220 \times 0.220}{1.56^2} \\ &= 0.01989 \\ &= 0.020 \end{aligned}$$

c The reaction quotient for this reaction is $\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$.

Calculate concentrations of reactants.

$$[\text{H}_2] = \frac{0.240 \text{ mol}}{2.00 \text{ L}} = 0.120 \text{ mol L}^{-1}$$

$$[\text{I}_2] = \frac{0.320 \text{ mol}}{2.00 \text{ L}} = 0.160 \text{ mol L}^{-1}$$

$$[\text{HI}] = \frac{1.00 \text{ mol}}{2.0 \text{ L}} = 0.500 \text{ mol L}^{-1}$$

The value of the reaction quotient is $\frac{0.120 \times 0.160}{0.500^2} = 0.077$.

The value of the reaction quotient is greater than the value of the equilibrium constant at the same temperature as calculated in part **b**. Thus, the system is not at equilibrium. A net reverse reaction will occur. As the reaction shifts towards equilibrium, the concentrations of H_2 and I_2 will decrease and the concentration of HI will increase until the value of the reaction quotient is equal to the equilibrium constant.

17

	$2\text{NO}(\text{g})$	+	$2\text{H}_2(\text{g})$	\rightleftharpoons	$\text{N}_2(\text{g})$	+	$2\text{H}_2\text{O}(\text{g})$
I	0.100		0.051		0		0.100
C	$-2x = -(0.100 - 0.062)$ $= -0.038$ (so $x = 0.019$)		$-2x = -0.038$		$+x$ $= +0.019$		$+2x$ $= 2 \times 0.019$ $= +0.038$
E	$0.100 - 2x$ $= 0.062$		$0.051 - 2x$ $= 0.051 - 0.038$ $= 0.013$		$0 + x$ $= 0 + 0.019$ $= 0.019$		$0.100 + 0.038$ $= 0.138$

volume of vessel = 1.00 L, so mol = concentration

$$K_c = \frac{[\text{H}_2\text{O}]^2[\text{N}_2]}{[\text{H}_2]^2[\text{NO}]^2}$$

$$= \frac{0.138^2 \times 0.019}{0.013^2 \times 0.062^2}$$

$$= 557$$

18 $K_c = \frac{[\text{B}]^2}{[\text{A}]}$

Initially, there is:

- 0.50 mol of $\text{A}(\text{g})$
- 0.0 mol of the product $\text{B}(\text{g})$.

Since K_c is very small, we assume that the number of moles of A at equilibrium is 0.50 mol.

Therefore, at equilibrium

$$[\text{A}] = \frac{0.50}{2.0}$$

$$= 0.25 \text{ M}$$

$$K_c = \frac{[\text{B}]^2}{0.25}$$

$$[\text{B}]^2 = K_c \times 0.25$$

$$[\text{B}]^2 = 4.4 \times 10^{-8} \times 0.25$$

$$= 1.1 \times 10^{-8}$$

Take the square root of both sides.

$$[\text{B}] = \sqrt{1.1 \times 10^{-8}}$$

$$[\text{B}] = 1.05 \times 10^{-4} \text{ mol L}^{-1}$$

CHAPTER 2 REVIEW

- 1 D. In a closed system, the reactants and products cannot be exchanged with the surroundings. In a closed system, the reactant and product particles cannot escape. This does not necessarily mean the reaction system must be sealed, unless a gas is involved. A reaction occurring in solution in a beaker might be an example of a closed system.
- 2 C. Chemical equilibria are dynamic, with reactants continuously forming products and products continually re-forming reactants at the same rate.
- 3 C. From Le Châtelier's principle, the addition of a product causes a net reverse reaction. The concentration of H_2 will decrease and the concentration of HI will increase.

