Mastering Chemistry

- Book 4B
- Topic 11 Chemical Equilibrium

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Content

39.1 Irreversible and reversible reactions (p.2)

- Water is produced when a mixture of hydrogen and oxygen in a 2 : 1 molar ratio is ignited. There is no hydrogen or oxygen remaining at the end of the reaction. The reaction has gone to completion.

- The equation for the reaction contains an arrow pointing from the reactants to the product.
  $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
  This reaction takes place in one direction only. This is an example of an **irreversible reaction (不可逆反應)**.

- Reactions that take place in both ‘forward’ and ‘backward’ directions are **reversible reactions (可逆反應)**.

39.1 Irreversible and reversible reactions (p.2)

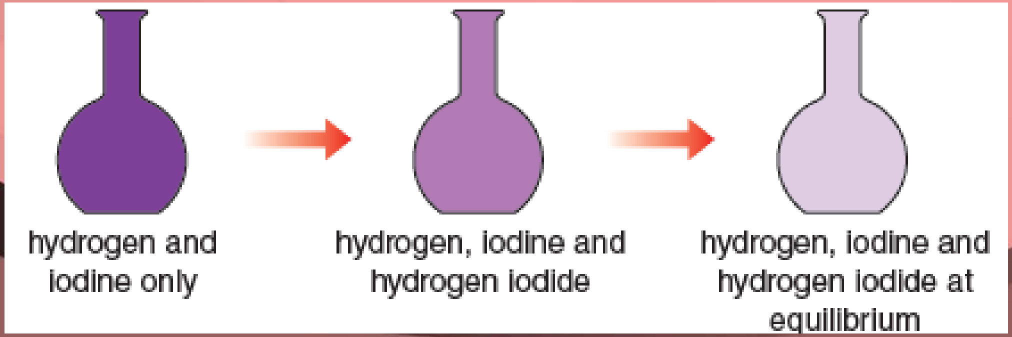
- When you heat calcium carbonate strongly, it decomposes to form calcium oxide and carbon dioxide. At the same time, calcium oxide reacts with carbon dioxide to form calcium carbonate. This is an example of a common reversible reaction.
  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
- The double arrow ($\rightleftharpoons$) in the above equation shows that the reaction is reversible. The reaction going from left to right is known as the **forward reaction (正向反應)**, the reaction going in the opposite direction is known as the **backward reaction (逆向反應)**.

39.2 The road to equilibrium (p.3)

- Many chemical reactions are reversible reactions, for example, the reaction between hydrogen and iodine to produce hydrogen iodide.

$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
colourless		purple		colourless

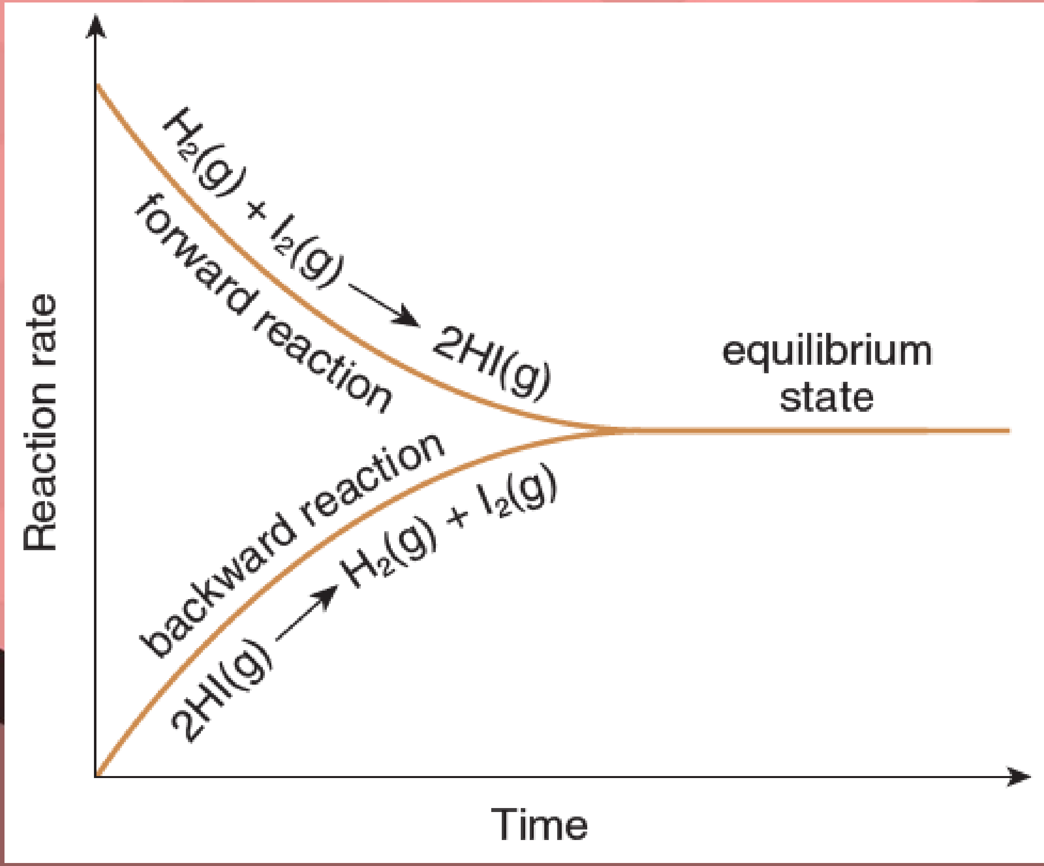
- When colourless hydrogen and purple iodine are mixed in a closed container at 230 °C, the purple colour becomes paler as iodine reacts with hydrogen. However, the purple colour will not disappear. After a while, the deepness of the pale purple colour stays constant.



Colour changes of the reaction between hydrogen and iodine

39.2 The road to equilibrium (p.3)

- When the mixture of hydrogen and iodine is heated, the two gases start to react and form hydrogen iodide. As the reaction proceeds, the concentrations of hydrogen and iodine decrease, so the rate of the forward reaction decreases.



Changes in the rates of the forward and backward reactions in a system of hydrogen, iodine and hydrogen iodide

39.2 The road to equilibrium (p.3)

- As soon as hydrogen iodide is formed, it starts to decompose slowly. As the reaction between hydrogen and iodine proceeds, the concentration of hydrogen iodide increases, so the rate of the backward reaction increases as well.
- Eventually, the rates of the forward and backward reactions become equal. Hydrogen, iodine and hydrogen iodide are all present and their concentrations remain constant. The system is now in **equilibrium (平衡)**. This type of equilibrium is known as **dynamic equilibrium (動態平衡)**.
- 'Dynamic' refers to movement. In dynamic equilibrium, there is constant movement. Reactants are changing to products and products are changing to reactants.

39.2 The road to equilibrium (p.3)

Three important features define a chemical system that is in dynamic equilibrium:

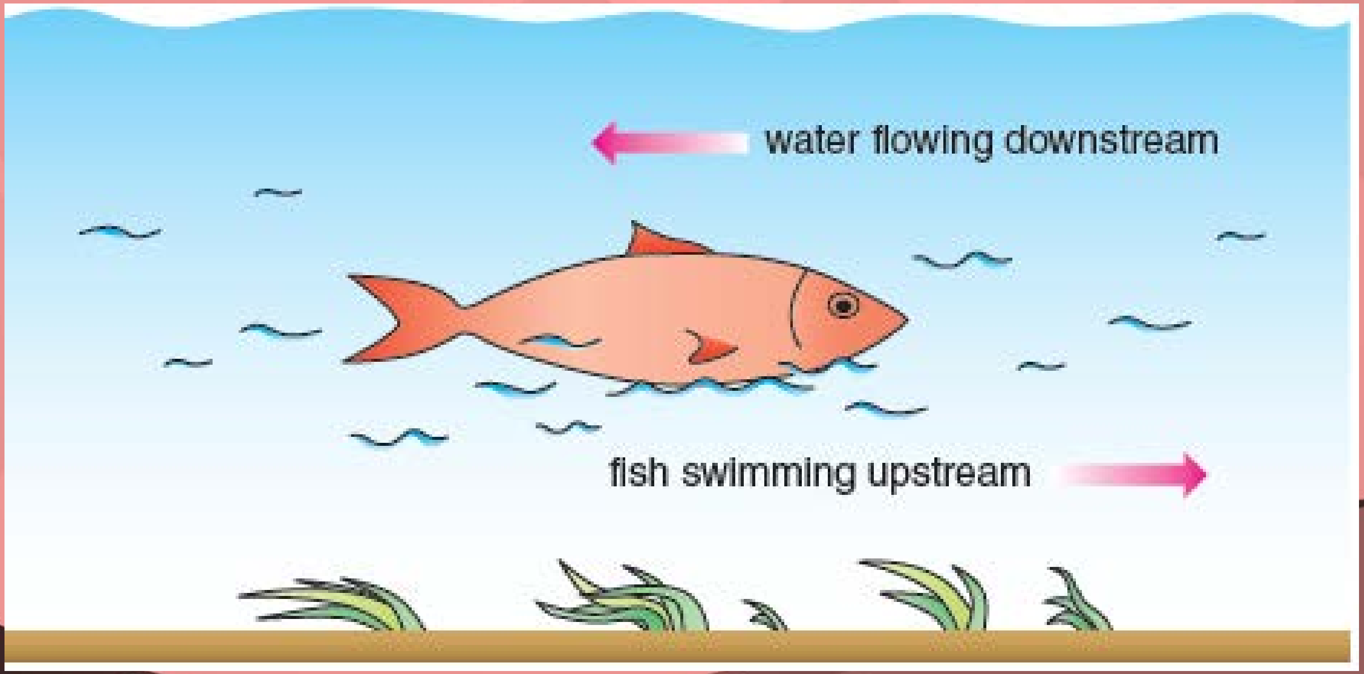
- **concentrations of reactants and products remain constant;**
- **forward and backward reactions are both happening (so ‘dynamic’);**
- **the rate of the forward reaction is equal to the rate of the backward reaction (and is NOT zero).**

Illustrating dynamic equilibrium *Ref.*

39.2 The road to equilibrium (p.3)

An analogy of dynamic equilibrium

- An analogy of dynamic equilibrium is a fish swimming upstream at the same speed as the water flowing downstream. The fish appears to be still, but it is in dynamic equilibrium with the flowing water.



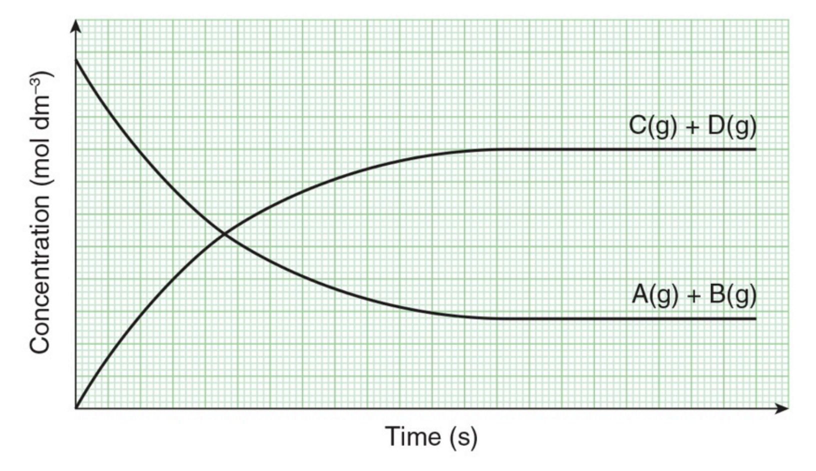
39.2 The road to equilibrium (p.3)

Practice 39.1

A dynamic equilibrium is attained when gas A is mixed with gas B at a given temperature.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

The figure below shows how the concentrations of reactants and products change with time.



Explain, in terms of the rate of forward reaction and the rate of backward reaction, how an equilibrium mixture containing the above four chemical species is obtained.

39.2 The road to equilibrium (p.3)

Practice 39.1 (continued)

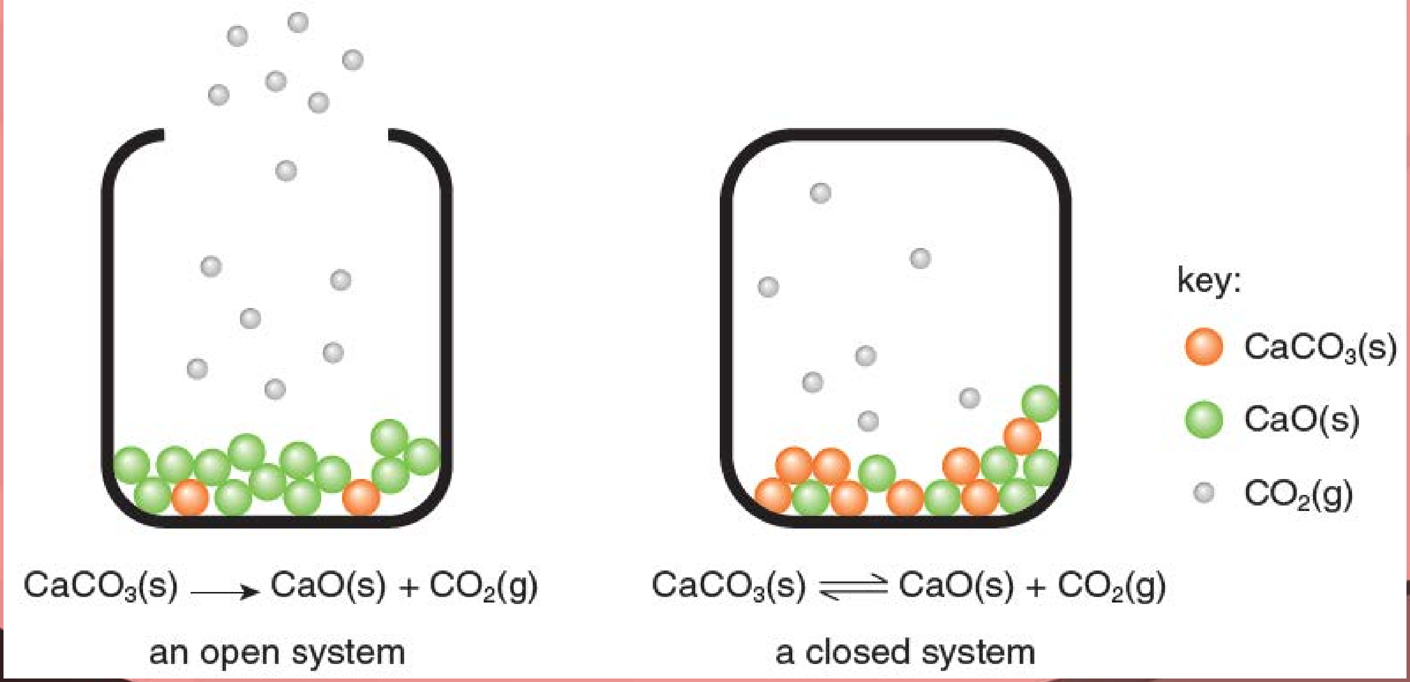
When A(g) and B(g) are mixed, the two gases start to react and form C(g) and D(g). As the reaction proceeds, the concentrations of A(g) and B(g) decrease, so the rate of the forward reaction decreases.

As soon as C(g) and D(g) are formed, they start to react slowly. As the reaction between A(g) and B(g) proceeds, the concentrations of C(g) and D(g) increase, so the rate of the backward reaction increases as well.

Eventually, the rates of the forward and backward reactions become equal. The concentrations of the four chemical species remain constant. An equilibrium mixture containing the four chemical species is obtained.

39.3 Equilibrium requires a closed system (p.5)

- An **open system (開放體系)** is a system in which substances can enter or leave.
- A **closed system (密閉體系)** is one in which no substances can enter or leave.



