Mastering Chemistry

- Book 4B
- Topic 11 Chemical Equilibrium

Content

Continued on next page

Content

40.1 Position of equilibrium (p.39)

- The '**position of equilibrium (平衡位置)**' refers to the proportion of products to reactants at equilibrium.
- Some reactions go almost to completion, for example:

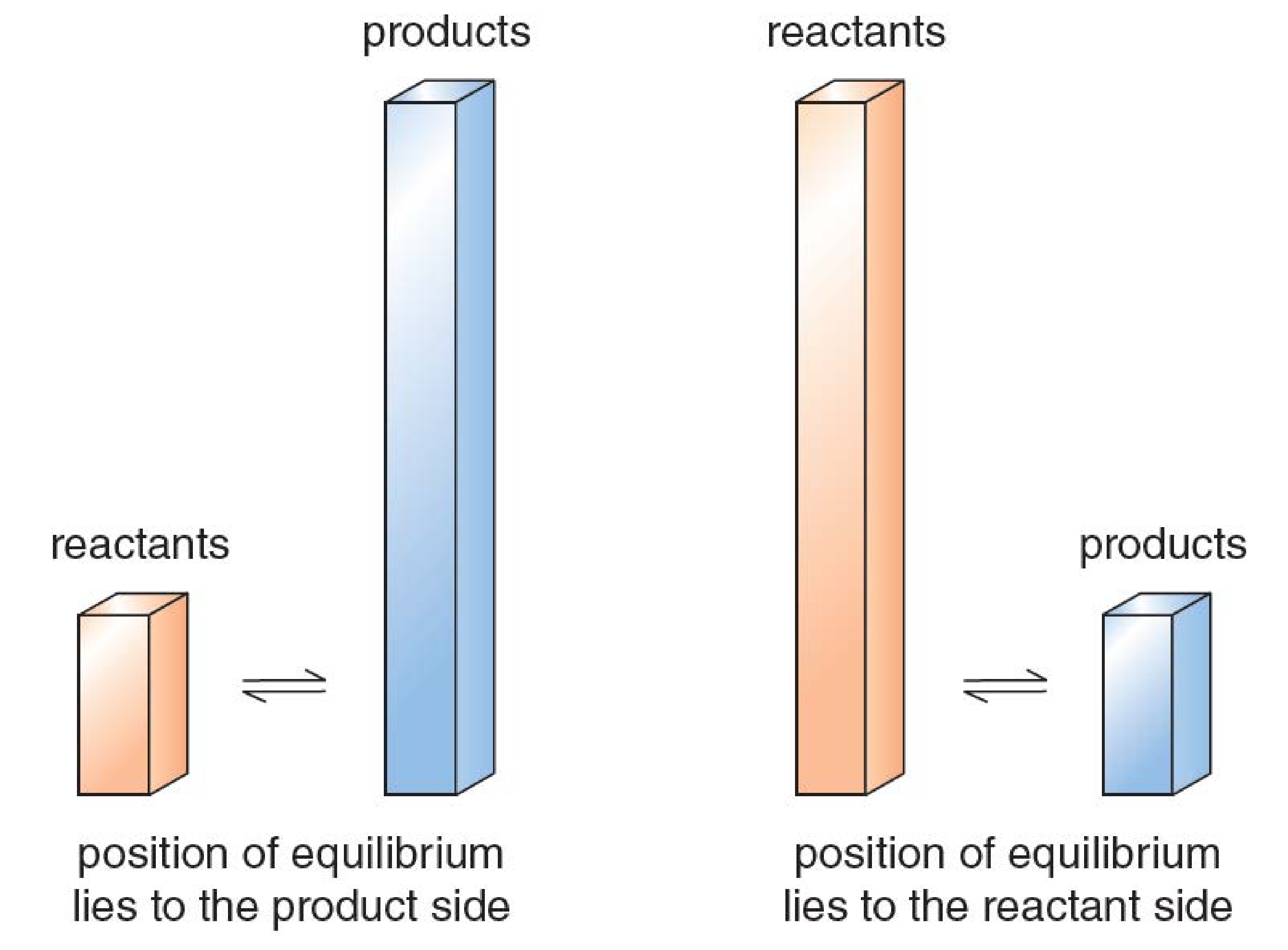
  $$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

  At 427 °C, the position of equilibrium lies a long way to the product side. There is a large amount of N_2(g) and O_2(g) and not very much NO(g) at equilibrium.
- Hydrogen chloride decomposes according to the following equation:

  $$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

  At 27 °C, the position of equilibrium lies a long way to the reactant side. There is a large amount of HCl(g) and not very much H_2(g) and Cl_2(g) at equilibrium.

40.1 Position of equilibrium (p.39)



The position of equilibrium refers to the proportion of products to reactants at equilibrium

40.2 Shifting the position of equilibrium by changing conditions (p.40)

- It is possible to change the amount of products in an equilibrium mixture. This can be achieved by shifting the position of equilibrium.
  - The position of equilibrium is shifted to the right if the amount of products in the equilibrium mixture is increased.
  - The position of equilibrium is shifted to the left if the amount of reactants in the equilibrium mixture is increased.
- The position of equilibrium can be shifted to the left or right by varying conditions such as the concentration of substances involved, temperature or pressure (in the case of reactions involving gases).

40.3 Le Chatelier's principle (p.40)

Le Chatelier's principle (勒沙得利爾原理) states that when the condition of a chemical equilibrium system is changed, the position of equilibrium shifts so as to reduce the change.

- The possible changes in conditions that you need to consider are:
  - changes in the concentration of either reactants or products;
  - changes in pressure for reactions involving gases;
  - changes in temperature.

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Effect of concentration changes on the chemical equilibrium system in aqueous bromine

- Consider again the chemical equilibrium system that exists in aqueous bromine:

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

- The colour changes of aqueous bromine upon the addition of sodium hydroxide solution or hydrochloric acid can be predicted by using Le Chatelier's principle.