- 4 D. Increasing the temperature of an endothermic equilibrium shifts the equilibrium in the forward direction. Since there are equal numbers of particles on both sides of the equation, decreasing the volume will not change the equilibrium position. A catalyst does not change the position of the equilibrium. The addition of CO will shift the equilibrium to the left.
- 5 C. Equilibria obey the equilibrium law, which can be represented as $K_c = \frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$.
- 6 D. Given the form of the expression for K_c , H_2 and CO must be products and CH_3OH must be the reactant. The expression for K_c also indicates that only H_2 has a coefficient of 2 in the equation.
- 7 reversible, Energy, matter, rates, remains constant, concentration
- 8 a open; both energy and matter (carbon dioxide and water vapour) are exchanged with the surroundings
 b closed; only energy is exchanged with the surroundings. While the door is shut, no matter is exchanged
 c open; both energy and matter are exchanged with the surroundings
 d closed; only energy is exchanged (temperature changes result in changes in volume) but there is no exchange of matter
- 9 iii, iv, ii, i
- 10 The addition of H_2 gas increases the concentration of H_2 molecules. This causes more frequent collisions between the H_2 molecules and other molecules. So, collisions between H_2 and I_2 mean the forward reaction occurs faster than the reverse reaction. As the forward reaction proceeds, there is a decrease in the rate of the forward reaction and an increase in the rate of the reverse reaction. The rates of the forward and reverse reactions become equal again and equilibrium is re-established. Therefore, there is a net forward reaction.
- 11 Reducing the volume of the system increases the total pressure of the gas mixture. The particles will collide more frequently and the rates of both the forward and reverse reactions will increase. However, the rate of the reverse reaction will increase more than the rate of the forward reaction because there are four particles on the right side of the equation compared with two on the left. As the reverse reaction proceeds, there is a decrease in the rate of the reverse reaction and an increase in the rate of the forward reaction. The rates of the forward and reverse reactions become equal again and equilibrium is re-established, but overall, there is a net reverse reaction.
- 12 The reaction quotient is the ratio of the concentrations of the products to the concentration of the reactants, with the index of each concentration the same as the coefficient of the substance in the reaction equation. The value of the reaction quotient becomes equal to the equilibrium constant at equilibrium.
- 13 a $K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$
 b $K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
 c $K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]}$
 d $K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$
- 14 a closed
 b open
 c closed
 d open
- 15 Initially, collisions between SO_2 and O_2 reactant molecules occur quickly, resulting in sufficient molecules having the correct energy and orientation to produce product molecules, SO_3 . As more product molecules are formed, they collide with sufficient energy to decompose into the reactant molecules, SO_2 and O_2 . The forward and reverse reactions continue to occur, with the rate of the forward reaction decreasing over time and the rate of the reverse reaction increasing over the same interval. Finally, the rates of both reactions become equal and equilibrium is established.
- 16 If Ca^{2+} ions were inefficiently absorbed from food, decreased concentrations of these ions could occur in body fluids. As a consequence, a net forward reaction would occur, raising the concentration of dissolved Ca^{2+} ions and resulting in decreased amounts of calcium phosphate in bones.
- 17 B. This gaseous equilibrium contains two particles on both sides of the equation. A volume decrease causes a pressure increase, resulting in an increase in the number of collisions between molecules. In reaction B, because there is an equal chance of reactant molecules colliding and forming a product or of product molecules colliding and forming the reactants (2 moles of reactants and 2 moles of products), there is no shift in the equilibrium position. The system is unable to oppose the change applied.

- 18 a increase
b increase
- 19 a net reverse reaction
b net forward reaction
c no effect
- 20 a $\text{CH}_3\text{OH}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{CO}(\text{g})$
b $\text{S}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{S}(\text{g})$
c $\text{NO}_2(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2\text{O}_4(\text{g})$
- 21 As Q_c for the reaction is larger than K_c , the reaction must shift to decrease Q_c . This will happen with a decrease in the concentration of the products. There will be a net reverse reaction, decreasing the concentration of ethyl ethanoate as the mixture reaches equilibrium.

- 22 a less than
b $\frac{[\text{H}_2\text{O}]^2[\text{N}_2]}{[\text{H}_2]^2[\text{NO}]^2}$
c shifts to the right
- 23 a no; K_c is very small
b 10^{10}
c yes; K_c is very large (provided the rate is sufficiently fast)

- 24 a $K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2}$
b i The coefficients of each species has been halved: $K_c = \sqrt{32} = 5.7$.
ii The reaction is the reverse of that in part a: $K_c = \frac{1}{32} = 0.031$.
iii Each of the coefficients has been doubled: $K_c = 32^2 = 1.0 \times 10^3$.
iv The reaction is reversed and the coefficients halved: $K_c = \frac{1}{\sqrt{32}} = 0.18$.

- 25 The reaction is not at equilibrium and will shift towards the left to reach equilibrium because $Q_c > K_c$.

