Chapter 2 Chemical equilibrium

2.1 Dynamic equilibrium

2.1 KEY QUESTIONS

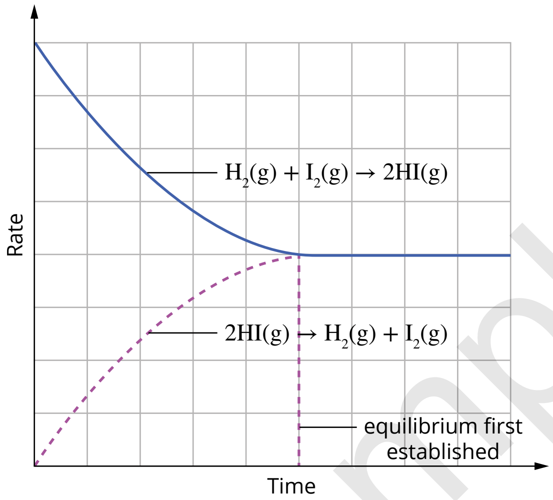
Describe

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

2 a false
  b false
  c true
  d false

Apply

3



4 The reversible arrow indicates:
- The reaction can proceed in both directions, the reactants can form products, and the products can also revert back to the reactants
- The system will reach an equilibrium where rate of the forward reaction equals the rate of the reverse reaction and the concentrations of all species are constant, however they may not be equal to each other.

Analyse

5 closed, decreases, less, reverse, increases, equal

6 a open; both energy and matter (carbon dioxide and water vapour) are exchanged with the surroundings
  b closed; only energy can be exchanged with the surroundings. While the can is unopened, no matter is exchanged.
  c open; both energy and matter are exchanged with the surroundings

7 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.

8 $130\,kJ\,mol^{-1}$. The activation energy is the difference between $390\,kJ\,mol^{-1}$ and $260\,kJ\,mol^{-1}$, which is $130\,kJ\,mol^{-1}$.

9 a Chemical equilibrium is ‘dynamic’ because both the forward and reverse reactions occur at the same rate. An equilibrium develops between water vapour and liquid water when wet clothes are in a sealed bag, with water evaporating as rapidly as water vapour condenses, so the clothes remain wet.
  b 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.

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10 **a** $0.07\,mol\,L^{-1}$

- **b** $0\,mol\,L^{-1}$
- **c** $0.03\,mol\,L^{-1}$
- **d** $0.08\,mol\,L^{-1}$
- **e** $0.07 - 0.03 = 0.04$ moles
- **f** 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.

11 This statement is false. Equilibrium represents a dynamic balance of forward and reverse reactions but the specific concentrations of reactants and products at equilibrium depends on characteristics of the reaction itself such as energy considerations (the activation energy of the forward and the reverse reactions) and reaction conditions such as temperature and pressure.

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:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

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 and the position of the equilibrium is said to have 'shifted to the left'.

2.2 KEY QUESTIONS

Describe

1 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 and the system will establish a new equilibrium.

Apply

2 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.

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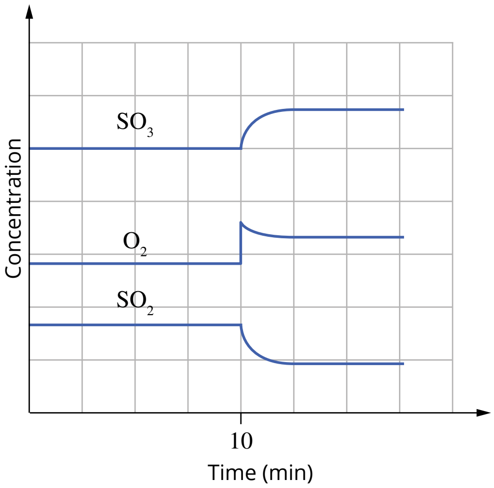
3



Analyse

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)

6 The mol L^{-1} changes as the reaction achieves equilibrium are as follows:

- $[H_2]$ decreases by 4 mol L^{-1}
- $[I_2]$ decreases by 2 mol L^{-1}
- $[H_I]$ increases by 6 mol L^{-1}.

  All three concentration changes shown in the graph are in error because the equation indicates that the concentration change for $[H_2]$ and $[I_2]$ should be the same and this change should be one-half of the concentration change of $[H_I]$. A correct graph would show, for example, a 2 mol L^{-1} change for $[H_2]$ and $[I_2]$ and a 4 mol L^{-1} change for $[H_I]$.

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:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

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. (When there is an increase in pressure, the system will shift in the direction of the fewest gaseous particles to reduce the pressure, and vice versa when there is a decrease in pressure.) 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.)