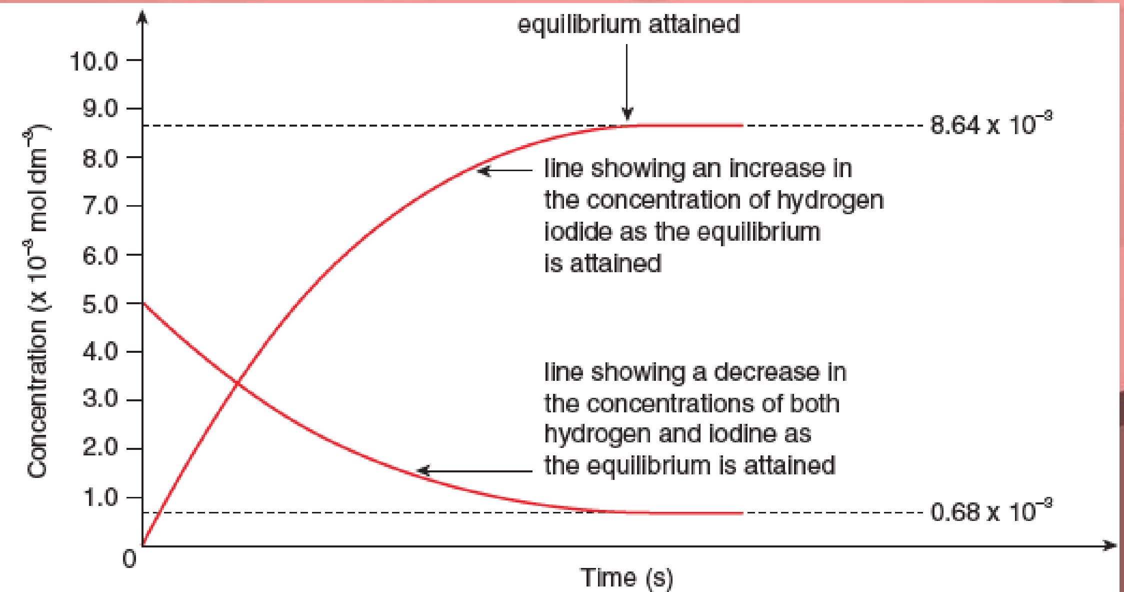
Heating calcium carbonate in an open system (left) and a closed system (right)

39.3 Equilibrium requires a closed system (p.5)

- In the open system, all the calcium carbonate are converted to calcium oxide because the carbon dioxide has escaped and thus no carbon dioxide is available to react with the calcium oxide to re-form calcium carbonate.
- If you do the experiment in a closed system, you find that no matter how long you continue with the experiment, there is still some calcium carbonate present. An equilibrium is attained. Calcium carbonate decomposes to give calcium oxide and carbon dioxide at exactly the same rate as the calcium oxide and carbon dioxide recombine to form calcium carbonate.

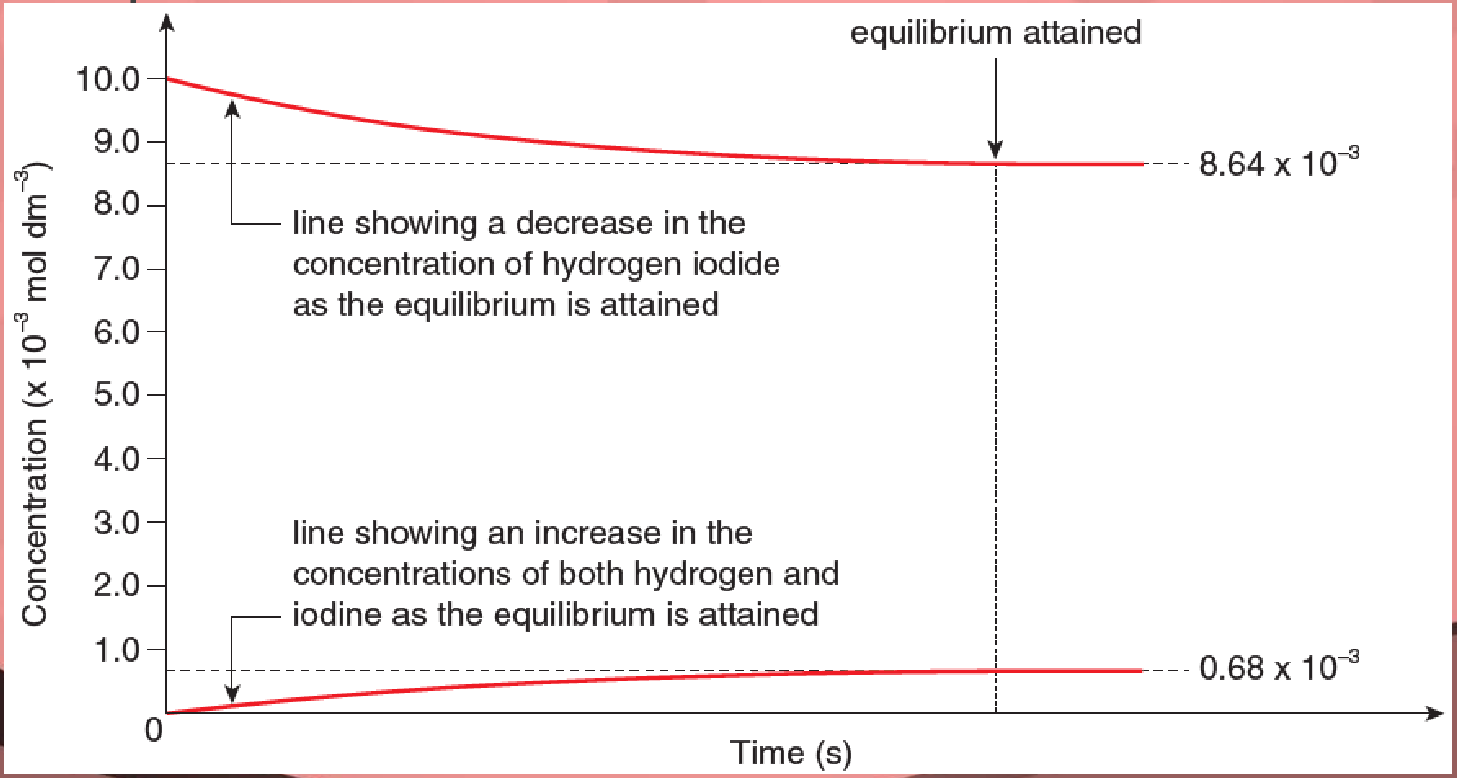
39.4 Equilibrium attained from either direction of a reaction (p.6)

- Consider again the reversible reaction between hydrogen and iodine: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
  The figure below shows what happens when 5.00×10^{-3} mole of hydrogen and 5.00×10^{-3} mole of iodine react at 230 °C in a closed vessel of volume 1.00 dm^3. At equilibrium, the mixture contains 0.68×10^{-3} mole of hydrogen, 0.68×10^{-3} mole of iodine and 8.64×10^{-3} mole of hydrogen iodide.



39.4 Equilibrium attained from either direction of a reaction (p.6)

- The figure below shows what happens when 1.00 x 10^{-2} mole of hydrogen iodide is allowed to decompose at the same temperature in a closed vessel of volume 1.00 dm^3.



39.4 Equilibrium attained from either direction of a reaction (p.6)

- From the above experiment, you can see that equilibrium can be attained from either direction, either starting with the substance on the right of the equation (i.e. HI(g)), or with the substances on the left (i.e. H_2(g) and I_2(g)).

39.5 Changing the conditions of a chemical equilibrium system (p.8)

- When a reaction mixture attains equilibrium, the composition of the equilibrium mixture (i.e. the concentration of each chemical species) will not alter as long as the conditions remain the same.
- If you make a change in one of the conditions (e.g. add some more of one of the chemical species, or change the temperature of the system), then the composition may change.

Investigating the effects of concentration changes on two chemical equilibrium systems
Ref.

39.5 Changing the conditions of a chemical equilibrium system (p.8)

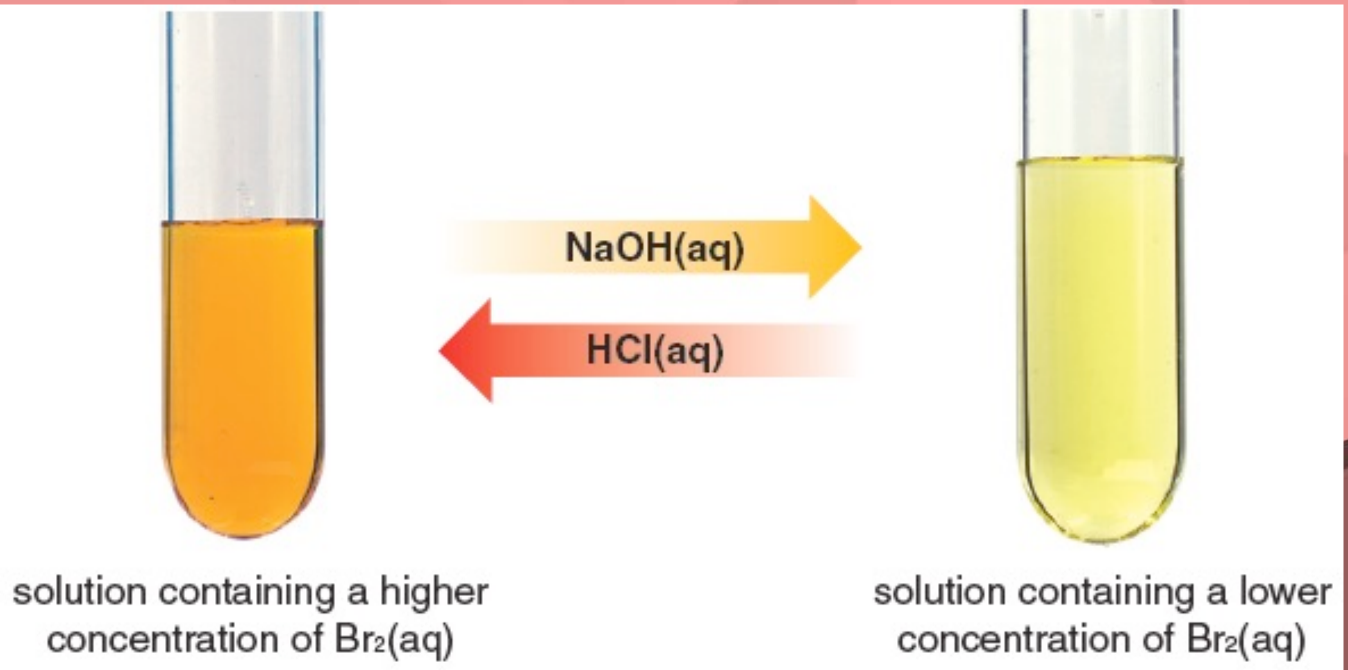
- Aqueous bromine can be used as a reagent to test for unsaturated hydrocarbons. The change in deepness of its colour indicates the concentration of bromine in the solution.

The following equilibrium system exists in aqueous bromine:

$$\underset{\text{yellow or light brown}}{Br_2(aq)} + H_2O(l) \rightleftharpoons \underbrace{HOBr(aq) + H^+(aq) + Br^-(aq)}_{\text{colourless}}$$

39.5 Changing the conditions of a chemical equilibrium system (p.8)

- If you add a small amount of sodium hydroxide solution to light brown aqueous bromine, the colour turns yellow. This indicates that the concentration of bromine has decreased.
- If you now add hydrochloric acid, the light brown colour returns. This indicates that the concentration of bromine has increased.



Effect of adding alkali or acid to an equilibrium system that exists in aqueous bromine

39.6 Characteristics of a chemical equilibrium system (p.9)

- The characteristics of a chemical equilibrium system are as follows:
  - it is dynamic;
  - the concentrations of reactants and products remain constant;
  - the rate of the forward reaction is equal to the rate of the backward reaction;
  - it requires a closed system;
  - it can be attained from either direction, either starting with the substances on the left of the equation or with the substances on the right of the equation;
  - it may be affected by a change in condition (e.g. concentration or temperature).

39.7 The equilibrium constant, K_c (p.9)

- Methanol is synthesised from a mixture of carbon monoxide and hydrogen. Methanol synthesis involves a reversible reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

- In an experiment, three 10.0 dm^3 containers were set up with different starting concentrations of carbon monoxide and hydrogen. The contents of the containers were allowed to attain equilibrium at 210 °C.

39.7 The equilibrium constant, K_c (p.9)

- The equilibrium concentrations of carbon monoxide, hydrogen and methanol in each container were determined. The table below shows the results obtained. The square brackets, [ ], in the last column refer to the concentration, in mol dm^{-3}, of the substance inside the brackets.

Trial	Equilibrium concentration (mol dm^{-3})			$\frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]^2}$ (dm^6 mol^{-2})
	$CO(g)$	$H_2(g)$	$CH_3OH(g)$	
1	0.0911	0.0822	0.00892	14.5
2	0.0753	0.151	0.0247	14.4
3	0.138	0.176	0.0620	14.5

39.7 The equilibrium constant, K_c (p.9)

- The last column in the above table shows the number obtained by arranging the equilibrium concentrations of CO(g), H_2(g) and CH_3OH(g) in a particular way.
  For the first row of data:

$$\frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]^2} = \frac{0.00892 \text{ mol dm}^{-3}}{(0.0911 \text{ mol dm}^{-3})(0.0822 \text{ mol dm}^{-3})^2}$$
$$= 14.5 \text{ dm}^6 \text{ mol}^{-2}$$

- This expression gives an approximately constant value close to 14.5 whatever the starting concentrations of carbon monoxide and hydrogen are. This constant is called the **equilibrium constant, K_c (平衡常數)**, for the reaction. The subscript ‘c’ refers to the fact that concentrations have been used in the calculations.

39.7 The equilibrium constant, K_c (p.9)

- In general, if an equilibrium mixture contains substances A, B, C and D that react according to the equation:
  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ (where *a*, *b*, *c* and *d* are the coefficients in the equation)

$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

- The expressions for the equilibrium constants for two systems are given below:

  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $$K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

39.7 The equilibrium constant, K_c (p.9)

- Notice that the concentration values fed into the expression must be those that occur at equilibrium, not the starting values.
- The value of equilibrium constant, K_c, is different for different systems. It also changes with temperature.

K is the symbol for the equilibrium constant.

The subscript '*c*' indicates the use of concentration values.

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Square brackets, [ ], refer to the concentrations of substances at equilibrium.

These 'powers' are the coefficients of substances in the equation for the reaction.

39.7 The equilibrium constant, K_c (p.9)

Practice 39.2

Write the expression for K_c for each of the following reactions.

a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$$

b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

$$K_c = \frac{[NO(g)]^4[H_2O(g)]^6}{[NH_3(g)]^4[O_2(g)]^5}$$

c) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

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

39.7 The equilibrium constant, K_c (p.9)

What are the units of equilibrium constant?

- In the expression for equilibrium constant, the square brackets refer to the concentration of the substance inside the brackets.
- The units of equilibrium constant therefore depend on the powers of concentrations of substances in the expression.

39.7 The equilibrium constant, K_c (p.9)

Q (Example 39.1)

State the unit of K_c for each of the following reactions:

a) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

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

A

a) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

$$K_c = \frac{[CO(g)][Cl_2(g)]}{[COCl_2(g)]}$$

Units of K_c are given by $\dfrac{\cancel{\text{mol dm}^{-3}} \times \text{mol dm}^{-3}}{\cancel{\text{mol dm}^{-3}}} = \text{mol dm}^{-3}$

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

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

Units of K_c are given by $\dfrac{\cancel{\text{mol dm}^{-3}} \times \cancel{\text{mol dm}^{-3}}}{\cancel{\text{mol dm}^{-3}} \times \cancel{\text{mol dm}^{-3}} \times \text{mol dm}^{-3}} = \text{dm}^3\ \text{mol}^{-1}$.