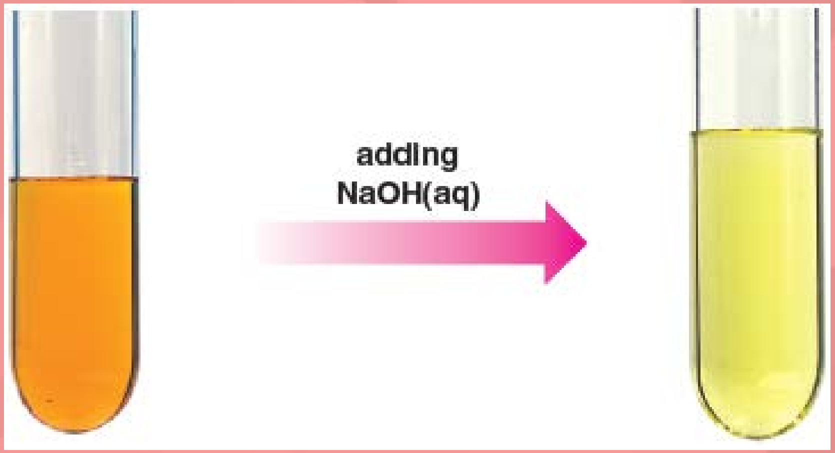
Investigating the effect of concentration changes on equilibrium *Ref.*

Effect of concentration changes on chemical equilibrium systems *Ref.*

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Effect of adding sodium hydroxide solution

- Adding a little sodium hydroxide solution to light brown aqueous bromine, the colour turns yellow. This indicates that there is less bromine and more colourless products in the mixture.



- The added hydroxide ion reacts with the hydrogen ion, decreasing the concentration of hydrogen ion.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

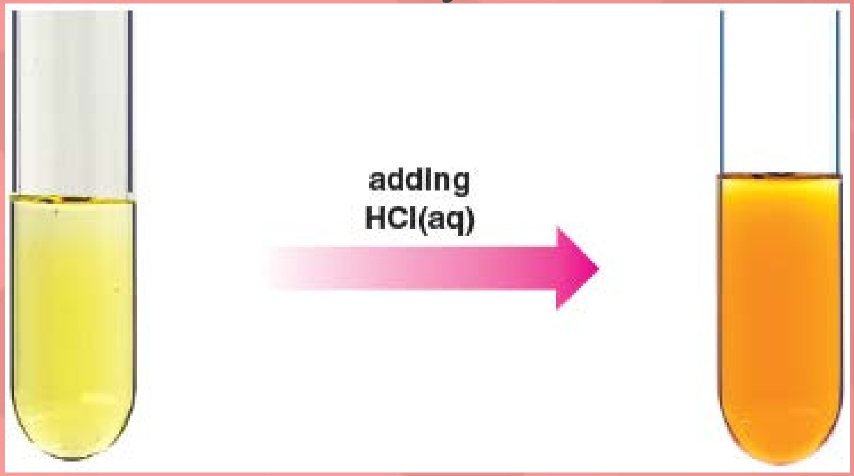
40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

- As the concentration of hydrogen ion falls, Le Chatelier's principle predicts that the position of equilibrium will shift so as to reduce this change, i.e. to raise the concentration of hydrogen ion. Hence the position of equilibrium will shift to the right. Some bromine is converted to the colourless products.
- Lowering the concentration of hydrogen ion slows down the backward reaction, while the forward reaction goes on as before. A net forward reaction occurs. The resulting increase in the concentrations of the products speeds up the backward reaction.
- The system attains a new equilibrium when the rates of the forward and backward reactions are the same.

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Effect of adding hydrochloric acid

- Adding a little hydrochloric acid to the yellow solution, the light brown colour returns.



- Adding hydrochloric acid increases the concentration of hydrogen ion. Le Chatelier's principle predicts that the position of equilibrium will shift so as to decrease the concentration of hydrogen ion. Hence the position of equilibrium will shift to the left. More colourless products are converted to bromine.

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

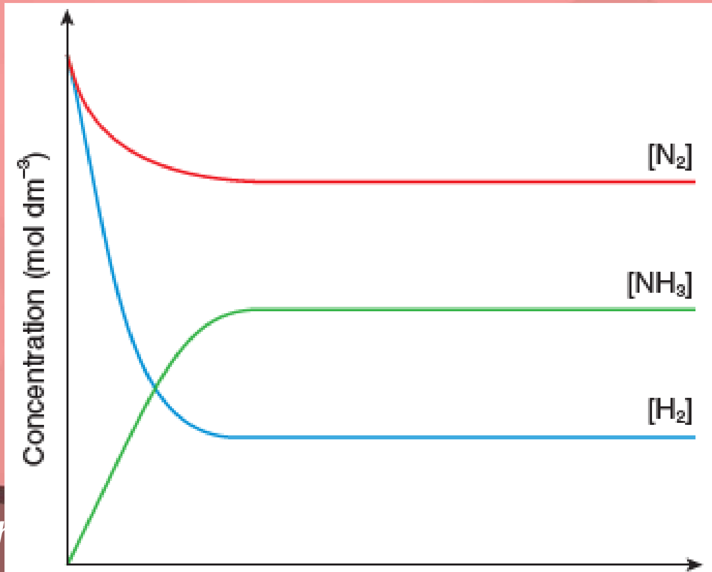
- Increasing the concentration of hydrogen ion speeds up the backward reaction, while the forward reaction goes on as before. A net backward reaction occurs until a new equilibrium is attained.
- The table below summarises the effects of adding sodium hydroxide solution and hydrochloric acid on the chemical equilibrium system in aqueous bromine.

Action on system	Colour change	Direction of net reaction	Shift of position of equilibrium
Adding NaOH(aq)	from light brown to yellow, i.e. concentration of Br_2(aq) decreases	backward reaction slows down while forward reaction goes on as before, i.e. a net forward reaction occurs	to the right (→) $Br_2(aq) + H_2O(l) \rightleftharpoons HOBr(aq) + H^+(aq) + Br^-(aq)$
Adding HCl(aq)	from yellow to light brown, i.e. concentration of Br_2(aq) increases	backward reaction speeds up while forward reaction goes on as before, i.e. a net backward reaction occurs	to the left (←) $Br_2(aq) + H_2O(l) \rightleftharpoons HOBr(aq) + H^+(aq) + Br^-(aq)$