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Try yourself 2.3.2

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

Consider the equilibrium:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \qquad \Delta H = -165\,\text{kJ mol}^{-1}$$

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 is an exothermic reaction, so the reverse reaction is endothermic. 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 concentrations of products decrease, the rate of the reverse reaction will decrease. As the concentrations of CO_2 and H_2 increase, 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

Describe

1 **a** true

b false; the amount of reactants increases because increasing the temperature of an exothermic reaction causes a net reverse reaction

c false the position of equilibrium shifts in whichever direction produces the lower 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 **increases** the rate at which an equilibrium is attained.

Apply

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 dissolved 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 of NO_2 compared to one particle of N_2O_4, so the frequency of the collisions for the forward reaction increases to a greater extent. This results in more N_2O_4 being formed. 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.

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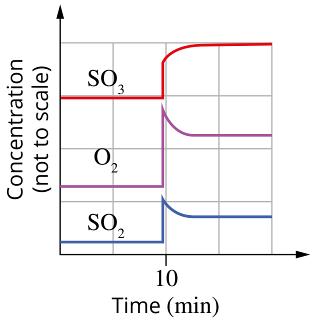
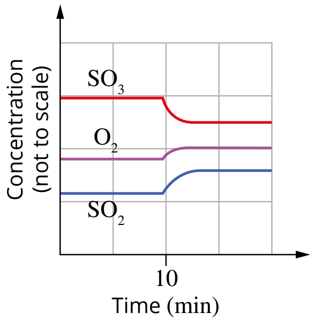
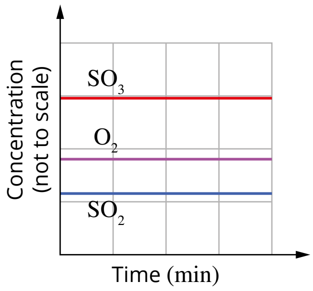
5 **a**



b



c



Analyse

6 **a** Reducing volume causes an increase in the concentration of all three gases and increases the pressure of the system. 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.

b 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 in this case.

c 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 shift in the equilibrium position.

7 **a** net forward reaction (i.e. shift to the right)

b no effect

c net forward reaction (i.e. shift to the right)

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.

a 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.

b 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.

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9 **a** decrease; since the reaction is endothermic, the equilibrium will shift to the left as temperature decreases and more H_2 will be consumed

b decrease; since the reaction is exothermic, the equilibrium will shift to the right as temperature decreases and more H_2 will be consumed

10 Adding a catalyst will increase the reaction rate as it will lower the activation energy of both the forward and reverse reactions. Adding a catalyst will not change the position of equilibrium or amounts of reactants and products at equilibrium.

11 The reaction must be endothermic as the addition of heat as described causes a forward reaction and more blue product is formed. As the system is opposing the energy added, energy must be a reactant.

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: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	
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: $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

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: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ 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 $c = \frac{n}{V}$.	$[N_2O_4] = \frac{n}{V}$ $= \frac{0.120}{3.00}$ $= 0.0400$ mol L^{-1} $[NO_2] = \frac{n}{V}$ $= \frac{0.500}{3.00}$ $= 0.167$ mol L^{-1}
State the expression for K_c.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute into the expression for K_c to determine the value of K_c.	$K_c = \frac{0.167^2}{0.0400}$ $= 0.697$

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Try yourself 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

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

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
Substitute the known values into the expression for K_c.	$0.720 = \frac{[NO_2]^2}{0.040}$
Rearrange the expression to make $[NO_2]$ the subject and calculate the concentration of this species.	$[NO_2] = \sqrt{0.720 \times 0.040}$ $= 0.17\ mol\ L^{-1}$

Try yourself 2.4.4

PREDICTING THE DIRECTION OF A REACTION

The value of the equilibrium constant, K_c, for the following reaction is 3.07×10^{-4} at 25 °C.

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

If the initial concentrations of reacting species are $[H_2] = 0.50$ M, $[N_2] = 0.40$ M and $[NH_3] = 0.30$ M, decide in which direction the reaction will proceed.

Thinking	Working
The concentrations given are not necessarily the equilibrium concentrations. If you calculate the reaction quotient, Q_c, for concentrations given, you can then compare the value of Q_c to the value of K_c to determine which direction the reaction will proceed. Write the Q_c expression for the reaction using the general expression as a guide: $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$	For this reaction the Q_c expression is $Q_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$ noting that the concentration terms for each substance are raised to the power indicated by the stoichiometric coefficient of each substance in the balanced chemical equation.
Substitute the given concentration values into the Q_c expression.	$Q_c = \frac{0.30^2}{0.50^3 \times 0.40}$ $= 1.8$
Compare the calculated Q_c value with the K_c value given in the question.	$Q_c = 1.8$; $K_c = 3.07 \times 10^{-4}$ Therefore, $Q_c > K_c$ and the reaction will proceed to the left.