39.7 The equilibrium constant, K_c (p.9)

Equilibrium constant with no units

- For the following reaction:

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

$$K_c = \frac{[CO(g)][H_2O(g)]}{[H_2(g)][CO_2(g)]}$$

Units of K_c are given by $\frac{\cancel{mol\ dm^{-3}} \times \cancel{mol\ dm^{-3}}}{\cancel{mol\ dm^{-3}} \times \cancel{mol\ dm^{-3}}}$, i.e. no units.

- In the above equation, the sum of the coefficients of the reactants equals to the sum of the coefficients of the products. There are identical powers in the numerator and the denominator of the expression for K_c. The concentration units in the expression cancel out. Thus, K_c has no units.

39.7 The equilibrium constant, K_c (p.9)

Practice 39.3

1 For each of the following reactions,

i) write an expression for the equilibrium constant, K_c;

ii) deduce the units of K_c.

a) $C_2H_4(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$

$$K_c = \frac{[CH_3CH_2OH(g)]}{[C_2H_4(g)][H_2O(g)]}$$

Units of K_c are given by $\dfrac{\cancel{\text{mol dm}^{-3}}}{(\cancel{\text{mol dm}^{-3}})(\text{mol dm}^{-3})}$ = $\text{dm}^3 \text{ mol}^{-1}$

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

$$K_c = \frac{[CH(g)][H_2(g)]^3}{[CH_4(g)][H_2O(g)]}$$

Units of K_c are given by $\dfrac{(\cancel{\text{mol dm}^{-3}})(\text{mol dm}^{-3})^{\cancel{3}\,2}}{(\cancel{\text{mol dm}^{-3}})(\cancel{\text{mol dm}^{-3}})}$ = $\text{mol}^2 \text{ dm}^{-6}$

39.7 The equilibrium constant, K_c (p.9)

Practice 39.3 (continued)

2 Consider the information below:

Reaction	Equilibrium constant at 25 °C
$P(aq) + Q(aq) \rightleftharpoons R(aq) + S(aq)$	K_1
$R(aq) + S(aq) \rightleftharpoons T(aq) + U(aq) + W(aq)$	K_2
$T(aq) + U(aq) + W(aq) \rightleftharpoons P(aq) + Q(aq)$	K_3

a) Show that $K_3 = \dfrac{1}{K_1 \times K_2}$.

$$K_1 = \frac{[R(aq)][S(aq)]}{[P(aq)][Q(aq)]} \quad K_2 = \frac{[T(aq)][U(aq)][W(aq)]}{[R(aq)][S(aq)]} \quad K_3 = \frac{[P(aq)][Q(aq)]}{[T(aq)][U(aq)][W(aq)]}$$

$$\frac{1}{K_1 \times K_2} = \frac{[P(aq)][Q(aq)]}{[R(aq)][S(aq)]} \times \frac{[R(aq)][S(aq)]}{[T(aq)][U(aq)][W(aq)]}$$

$$= \frac{[P(aq)][Q(aq)]}{[T(aq)][U(aq)][W(aq)]}$$

$$= K_3$$

39.7 The equilibrium constant, K_c (p.9)

Practice 39.3 (continued)

2 b) What are the units of K_3?

Units of K_3 are given by

$$\frac{(\cancel{\text{mol dm}^{-3}})(\cancel{\text{mol dm}^{-3}})}{(\cancel{\text{mol dm}^{-3}})(\cancel{\text{mol dm}^{-3}})\ (\text{mol dm}^{-3})}$$

$= \text{dm}^3\ \text{mol}^{-1}$

39.7 The equilibrium constant, K_c (p.9)

Different values of equilibrium constant for the same system

- The expression for the equilibrium constant for a system depends on the balanced equation quoted.
- There can be different values of equilibrium constant for a system involving the same substances under the same conditions, depending on the form of the balanced equation.
- Consider the chemical equilibrium system of $NO_2(g)$ and $N_2O_4(g)$. The chemical equation for the reaction is:

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

  The expression for its equilibrium constant is:

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

39.7 The equilibrium constant, K_c (p.9)

- The equilibrium constant is 0.690 $dm^3\ mol^{-1}$ at 127 °C. However, the chemical equation for the reaction could also be written in the other way round:

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

  The expression for the equilibrium constant in this case is:

  $$K_c' = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

  The value of the equilibrium constant for this system at 127 °C is $\frac{1}{0.690}$ or 1.45 $mol\ dm^{-3}$.

- The relationship between the two equilibrium constants is:

  $$K_c' = \frac{1}{K_c}$$

39.7 The equilibrium constant, K_c (p.9)

- Consider the chemical equilibrium system of $H_2(g)$, $I_2(g)$ and HI(g). The chemical equation for the reaction is:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

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

which can also be written as:

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

$$K_c' = \frac{[HI(g)]}{[H_2(g)]^{\frac{1}{2}}[I_2(g)]^{\frac{1}{2}}}$$

- The relationship between the two equilibrium constants is:

$$K_c' = \sqrt{K_c}$$

- When quoting a value of equilibrium constant, you must specify the balanced equation to which it applies.

39.7 The equilibrium constant, K_c (p.9)

Practice 39.4

1 The following equation represents an esterification reaction producing ethyl ethanoate:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The value of K_c for the above reaction at 25 °C is 4.0. This equilibrium can be attained from the opposite direction. What is the value of K_c for the reaction shown below at 25 °C?

$$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$$

$$K_c = 4.0 = \frac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[CH_3COOH(l)][C_2H_5OH(l)]}$$

$$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$$

$$K_c \text{ for the above reaction} = \frac{[CH_3COOH(l)][C_2H_5OH(l)]}{[CH_3COOC_2H_5(l)][H_2O(l)]}$$

$$= \frac{1}{4.0}$$

$$= 0.25$$

39.7 The equilibrium constant, K_c (p.9)

Practice 39.4 (continued)

2 Nitrogen and hydrogen react to form ammonia in the presence of a catalyst.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 626\ dm^6\ mol^{-2}$ at 200 °C

What is the value of K_c for the reaction shown below at 200 °C?

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

$$K_c = 626\ dm^6\ mol^{-2} = \frac{[NH_3(g)]^2}{[N_3(g)][H_2(g)]^3}$$

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$K_c \text{ for the above reaction} = \frac{[NH_3(g)]}{[N_2(g)]^{\frac{1}{2}}[H_2(g)]^{\frac{3}{2}}}$$

$$= \sqrt{626}\ dm^3\ mol^{-1}$$

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

K_c for the above reaction

$$= \frac{[N_2(g)]^{\frac{1}{2}}[H_2(g)]^{\frac{3}{2}}}{[NH_3(g)]}$$

$$= \frac{1}{\sqrt{626}}\ mol\ dm^{-3}$$

$$= 0.0400\ mol\ dm^{-3}$$

39.8 Calculating equilibrium constant, K_c (p.15)

- Calculating a value of equilibrium constant, K_c, may involve determining and using equilibrium concentrations.
- The equilibrium concentrations may be determined by dividing the equilibrium amounts, in moles, by the volume (use V if volume is not given).
- The equilibrium concentrations may then be substituted into the K_c expression to calculate a value of K_c.

1 Calculate the quantity of each substance at equilibrium using the balanced equation involved.	2 Calculate the equilibrium concentration of each substance.	3 Substitute the equilibrium concentrations into the expression for K_c and calculate K_c.

The steps of calculating equilibrium constant

- The equilibrium constant, K_c, for a system is only constant at a constant temperature.

39.8 Calculating equilibrium constant, K_c (p.15)

Q (Example 39.2)

Phosgene ($COCl_2$) is an important chemical. It can be produced from the reaction of CO(g) with Cl_2(g).

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

A 4.00 dm^3 sealed container, which was maintained at 1 000 K, initially contained 2.00 moles of CO(g) and 1.00 mole of Cl_2(g). When the system attained equilibrium, the concentration of $COCl_2$(g) was 0.120 mol dm^{-3}.

Calculate the equilibrium constant, K_c for the reaction at 1 000 K.

39.8 Calculating equilibrium constant, K_c (p.15)

Q (Example 39.2) (continued)

A Number of moles of $COCl_2$(g) at equilibrium = 0.120 mol dm^{-3} x 4.00 dm^3

= 0.480 mol

According to the equation, 1 mole of CO(g) and 1 mole of Cl_2(g) react to form 1 mole of $COCl_2$(g).

i.e. number of moles of CO(g) or Cl_2(g) consumed at equilibrium = 0.480 mol

	CO(g)	+	Cl_2(g)	$\rightleftharpoons$	$COCl_2$(g)
Initial concentration (mol dm^{-3})	$\frac{2.00}{4.00}$		$\frac{1.00}{4.00}$		0
Equilibrium concentration (mol dm^{-3})	$\frac{2.00 - 0.480}{4.00}$ = 0.380		$\frac{1.00 - 0.480}{4.00}$ = 0.130		0.120

$$K_c = \frac{[COCl_2(g)]}{[CO(g)][Cl_2(g)]}$$

$$= \frac{0.0120 \text{ mol dm}^{-3}}{(0.380 \text{ mol dm}^{-3})(0.130 \text{ mol dm}^{-3})}$$

$$= 2.43 \text{ dm}^3 \text{ mol}^{-1}$$

$\therefore$ the equilibrium constant, K_c for the reaction is 2.43 dm^3 mol^{-1} at 1 000 K.

39.8 Calculating equilibrium constant, K_c (p.15)

Q (Example 39.3)

Consider the reaction represented by the equation below:

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

In an experiment, 1.20 moles of NO(g) and 1.00 mole of O_2(g) were mixed in a 10.0 dm^3 closed container maintained at temperature T. When equilibrium was attained, 78.0% of NO(g) was consumed.

Calculate the equilibrium constant, K_c for the reaction under the experimental conditions.

39.8 Calculating equilibrium constant, K_c (p.15)

Q (Example 39.3) (continued)

A Number of moles of NO(g) consumed = 1.20 mol x 78.0%

= 0.936 mol

According to the equation, 2 moles of NO(g) react with 1 mole of O_2(g) to form 2 moles of NO_2(g).

i.e. number of moles of O_2(g) consumed = $\frac{0.936}{2}$ mol = 0.468 mol

number of moles of NO_2(g) formed = 0.936 mol

	$2NO(g)$	+ $O_2(g)$ $\rightleftharpoons$	$2NO_2(g)$
Initial concentration (mol dm^{-3})	$\frac{1.20}{10.0}$	$\frac{1.00}{10.0}$	0
Equilibrium concentration (mol dm^{-3})	$\frac{1.20 - 0.936}{10.00}$ = 0.0264	$\frac{1.00 - 0.468}{10.00}$ = 0.0532	$\frac{0.936}{10.0}$ = 0.0936

$$K_c = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$$

$$= \frac{(0.0936 \text{ mol dm}^{-3})^2}{(0.0264 \text{ mol dm}^{-3})^2(0.0532 \text{ mol dm}^{-3})}$$

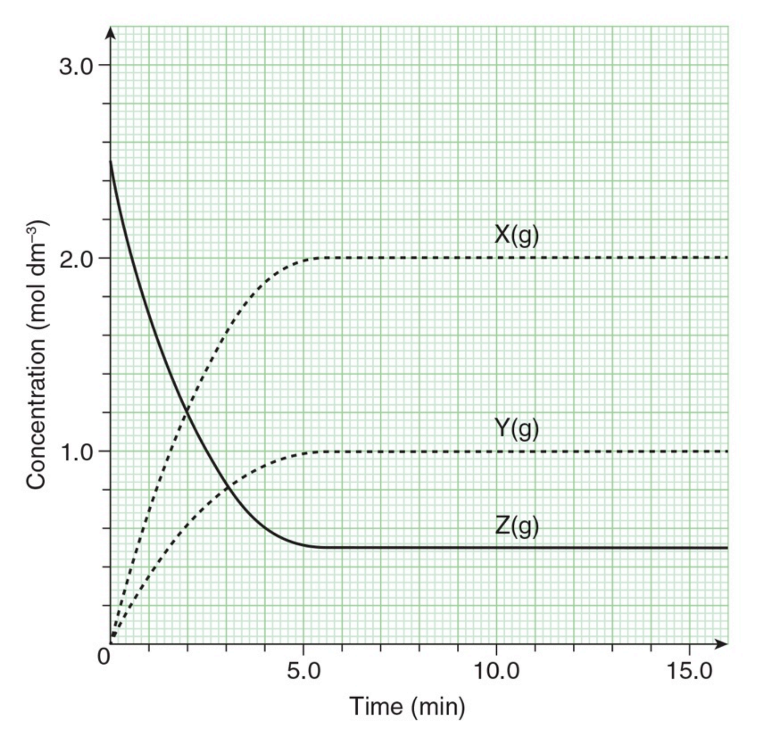
$$= 236 \text{ dm}^3 \text{ mol}^{-1}$$

∴ the equilibrium constant, K_c for the reaction is 236 dm^3 mol^{-1} under the experimental conditions.

39.8 Calculating equilibrium constant, K_c (p.15)

Practice 39.5

1 An experiment was performed for a reversible reaction involving X(g), Y(g) and Z(g) in a closed container of 1.00 dm^3 at a constant temperature. The graph below shows the relevant experimental data.



39.8 Calculating equilibrium constant, K_c (p.15)

Practice 39.5 (continued)

1 a) According to the graph, how do you know that the reaction is reversible?

None of the final concentrations of X(g), Y(g) and Z(g) is equal to zero. / X(g), Y(g) and Z(g) co-exist in the systems, and their concentrations remain unchanged after a long period of time.

b) Calculate the equilibrium constant K_c for the reaction at the temperature of the experiment.

Z(g) decomposes to give X(g) and Y(g) according to the equation below.

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

$$K_c = \frac{[X(g)]^2[Y(g)]}{[Z(g)]^2}$$

$$= \frac{(2.0\ \text{mol dm}^{-3})^2(1.0\ \text{mol dm}^{-3})}{(0.50\ \text{mol dm}^{-3})^2}$$

$$= 16\ \text{mol dm}^{-3}$$

∴ the equilibrium constant, K_c, for the reaction at the temperature of the experiment is 16 mol dm^{-3}.

39.8 Calculating equilibrium constant, K_c (p.15)

Practice 39.5 (continued)

2 $PCl_5(g)$ decomposes to form $PCl_3(g)$ and $Cl_2(g)$ according to the equation below.

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

4.00 moles of $PCl_5(g)$, 8.00 moles of $PCl_3(g)$ and 6.00 moles of $Cl_2(g)$ are placed in a container of volume 12.0 dm^3 kept at temperature T.

The equilibrium concentration of $PCl_5(g)$ is 0.750 mol dm^{-3}. Calculate the equilibrium constant, K_c, for the reaction at temperature T.

39.8 Calculating equilibrium constant, K_c (p.15)

Practice 39.5 (continued)

2 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Initial concentration (mol dm^{-3}) $\frac{4.00}{12.0}$ $\frac{8.00}{12.0}$ $\frac{6.00}{12.0}$

Number of moles of $PCl_5(g)$ at equilibrium = 0.750 mol dm^{-3} x 12.0 dm^3
= 9.00 mol

Number of moles of $PCl_5(g)$ produced from $PCl_3(g)$ and $Cl_2(g)$
= (9.00 – 4.00) mol
= 5.00 mol
= Number of moles of $PCl_3(g)$ / $Cl_2(g)$ consumed

Number of moles of $PCl_3(g)$ at equilibrium = (8.00 – 5.00) mol
= 3.00 mol

Number of moles of $Cl_2(g)$ at equilibrium = (6.00 – 5.00) mol
= 1.00 mol

$$K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$$

$$= \frac{\left(\frac{3.00}{12.0} \text{ mol dm}^{-3}\right)\left(\frac{1.00}{12.0} \text{ mol dm}^{-3}\right)}{0.750 \text{ mol dm}^{-3}} = 0.0278 \text{ mol dm}^{-3}$$

∴ the equilibrium constant, K_c, for the reaction at temperature T is 0.0278 mol dm^{-3}.