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{0.250^2}{1.00 \times 1.00^3} = 0.063$$

- 26 The volume of the container is 2.00L:

$$[\text{H}_2\text{O}] = \frac{0.020}{2.00} = 0.010 \text{ mol L}^{-1}$$

$$[\text{H}_2] = \frac{0.030}{2.00} = 0.015 \text{ mol L}^{-1}$$

$$[\text{CO}] = \frac{0.040}{2.00} = 0.020 \text{ mol L}^{-1}$$

$$[\text{CO}_2] = \frac{0.050}{2.00} = 0.025 \text{ mol L}^{-1}$$

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{0.010 \times 0.020}{0.015 \times 0.025} = 0.533$$

- 27 a $K_c = \frac{[\text{Fe}^{2+}]^2[\text{Sn}^{4+}]}{[\text{Fe}^{3+}]^2[\text{Sn}^{2+}]}$
b $K_c = \frac{0.40^2 \times 0.20}{0.30^2 \times 0.10} = 3.6$

- 28 Write the expression for the equilibrium constant.

$$K_c = \frac{[\text{C}_3\text{H}_6\text{O}][\text{H}_2]}{[\text{C}_3\text{H}_8\text{O}]}$$

Calculate equilibrium concentrations of reactants and products.

$$[\text{C}_3\text{H}_6\text{O}] = \frac{0.082 \text{ mol}}{20.0 \text{ L}} = 0.0041 \text{ mol L}^{-1}$$

$$[\text{H}_2] = \frac{0.082 \text{ mol}}{20.0 \text{ L}} = 0.0041 \text{ mol L}^{-1}$$

$$[\text{C}_3\text{H}_8\text{O}] = \frac{0.018 \text{ mol}}{20.0 \text{ L}} = 0.0009 \text{ mol L}^{-1}$$

Substitute equilibrium concentrations in the equilibrium expression and find the value of the equilibrium constant.

$$\begin{aligned} K_c &= \frac{0.0041 \times 0.0041}{0.0009} \\ &= 0.0187 \\ &= 0.019 \end{aligned}$$

29 a $K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

b Calculate equilibrium concentrations of reactants and products.

$$[\text{PCl}_5] = \frac{4.50 \text{ mol}}{3.00 \text{ L}} = 1.50 \text{ mol L}^{-1}$$

$$[\text{Cl}_2] = \frac{0.900 \text{ mol}}{3.00 \text{ L}} = 0.300 \text{ mol L}^{-1}$$

$$[\text{PCl}_3] = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ mol L}^{-1}$$

Use the expression for the equilibrium constant from part a.

Substitute equilibrium concentrations in the equilibrium expression.

$$\begin{aligned} K_c &= \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \\ &= 0.400 \end{aligned}$$

c Rearrange the expression to find $[\text{Cl}_2]$.

$$[\text{Cl}_2] = K_c \times \frac{[\text{PCl}_5]}{[\text{PCl}_3]}$$

Substitute equilibrium concentrations in the equilibrium constant expression and find the value of $[\text{Cl}_2]$.

$$\begin{aligned} [\text{Cl}_2] &= 0.400 \times \frac{0.002}{0.001} \\ &= 0.800 \text{ mol L}^{-1} \end{aligned}$$

d Note that the equation is reversed and the temperature is constant. For the reverse reaction, the equilibrium constant is the reciprocal of the forward reaction.

$$\begin{aligned} K_c &= \frac{1}{0.400} \\ &= 2.50 \end{aligned}$$

30 a Write the expression for the equilibrium constant.

$$K_c = \frac{[\text{C}]^2[\text{D}]}{[\text{A}][\text{B}]^3}$$

Calculate equilibrium concentrations of reactants and products.

$$[\text{A}] = \frac{2.00 \text{ mol}}{2.00 \text{ L}} = 1.00 \text{ mol L}^{-1}$$

$$[\text{B}] = \frac{0.500 \text{ mol}}{2.00 \text{ L}} = 0.250 \text{ mol L}^{-1}$$

$$[\text{D}] = \frac{3.00 \text{ mol}}{2.00 \text{ L}} = 1.50 \text{ mol L}^{-1}$$

b Substitute equilibrium concentrations in the equilibrium expression and calculate the equilibrium concentration of C.