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Try yourself 2.4.5

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

<table>
<tr><td colspan="2">At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetraoxide (N_2O_4) at 60°C:
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
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.</td></tr>
<tr><td>Thinking</td><td>Working</td></tr>
<tr><td>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):
<table>
<tr><th></th><th colspan="2">Reactants $\rightleftharpoons$ Products</th></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
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.</td>
<td>Initially, there is:
• 0.350 mol of $N_2O_4(g)$
• 0.0 mol of the product $NO_2(g)$.
Let x mol of N_2O_4 react and $2x$ mol of NO_2 is produced.
At equilibrium, there is 0.120 mol of $NO_2(g)$.
<table>
<tr><th></th><th colspan="2">$N_2O_4(g) \rightleftharpoons 2NO_2(g)$</th></tr>
<tr><td>I</td><td>0.350 mol</td><td>0.0 mol</td></tr>
<tr><td>C</td><td>$-x$ mol</td><td>$+2x$ mol</td></tr>
<tr><td>E</td><td>$0.350 - x$ mol</td><td>$2x = 0.120$ mol</td></tr>
</table></td></tr>
<tr><td>Using the coefficients from the equation, calculate the number of moles of all species at equilibrium.</td>
<td>Initially, no NO_2 was present, so because 0.120 mol NO_2 has been produced at equilibrium:
$2x = 0.120$ mol
$x = 0.060$ mol
We can enter these values in the table:
<table>
<tr><th></th><th colspan="2">$N_2O_4(g) \rightleftharpoons 2NO_2(g)$</th></tr>
<tr><td>I</td><td>0.350 mol</td><td>0.0 mol</td></tr>
<tr><td>C</td><td>$-x = -0.060$ mol</td><td>$+2x = 0.120$ mol</td></tr>
<tr><td>E</td><td>$0.350 - 0.060$
$= 0.290$ mol</td><td>$2x = 0.120$ mol</td></tr>
</table></td></tr>
<tr><td>Using the volume of the vessel, calculate the equilibrium concentrations for all species at equilibrium.
Use the formula $c = \frac{n}{V}$.</td>
<td>The volume of the vessel is 2.00 L.
$$[N_2O_4] = \frac{n}{V} = \frac{0.290}{2.00} = 0.145\ \text{mol L}^{-1}$$
$$[NO_2] = \frac{n}{V} = \frac{0.120}{2.00} = 0.060\ \text{mol L}^{-1}$$</td></tr>
<tr><td>State the expression for K_c and substitute the equilibrium concentrations.
Calculate the equilibrium constant, K_c.</td>
<td>$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.060^2}{0.145} = 0.025$$</td></tr>
</table>

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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:

$$X(g) \rightleftharpoons 2Y(g)$$

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.	$K_c = \frac{[Y]^2}{[X]}$
Decide if any assumptions can be made in the calculation.	Initially, there is: • 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.	$[X] = \frac{n}{V}$ $= \frac{0.30}{2.0}$ $= 0.15\ \text{mol L}^{-1}$
Substitute into the expression for K_c.	$4.4 \times 10^{-8} = \frac{[Y]^2}{0.15}$
Calculate the unknown concentration, stating the assumption you made in the calculation.	$[Y]^2 = 0.15 \times 4.4 \times 10^{-8}$ $= 6.6 \times 10^{-9}$ Take the square root of both sides: $[Y] = 8.1 \times 10^{-5}\ \text{mol L}^{-1}$ 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

Write equilibrium expressions for the following chemical reactions:

a $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
b $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$
c $Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$

Thinking	**Working**
Identify the coefficients of the products and the reactants in the equation. These will be the indices of the concentration terms in the equilibrium expression. Write the expression for K_c: $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ Only gases and dissolved substances should be included in the equilibrium expressions. Leave out pure solids, pure liquids and solvents.	**a** $K_c = \frac{[CO][H_2]}{[H_2O]}$ **b** $K_c = \frac{[CO]}{[CO_2][H_2]}$ **c** $K_c = [Ag^+]^2[S^{2-}]$ or $K_{sp} = [Ag^+]^2[S^{2-}]$ Note that when the equilibrium reaction involves the dissolution of a sparingly soluble salt like Ag_2S, the equilibrium constant is given a special name (the solubility product) and symbol (K_{sp}).