39.9 Using given values of equilibrium constants in calculations (p.19)

- Some calculations require you to use a given value of equilibrium constant, K_c, at a certain temperature to calculate the equilibrium concentration of one component in a system or the volume of the container.

39.9 Using given values of equilibrium constants in calculations (p.19)

Q (Example 39.4)

In an experiment, 1.00 mole of SO_2(g) and 2.00 moles of Cl_2(g) were allowed to react in a 2.00 dm^3 closed container maintained at 375 °C. The chemical equation for the reaction is shown below:

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$$

At 375 °C, the equilibrium constant, K_c, for the reaction is 12.6 dm^3 mol^{-1}. Calculate the equilibrium concentration of SO_2Cl_2(g).

39.9 Using given values of equilibrium constants in calculations (p.19)

Example 39.4 (continued)

A Suppose there was x mole(s) of $SO_2Cl_2(g)$ at equilibrium.

	$SO_2(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$SO_2Cl_2(g)$
Initial concentration (mol dm^{-3})	$\frac{1.00}{2.00}$		$\frac{2.00}{2.00}$		0
Equilibrium concentration (mol dm^{-3})	$\frac{1.00 - x}{2.00}$		$\frac{2.00 - x}{2.00}$		$\frac{x}{2.00}$

$$K_c = 12.6\ \text{dm}^3\ \text{mol}^{-1} = \frac{[SO_2Cl_2(g)]}{[SO_2(g)][Cl_2(g)]} = \frac{\frac{x}{2.00}}{\left(\frac{1.00 - x}{2.00}\right)\left(\frac{2.00 - x}{2.00}\right)}$$

$$12.6 = \frac{2.00x}{(1.00 - x)(2.00 - x)}$$

Rearranging the equation gives $12.6(1.00 - x)(2.00 - x) = 2.00x$

$$12.6x^2 - 39.8x + 25.2 = 0$$

Solving the quadratic equation gives two solutions:

$x = 0.876$ or 2.28 (rejected)

Equilibrium concentration of $SO_2Cl_2(g)$ = $\frac{0.876\ \text{mol}}{2.00\ \text{dm}^3}$

$= 0.438$ mol dm^{-3}

$\therefore$ the equilibrium concentration of $SO_2Cl_2(g)$ was 0.438 mol dm^{-3}.

39.9 Using given values of equilibrium constants in calculations (p.19)

Q (Example 39.5)

The following reversible reaction is used to make methanol in industry:

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

In an experiment, 2.00 moles of CO(g) and 3.00 moles of H_2(g) were mixed in a sealed container maintained at 230 °C. When the system attained equilibrium, 0.860 mole of CH_3OH(g) was obtained.

At 230 °C, the equilibrium constant, K_c for the reaction is 20.9 $dm^6\ mol^{-2}$. Calculate the volume of the container.

39.9 Using given values of equilibrium constants in calculations (p.19)

Q (Example 39.5) (continued)

A Suppose the volume of the container was V dm^3. According to the equation, 1 mole of CO(g) reacts with 2 moles of H_2(g) to give 1 mole of CH_3OH(g).

i.e. number of moles of CO(g) consumed = 0.860 mol

number of moles of H_2(g) consumed = 2 x 0.860 mol = 1.72 mol

	CO(g) +	2H$_2$(g) $\rightleftharpoons$	CH$_3$OH(g)
Initial concentration (mol dm^{-3})	$\frac{2.00}{V}$	$\frac{3.00}{V}$	0
Equilibrium concentration (mol dm^{-3})	$\frac{2.00-0.860}{V} = \frac{1.14}{V}$	$\frac{3.00-1.72}{V} = \frac{1.28}{V}$	$\frac{0.860}{V}$

$$K_c = 20.9\ \text{dm}^6\ \text{mol}^{-2} = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]} = \frac{\frac{0.860}{V}\ \text{mol dm}^{-3}}{(\frac{1.14}{V}\ \text{mol dm}^{-3})(\frac{1.28}{V}\ \text{mol dm}^{-3})^2}$$

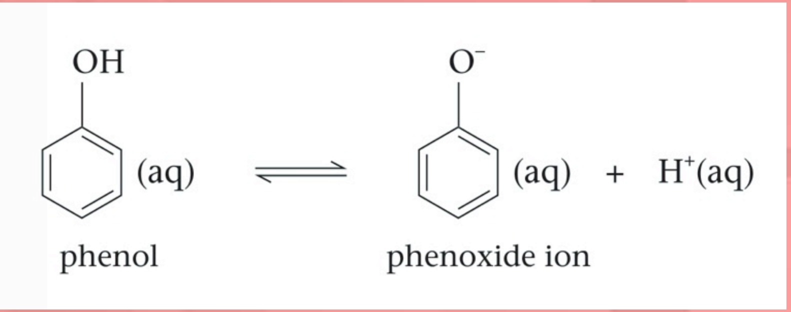
$V = 6.74$

∴ the volume of the container was 6.74 dm^3.

39.9 Using given values of equilibrium constants in calculations (p.19)

Q (Example 39.6)

Q: Phenol is a powerful disinfectant and antiseptic. The equation below shows the ionisation of phenol in water:



At 25 °C, the equilibrium constant, K_c for the ionisation is 1.05×10^{-10} mol dm^{-3}.

When the above ionisation attains equilibrium at 25 °C, the pH of the aqueous solution is 5.6. Calculate the ratio of the concentration of phenol to phenoxide ion in this solution.

39.9 Using given values of equilibrium constants in calculations (p.19)

Q (Example 39.6) (continued)

A The pH of the solution is 5.6.

i.e. $-\log[H^+(aq)] = 5.6$

$[H^+(aq)] = 2.5 \times 10^{-6}$ mol dm^{-3}

$$K_c = 1.05 \times 10^{-10} \text{ mol dm}^{-3}$$

$$= \frac{[H^+(aq)][C_6H_5O^-(aq)]}{[C_6H_5OH(aq)]} = \frac{(2.5 \times 10^{-6} \text{ mol dm}^{-3})[C_6H_5O^-(aq)]}{[C_6H_5OH(aq)]}$$

$$\frac{[C_6H_5OH(aq)]}{[C_6H_5O^-(aq)]} = \frac{2.5 \times 10^{-6} \text{ mol dm}^{-3}}{1.05 \times 10^{-10} \text{ mol dm}^{-3}}$$

$$= 23\ 800$$

∴ the ratio of the concentration of phenoxide ion in this solution is 23 800.

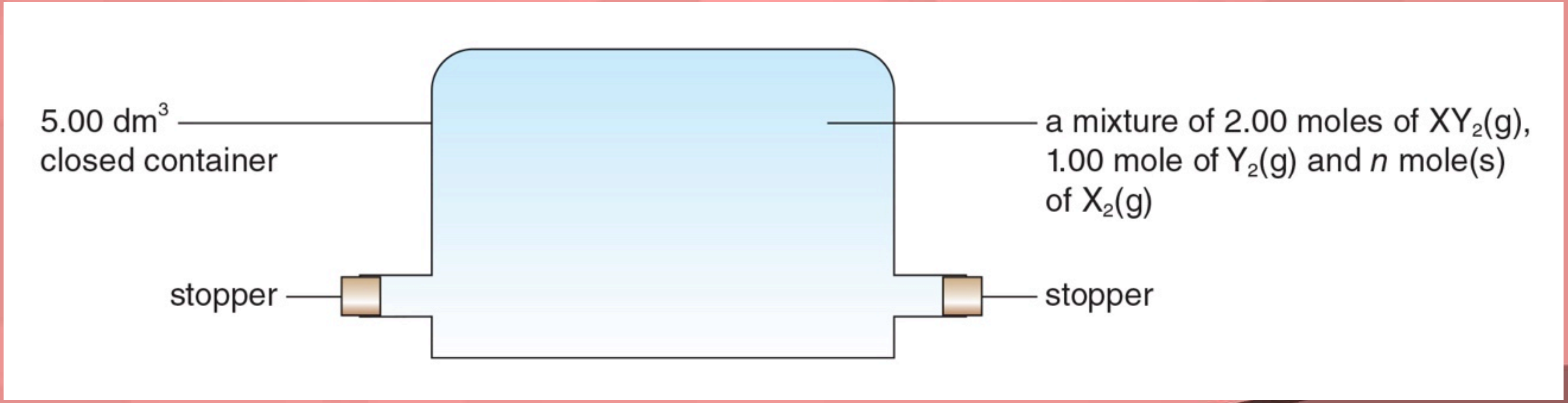
39.9 Using given values of equilibrium constants in calculations (p.19)

Practice 39.6

1 Consider the following reaction at a certain temperature:

$2XY_2(g) \rightleftharpoons X_2(g) + 2Y_2(g)$ $K_c = 8.00 \times 10^{-2}$ mol dm^{-3}

An equilibrium mixture was obtained at this temperature as shown below:



What was *n*?

39.9 Using given values of equilibrium constants in calculations (p.19)

Practice 39.6 (continued)

1

	$2XY_2(g) \rightleftharpoons$	$X_2(g)$ +	$2Y_2(g)$
Equilibrium concentration (mol dm^{-3})	$\frac{2.00}{5.00}$	$\frac{n}{5.00}$	$\frac{1.00}{5.00}$

$$K_c = 8.00 \times 10^{-2}\ \text{mol dm}^{-3} = \frac{[X_2(g)][Y_2(g)]^2}{[XY_2(g)]^2}$$

$$= \frac{\left(\frac{n}{5.00}\ \text{mol dm}^{-3}\right)\left(\frac{1.00}{5.00}\ \text{mol dm}^{-3}\right)^2}{\left(\frac{2.00}{5.00}\ \text{mol dm}^{-3}\right)^2}$$

$$= \frac{n}{(5.00)(2.00)^2}\ \text{mol dm}^{-3}$$

$$n = 1.60$$

∴ the value of n was 1.60.

39.9 Using given values of equilibrium constants in calculations (p.19)

Practice 39.6 (continued)

2 In an experiment, 1.00 mole of C_2H_4(g) and 1.50 moles of H_2O(g) were allowed to react in a closed container maintained at 573 K. The chemical equation for the reaction is shown below:

$$C_2H_4(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

When the system attained equilibrium, 0.0800 mole of CH_3CH_2OH(g) was obtained. The equilibrium constant, K_c, for the reaction is 0.115 dm^3 mol^{-1} at 573 K. Calculate the volume of the container.

39.9 Using given values of equilibrium constants in calculations (p.19)

Practice 39.6 (continued)

2 Suppose the volume of the container was V dm^3.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

	$C_2H_4(g)$	$H_2O(g)$	$CH_3CH_2OH(g)$
Initial concentration (mol dm^{-3})	$\frac{1.00}{V}$	$\frac{1.50}{V}$	0

Number of moles of $C_2H_4(g)$ / $H_2O(g)$ consumed = 0.0800 mol

Number of moles of $C_2H_4(g)$ at equilibrium = (1.00 – 0.0800) mol

= 0.920 mol

Number of moles of $H_2O(g)$ at equilibrium = (1.50 – 0.0800) mol

= 1.42 mol

$$K_c = 0.115 \text{ dm}^3 \text{ mol}^{-1} = \frac{[CH_3CH_2OH(g)]}{[C_2H_4(g)][H_2O(g)]}$$

$$= \frac{\frac{0.0800}{V} \text{ mol dm}^{-3}}{\left(\frac{0.920}{V} \text{ mol dm}^{-3}\right)\left(\frac{1.42}{V} \text{ mol dm}^{-3}\right)}$$

$V = 1.88$

∴ the volume of the container was 1.88 dm^3.

39.10 What does the value of equilibrium constant tell you? (p.22)

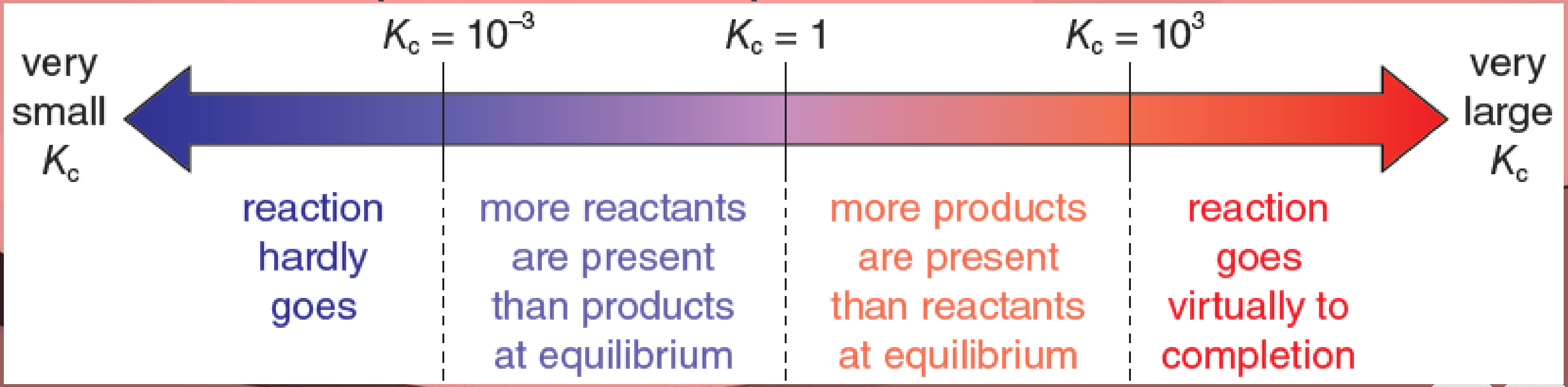
- Values of equilibrium constants vary enormously. The table below shows values of K_c for two systems at the same temperature.

	System	Value of K_c	K_c expression
I	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	801 at 25 °C	$K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$
II	$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	10^{-31} at 25 °C	$K_c = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$

- A large value of K_c for system I shows that there is a high proportion of the product compared to the reactants at equilibrium.
- A small value of K_c for system II shows that only a very small amount of the reactants have been converted into the product at equilibrium.

39.10 What does the value of equilibrium constant tell you? (p.22)

- If $K_c >> 1$, then the reaction is said to have gone almost to completion. There is an almost complete conversion of reactants to products.
- If $K_c << 1$, the reaction has hardly taken place at all. Only a small amount of the reactants has been converted to products.
- The value of equilibrium constant indicates the extent of a reaction at a particular temperature.



39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

- The same general expression for K_c can be used to predict the direction of the net reaction of a system if the expression is fed with non-equilibrium concentration values. In this case, the value calculated is known as **reaction quotient, Q_c (反應商數)**.