$$\begin{aligned} K_c &= 0.024 = \frac{[\text{C}]^2 \times 1.50}{1.00 \times 0.250^3} \\ [\text{C}]^2 &= \frac{0.024 \times 1.00 \times 0.250^3}{1.50} \\ [\text{C}] &= \sqrt{\frac{0.024 \times 1.00 \times 0.250^3}{1.50}} \\ &= 0.0158 \\ &= 0.016 \text{ mol L}^{-1} \end{aligned}$$

- c Convert the equilibrium concentration of C into number of moles.

$$[C] = 0.016 \text{ mol L}^{-1}$$

$$n(C) = c \times V$$

$$= 0.016 \text{ mol L}^{-1} \times 2.00 \text{ L}$$

$$= 0.032 \text{ mol}$$

- 31 a i net forward reaction
 ii no change
 iii net forward reaction

- b i increase
 ii no change
 iii no change

- c likely to be large

- 32 a For the initial mixture, the ratio $\frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{0.300 \times 0.400}{0.100 \times 0.200^3} = 150$

A net reverse reaction will occur, so this ratio becomes equal to K_c .

- i increase
 ii increase
 iii decrease
 iv decrease

- b it is endothermic

33	Colour change (lighter or darker)	Explanation
a The temperature is increased to 450°C at constant volume.	lighter	It is an exothermic reaction, so K_c will decrease as temperature increases, so a net reverse reaction occurs.
b The volume of the container is increased at constant temperature.	lighter	As volume increases, the colour of the gas mixture will decrease. (A net reverse reaction will also occur, further lightening the colour.)
c A catalyst is added at constant volume and temperature.	no colour change	The addition of a catalyst would not change the colour because the rates of the forward and reverse reactions are increased equally.
d More oxygen is added at constant volume and temperature.	darker	The addition of oxygen will cause a net forward reaction to occur.

- 34 a i decrease
 ii decrease
 iii increase
 iv no change
 v no change

- b i increase
 ii increase
 iii increase
 iv increase
 v no change

- 35 a Write the expression for the equilibrium constant.

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$= 0.052$$

Because a 1.00 L vessel is used, the concentrations are the same as the amount in moles. Substitute the concentration values into the reaction quotient.

$$Q_c = \frac{0.200^2}{0.200 \times 0.200^3}$$

$$= 25$$

$Q_c > K_c$; therefore the system is not at equilibrium. The system will shift in the direction that makes $Q_c = K_c$. Since $Q_c > K_c$, the reaction must shift to the left, resulting in a net reverse reaction.

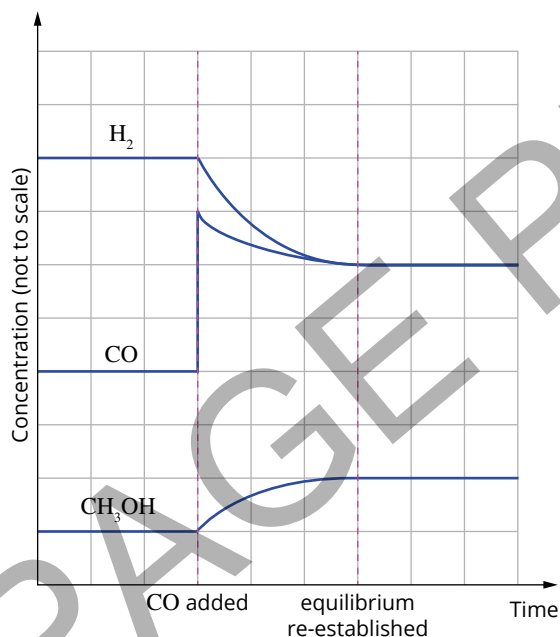
- b** Because a 1.00L vessel is used, the concentrations are the same as the amount in moles. Substitute the given concentration values into the reaction quotient.