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Try yourself 2.4.8

CALCULATING MOLAR SOLUBILITY FROM K_{sp} VALUES

<table>
<tr><td colspan="2">Use the K_{sp} values in Table 2.4.4 to calculate the molar solubility of lead(II) iodide, PbI_2, at 25°C.</td></tr>
<tr><td>Thinking</td><td>Working</td></tr>
<tr><td>Write the balanced chemical equation of the dissolution of PbI_2.
Write the K_{sp} expression and equate it to K_{sp} value from Table 2.4.4.</td><td>$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$
$K_{sp} = [Pb^{2+}][I^-]^2 = 9.8 \times 10^{-9}$</td></tr>
<tr><td>Construct an ICE table with three rows in the table labelled ‘I’ (initial), ‘C’ (change) and ‘E’ (equilibrium):
<table>
<tr><td></td><td colspan="2">Reactants ⇌ Products</td></tr>
<tr><td>I</td><td></td><td></td></tr>
<tr><td>C</td><td></td><td></td></tr>
<tr><td>E</td><td></td><td></td></tr>
</table>
In this case we note the solid reactant is irrelevant (i.e. not applicable—N/A) since the solid term does not appear in the K_{sp} expression.
We therefore only need consider the concentrations of the products.</td><td>The initial concentration of the products is zero.
Let $+x$ mol L^{-1} represent the change in concentration of Pb^{2+} as the dissolution process comes to equilibrium.
Since there is a 1:2 ratio between Pb^{2+} ions and I^- ions, the change in concentration for I^- will be $+2x$ mol L^{-1}
At equilibrium the concentrations of Pb^{2+} and I^- are x molL^{-1} and $2x$ mol L^{-1} respectively.
<table>
<tr><td></td><td colspan="3">$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$</td></tr>
<tr><td>I</td><td>N/A</td><td>0.0 mol L^{-1}</td><td>0.0 mol L^{-1}</td></tr>
<tr><td>C</td><td>N/A</td><td>$+x$ mol L^{-1}</td><td>$+2x$ mol L^{-1}</td></tr>
<tr><td>E</td><td>N/A</td><td>x mol L^{-1}</td><td>$2x$ mol L^{-1}</td></tr>
</table></td></tr>
<tr><td>Substitute the equilibrium concentration values into the K_{sp} expression and solve for x.</td><td>$$\begin{aligned} K_{sp} &= [Pb^{2+}][I^-]^2 = 9.8 \times 10^{-9} \\ x \times (2x)^2 &= 9.8 \times 10^{-9} \\ 4x^3 &= 9.8 \times 10^{-9} \\ x^3 &= 2.45 \times 10^{-9} \\ x &= \sqrt[3]{2.45 \times 10^{-9}} \\ x &= 1.35 \times 10^{-3} \end{aligned}$$
Therefore, $[Pb^{2+}] = 1.35 \times 10^{-3}$ mol L^{-1}</td></tr>
<tr><td>Determine the molar solubility.</td><td>Since Pb^{2+} and PbI_2 are in a 1:1 ratio in the balanced chemical equation, the molar solubility of PbI_2 is therefore 1.35×10^{-3} mol L^{-1}.</td></tr>
</table>

Sample pages

2.4 KEY QUESTIONS

Describe

1 **a** A homogeneous system is a system in which all the species are in the same state.

b For the general equation:

$aA + bB \rightleftharpoons cC + dD$

the reaction quotient, Q_c, can be written as: $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Q_c is equal to K_c at equilibrium.

c The equilibrium constant is the ratio of the equilibrium concentrations of the products to 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.

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Apply

2 $Q_c = \frac{[HCl]^2}{[H_2][Cl_2]}$

3 **a** $K_c = \frac{[HI]^2}{[H_2][I_2]}$

b $K_c = \frac{[N_2]^2[O_2]}{[N_2O]^2}$

c $K_c = \frac{[NO_2]}{[NO][O_2]^{\frac{1}{2}}}$

d $K_c = \frac{[N_2]^2[H_2O]^6}{[NH_3]^4[O_2]^3}$

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

Analyse

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 $Q_c = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

As $Q_c > K_c$, in order to reach equilibrium, the concentration of $[Cu(NH_3)_4]^{2+}$ must decrease and the concentration of the reactants increase. The reaction thus shifts to the left, producing more reactants.