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

- Look at the reversible reaction between dinitrogen tetroxide and nitrogen dioxide:

$$N_2O_4(aq) \rightleftharpoons 2NO_2(g) \qquad K_c = 41.0\ \text{mol dm}^{-3} \text{ at } 500\ \text{K}$$

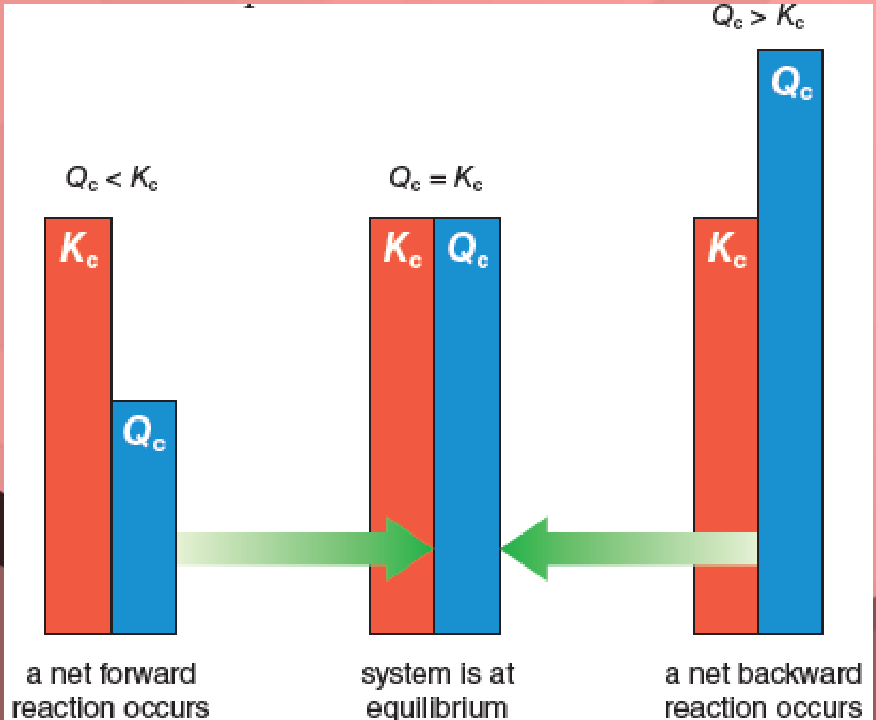
- Suppose a mixture of 2.00 moles of dinitrogen tetroxide and 6.00 moles of nitrogen dioxide is placed in a 1.00 dm^3 closed container at 500 K.

$$Q_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]} = \frac{(6.00\ \text{mol dm}^{-3})^2}{2.00\ \text{mol dm}^{-3}}$$
$$= 18.0\ \text{mol dm}^{-3}$$

- Q_c is smaller than K_c. The system is not at equilibrium.

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

- To attain equilibrium, $[NO_2(g)]$ must increase while $[N_2O_4(g)]$ must decrease.
- A net forward reaction occurs (i.e. forward reaction rate > backward reaction rate). Q_c increases until $Q_c = K_c$. Now the system has attained equilibrium.



The direction of the net reaction can be predicted by comparing the values of Q_c and K_c

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

Q (Example 39.7)

Methoxymethane (CH_3OCH_3) is used as a propellant in spray cans. It can be produced from methanol according to the equation below.

$2CH_3OH(g) \rightleftharpoons CH_3OCH_3(g) + H_2O(g)$

The equilibrium constant, K_c, for this reaction is 5.76 at 350 °C.

In an experiment, a 10.0 dm^3 closed container initially contained 1.50 moles of $CH_3OH(g)$, 4.00 moles of $CH_3OCH_3(g)$ and 5.00 moles of $H_2O(g)$ at 350 °C.

a) i) For this system under the initial conditions, calculate the reaction quotient.

ii) Predict and explain, under the initial conditions, whether the forward reaction rate or the backward reaction rate was greater.

b) Calculate the concentration of $CH_3OCH_3(g)$ when the system attained equilibrium.

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

Q (Example 39.7) (continued)

A

a) i) $$Q_c = \frac{\left(\frac{4.00}{10.0}\ \text{mol dm}^{-3}\right)\left(\frac{5.00}{10.0}\ \text{mol dm}^{-3}\right)}{\left(\frac{1.50}{10.0}\ \text{mol dm}^{-3}\right)^{2}} = 8.89$$

ii) As $Q_c > K_c$, $[CH_3OH(g)]$ must increase while $[CH_3OCH_3(g)]$ and $[H_2O(g)]$ must decrease unit $Q_c = K_c$.

A net backward reaction occurred, i.e. the backward reaction rate was greater than the forward reaction rate.

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

Q (Example 39.7) (continued)

A b) Suppose x mole(s) of $CH_3OCH_3(g)$ was(were) consumed when the system attained equilibrium.

	$2CH_3OH(g)$ $\rightleftharpoons$	$CH_3OCH_3(g)$ +	$H_2O(g)$
Equilibrium concentration ($mol\ dm^{-3}$)	$\dfrac{1.50 + 2x}{10.0}$	$\dfrac{4.00 - x}{10.0}$	$\dfrac{5.00 - x}{10.0}$

$$K_c = 5.76 = \frac{\left(\dfrac{4.00 - x}{10.0}\ mol\ dm^{-3}\right)\left(\dfrac{5.00 - x}{10.0}\ mol\ dm^{-3}\right)}{\left(\dfrac{1.50 + 2x}{10.0}\ mol\ dm^{-3}\right)^2} = \frac{(4.00 - x)(5.00 - x)}{(1.50 + 2x)^2}$$

Rearranging the equation gives $5.76(1.50 + 2x)^2 = (4.00 - x)(5.00 - x)$

$$22.04x^2 + 43.56x - 7.04 = 0$$

$$x = 0.150 \text{ or } -2.13 \text{ (rejected)}$$

Equilibrium concentration of $CH_3OCH_3(g) = \dfrac{4.00 - 0.150}{10.0}\ mol\ dm^{-3}$

$= 0.385\ mol\ dm^{-3}$

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

Practice 39.7

I_2(g) and Cl_2(g) react to form ICl(g).

$I_2(g) + Cl_2(g) \rightleftharpoons 2ICl(g)$

The equilibrium constant, K_c, for this reaction is 81.9 at a given temperature. In an experiment, 1.00 mole of I_2(g), 2.00 moles of Cl_2(g) and 3.00 moles of ICl(g) were mixed in a 5.00 dm^3 closed container maintained at the given temperature.

a) i) For this system under the initial conditions, calculate the reaction quotient.

$$Q_c = \frac{\left(\frac{3.00}{5.00}\ \text{mol dm}^{-3}\right)^2}{\left(\frac{1.00}{5.00}\ \text{mol dm}^{-3}\right)\left(\frac{2.00}{5.00}\ \text{mol dm}^{-3}\right)}$$

$$= 4.50$$

ii) Predict and explain, under the initial conditions, whether the forward reaction rate or the backward reaction rate was greater.

As $Q_c < K_c$, [ICl(g)] must increase while [I_2(g)] and [Cl_2(g)] must decrease until $Q_c = K_c$. A net forward reaction occurred, i.e. the forward reaction rate was greater than the backward reaction rate.

39.11 The relationship between equilibrium constant (K_c) and reaction quotient (Q_c) (p.23)

Practice 39.7 (continued)

b) Calculate the concentration of ICl(g) when the system attained equilibrium.

Suppose 2*x* mole(s) of ICl(g) was / were formed when the system attained equilibrium.

	$I_2(g)$ +	$Cl_2(g)$	$\rightleftharpoons$	$2ICl(g)$
Equilibrium concentration ($mol\ dm^{-3}$)	$\frac{1.00 - x}{5.00}$	$\frac{2.00 - x}{5.00}$		$\frac{3.00 + x}{5.00}$

$$K_c = 81.9 = \frac{[ICl(g)]^2}{[I_2(g)][Cl_2(g)]}$$

$$= \frac{(\frac{3.00 + 2x}{5.00}\ mol\ dm^{-3})^2}{(\frac{1.00 - x}{5.00}\ mol\ dm^{-3})(\frac{2.00 - x}{5.00}\ mol\ dm^{-3})}$$

Rearranging the equation gives

$81.9(1.00 - x)(2.00 - x) = (3.00 + 2x)^2$

$163.8 - 245.7x + 81.9x^2 = 9.00 + 12.0x + 4x^2$

$154.8 - 257.7x + 77.9x^2 = 0$

$x = 0.789$ or 2.52 (rejected)

Equilibrium concentration of ICl(g) $= \frac{3.00 + 2(0.789)}{5.00}\ mol\ dm^{-3}$

$= 0.916\ mol\ dm^{-3}$

∴ the concentration of ICl(g) at equilibrium is $0.916\ mol\ dm^{-3}$.

39.12 Determining the equilibrium constant for an esterification reaction (p.26)

- Esterification is a reversible reaction.
  $CH_3COOH(l) + (CH_3)_2CHOH(l) \rightleftharpoons CH_3COOCH(CH_3)_2(l) + H_2O(l)$
- Suppose a mixture of ethanoic acid and propan-2-ol is heated under reflux in the presence of concentrated sulphuric acid until equilibrium is attained. Both the reactants and products are present in the equilibrium mixture.
- The concentrations of ethanoic acid in the reaction mixture before and after reflux can be found by withdrawing samples and titrating with standard sodium hydroxide solution (allowing for the amount of acid catalyst added). Subsequently, the concentrations of other substances in the equilibrium mixture can be determined. The equilibrium constant for the reaction can be calculated.

Determining the equilibrium constant, K_c, for an esterification reaction *Ref.*

39.12 Determining the equilibrium constant for an esterification reaction (p.26)

Practice 39.8

An experiment, consisting of three stages, was conducted to determine the equilibrium constant, K_c, for an esterification reaction.

Stage 1 0.250 mole of ethanoic acid and 0.250 mole of propan-2-ol were mixed in a pear-shaped flask. 1.00 cm^3 of this mixture was withdrawn and added to a conical flask containing 25 cm^3 of deionised water. The contents of the conical flask were then titrated against 0.400 mol dm^{-3} sodium hydroxide solution.

Stage 2 A few drops of concentrated sulphuric acid were added to the remaining acid-alcohol mixture in the pear-shaped flask with shaking. 1.00 cm^3 of the resulting mixture was withdrawn and added to a conical flask containing 25 cm^3 of deionised water. The contents of the conical flask were immediately titrated against 0.400 mol dm^{-3} sodium hydroxide solution as in *Stage 1*.

Stage 3 Some anti-bumping granules were added to the pear-shaped flask which was then heated under reflux for two hours. After cooling, 1.00 cm^3 of the mixture was withdrawn and added to a conical flask containing 25 cm^3 of deionised water. The contents of the conical flask were immediately titrated against 0.400 mol dm^{-3} sodium hydroxide solution as in *Stage 1*.

39.12 Determining the equilibrium constant for an esterification reaction (p.26)

Practice 39.8 (continued)

The table below lists the titration results:

	Volume of 0.400 mol dm^{-3} NaOH(aq) used (cm^3)
Stage 1	27.60
Stage 2	27.70
Stage 3	12.85

a) From the titration result in *Stage 1*, calculate the concentration of ethanoic acid in the original mixture.

NaOH(aq) reacts with $CH_3COOH(l)$ according to the following equation:

$CH_3COOH(l) + NaOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$

Number of moles of NaOH = number of moles of CH_3COOH

$$0.400 \text{ mol dm}^{-3} \times \frac{27.60}{1\ 000} \text{ dm}^3 = [CH_3COOH(l)] \times \frac{1.00}{1\ 000} \text{ dm}^3$$

$$[CH_3COOH(l)] = 11.04 \text{ mol dm}^{-3}$$

$\therefore$ the concentration of $CH_3COOH(l)$ in the original mixture is 11.04 mol dm^{-3}.

39.12 Determining the equilibrium constant for an esterification reaction (p.26)

Practice 39.8 (continued)

b) From the titration results in *Stages 2* and *3*, calculate the concentration of ethanoic acid in the equilibrium mixture.

From the titration results of *Stages 1* and *2*, it can be deduced that the sulphuric acid catalyst in 1.00 cm^3 of the mixture required 0.1 cm^3 of the alkali for neutralisation.

∴ volume of NaOH(aq) required to neutralise $CH_3COOH(l)$ in 1.00 cm^3 of the mixture after reflux = (12.85 – 0.1) cm^3 = 12.75 cm^3

Number of moles of NaOH = number of moles of CH_3COOH

$$0.400 \text{ mol dm}^{-3} \times \frac{12.75}{1\,000} \text{ dm}^3 = [CH_3COOH(l)] \times \frac{1.00}{1\,000} \text{ dm}^3$$

$$[CH_3COOH(l)] = 5.10 \text{ mol dm}^{-3}$$

∴ concentration of $CH_3COOH(l)$ in the mixture after reflux is 5.10 mol dm^{-3}.

39.12 Determining the equilibrium constant for an esterification reaction (p.26)

Practice 39.8 (continued)

c) Calculate the concentrations of other chemical species in the equilibrium mixture.

Consider the equation for the esterification reaction:

$CH_3COOH(l) + (CH_3)_2CHOH(l) \rightleftharpoons CH_3COOCH(CH_3)_2(l) + H_2O(l)$

According to the equation, 1 mole of CH_3COOH reacts with 1 mole of $(CH_3)_2CHOH$ to give 1 mole of $CH_3COOCH(CH_3)_2$ and 1 mole of H_2O.

Change in concentration of $CH_3COOH(l)$
= concentration of $CH_3COOH(l)$ in mixture after reflux – concentration of $CH_3COOH(l)$ in original mixture = (5.10 – 11.04) mol dm^{-3}
= –5.94 mol dm^{-3}

Concentration of $(CH_3)_2CHOH(l)$ in mixture after reflux = 5.10 mol dm^{-3}
Concentration of $CH_3COOCH(CH_3)_2(l)$ in mixture after reflux = 5.94 mol dm^{-3}
Concentration of $H_2O(l)$ in mixture after reflux = 5.94 mol dm^{-3}

39.12 Determining the equilibrium constant for an esterification reaction (p.26)

Practice 39.8 (continued)

d) Calculate the equilibrium constant for the esterification reaction.

$$K_c = \frac{[CH_3COOCH(CH_3)_2(l)][H_2O(l)]}{[CH_3COOH(l)][(CH_3)_2CHOH(l)]}$$

$$= \frac{(5.94\ \text{mol dm}^{-3})(5.94\ \text{mol dm}^{-3})}{(5.10\ \text{mol dm}^{-3})(5.10\ \text{mol dm}^{-3})}$$

$$= 1.36$$

∴ the equilibrium constant for the esterification reaction is 1.36.

Key terms (p.28)

irreversible reaction	不可逆反應	dynamic equilibrium	動態平衡
reversible reaction	可逆反應	open system	開放體系
forward reaction	正向反應	closed system	密閉體系
backward reaction	逆向反應	equilibrium constant, K_c	平衡常數
equilibrium	平衡	reaction quotient, Q_c	反應商數

Summary (p.29)

1 a) Irreversible reactions are chemical reactions that take place in one direction only.

b) Reversible reactions are chemical reactions that take place in both the 'forward' and 'backward' directions.

2 A dynamic equilibrium is attained when the rate of the forward reaction is equal to the rate of the backward reaction.

3 Three important features define a chemical system that is in dynamic equilibrium:

- concentrations of reactants and products remain constant;
- forward and backward reactions are both happening (so 'dynamic');
- the rate of the forward reaction is equal to the rate of the backward reaction (and is NOT zero).

Summary (p.29)

4 For a reversible reaction:

$aA + bB \rightleftharpoons cC + dD$

Enter the equilibrium concentrations of the substances into the following expression to calculate the equilibrium constant, K_c:

$$K_c = \frac{[C]_{eqm}^c[D]_{eqm}^d}{[A]_{eqm}^a[B]_{eqm}^b}$$

5 Steps used to calculate the equilibrium constant, K_c, for a reaction:

1 Calculate the quantity of each substance at equilibrium using the balanced equation involved.

2 Calculate the equilibrium concentration of each substance.

3 Substitute the equilibrium concentrations into the expression for K_c and calculate K_c.

Summary (p.29)

6 For a reversible reaction:

$aA + bB \rightleftharpoons cC + dD$

Enter the concentrations of substances at any time (t) during a reaction into the following expression to calculate reaction quotient, Q_c:

$$Q_c = \frac{[C]_t^c\,[D]_t^d}{[A]_t^a\,[B]_t^b}$$

- If $Q_c < K_c$, a net forward reaction occurs to generate more products until equilibrium is attained.
- If $Q_c = K_c$, the system is at equilibrium.
- If $Q_c > K_c$, a net backward reaction occurs to generate more reactants until equilibrium is attained.