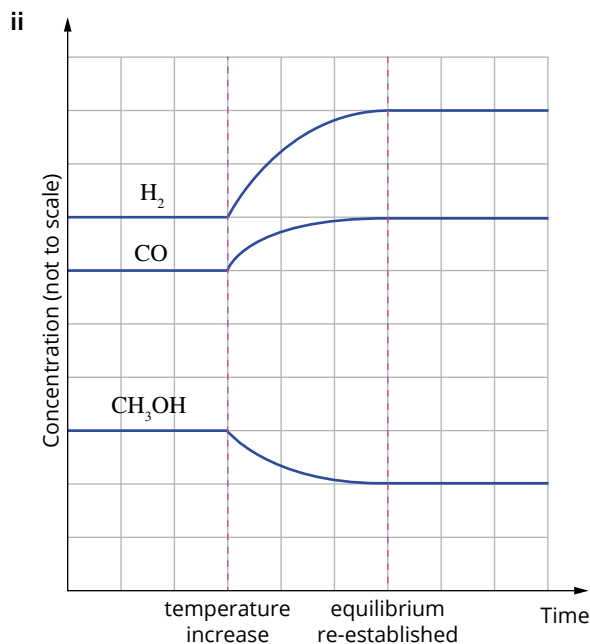
$$Q_c = \frac{0.0^2}{0.050 \times 0.500^3} = 0.0$$

$Q_c < K_c$; therefore, the system is not at equilibrium. The system will shift in the direction that makes $Q_c = K_c$. Since $Q_c < K_c$, the reaction must shift to the right, resulting in a net forward reaction.

36 a $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$

- b** 15–20 minutes, 25–30 minutes, 35–40 minutes
c 1.56 (answer depends on concentrations obtained from the graph)
d 10 minutes; before 10 minutes the concentrations were changing slowly, but the catalyst caused the equilibrium to be reached more rapidly
e 3.50 (answer depends on concentrations obtained from the graph)
f At 20 minutes, the pressure was increased by reducing volume. Also, because the value of K_c at 25–30 minutes is larger than at 15–20 minutes, and this is an exothermic reaction, a decrease in temperature must have occurred as well.
- 37 a** **i** high temperature; high pressure
ii low temperature; high pressure
b temperature
c use a catalyst
d i





- 38 a i increase
 ii increase
- b In practice, satisfactorily high equilibrium yields of sulfur trioxide can be obtained without needing to use high pressures, which would involve more expensive equipment.
- c The purpose of recycling the gases from the absorption tower is to increase the yield of sulfur trioxide and to minimise emissions of sulfur oxides, which act as pollutants.
- d the rate of reaction and the magnitude of K_c
- 39 a $2\text{SO}_3(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 4\text{O}_2(\text{g})$
- b $K_c = \frac{[\text{CS}_2][\text{O}_2]^4}{[\text{SO}_3]^2[\text{CO}_2]}$
- c i $n(\text{O}_2) = 4 \times n(\text{CS}_2) = 4 \times 0.028 = 0.112 \text{ mol}$
- ii $[\text{CS}_2] = \frac{0.028}{20.0} = 0.0014 \text{ mol L}^{-1}$
- $[\text{O}_2] = \frac{0.112}{20.0} = 0.0056 \text{ mol L}^{-1}$
- $[\text{SO}_3] = \frac{0.022}{20.0} = 0.0011 \text{ mol L}^{-1}$
- $[\text{CO}_2] = \frac{0.014}{20.0} = 0.0007 \text{ mol L}^{-1}$
- $K_c = \frac{[\text{CS}_2][\text{O}_2]^4}{[\text{SO}_3]^2[\text{CO}_2]}$
- $= \frac{0.0014 \times 0.0056^4}{0.0011^2 \times 0.0007}$
- $= 1.6 \times 10^{-3}$
- d i increase
 ii increase
 iii no effect
 iv decrease
 v no effect

Data analysis

Question 1 (1 mark)

Equilibrium is established four times.

Question 2 (2 marks)

The increase in volume at 450 seconds would show on the graph as a rapid decrease in concentration of all three gases (three vertical lines at 450 seconds). This is a decrease in pressure of the system. As the new equilibrium is established, the system will respond to increase pressure (according to Le Châtelier's principle), and this means that the side of the equation with more moles of gas is favoured (reactant side). The graph, after 450 seconds, will show an increase in Cl_2 and CO concentrations and a decrease in COCl_2 concentrations.

Question 3 (3 marks)

At 120 seconds, the system was cooled. At 120 seconds, we see the system favours the products after the temperature change, and as it is known to be an exothermic reaction (heat is a product), heat must have been removed. K_c will increase due to the new equilibrium favouring the products.

Question 4 (2 marks)

(The values used in the calculations will vary depending on the numbers obtained from the graph. A range of possible values is shown.)

COCl_2 0.007 mol L^{-1}

CO 0.018 mol L^{-1}

Cl_2 0.008 mol L^{-1}

$$K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{0.007}{0.018 \times 0.008}$$