7 **a** $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

b Since $\frac{[N_2][H_2]^3}{[NH_3]^2} = 100$

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1}{100}$$
$$= 0.01$$

c $K_c = \frac{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}{[NH_3]}$

d The expression in part **c** is equal to the square root of $\frac{[N_2][H_2]^3}{[NH_3]^2}$, which is 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 **a** $K_c = \frac{[HCl]^2[O_2]^{\frac{1}{2}}}{[H_2O][Cl_2]}$

$$= \sqrt{4.0 \times 10^{-4}}$$
$$= 0.020$$

b $K_c = \frac{[H_2O][Cl_2]}{[HCl]^2[O_2]^{\frac{1}{2}}}$

$$= \frac{1}{0.020}$$
$$= 50$$

9 **a** $K_c = (1.75)^4 = 8.35$

b $K_c = \frac{1}{\sqrt{1.70}} = 0.767$

c $K_c = \sqrt{1.70} = 1.30$

d $K_c = \frac{1}{1.70^2} = 0.346$

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10 **a** increased
- **b** decreased
- **c** increased
- **d** decreased

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Calculate equilibrium concentrations of reactants and products.

$$[NO_2] = \frac{0.40\,\text{mol}}{2.0\,\text{L}}$$
$$= 0.20\,\text{mol}\,\text{L}^{-1}$$
$$[N_2O_4] = \frac{0.80\,\text{mol}}{2.0\,\text{L}}$$
$$= 0.40\,\text{mol}\,\text{L}^{-1}$$

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 $$K_c = \frac{[COCl_2]}{[CO][Cl_2]}$$
$$= \frac{0.280}{2.4 \times 10^{-2} \times 0.108}$$
$$= 1.1 \times 10^2$$

13 $$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$
$$6.44 \times 10^5 = \frac{15.50^2}{0.0542^2 \times [O_2]}$$
$$[O_2] = \frac{15.50^2}{0.0542^2 \times (6.44 \times 10^5)}$$
$$= 0.127\,\text{mol}\,\text{L}^{-1}$$

14

	$PCl_3(g)$ +	**$Cl_2(g)$ ⇌**	**$PCl_5(g)$**
I	4.45 mol	5.50 mol	0.0 mol
C	−*x* = −0.350 mol	−*x* = −0.350 mol	+*x* = 0.350 mol
E	4.45 − *x* = 4.45 − 0.350 = 4.10 mol	5.50 − *x* = 5.50 − 0.350 = 5.15 mol	*x* = 0.350 mol

volume of vessel = 2.00 L

$$[PCl_3] = \frac{4.10}{2.00} = 2.05\,\text{mol}\,\text{L}^{-1}$$
$$[Cl_2] = \frac{5.15}{2.00} = 2.58\,\text{mol}\,\text{L}^{-1}$$
$$[PCl_5] = \frac{0.350}{2.00} = 0.175\,\text{mol}\,\text{L}^{-1}$$
$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$
$$= \frac{0.175}{2.05 \times 2.58}$$
$$= 0.0330$$

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15

	$N_2(g)$ +	**$3H_2(g)$ ⇌**	**$2NH_3(g)$**
I	5.89 mol	8.23 mol	0.0 mol
C	$-x = -0.240$ mol	$-3x = -0.720$ mol	$+2x = 0.480$ mol
E	$5.89 - x$ $= 5.89 - 0.240$ $= 5.65$ mol	$8.23 - 3x$ $= 8.23 - 0.720$ $= 7.51$ mol	$2x = 0.480$ mol

volume of vessel = 5.00 L

$$[N_2] = \frac{5.65}{5.00} = 1.13\,\text{mol}\,\text{L}^{-1}$$

$$[H_2] = \frac{7.51}{5.00} = 1.50\,\text{mol}\,\text{L}^{-1}$$

$$[NH_3] = \frac{0.480}{5.00} = 0.096\,\text{mol}\,\text{L}^{-1}$$

$$\begin{aligned} K_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ &= \frac{0.096^2}{1.13 \times 1.50^3} \\ &= 2.4 \times 10^{-3} \end{aligned}$$

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

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

Calculate equilibrium concentrations of reactants.

$$[H_2] = \frac{0.220\,\text{mol}}{2.00\,\text{L}} = 0.110\,\text{mol}\,\text{L}^{-1}$$

$$[I_2] = \frac{0.110\,\text{mol}}{2.00\,\text{L}} = 0.055\,\text{mol}\,\text{L}^{-1}$$