Unit Exercise (p.31)

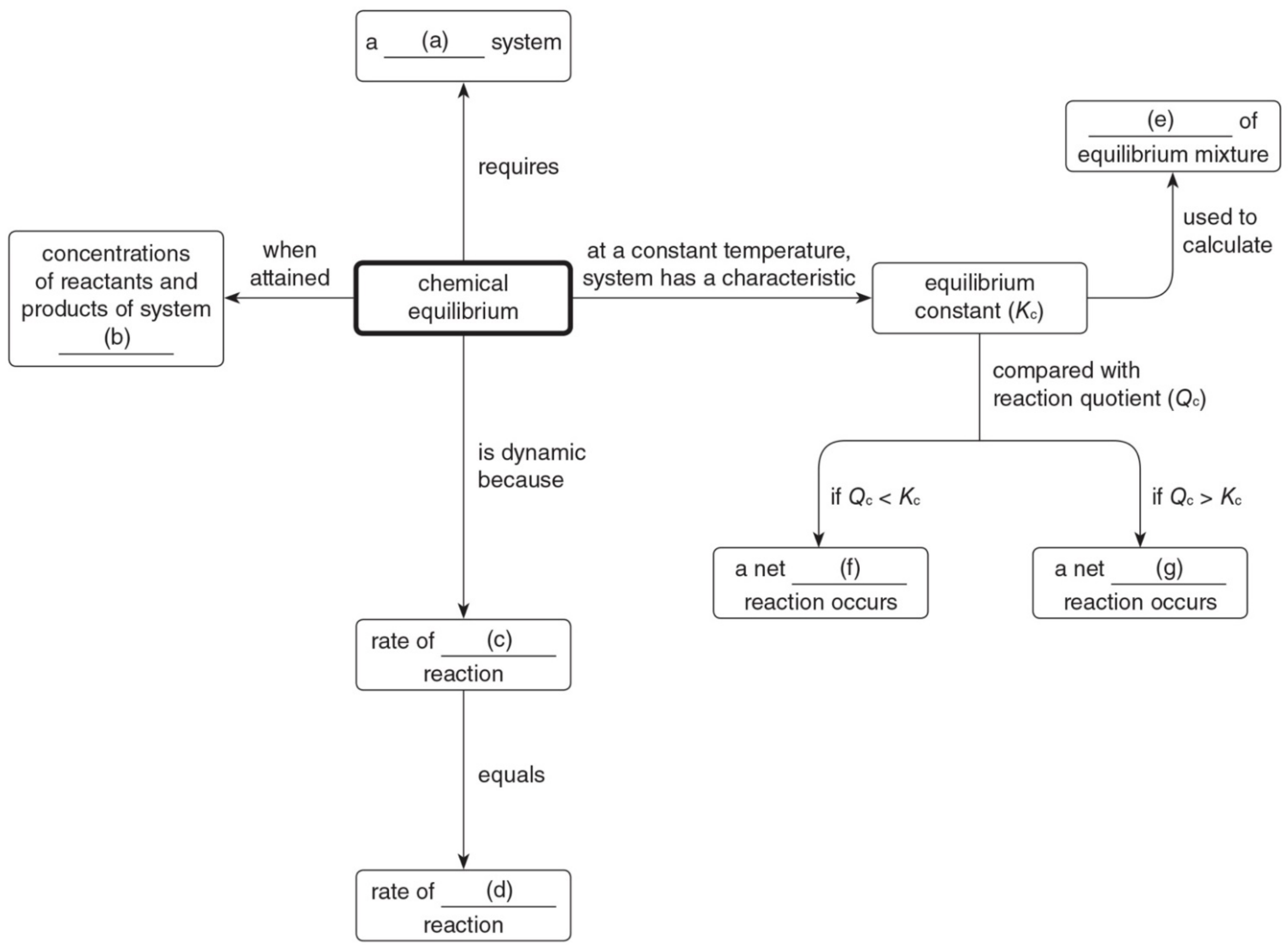
Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

question targeted at level 3 and above;
question targeted at level 4 and above;
question targeted at level 5.
‘ * ’ indicates 1 mark is given for effective communication.

Unit Exercise (p.31)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.



a) closed
b) remain constant
c) forward
d) backward
e) concentrations of chemical species
f) forward
g) backward

Unit Exercise (p.31)

PART II MULTIPLE CHOICE QUESTIONS

2 Hydrogen is manufactured from methane via the reaction below.

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

What is the K_c expression for this reaction?

A $\dfrac{[CO(g)] \times 3[H_2(g)]}{[CH_4(g)] \times [H_2O(g)]}$

B $\dfrac{[CO(g)] \times [H_2(g)]^3}{[CH_4(g)] \times [H_2O(g)]}$

C $\dfrac{[CH_4(g)] \times [H_2O(g)]}{[CO(g)] \times 3[H_2(g)]}$

D $\dfrac{[CH_4(g)] \times [H_2O(g)]}{[CO(g)] \times [H_2(g)]^3}$

Answer: B

Unit Exercise (p.31)

3 What are the units of the equilibrium constant, K_c, for the hypothetical reaction below?

$$A(aq) + 3B(aq) \rightleftharpoons 2C(aq) + D(aq)$$

A dm^3 mol^{-1}
B dm^6 mol^{-2}
C mol^2 dm^{-6}
D mol dm^{-3}

Explanation:

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

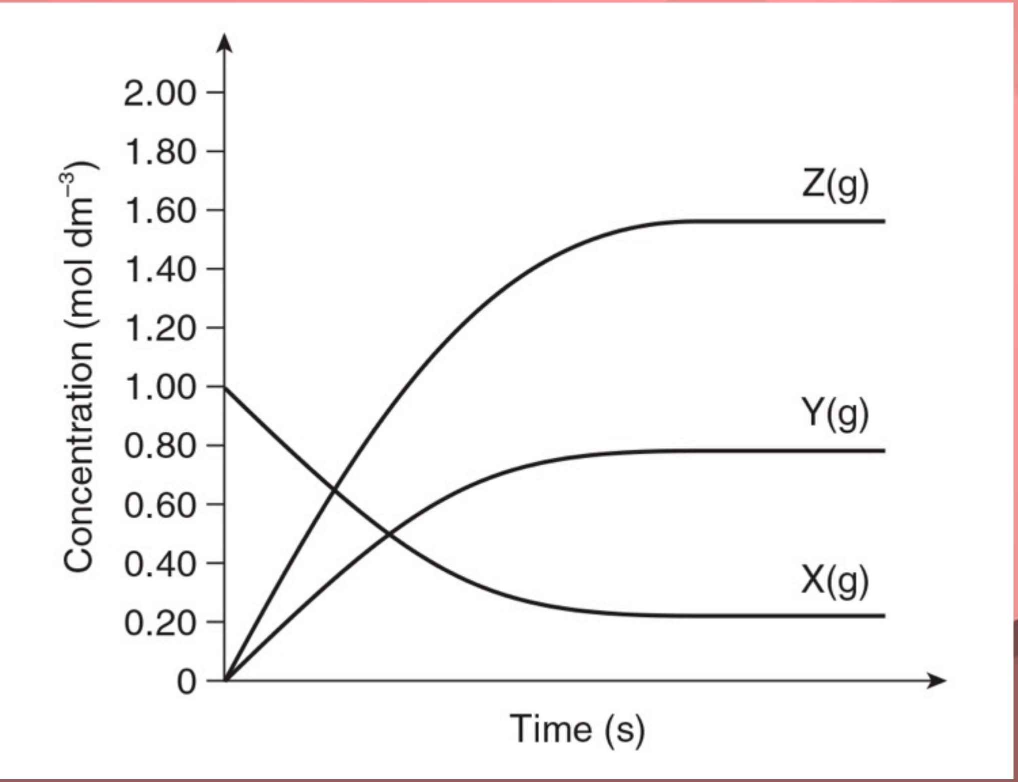
Units of K_c are given by

$$\frac{\cancel{(mol\ dm^{-3})^2}\cancel{(mol\ dm^{-3})}}{(mol\ dm^{-3})\cancel{(mol\ dm^{-3})^3}} = dm^3\ mol^{-1}$$

Answer: A

Unit Exercise (p.31)

4 X(g) decomposes reversibly to give Y(g) and Z(g). A sample of X(g) is placed in a closed container of volume 1.00 dm^3 kept at constant temperature. The graph below shows the changes in concentrations of X(g), Y(g) and Z(g) in the container with time.



Unit Exercise (p.31)

4 (continued)

What is the K_c expression for this reaction?

A $\dfrac{[X(g)]}{[Y(g)][Z(g)]}$

B $\dfrac{[X(g)]}{[Y(g)][Z(g)]^2}$

C $\dfrac{[Y(g)][Z(g)]}{[X(g)]}$

D $\dfrac{[Y(g)][Z(g)]^2}{[X(g)]}$

Explanation:

X(g) decomposes to give Y(g) and Z(g) according to the equation below.

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

$$K_c = \frac{[Y(g)][Z(g)]^2}{[X(g)]}$$

Answer: D

Unit Exercise (p.31)

5 Consider the information below:

Reaction	Equilibrium constant at temperature T
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	K_1
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	K_2
$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$	K_3

Which of the following combinations is correct?

	Relationship of K_1, K_2 and K_3	Units of K_3
A	$K_3 = K_1 \times K_2$	mol dm^{-3}
B	$K_3 = K_1 \times K_2$	dm^3 mol^{-1}
C	$K_3 = \dfrac{1}{K_1 \times K_2}$	mol dm^{-3}
D	$K_3 = \dfrac{1}{K_1 \times K_2}$	dm^3 mol^{-1}

Answer: B

Unit Exercise (p.31)

5 (continued)

Explanation:

$$K_1 = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$$

$$K_2 = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$$

$$K_3 = \frac{[NO_2(g)]^2}{[N_2(g)][O_2(g)]^2}$$

$$K_1 \times K_2 = \frac{\cancel{[NO(g)]^2}}{[N_2(g)][O_2(g)]} \times \frac{[NO_2(g)]^2}{\cancel{[NO(g)]^2}[O_2(g)]}$$

$$= \frac{[NO_2(g)]^2}{[N_2(g)][O_2(g)]^2}$$

$$= K_3$$

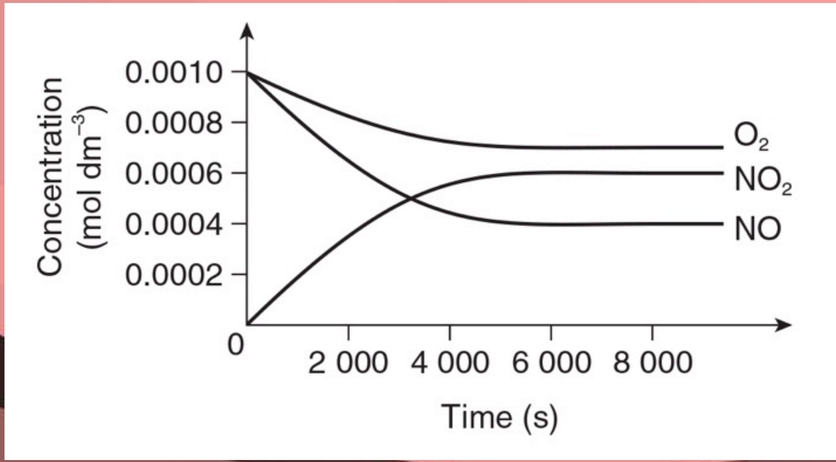
Units of K_3 are given by $\frac{\cancel{(mol\ dm^{-3})^2}}{(mol\ dm^{-3})\cancel{(mol\ dm^{-3})^2}} = dm^3\ mol^{-1}$

Unit Exercise (p.31)

6 NO(g) reacts with O_2(g) to give NO_2(g) according to the equation below.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

A mixture of NO(g) and O_2(g) was allowed to attain equilibrium at constant temperature. The graph below shows the changes in concentrations of the three gases.



Unit Exercise (p.31)

6 (continued)

What is the value of K_c for the reaction at this temperature?

A 3.11×10^{-4} dm^3 mol^{-1}

B 4.67×10^{-4} dm^3 mol^{-1}

C 2 143 dm^3 mol^{-1}

D 3 214 dm^3 mol^{-1}

Explanation:

$$K_c = \frac{[NO_2(g)]^2}{[NO(g)]^2\,[O_2(g)]}$$

$$= \frac{(0.00060 \text{ mol dm}^{-3})^2}{(0.00040 \text{ mol dm}^{-3})^2(0.00070 \text{ mol dm}^{-3})}$$

$$= 3\,214 \text{ dm}^3 \text{ mol}^{-1}$$

Answer: D

Unit Exercise (p.31)

7 This question is about the reversible reaction below.

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

A chemist investigating this reaction started with 10 moles of NO_2 and allowed the system to reach equilibrium. If 3 moles of N_2O_4 are formed, the number of moles of NO_2 at equilibrium is

A 8.5.
B 7.
C 6.
D 4.

Explanation:
Number of moles of NO_2 consumed at equilibrium
= 2 x 3 mol = 6 mol
Number of moles of NO_2 at equilibrium
= (10 – 6) mol = 4 mol

Answer: D

(Edexcel Advanced Level GCE, Unit 4, Jun. 2015, 6(a))

Unit Exercise (p.31)

8 Ammonia is manufactured by the reversible reaction between nitrogen and hydrogen.

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

At a certain temperature, the value of K_c for the above reaction is 75.0 dm6 mol^{-2}. At equilibrium, the concentrations of $N_2(g)$ and $H_2(g)$ are 0.0230 mol dm^{-3} and 0.0780 mol dm^{-3} respectively. What is the equilibrium concentration of $NH_3(g)$?

A 3.8×10^{-4} mol dm^{-3}
B 4.4×10^{-3} mol dm^{-3}
C 0.029 mol dm^{-3}
D 0.37 mol dm^{-3}

Answer: C

Unit Exercise (p.31)

8 (continued)

Explanation:

$$K_c = 75.0\ \text{dm}^6\ \text{mol}^{-2} = \frac{[NH_3(g)]^2}{[N_2(g)]\,[H_2(g)]^3}$$

$$= \frac{[NH_3(g)]^2}{(0.0230\ \text{mol dm}^{-3})(0.00780\ \text{mol dm}^{-3})^3}$$

$$[NH_3(g)]^2 = 8.19 \times 10^{-4}\ \text{mol}^2\ \text{dm}^{-6}$$

$$[NH_3(g)] = 0.029\ \text{mol dm}^{-3}$$

Unit Exercise (p.31)

9 The following equation represents an esterification reaction producing ethyl ethanoate:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

K_c = 4.0 at 25 °C

In an experiment, 0.60 mole of $CH_3COOH(l)$ and 0.60 mole of $C_2H_5OH(l)$ are placed in a 2.00 dm^3 closed container kept at 25 °C. How many moles of $CH_3COOC_2H_5(l)$ are present when the system attains equilibrium?