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

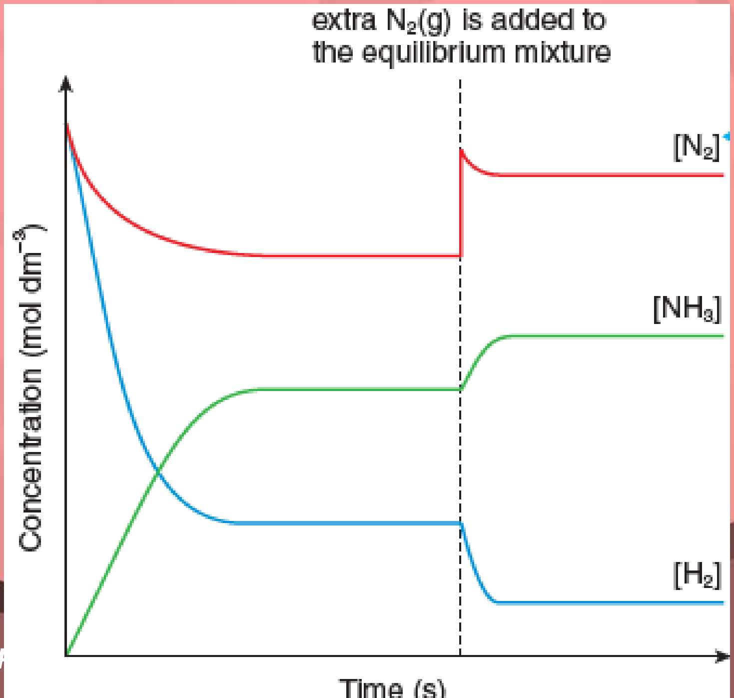
Effect of concentration changes on the chemical equilibrium system of nitrogen, hydrogen and ammonia

- One important industrial process that depends on a reversible reaction is the production of ammonia. The reaction involved is: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- Before extra nitrogen is added, concentrations of the reactants and the product in the equilibrium mixture are constant.



40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

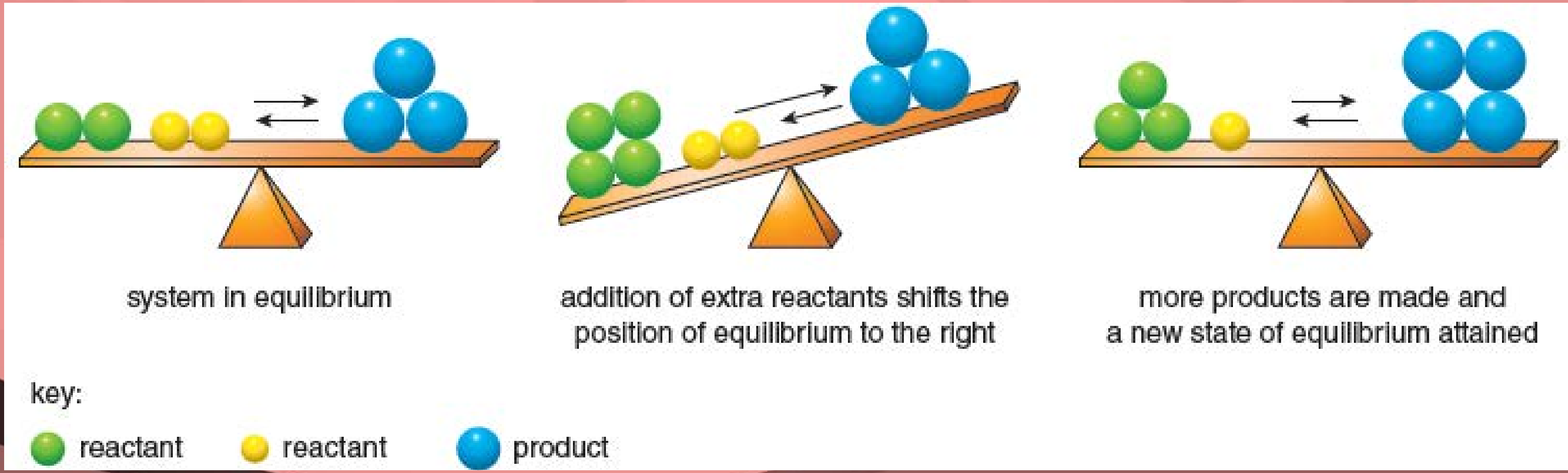
- Suppose extra nitrogen gas is added to the equilibrium mixture while the volume and the temperature are both kept constant. The system is no longer at equilibrium. The position of equilibrium shifts to the right. Some of the extra nitrogen is consumed and more ammonia is formed.
- The system attains a new equilibrium after some time, with different concentrations of the reactants and the product. Notice that the equilibrium concentration of ammonia has increased.



40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Summarising the effect of concentration changes on chemical equilibrium systems

- The effect of adding extra reactants to a chemical equilibrium system can be illustrated using the analogy of the 'see-saw'. If extra reactants are added, the position of equilibrium shifts to the right. More products are made until a new equilibriumis attained.



40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

In general, if the concentration of one of the substances in an equilibrium mixture is increased, the position of equilibrium shifts to the opposite side to reduce the concentration of this substance.

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Practice 40.1

1 Consider the following chemical equilibrium system involving four miscible liquids:

$W(l) + X(l) \rightleftharpoons Y(l) + Z(l)$

Predict and explain the effect on the number of moles of Y(l) when

a) extra W(l) is added to the equilibrium mixture;

The position of equilibrium shifts to the right.

Some of the extra W(l) is consumed and more Y(l) is formed.

b) Z(l) is removed from the equilibrium mixture.

The position of equilibrium shifts to the right. W(l) and X(l) react to produce more Z(l). More Y(l) is also formed.

40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Practice 40.1 (continued)

2 At 250 °C, PCl_3(g) and Cl_2(g) reacted to give PCl_5(g) according to the equation below.

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

At 250°C, an equilibrium mixture in a 10.0 dm^3 container contained 0.552 mole of PCl_3(g), 0.252 mole of Cl_2(g) and 0.348 mole of PCl_5(g).

a) Calculate the equilibrium constant, K_c, for the reaction at 250°C.