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

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

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

$$\begin{aligned} [HI] &= \sqrt{\frac{0.110 \times 0.055}{48.8}} \\ &= 0.011\,13\,\text{mol}\,\text{L}^{-1} \\ &= 0.011\,\text{mol}\,\text{L}^{-1} \end{aligned}$$

b

	$2HI(g)$ ⇌	**$H_2(g)$ +**	**$I_2(g)$**
I	4.00 mol	0.0 mol	0.0 mol
C	$-2x = -0.880$ mol (so $x = 0.440$)	$+x = 0.440$ mol	$+x = 0.440$ mol
E	$4.00 - 2x$ $= 4.00 - 0.880$ $= 3.12$ mol $[HI] = \frac{3.12\,\text{mol}}{2.00\,\text{L}}$ $= 1.56\,\text{mol}\,\text{L}^{-1}$	$x = 0.440$ mol $[H_2] = \frac{0.440\,\text{mol}}{2.00\,\text{L}}$ $= 0.220\,\text{mol}\,\text{L}^{-1}$	$x = 0.440$ mol $[I_2] = \frac{0.440\,\text{mol}}{2.00\,\text{L}}$ $= 0.220\,\text{mol}\,\text{L}^{-1}$

$$\begin{aligned} K_c &= \frac{[H_2][I_2]}{[HI]^2} \\ &= \frac{0.220 \times 0.220}{1.56^2} \\ &= 0.019\,89 \\ &= 0.020 \end{aligned}$$

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c The reaction quotient for this reaction is $\frac{[H_2][I_2]}{[HI]^2}$.

Calculate concentrations of reactants.

$[H_2] = \frac{0.240\text{ mol}}{2.00\text{L}} = 0.120\text{ mol L}^{-1}$

$[I_2] = \frac{0.320\text{mol}}{2.00\text{L}} = 0.160\text{ mol L}^{-1}$

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

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

	$2NO(g)$ +	**$2H_2(g)$ ⇌**	**$N_2(g)$ +**	**$2H_2O(g)$**
I	0.100 mol	0.051 mol	0.0 mol	0.100 mol
C	$-2x = -(0.100 - 0.062)$ $= -0.038$ mol (so $x = 0.019$ mol)	$-2x = -0.038$ mol	$+x$ $= +0.019$ mol	$+2x$ $= 2 \times 0.019$ $= +0.038$ mol
E	$0.100 - 2x$ $= 0.062$ mol	$0.051 - 2x$ $= 0.051 - 0.038$ $= 0.013$ mol	$0 + x$ $= 0 + 0.019$ $= 0.019$ mol	$0.100 + 0.038$ $= 0.138$ mol

volume of vessel = 1.00 L, so mol = concentration

$$K_c = \frac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$$

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

$$= 557$$

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

Initially, there is:

- 0.50 mol of A(g)
- 0.0 mol of the product B(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:

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

$$= 0.25\text{ M}$$

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

$[B]^2 = K_c \times 0.25$

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

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

Take the square root of both sides.

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

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

19 $PbI_2(s) \rightleftharpoons Pb(aq) + 2I(aq)$

Let x be the amount of lead iodide dissolved.

$9.8 \times 10^{-9} = [Pb] \times [I]^2$; $9.8 \times 10^{-9} = x \times (2x)^2$

$9.8 \times 10^{-9} = 4x^3$; $x^3 = 2.45 \times 10^{-9}$; $x = 1.35 \times 10^{-3}$

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20 First, determine the concentrations of the Ca^{2+} and CO_3^{2-} ions in the mixed solution. The formula for calculating dilutions is $c_1v_1 = c_2v_2$. This gives a final concentration of 0.001 M Ca^{2+} and 0.005 M CO_3^{2-}.

$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}] = 0.001 \times 0.005 = 5 \times 10^{-6}$

This solubility product is much greater than the K_{sp} in Table 2.4.4 (3.36×10^{-9}), and therefore, the $CaCO_3$ will not be all dissolved. Yes, a precipitate will form.

21 First, write the chemical equation and determine which product will possibly have low solubility using the data book. We see that this is silver chloride.

$Ag(NO_3) + NaCl \rightleftharpoons Na(NO_3) + AgCl$

Determine the concentrations of the Ag and Cl^- ions in the mixed solution. The formula for calculating dilutions is $c_1v_1 = c_2v_2$. This gives a final concentration of 0.02 M Ag^+ and 0.04 M Cl^-.

$K_{sp} = [Ag^+]\,[Cl^-] = 0.02 \times 0.04 = 8 \times 10–4$

This solubility product is much greater than the K_{sp} for AgCl in Table 2.4.4 (1.77×10^{-10}), and therefore, the AgCl will not be all dissolved. Yes, a precipitate will form.

CHAPTER 2 REVIEW

Describe

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 $K_c = \dfrac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$.

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

Apply

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 until the rates of the forward and reverse reactions become equal again and equilibrium is re-established. Therefore, there is a net forward reaction.