A 0.40 mole
B 0.30 mole
C 0.20 mole
D 0.10 mole

Answer: A

Unit Exercise (p.31)

9 (continued)

Suppose x mole(s) of $CH_3COOC_2H_5(l)$ is / are present when the system attains equilibrium.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

	$CH_3COOH(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$H_2O(l)$
Initial concentration (mol dm^{-3})	$\frac{0.60}{2.00}$	$\frac{0.60}{2.00}$		
Equilibrium concentration (mol dm^{-3})	$\frac{0.60 - x}{2.00}$	$\frac{0.60 - x}{2.00}$	$\frac{x}{2.00}$	$\frac{x}{2.00}$

$$K_c = 4.0 = \frac{[CH_3COOC_2H_5(l)]\,[H_2O(l)]}{[CH_3COOH(l)]\,[C_2H_5OH(l)]}$$

$$= \frac{\left(\frac{x}{2.00}\text{ mol dm}^{-3}\right)\left(\frac{x}{2.00}\text{ mol dm}^{-3}\right)}{\left(\frac{0.60 - x}{2.00}\text{ mol dm}^{-3}\right)\left(\frac{0.60 - x}{2.00}\text{ mol dm}^{-3}\right)}$$

$$4.0 = \frac{x^2}{(0.60 - x)^2}$$

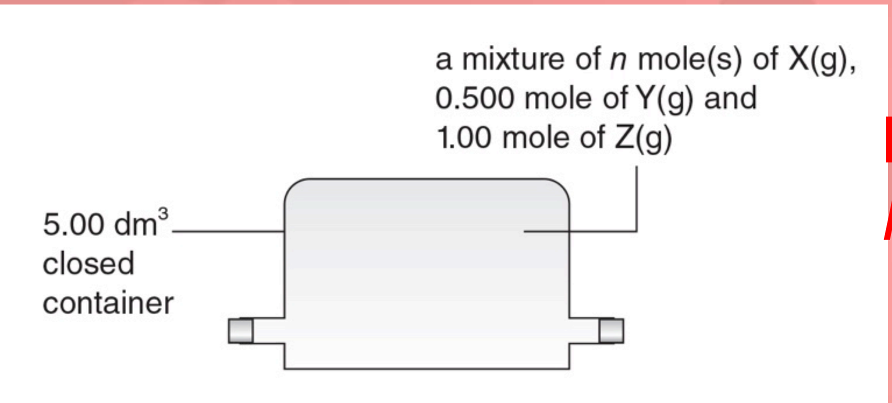
$x = 0.40$ or 1.2 (rejected)

Unit Exercise (p.31)

10 Consider the following reaction at a certain temperature:

$2X(g) \rightleftharpoons 2Y(g) + Z(g)$ $K_c = 0.0222 \text{ mol dm}^{-3}$

An equilibrium mixture was obtained at this temperature as shown below:



What is *n*?

A 1.50
B 0.950
C 0.300
D 0.190

Answer: A

Explanation:

$K_c = 0.0222 \text{ mol dm}^{-3}$

$$= \frac{[Y(g)]^2[Z(g)]}{[X(g)]^2}$$

$$= \frac{\left(\frac{0.500}{5.00} \text{ mol dm}^{-3}\right)^2 \left(\frac{1.00}{5.00} \text{ mol dm}^{-3}\right)}{\left(\frac{n}{5.00} \text{ mol dm}^{-3}\right)^2}$$

$n = 1.50$

Unit Exercise (p.31)

11 The equilibrium constant, K_c, for the reaction below is 0.200 $dm^3\ mol^{-1}$ at 873 K.

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

A mixture of 2.00 moles of CO(g), 1.00 mole of $Cl_2(g)$ and 0.500 mole of $COCl_2(g)$ is introduced into a closed container maintained at 873 K.

When the system attains equilibrium, 0.160 mole of $COCl_2(g)$ is present.

What is the volume of the container?

A 2.55 dm^3
B 2.84 dm^3
C 3.13 dm^3
D 3.92 dm^3

Answer: D

Unit Exercise (p.31)

11 (continued)

Explanation:

Suppose the volume of the container is V dm^3.

	$CO(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$
Initial concentration (mol dm^{-3})	$\frac{2.00}{V}$		$\frac{1.00}{V}$		$\frac{0.500}{V}$
Equilibrium concentration (mol dm^{-3})	$\frac{2.00+0.34}{V}$		$\frac{1.00+0.34}{V}$		$\frac{0.160}{V}$

$$K_c = 0.200 \text{ dm}^3 \text{ mol}^{-1} = \frac{[COCl_2(g)]}{[CO(g)][Cl_2(g)]}$$

$$= \frac{\frac{0.160}{V} \text{ mol dm}^{-3}}{\left(\frac{2.34}{V} \text{ mol dm}^{-3}\right)\left(\frac{1.34}{V} \text{ mol dm}^{-3}\right)}$$

$$V = 3.92$$

$\therefore$ the volume of the container is 3.92 dm^3.

Unit Exercise (p.31)

12 The value of K_c for the reaction below is 46.4 at 458 °C.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What is the value of K_c for the reaction below at the same temperature?

$$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$$

A 0.147
B 0.215
C 2.61
D 6.81

Answer: A

Unit Exercise (p.31)

12 (continued)

Explanation:

$$K_c = 46.4 = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(aq) \rightleftharpoons HI(g)$$

$$K_c \text{ for the above reaction} = \frac{[HI(g)]}{[H_2(g)]^{\frac{1}{2}}[I_2(g)]^{\frac{1}{2}}}$$

$$= \sqrt{46.4}$$

$$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(aq)$$

$$K_c \text{ for the above reaction} = \frac{[H_2(g)]^{\frac{1}{2}}[I_2(g)]^{\frac{1}{2}}}{[HI(g)]}$$

$$= \frac{1}{\sqrt{46.4}}$$

$$= 0.147$$

Unit Exercise (p.31)

13 NO_2(g) is involved in the formation of smog and acid rain. The reaction below is important in the formation of NO_2(g):

$$O_3(g) + NO(g) \rightleftharpoons O_2(g) + NO_2(g) \qquad K_c = 6.0 \times 10^{34}$$

A sample of air contained 1.0×10^{-6} mol dm^{-3} O_3(g), 1.0×10^{-5} mol dm^{-3} NO(g), 2.5×10^{-4} mol dm^{-3} NO_2(g) and 8.2×10^{-3} mol dm^{-3} O_2(g).

Which of the following statements is correct?

Answer: B

A There is a tendency to form more NO(g) and O_3(g).

B There is a tendency to form more NO_2(g) and O_2(g).

C There is a tendency to form more NO_2(g) and O_3(g).

D There is no tendency to change because the system is at equilibrium.

Unit Exercise (p.31)

13 (continued)

Explanation:

$$Q_c = \frac{[O_2(g)]\,[NO_2(g)]}{[O_3(g)]\,[NO(g)]}$$

$$= \frac{(8.2 \times 10^{-3}\ \text{mol dm}^{-3})(2.5 \times 10^{-4}\ \text{mol dm}^{-3})}{(1.0 \times 10^{-6}\ \text{mol dm}^{-3})(1.0 \times 10^{-5}\ \text{mol dm}^{-3})}$$

$$= 2.05 \times 10^{5}$$

As $Q_c < K_c$, $[O_2(g)]$ and $[NO_2(g)]$ must increase while $[O_3(g)]$ and $[NO(g)]$ must decrease until $Q_c = K_c$. There is a tendency to form more $O_2(g)$ and $NO_2(g)$.

Unit Exercise (p.31)

14 The equilibrium constant K_c for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 70 °C is 0.13 mol dm^{-3}. In a 5.0 dm^3 closed container kept at 70 °C, there is a mixture of 0.20 mol of $N_2O_4(g)$ and 0.30 mol of $NO_2(g)$ at a certain moment. Which of the following combinations is correct at that moment?

	Reaction quotient Q_c (mol dm^{-3})	Rate of the reaction
A	0.09	backward > forward
B	0.09	forward > backward
C	0.45	backward > forward
D	0.45	forward > backward

(HKDSE, Paper 1A, 2018, 29)

Answer: B

Unit Exercise (p.31)

15 Which of the following statements must be true for a chemical equilibrium system?

(1) The forward and backward reactions both continue.
(2) The rates of the forward and backward reactions are equal.
(3) The concentrations of reactants and products are equal.

A (1) and (2) only
B (1) and (3) only
C (2) and (3) only
D (1), (2) and (3)

Answer: A

Unit Exercise (p.31)

16 Consider the following equilibrium system:

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

Which of the following statements are INCORRECT?

(1) $[CrO_4^{2-}(aq)]$ must be equal to $[Cr_2O_7^{2-}(aq)]$.

(2) Both the forward reaction and the backward reaction have stopped.

(3) The number of moles of $CrO_4^{2-}(aq)$ must be double the number of moles of $Cr_2O_7^{2-}(aq)$.

A (1) and (2) only

B (1) and (3) only

C (2) and (3) only

D (1), (2) and (3)

Answer: D

(HKDSE, Paper 1A, 2017, 34)

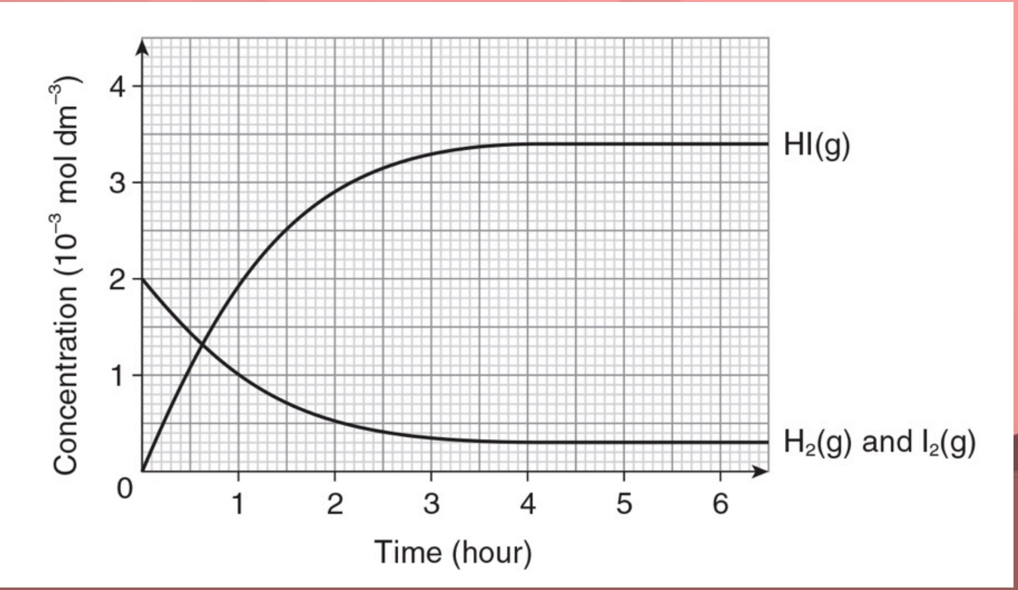
Unit Exercise (p.31)

PART III STRUCTURED QUESTIONS

17 The reaction between hydrogen and iodine is a reversible reaction.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

The graph below shows the changes in concentrations when 2.0×10^{-3} mole of $H_2(g)$ was mixed with 2.0×10^{-3} mole of $I_2(g)$ in a closed container of volume 1.00 dm^3 and left to attain dynamic equilibrium at temperature T.



Unit Exercise (p.31)

17 (continued)

a) What is meant by the term 'dynamic equilibrium'?

At dynamic equilibrium, the rate of forward reaction is equal to the rate of backward reaction, and not equals to zero. (1)

b) Use the graph to determine the equilibrium concentrations of HI(g), H_2(g) and I_2(g).

Concentration of HI(g) = 3.4×10^{-3} mol dm^{-3}
Concentration of H_2(g) / I_2(g) = 0.30×10^{-3} mol dm^{-3}
(1)

Unit Exercise (p.31)

17 (continued)

c) Calculate the equilibrium constant, K_c, for this reaction at temperature T.

$$K_c = \frac{[HI(g)]^2}{[H_2(g)]\,[I_2(g)]}$$

$$= \frac{(3.4 \times 10^{-3}\ \text{mol dm}^{-3})}{(0.30 \times 10^{-3}\ \text{mol dm}^{-3})\ (0.30 \times 10^{-3}\ \text{mol dm}^{-3})}\ (1)$$

$$= 128\ (1)$$

∴ the equilibrium constant, K_c, for this reaction is 128.

Unit Exercise (p.31)

18 A chemist carried out an investigation on the chemical equilibrium system shown below.

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

A mixture of 0.100 mol dm^{-3} NO(g), 0.0500 mol dm^{-3} H_2(g) and 0.100 mol dm^{-3} H_2O(g) was allowed to attain equilibrium at a certain temperature. The equilibrium concentration of NO(g) was found to be 0.0620 mol dm^{-3}.

Determine the value of equilibrium constant, K_c, at this temperature.

Unit Exercise (p.31)

18 (continued)

Concentration decrease of NO(g) = (0.100 – 0.0620) mol dm^{-3}
= 0.0380 mol dm^{-3}
= concentration decrease of H_2(g)

Concentration increase of N_2(g) = $\dfrac{0.0380}{2}$ mol dm^{-3} = 0.0190 mol dm^{-3}

Concentration increase of H_2O(g) = 0.0380 mol dm^{-3}

	2NO(g) +	2H_2(g) ⇌	N_2(g) +	2H_2O(g)
Equilibrium concentration (mol dm^{-3})	0.0620	0.0500 – 0.0380 = 0.0120	0.0190	0.100 + 0.0380 = 0.138 (1)

$$K_c = \frac{[N_2(g)]\,[H_2O(g)]^2}{[NO(g)]^2\,[H_2(g)]^2}$$

$$= \frac{(0.0190 \text{ mol dm}^{-3})(0.138 \text{ mol dm}^{-3})^2}{(0.0620 \text{ mol dm}^{-3})^2(0.0120 \text{ mol dm}^{-3})^2} \quad (1)$$

$= 654$ dm^3 mol^{-1} (1)

∴ the equilibrium constant, K_c, is 654 dm^3 mol^{-1}.

Unit Exercise (p.31)

19 Ethene reacts with steam in the presence of an acid catalyst to form ethanol.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

A mixture of 5.00 moles of $C_2H_4(g)$ and 5.60 moles of $H_2O(g)$ was introduced into a 2.00 dm^3 closed container kept at 573 K. At equilibrium, 20.8% of the $C_2H_4(g)$ had reacted.

Calculate the equilibrium constant, K_c, for this reaction.

Unit Exercise (p.31)

19 (continued)

Number of moles of $C_2H_4(g)$ consumed = 5.00 x 20.8% mol
= 1.04 mol
= number of moles of $H_2O(g)$ consumed

Number of moles of $CH_3CH_2OH(g)$ formed = 1.04 mol

	$C_2H_4(g)$ +	$H_2O(g)$ $\rightleftharpoons$	$CH_3CH_2OH(g)$
Initial concentration (mol dm^{-3})	$\frac{5.00}{2.00}$	$\frac{5.60}{2.00}$	0
Equilibrium concentration (mol dm^{-3})	$\frac{5.00 - 1.04}{2.00}$ = 1.98	$\frac{5.60 - 1.04}{2.00}$ = 2.28	$\frac{1.04}{2.00}$ = 0.520 (1)

$$K_c = \frac{[CH_3CH_2OH(g)]}{[C_2H_4(g)]\,[H_2O(g)]}$$

$$= \frac{0.520 \text{ mol dm}^{-3}}{(1.98 \text{ mol dm}^{-3})\,(2.28 \text{ mol dm}^{-3})} \quad (1)$$

$$= 0.115 \text{ dm}^3 \text{ mol}^{-1} \quad (1)$$

∴ the equilibrium constant, K_c, for this reaction is 0.115 dm^3 mol^{-1}.

Unit Exercise (p.31)

20 The air pollutant NO(g) is produced in car engines because of the high temperature reaction between N_2(g) and O_2(g).

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 1.7 \times 10^{-3}$ at 2 300 K

The initial concentrations of both N_2(g) and O_2(g) were 1.40 mol dm^{-3}. What was the concentration of NO(g) at equilibrium?

Unit Exercise (p.31)

20 (continued)

Suppose the concentration of NO(g) at equilibrium is x mol dm^{-3}.

	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2NO(g)$
Initial concentration (mol dm^{-3})	1.40		1.40		0
Equilibrium concentration (mol dm^{-3})	$1.40 - \frac{x}{2}$		$1.40 - \frac{x}{2}$		x (1)

$$K_c = 1.7 \times 10^{-3} = \frac{(x \text{ mol dm}^{-3})^2}{(1.4 - \frac{x}{2}) \text{ mol dm}^{-3} (1.4 - \frac{x}{2}) \text{mol dm}^{-3}}$$

$$1.7 \times 10^{-3} = \frac{x^2}{\left(1.4 - \frac{x}{2}\right)^2} \quad (1)$$

$$x = 0.0566 \text{ or } -0.0590 \text{ (rejected) (1)}$$

$\therefore$ the concentration of NO(g) at equilibrium is 0.0566 mol dm^{-3}.