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

$$= \frac{(\frac{0.348}{10.0} \text{ mol dm}^{-3})}{(\frac{0.552}{10.0} \text{ mol dm}^{-3})(\frac{0.252}{10.0} \text{ mol dm}^{-3})}$$

$$= 25.0 \text{ dm}^3 \text{ mol}^{-1}$$

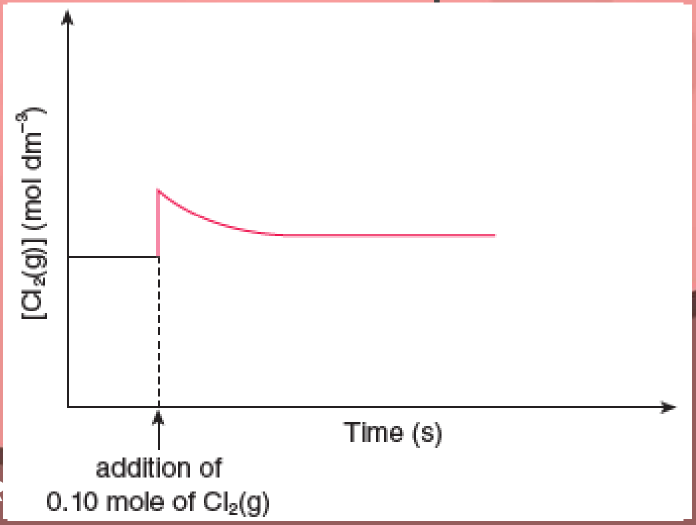
40.4 Effect of concentration changes on chemical equilibrium systems (p.41)

Practice 40.1 (continued)

2 b) 0.10 mole of $Cl_2(g)$ was added to the equilibrium mixture. (Assume that the temperature of the system remained at 250 °C.)

i) What would happen to the rate of formation of $PCl_5(g)$?
Increase

ii) Sketch below the variation of the concentration of $Cl_2(g)$ with time until a new state of equilibrium was attained.



40.5 The link between Le Chatelier's principle and the reaction quotient, Q_c (p.46)

- Le Chatelier's principle provides a very useful descriptive tool that helps you predict the outcome of a change in conditions on a chemical equilibrium system. However, it does not provide an explanation for these effects.
- Using the reaction quotient, Qc, can give an insight into why changing the concentration of a component of an equilibrium mixture gives rise to the effect it does. Take the following reaction system as an example:

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

At equilibrium:

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

- If extra nitrogen is added to the equilibrium mixture, the value of the denominator in Q_c increases. The value of Q_c will be lower than that of K_c. Hence the system will adjust to increase Q_c by producing more ammonia, i.e. the position of equilibrium shifts to the right.

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

- Changing the pressure of a system containing gases at equilibrium may change the position of equilibrium, but only if there are more number of moles of gas on one side of the equation than the other.

Effect of pressure changes on chemical equilibrium systems *Ref.*

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

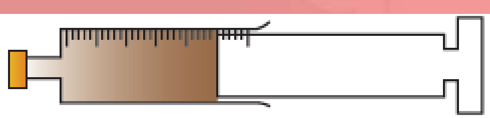
Effect of pressure change on the chemical equilibrium system of dinitrogen tetroxide and nitrogen dioxide

- Consider this chemical equilibrium system:

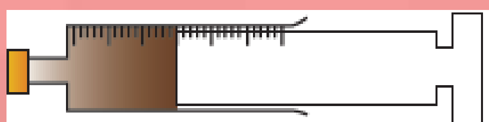
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$N_2O_4(g)$	$2NO_2(g)$
dinitrogen tetroxide	nitrogen dioxide
pale yellow	dark brown

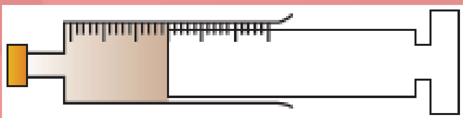
increase the pressure by pushing in the plunger



(a) a syringe containing an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$



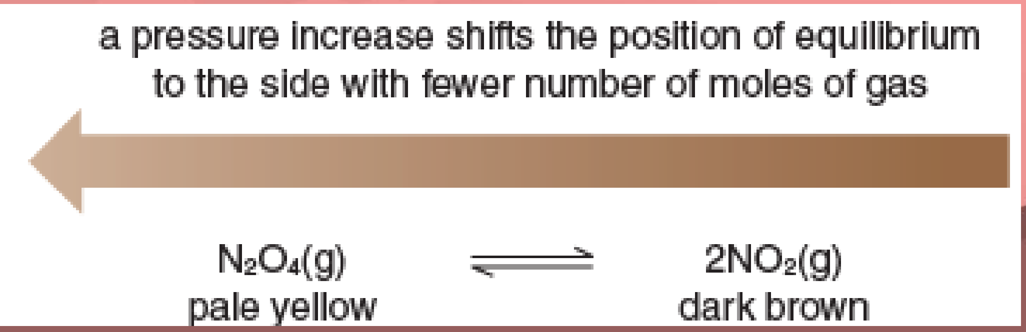
(b) the mixture initially gets slightly darker



(c) the colour of the mixture becomes paler as a new state of equilibrium is attained

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

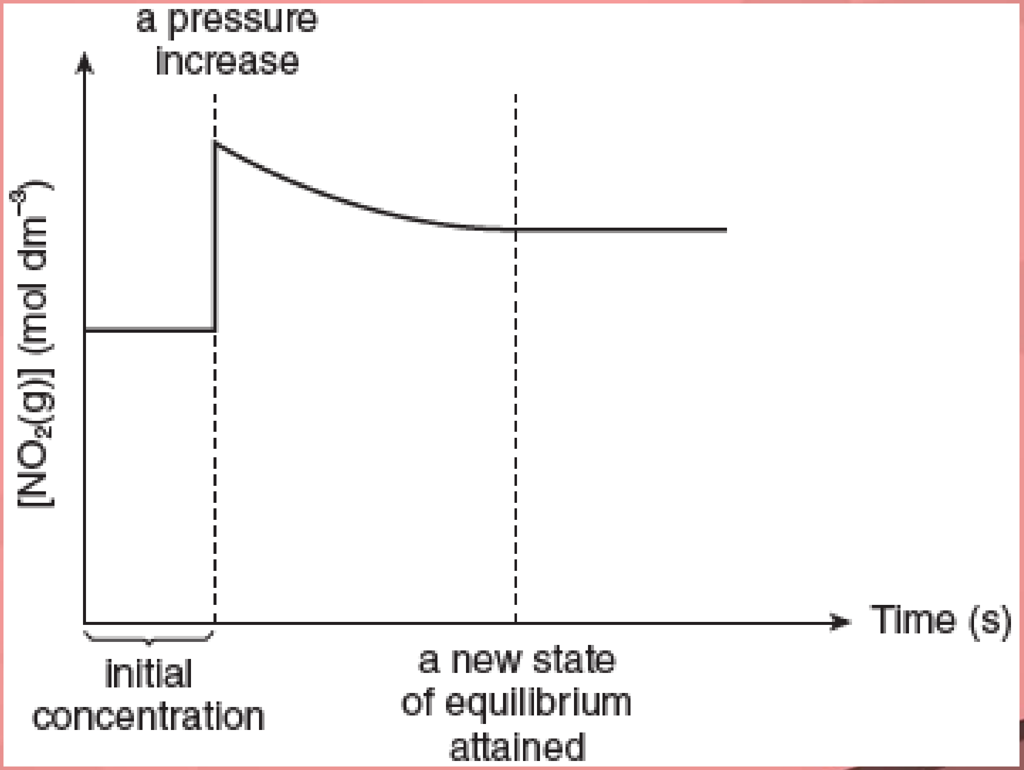
- Pressure is caused by the bombardment of gas molecules on the walls of the container. At a certain temperature, the pressure depends only on the number of gas molecules in a given volume.
- If the pressure of a chemical equilibrium system is increased, Le Chatelier's principle predicts that the system will adjust in order to bring the pressure down. A net reaction that decreases the number of moles of gas occurs, i.e. the position of equilibrium shifts to the side of the equation with fewer number of moles of gas.