11 When the total pressure of the system is increased, 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 until 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 expression can be written for reactant and product concentrations at any time during the reaction. The equilibrium constant expression can only be written for reactant and product concentrations when the reaction is at equilibrium.

sample pages

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13 **a** $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

b $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$

c $K_c = \dfrac{[H_2O][CO]}{[H_2][CO_2]}$

d $K_c = \dfrac{[CH_4][H_2O]}{[CO][H_2]^3}$

Analyse

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** $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$
b $S_2(g) + 2H_2(g) \rightleftharpoons 2H_2S(g)$
c $NO_2(g) \rightleftharpoons \frac{1}{2}\,N_2O_4(g)$

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 $\dfrac{[H_2O]^2[N_2]}{[H_2]^2[NO]^2}$
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** $K_c = \dfrac{[Br_2][Cl_2]}{[BrCl]^2}$

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**: $K_c = \dfrac{1}{32} = 0.031$.

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: $K_c = \dfrac{1}{\sqrt{32}} = 0.18$.

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

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.250^2}{1.00 \times 1.00^3} = 0.063$$

26 The volume of the container is 2.00 L:

$$[H_2O] = \frac{0.020}{2.00} = 0.010\,mol\,L^{-1}$$

$$[H_2] = \frac{0.030}{2.00} = 0.015\,mol\,L^{-1}$$

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

$$[CO_2] = \frac{0.050}{2.00} = 0.025\,mol\,L^{-1}$$

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{0.010 \times 0.020}{0.015 \times 0.025} = 0.533$$

27 **a** $K_c = \frac{[Fe^{2+}]^2[Sn^{4+}]}{[Fe^{3+}]^2[Sn^{2+}]}$

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.

$$K_c = \frac{[C_3H_6O][H_2]}{[C_3H_8O]}$$

Calculate equilibrium concentrations of reactants and products.

$$[C_3H_6O] = \frac{0.082\,mol}{20.0\,L} = 0.0041\,mol\,L^{-1}$$

$$[H_2] = \frac{0.082\,mol}{20.0\,L} = 0.0041\,mol\,L^{-1}$$

$$[C_3H_8O] = \frac{0.018\ mol}{20.0\ L} = 0.0009\,mol\,L^{-1}$$

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

$$K_c = \frac{0.0041 \times 0.0041}{0.0009} = 0.0187 = 0.019$$

29 **a** $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b Calculate equilibrium concentrations of reactants and products.

$$[PCl_5] = \frac{4.50\,mol}{3.00\,L} = 1.50\,mol\,L^{-1}$$

$$[Cl_2] = \frac{0.900\,mol}{3.00\,L} = 0.300\,mol\,L^{-1}$$

$$[PCl_3] = \frac{6.00\ mol}{3.00\ L} = 2.00\,mol\,L^{-1}$$

Use the expression for the equilibrium constant from part **a**.
Substitute equilibrium concentrations in the equilibrium expression.

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.400$$

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c Rearrange the expression to find $[Cl_2]$.

$$[Cl_2] = K_c \times \frac{[PCl_5]}{[PCl_3]}$$

Substitute equilibrium concentrations in the equilibrium constant expression and find the value of $[Cl_2]$.

$$\begin{aligned}[Cl_2] &= 0.400 \times \frac{0.002}{0.001} \\ &= 0.800\,\text{mol L}^{-1}\end{aligned}$$

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.

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

Calculate equilibrium concentrations of reactants and products.

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

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

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

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

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

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

$$\begin{aligned}[C] &= 0.016\,\text{mol L}^{-1} \\ n(C) &= c \times V \\ &= 0.016\,\text{mol L}^{-1} \times 2.00\,\text{L} \\ &= 0.032\,\text{mol}\end{aligned}$$

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 $\frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{0.300 \times 0.400}{0.100 \times 0.200^3} = 150$, which is greater than the equilibrium constant.

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

i increase

ii increase

iii decrease

iv decrease

b It is endothermic.

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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, a net reverse reaction occurs and the colour of the gas mixture will become lighter.
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.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
$$= 0.052$$

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 1.00 L 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** $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

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 Water is a product of the esterification (ester production) reaction, so conditions with low water such as concentrated acids will, according to Le Châtelier’s principle, promote the forward reaction.

Conversely, when esters are broken down (reverse reaction), water is required as a reactant, so dilute acid will promote the reaction.

Sample pages

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38 $BaCl_2 + CuSO_4 \rightleftharpoons BaSO_4 + CuCl_2$

The data book indicates that barium sulfate could be precipitated. The mixed (diluted) concentrations are: [Ba] 4×10^{-5} and $[SO_4]$ 8×10^{-6}; $K_{sp} = 4 \times 10^{-5} \times 8 \times 10^{-6} = 3.2 \times 10^{-10}$

The data book K_{sp} value for $BaSO_4$ is 1.08×10^{-10}.