Unit Exercise (p.31)

21 In a study on the production of hydrogen from methane, methane and steam were allowed to attain equilibrium in a closed container of volume 0.320 dm^3 at 1 200 K.

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

$K_c = 0.260\ mol^2\ dm^{-6}$ at 1 200 K

At equilibrium, the container contained 0.260 mole of CO(g), 0.0910 mole of $H_2(g)$ and 0.0410 mole of $CH_4(g)$. What was the equilibrium concentration of $H_2O(g)$?

Unit Exercise (p.31)

21 (continued)

	$CH_4(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO(g)$	+	$3H_2(g)$
Equilibrium concentration ($mol\ dm^{-3}$)	$\frac{0.0410}{0.320}$				$\frac{0.260}{0.320}$		$\frac{0.0910}{0.320}$

$$K_c = 0.260\ mol^2\ dm^{-6} = \frac{[CO(g)]\,[H_2(g)]^3}{[CH_4(g)]\,[H_2O(g)]} \quad (1)$$

$$[H_2O(g)] = \frac{[CO(g)]\,[H_2(g)]^3}{0.260\,[CH_4(g)]}\ mol\ dm^{-3}$$

$$= \frac{\left(\frac{0.260}{0.320}\right)\left(\frac{0.0910}{0.320}\right)^3}{0.260\left(\frac{0.0410}{0.320}\right)}\ mol\ dm^{-3} \quad (1)$$

$$= 0.561\ mol\ dm^{-3} \quad (1)$$

∴ the equilibrium concentration of $H_2O(g)$ was 0.561 $mol\ dm^{-3}$.

Unit Exercise (p.31)

22 Solutions P(aq) and Q(aq) react to give an orange solution R(aq) according to the chemical equation below.

$$P(aq) + 2Q(aq) \rightleftharpoons 2R(aq)$$

A student mixed 50.0 cm^3 of 0.100 mol dm^{-3} P(aq) and 50.0 cm^3 of 0.100 mol dm^{-3} Q(aq) at room temperature and shook the mixture.

After 30 seconds, there was no further change in colour. The concentration of R(aq) at equilibrium was 0.0220 mol dm^{-3}.

a) What were the initial concentrations of P(aq) and Q(aq) after mixing?

Initial concentration of P(aq) / Q(aq) after mixing $= \dfrac{0.100}{2}$ mol dm^{-3}

$= 0.0500$ mol dm^{-3} (1)

Unit Exercise (p.31)

22 (continued)

b) What were the equilibrium concentrations of P(aq) and Q(aq)?

Concentration decrease of P(aq) = $\frac{0.0220}{2}$ mol dm^{-3}

= 0.0110 mol dm^{-3}

Concentration decrease of Q(aq) = 0.0220 mol dm^{-3}

Equilibrium concentration of P(aq) = (0.0500 – 0.0110) mol dm^{-3}
= 0.0390 mol dm^{-3}

Equilibrium concentration of Q(aq) = (0.0500 – 0.0220) mol dm^{-3}
= 0.0280 mol dm^{-3}

(1)

Unit Exercise (p.31)

22 (continued)

c) Calculate the equilibrium constant, K_c, for this reaction at room temperature.

$$K_c = \frac{[R(aq)]^2}{[P(aq)]\,[Q(aq)]^2}$$

$$= \frac{(0.0220 \text{ mol dm}^{-3})^2}{(0.0390 \text{ mol dm}^{-3})\,(0.0280 \text{ mol dm}^{-3})^2} \quad (1)$$

$$= 15.8 \text{ dm}^3 \text{ mol}^{-1} \quad (1)$$

d) On the grid below, draw a graph to show how the concentration of R(aq) changed from the time of initial mixing until 60 seconds had elapsed.

Curve starts at the origin.
Then flattens at 30 s at 0.0220 mol dm^{-3}. (1)

Unit Exercise (p.31)

23 Methanol can be produced by the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

K_c = 10.5 dm^6 mol^{-2} at 500 K

In an experiment, 2.00 moles of CO(g) and 4.00 moles of H_2(g) are allowed to react in a closed container maintained at 500 K. When the system attains equilibrium, 1.61 moles of CH_3OH(g) are obtained.

Calculate the volume of the container.

Unit Exercise (p.31)

23 (continued)

Number of moles of CO(g) consumed at equilibrium = 1.61 mol

Number of moles of H_2(g) consumed at equilibrium = 2 x 1.61 mol
= 3.22 mol

Suppose the volume of the container is V dm^3.

	CO(g)	+	$2H_2$(g)	$\rightleftharpoons$	CH_3OH(g)
Equilibrium concentration (mol dm^{-3})	$\frac{2.00 - 1.61}{V}$		$\frac{4.00 - 3.22}{V}$		$\frac{1.61}{V}$
	$= \frac{0.39}{V}$		$= \frac{0.78}{V}$		(1)

$$K_c = 10.5 \text{ dm}^6 \text{ mol}^{-2} = \frac{[CH_3OH(g)]}{[CO(g)]\,[H_2(g)]^2}$$

$$= \frac{\frac{1.60}{V} \text{ mol dm}^{-3}}{\left(\frac{0.39}{V} \text{ mol dm}^{-3}\right)\left(\frac{0.78}{V} \text{ mol dm}^{-3}\right)^2} \quad (1)$$

$V = 1.24$ (1)

∴ the volume of the container is 1.24 dm^3.

Unit Exercise (p.31)

24 In an experiment, 2.00 moles of NO(g) and 2.00 moles of Cl_2(g) were allowed to react in a closed container maintained at 230 °C. The chemical equation for the reaction is shown below:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

When the reaction system attained equilibrium, 1.60 moles of NOCl(g) were obtained.

At 230 °C, the equilibrium constant, K_c, for the reaction is 221 $dm^3\ mol^{-1}$. Calculate the volume of the container.

Unit Exercise (p.31)

24 (continued)

Number of moles of NO(g) consumed = 1.60 mol

Number of moles of Cl_2(g) consumed = $\frac{1.60}{2}$ mol

= 0.800 mol

Suppose the volume of the container is V dm^3.

	2NO(g) +	Cl_2(g) $\rightleftharpoons$	2NOCl(g)
Equilibrium concentration (mol dm^{-3})	$\frac{2.00 - 1.60}{V}$	$\frac{2.00 - 0.800}{V}$	$\frac{1.60}{V}$
	$= \frac{0.40}{V}$	$= \frac{1.20}{V}$	(1)

$$K_c = 221 \text{ dm}^3 \text{ mol}^{-1} = \frac{[\text{NOCl(g)}]^2}{[\text{NO(g)}]^2\,[\text{Cl}_2\text{(g)}]}$$

$$= \frac{\left(\frac{1.60}{V} \text{ mol dm}^{-3}\right)^2}{\left(\frac{0.40}{V} \text{ mol dm}^{-3}\right)^2 \left(\frac{1.20}{V} \text{ mol dm}^{-3}\right)} \quad (1)$$

$V = 16.6$ (1)

∴ the volume of the container is 16.6 dm^3.

Unit Exercise (p.31)

25 At 74 °C, the equilibrium constant, K_c, for the reaction below is 220 $dm^3\ mol^{-1}$.

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

A 10.0 dm^3 sealed container, which is maintained at 74 °C, initially contains 1.20 moles of CO(g), 1.00 mole of $Cl_2(g)$ and 1.50 moles of $COCl_2(g)$.

a) For this system under the initial conditions, calculate the reaction quotient.

$$Q_c = \frac{\frac{1.50}{10.0}\ \text{mol dm}^{-3}}{\left(\frac{1.20}{10.0}\ \text{mol dm}^{-3}\right)\left(\frac{1.00}{10.0}\ \text{mol dm}^{-3}\right)}$$

$$= 12.5\ dm^3\ mol^{-1} \qquad (1)$$

Unit Exercise (p.31)

25 (continued)

b) Predict and explain, under the initial conditions, whether the forward reaction rate or the backward reaction rate is greater.

As $Q_c < K_c$, [$COCl_2$(g)] must increase while [CO(g)] and [Cl_2(g)] must decrease until $Q_c = K_c$.
A net forward reaction occurs, i.e. the forward reaction rate is greater than the backward reaction rate. (1)

Unit Exercise (p.31)

25 (continued)

c) Calculate the concentration of $COCl_2(g)$ when the system attains equilibrium.

Suppose x mole of $COCl_2(g)$ is formed when the system attains equilibrium.

	$CO(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$
Equilibrium concentration (mol dm^{-3})	$\frac{1.20 - x}{10.0}$		$\frac{1.00 - x}{10.0}$		$\frac{1.50 + x}{10.0}$

$$K_c = 220 \text{ dm}^3 \text{ mol}^{-1} = \frac{\frac{1.50 + x}{10.0} \text{ mol dm}^{-3}}{\left(\frac{1.20 - x}{10.0} \text{ mol dm}^{-3}\right)\left(\frac{1.00 - x}{10.0} \text{ mol dm}^{-3}\right)}$$

Rearranging the equation gives

$$220(1.20 - x)(1.00 - x) = 10.0(1.50 + x)$$
$$26.4 - 48.4x + 22x^2 = 1.50 + x$$
$$22x^2 - 49.4x + 24.9 = 0$$
$$x = 0.764 \text{ or } 1.48 \text{ (rejected) (1)}$$

Equilibrium concentration of $COCl_2(g)$ = $\frac{1.50 + 0.764}{10.0}$ mol dm^{-3}

= 0.226 mol dm^{-3} (1)

Unit Exercise (p.31)

26 Consider the reaction between $H_2(g)$ and $I_2(g)$ at 430 °C.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The equilibrium constant for this reaction is 54.0 at 430 °C. 0.200 mole of $H_2(g)$, 0.240 mole of $I_2(g)$ and 1.80 moles of HI(g) were mixed in a 2.00 dm^3 closed container maintained at 430 °C.

a) i) For this system under the initial conditions, calculate the reaction quotient.

$$Q_c = \frac{[HI(g)]^2}{[H_2(g)]\,[I_2(g)]}$$

$$= \frac{\left(\frac{1.80}{2.00}\ \text{mol dm}^{-3}\right)^2}{\left(\frac{0.200}{2.00}\ \text{mol dm}^{-3}\right)\left(\frac{0.240}{2.00}\ \text{mol dm}^{-3}\right)}$$

$$= 67.5 \quad (1)$$

Unit Exercise (p.31)

26 (Continued)

a) ii) Predict and explain, under the initial conditions, whether the forward reaction rate or the backward reaction rate was greater.

As $Q_c > K_c$, [H_2(g)] and [I_2(g)] must increase while [HI(g)] must decrease until $Q_c = K_c$.
A net backward reaction occurs, i.e. the backward reaction rate was greater than the forward reaction rate. (1)

Unit Exercise (p.31)

26 (Continued)

b) Calculate the concentration of HI(g) when the system attained equilibrium.

Suppose 2*x* mole of HI(g) was consumed when the system attained equilibrium.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Equilibrium concentration (mol dm^{-3})	$\frac{0.200 + x}{2.00}$	$\frac{0.240 + x}{2.00}$	$\frac{1.80 - 2x}{2.00}$

$$K_c = 54.0 = \frac{\left(\frac{1.80 - 2x}{2.00}\ \text{mol dm}^{-3}\right)^2}{\left(\frac{0.200 + x}{2.00}\ \text{mol dm}^{-3}\right)\left(\frac{0.240 + x}{2.00}\ \text{mol dm}^{-3}\right)}$$

$$= \frac{(1.80 - 2x)^2}{(0.200 + x)(0.240 + x)}$$

Rearranging the equation gives

$54.0(0.200 + x)(0.240 + x) = (1.80 - 2x)^2$

$2.592 + 23.76x + 54x^2 = 3.24 - 7.2x + 4x^2$

$50x^2 + 30.96x - 0.648 = 0$

$x = 0.0203$ or -0.639(rejected) (1)

Equilibrium concentration of HI(g) $= \frac{1.80 - 2(0.0203)}{2.00}$ mol dm^{-3}

$= 0.880$ mol dm^{-3}

Unit Exercise (p.31)

27 This question is about an experiment to determine the equilibrium constant, K_c, for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water.

Two sealed test tubes were prepared.

The first test tube contained 0.0400 mole ethanoic acid, 0.0400 mole of ethanol and 0.20 cm^3 of concentrated hydrochloric acid.

The second test tube contained 0.0400 mole ethyl ethanoate, 0.0400 mole of water and 0.20 cm^3 of concentrated hydrochloric acid.

Unit Exercise (p.31)

27 (Continued)

After standing at 25 °C for two weeks, to ensure equilibrium is reached, the contents of each test tube were separately titrated with 0.200 mol dm^{-3} sodium hydroxide solution.

0.20 cm^3 of concentrated hydrochloric acid was also titrated with the same sodium hydroxide solution.

a) Suggest a reason why the test tubes were sealed.

Any one of the following:

- To prevent evaporation / vapour escaping / water vapour entering. (1)
- To maintain a closed system. (1)

Unit Exercise (p.31)

27 (Continued)

b) In this experiment, the following titres were obtained.

Titration	Volume of 0.200 mol dm^{-3} sodium hydroxide solution (cm^3)
Contents of first test tube	77.10
Contents of second test tube	77.05
0.20 cm^3 concentrated hydrochloric acid	11.70

i) Write the equation for the reaction between ethanoic acid and ethanol to form ethyl ethanoate and water, using structural formulae.

$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ (1)

Unit Exercise (p.31)

27 (Continued)

b) ii) Calculate the number of moles of ethanoic acid present at equilibrium in the first test tube.

Volume of alkali reacting with ethanoic acid = $(77.10 - 11.70)\ cm^3$
$= 65.40\ cm^3$

Number of moles of NaOH = $0.200\ mol\ dm^{-3} \times \frac{65.40}{1\ 000}\ dm^3$
$= 0.0131$ mol
= number of moles of ethanoic acid (1)

iii) Deduce the number of moles of ethanol present at equilibrium in the first test tube.

Number of moles of ethanol = 0.0131 mol (1)

iv) Calculate the number of moles of ethyl ethanoate formed at equilibrium in the first test tube.

Number of moles of ethyl ethanoate = $(0.0400 - 0.0131)$ mol
$= 0.0269$ mol (1)

Unit Exercise (p.31)

27 (Continued)

b) v) Write an expression for the equilibrium constant, K_c, for the reaction.
Assuming the number of moles of water and ethyl ethanoate present at equilibrium are the same, calculate the equilibrium constant, K_c.

$$K_c = \frac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$$

$$= \frac{(0.0269 \text{ mol dm}^{-3})(0.0269 \text{ mol dm}^{-3})}{(0.0131 \text{ mol dm}^{-3})(0.0131 \text{ mol dm}^{-3})} \quad (1)$$

$$= 4.22 \quad (1)$$

vi) Explain why the equilibrium constant for this reaction has no units.

Units of K_c are given by

$$\frac{\cancel{(\text{mol dm}^{-3})}\cancel{(\text{mol dm}^{-3})}}{\cancel{(\text{mol dm}^{-3})}\cancel{(\text{mol dm}^{-3})}} \quad (1)$$

$\therefore$ no units

Unit Exercise (p.31)

27 (Continued)

c) i) What is the type of reaction that took place in each test tube?

First test tube = esterification (1)

Second test tube = hydrolysis (1)

ii) Comment on the value of the titre for the equilibrium mixture in the second test tube compared to the first test tube.

What characteristic feature of equilibrium reactions is demonstrated by the values of these titres?

The values are the same within experimental error. / The values are concordant. (1)

Equilibrium can be attained from either direction of a reaction. (1)

iii) State the role of the concentrated hydrochloric acid in the equilibrium reaction.

Acid catalyst (1)

(Edexcel Advanced Level GCE, Unit 4, Jun. 2014, 12)