When the pressure of a chemical equilibrium system is increased, Le Chatelier's principle predicts that the system will adjust so as to reduce the pressure

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

- The figure below shows how the concentration of nitrogen dioxide in the system changes with time.

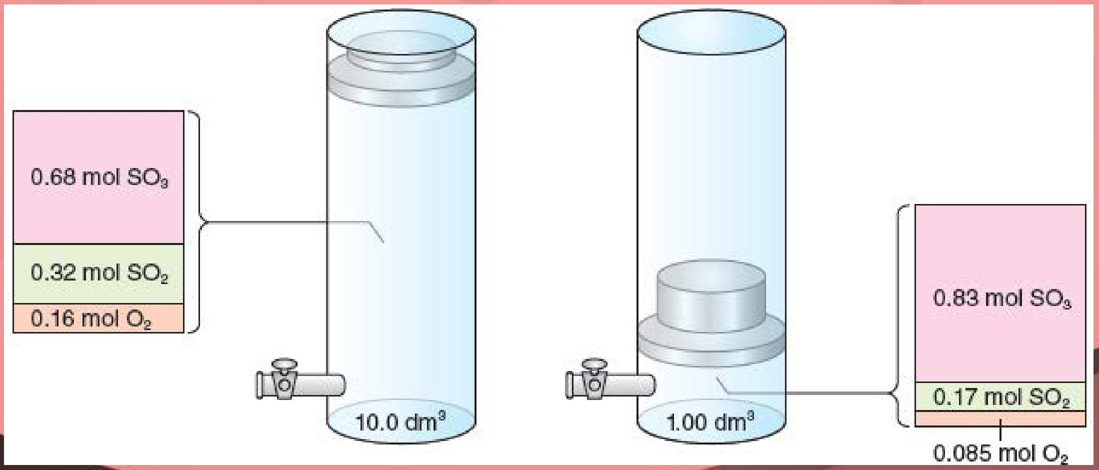


The concentration-time graph of $NO_2(g)$ for the system of $N_2O_4(g)$ and $NO_2(g)$

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

Effect of pressure changes on the chemical equilibrium system of sulphur dioxide, oxygen and sulphur trioxide

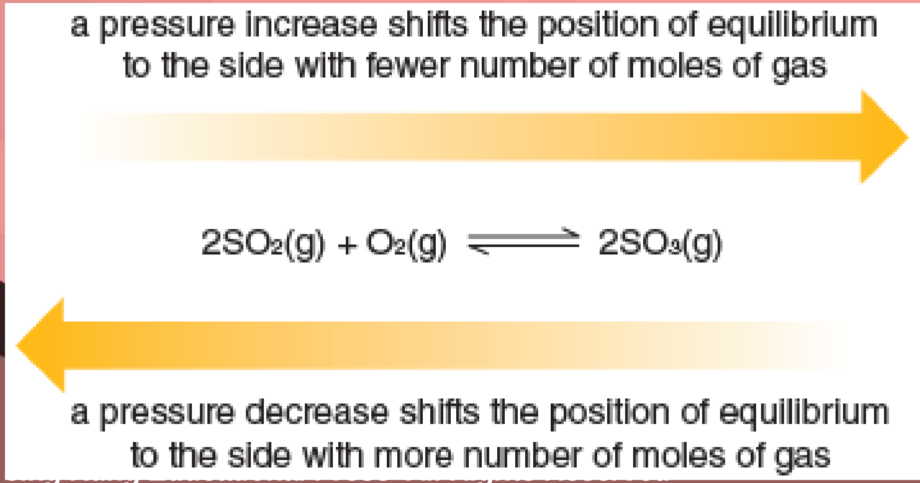
- The manufacture of sulphuric acid in the Contact process involves the conversion of sulphur dioxide to sulphur trioxide, as shown by the equation: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- The figure below shows the composition of an equilibrium mixture in a 10.0 dm^3 container at a certain temperature. The volume of the container is reduced to 1.00 dm^3 while the temperature remains the same.



A decrease in volume of a container containing $SO_2(g)$, $O_2(g)$ and $SO_3(g)$ causes an increase in pressure and a shift of the position of equilibrium to the right

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

- When the pressure of the chemical equilibrium system is increased at constant temperature, the position of equilibrium shifts to the right, i.e. to the side of the equation with fewer number of moles of gas. This is as Le Chatelier's principle predicts.
- The reverse is true if the pressure is decreased. The position of equilibrium shifts to the left, i.e. to the side of the equation with more number of moles of gas.



Le Chatelier's principle predicts the effect of pressure changes on the chemical equilibrium system of SO_2(g), O_2(g) and SO_3(g)

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

Effect of pressure change on the chemical equilibrium system of hydrogen iodide, hydrogen and iodine

- If there is no change in the number of moles of gas during the course of a reaction, then changes in pressure have no effect on the position of equilibrium of the chemical equilibrium system at a given temperature. This is illustrated by the reaction of hydrogen and iodine to form hydrogen iodide:

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

- When the pressure is increased, the rates of both the forward and backward reactions increase by the same extent. When the pressure is decreased, the rates of both the forward and backward reactions decrease by the same extent.

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

Summarising the effect of pressure changes on chemical equilibrium systems

- The effect of pressure changes on a chemical equilibrium system depends on the total number of moles of gas on each side of the equation, and is summarised below:

Number of moles of reactants	Number of moles of products	A pressure increase (rates of both forward and backward reactions increase)		A pressure decrease (rates of both forward and backward reactions decrease)	
		Direction of net reaction	Shift of position of equilibrium	Direction of net reaction	Shift of position of equilibrium
more	fewer	a net forward reaction occurs	to the right (more products are formed)	a net backward reaction occurs	to the left (more reactants are formed)
fewer	more	a net backward reaction occurs	to the left (more reactants are formed)	a net forward reaction occurs	to the right (more products are formed)
same	same	no net reaction	no change	no net reaction	no change

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

For a chemical equilibrium system containing gases where there are more number of moles of gas on one side of the equation than the other,

- **a pressure increase (a volume decrease) shifts the position of equilibrium to the side with fewer number of moles of gas;**
- **a pressure decrease (a volume increase) shifts the position of equilibrium to the side with more number of moles of gas.**

- None of these changes results in a change in the value of K_c.