Interpret

39 Include the existing Cl^- concentration in your K_{sp} calculations.

$K_{sp} = 1.77 \times 10^{-10} = x \times (0.1 + x)$

As this calculation results in a quadratic calculation and K_{sp} is very small, we can approximate that $(0.1 + x)$ is approximately equal to 0.1.

$1.77 \times 10^{-10} = 0.1x$

$1.77 \times 10^{-9} = x$

The solubility of silver chloride in a 0.1 M solution of NaCl is 1.77×10^{-9}.

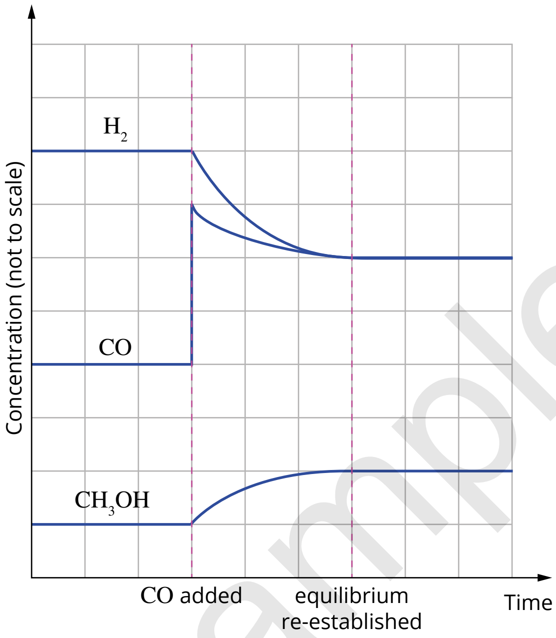
40 **a** **i** high temperature; high pressure

ii low temperature; high pressure

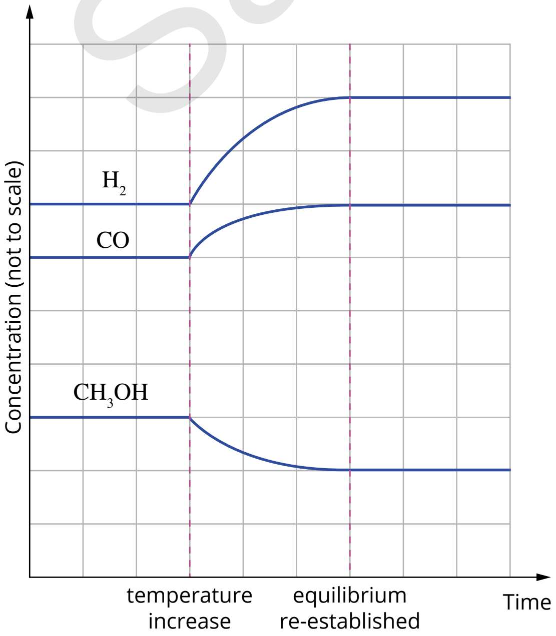
b temperature

c use a catalyst

d **i**



ii



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41 **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

42 **a** $2SO_3(g) + CO_2(g) \rightleftharpoons CS_2(g) + 4O_2(g)$

b $K_c = \dfrac{[CS_2][O_2]^4}{[SO_3]^2[CO_2]}$

c **i** $n(O_2) = 4 \times n(CS_2) = 4 \times 0.028 = 0.112\,\text{mol}$

ii $[CS_2] = \dfrac{0.028}{20.0} = 0.0014\,\text{mol L}^{-1}$

$[O_2] = \dfrac{0.112}{20.0} = 0.0056\,\text{mol L}^{-1}$

$[SO_3] = \dfrac{0.022}{20.0} = 0.0011\,\text{mol L}^{-1}$

$[CO_2] = \dfrac{0.014}{20.0} = 0.0007\,\text{mol L}^{-1}$

$$K_c = \frac{[CS_2][O_2]^4}{[SO_3]^2[CO_2]}$$

$$= \frac{0.0014 \times 0.0056^4}{0.0011^2 \times 0.0007}$$

$$= 1.6 \times 10^{-3}$$

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 500 seconds would show on the graph as a rapid decrease in concentration of all three gases (three vertical lines at 500 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 500 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)

$COCl_2$ 0.007 mol L^{-1}
CO 0.018 mol L^{-1}
Cl_2 0.008 mol L^{-1}

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.007}{0.018 \times 0.008} = 48.61 = 50 \text{ (rounded to 1 significant figure)}$$

sample pages

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