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

Practice 40.2

1 The following system attains equilibrium at a certain temperature:

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

The volume of the container of the system is decreased while the temperature remains the same.

Predict and explain the effect of this change on:

a) the position of equilibrium;

The position of equilibrium shifts to the right, i.e. to the side of the equation with fewer number of moles of gas.

b) the rate of decomposition of $CH_3OH(g)$;

The rate of decomposition of $CH_3OH(g)$ increases because the concentrations of substances in the container increase. The chance of collision of particles increases, so there are more effective collisions in a unit volume per unit time.

40.6 Effect of pressure changes on chemical equilibrium systems (p.47)

Practice 40.2 (continued)

1 c) the value of K_c.

The value of K_c does not change because the temperature remains the same.

2 Consider the following chemical equilibrium system in a container kept at constant temperature:

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

The volume of the container is increased while the temperature remains the same.

Predict and explain the effect of this change on:

a) the rate of formation of $H_2(g)$;

The rate of formation of $H_2(g)$ decreases because the concentrations of substances in the container decrease. The chance of collision of particles decreases, so there are less effective collisions in a unit volume per unit time.

b) the position of equilibrium.

The position of equilibrium has no change because there is no change in the number of moles of gas during the course of the reaction.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- Le Chatelier's principle can be used to predict the effect of temperature changes on the position of equilibrium. The key factor to be considered here is whether the forward reaction is exothermic (a negative ΔH value) or endothermic (a positive ΔH value).

- In a reversible reaction, the backward reaction has an enthalpy change that is equal and opposite to that of the forward reaction.

Investigating the effect of pressure and temperature changes on equilibrium Ref.

Effect of temperature changes on chemical equilibrium systems Ref.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Effect of temperature changes on the chemical equilibrium system of two types of cobalt(II) ion

- Cobalt(II) chloride dissolves in water to form a pink solution. The dissolving process actually produces an equilibrium mixture containing two types of cobalt(II) ion of different colours:

$$\underset{\text{pink}}{Co^{2+}(aq)} + 4Cl^{-}(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} \qquad \Delta H > 0$$

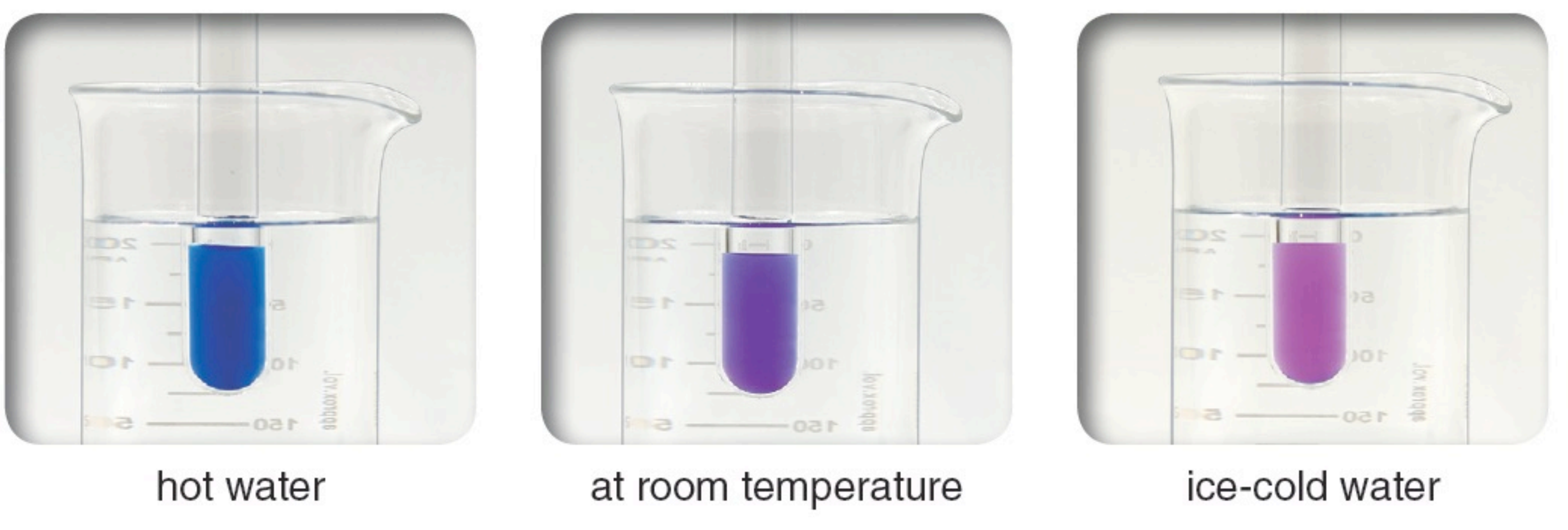
40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- Carry out the following experiment to show the effect of temperature changes on the equilibrium mixture of these two types of cobalt(II) ion.

Step 1 Dissolve cobalt(II) chloride in water. Add a small amount of hydrochloric acid to form a violet equilibrium mixture containing the two types of cobalt(II) ion.

Step 2 Prepare three tubes of the violet equilibrium mixture, and keep one tube at room temperature as a control. Place another tube in hot water (over 90 °C) and the third tube in ice-cold water.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

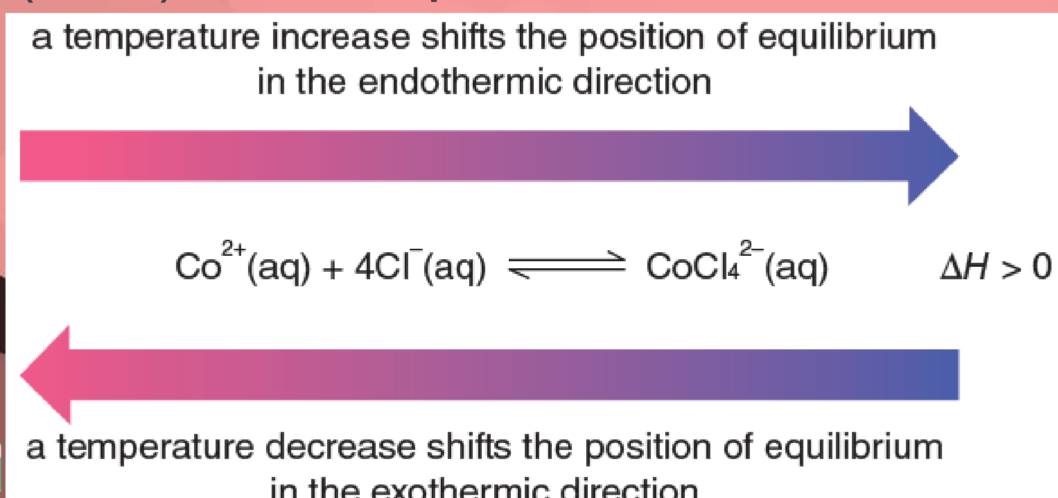


The equilibrium mixture of Co^{2+}(aq) and $CoCl_4^{2-}$(aq) at different temperatures

- If the temperature of a chemical equilibrium system is increased, Le Chatelier's principle predicts that the system will adjust in order to bring the temperature down. A net reaction that absorbs heat occurs, i.e. the position of equilibrium shifts in the endothermic direction.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- The equilibrium mixture at higher temperature is blue while the one at room temperature is violet. This indicates that there are more $CoCl_4^{2-}(aq)$ ions (blue) and less $Co^{2+}(aq)$ ions (pink) in the equilibrium mixture at higher temperature.
- The equilibrium mixture at lower temperature is pink while the one at room temperature is violet. This indicates that there are more $Co^{2+}(aq)$ ions (pink) and less $CoCl_4^{2-}(aq)$ ions (blue) in the equilibrium mixture at lower temperature.



Le Chatelier's principle predicts the effect of temperature changes on the chemical equilibrium system of $Co^{2+}(aq)$ and $CoCl_4^{2-}(aq)$

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Effect of temperature changes on the chemical equilibrium system of nitrogen, hydrogen and ammonia

- Consider another chemical equilibrium system:

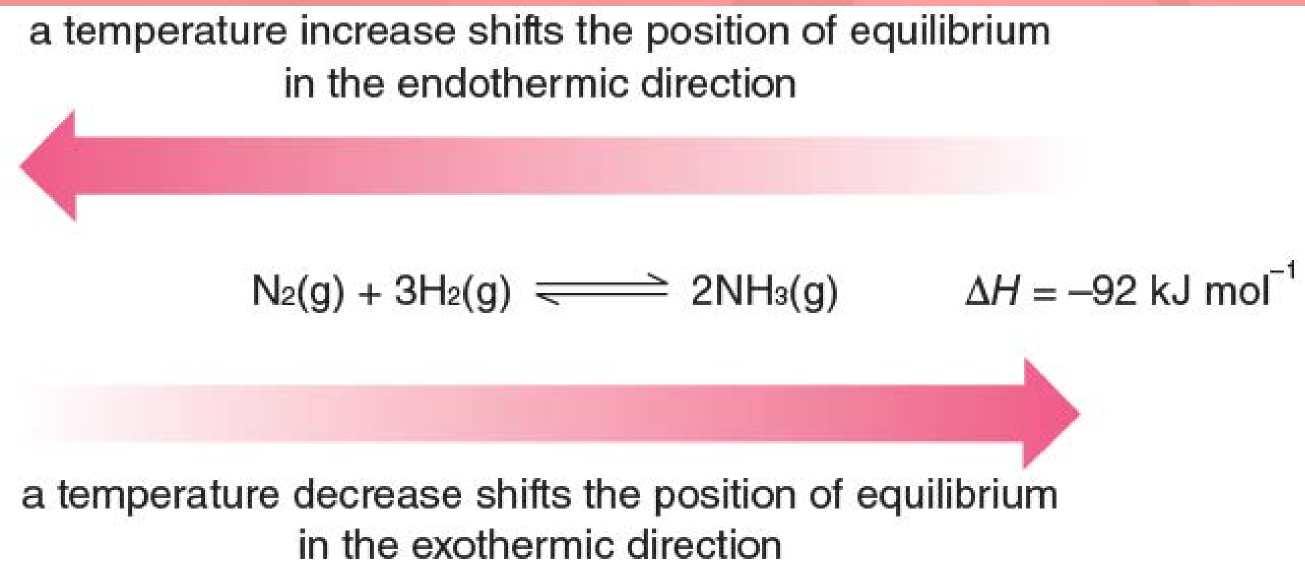
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

The table below shows the percentage of ammonia in the equilibrium mixture at different temperatures and at constant pressure.

Temperature (°C)	Percentage of $NH_3(g)$ in the equilibrium mixture (%)
300	27.4
400	8.7
500	2.9

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- When the temperature of the chemical equilibrium system is increased, the position of equilibrium shifts in the endothermic direction, i.e. to the left. More reactants are formed.
- When the temperature of the chemical equilibrium system is decreased, the position of equilibrium shifts in the exothermic direction, i.e. to the right. More product is formed.



Le Chatelier's principle predicts the effect of temperature changes on the chemical equilibrium system of $N_2(g)$, $H_2(g)$ and $NH_3(g)$

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

The link between the value of equilibrium constant and temperature changes

- For the endothermic reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +190\ \text{kJ mol}^{-1}$$

The concentration of NO(g) increases while those of N_2(g) and O_2(g) decrease as the temperature is increased.

- The value of K_c must increase with increasing temperature. This is because [NO(g)] is increasing while [N_2(g)] and [O_2(g)] are decreasing.

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

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- The table below shows how the value of K_c for this reaction changes with temperature.

temperature increases

Temperature (°C)	Value of K_c
300	4.5×10^{-15}
400	8.4×10^{-13}
500	4.0×10^{-11}

value of K_c increases

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- For the exothermic reaction:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -114 \text{ kJ mol}^{-1}$$

The concentrations of NO(g) and O_2(g) increase while that of NO_2(g) decreases as the temperature is increased.

- The value of K_c must decrease with increasing temperature. This is because [NO(g)] and [O_2(g)] are increasing while [NO_2(g)] is decreasing.

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

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

- The table below shows how the value of K_c for this reaction changes with temperature.

temperature increases ↓

Temperature (°C)	Value of K_c ($dm^3\ mol^{-1}$)
300	1.9×10^7
400	6.3×10^5
500	5.0×10^4

value of K_c decreases ↓

- Unlike changing the concentration or the pressure, a change in temperature will change the value of K_c.
- For endothermic reactions, an increase in temperature results in an increase in the concentration of products in the equilibrium mixture and therefore an increased K_c. The opposite is true for exothermic reactions.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Summarising the effect of temperature changes on chemical equilibrium systems

- The effect of temperature changes on a chemical equilibrium system depends on whether the forward reaction is exothermic or endothermic, and is summarised in the table below.

Forward reaction	A temperature increase (rates of both forward and backward reactions increase, but not to the same extent)			A temperature decrease (rates of both forward and backward reactions decrease, but not to the same extent)		
	Direction of net reaction	Shift of position of equilibrium	Value of K_c	Direction of net reaction	Shift of position of equilibrium	Value of K_c
Exothermic (ΔH is negative)	a net backward reaction occurs	to the left	decreases	a net forward reaction occurs	to the right	increases
Endothermic (ΔH is positive)	a net forward reaction occurs	to the right	increases	a net backward reaction occurs	to the left	decreases

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

When the temperature of a chemical equilibrium system is increased, the position of equilibrium shifts in the endothermic direction.

When the temperature of a chemical equilibrium system is decreased, the position of equilibrium shifts in the exothermic direction.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Q (Example 40.1)

The dissociation of water is a reversible reaction.

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

Under fixed conditions, $[H_2O(l)]$ is considered as a constant. In consideration of the definition of K_c, $[H^+(aq)][OH^-(aq)]$ would also be a constant.

a) The pH of water equals 7.0 at 298 K. Find, at this temperature, the value of $[H^+(aq)][OH^-(aq)]$.

b) The pH of water at 323 K is 6.6. Deduce whether the dissociation of water is exothermic or endothermic.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Q (Example 40.1) (continued)

A

a) At 298 K,

$pH = -\log[H^+(aq)] = 7.0$

$[H^+(aq)] = 1.0 \times 10^{-7}$ mol dm^{-3}

As $[H^+(aq)] = [OH^-(aq)]$,

$[H^+(aq)][OH^-(aq)] = (1.0 \times 10^{-7}$ mol dm$^{-3})^2$

$= 1.0 \times 10^{-14}$ mol^2 dm^{-6}

b) At 323 K,

$pH = -\log[H^+(aq)] = 6.6$

$[H^+(aq)] = 2.5 \times 10^{-7}$ mol dm^{-3}

It can be deduced that increasing the temperature shifts the position of equilibrium to the right. Hence the dissociation of water is endothermic.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Practice 40.3

1 Consider the following chemical equilibrium system in a container:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H = -41 \text{ kJ mol}^{-1}$$

The temperature of the system is increased. Predict and explain the effect of this change on:

a) the position of equilibrium;

When the temperature of the system is increased, the position of equilibrium shifts in the endothermic direction, i.e. to the left.

b) the number of moles of $H_2(g)$ obtained;

The number of moles of $H_2(g)$ decreases.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Practice 40.3 (continued)

1 c) the rate of the forward reaction;

The rate of the forward reaction increases.

d) the value of K_c.

The value of K_c decreases.

2 A chemical equilibrium system is obtained when iron(III) ions (Fe^{3+}(aq)) are added to thiocyanate ions (SCN^-(aq)). The resulting equilibrium mixture has a deep red colour.

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

yellowish brown   colourless   deep red

The resulting equilibrium mixture is divided into four equal portions and placed in test tubes. Keep one test tube at room temperature as a control.

40.7 Effect of temperature changes on chemical equilibrium systems (p.52)

Practice 40.3 (continued)

Predict and explain the effect of each of the following changes on each test tube containing the equilibrium mixture:

a) Adding 1 drop of $Fe(NO_3)_3$(aq)

The position of equilibrium shifts to the right.

The deep red colour becomes more intense.

b) Adding 1 drop of $AgNO_3$(aq) (it is known that AgSCN(s) is insoluble in water)

The position of equilibrium shifts to the left.

The deep red colour becomes less intense.

c) Placing the mixture in a hot water bath (70–80 °C)

The position of equilibrium shifts in the endothermic direction, i.e. to the left.

The deep red colour becomes less intense

40.8 Effect of catalysts on chemical equilibrium systems (p.59)

- Catalysts have no effect on the position of equilibrium so they do not alter the composition of the equilibrium mixture.
- Catalysts work by providing an alternative pathway with a lower activation energy for the reaction.
- The presence of a catalyst increases the rates of both the forward and backward reactions equally.
- Catalyst do allow equilibrium to be attained more quickly and are therefore important in industry.

40.9 Chemical equilibrium systems in industry (p.59)

- A number of industrial processes involve reversible reactions. In these cases, the equilibrium yield of the reaction is important and Le Chatelier's principle can be used to find the best conditions for increasing it.
- Yield is not the only consideration. Sometimes a low temperature would give the best yield but this would slow the reaction down.
- The costs of building and running a plant that operates at high temperatures and pressures must also be taken into account.

40.9 Chemical equilibrium systems in industry (p.59)

The Contact process

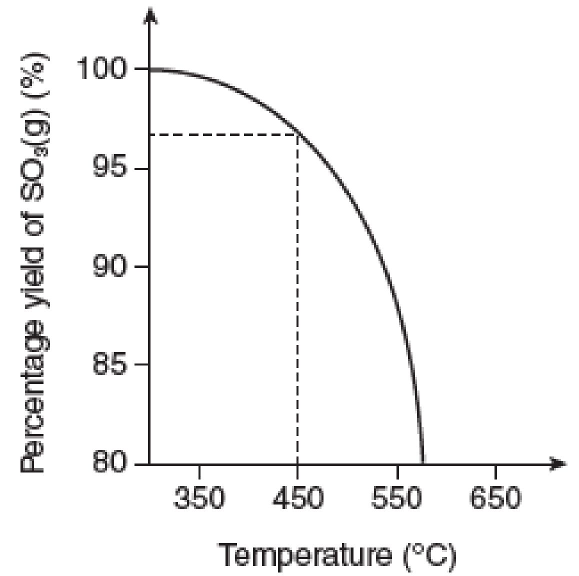
- Sulphuric acid is manufactured by the **Contact process (接觸法)**. This process has three stages.

- This process gets its name from the stage that involves the reaction between sulphur dioxide and oxygen (from air) at the surface of a solid vanadium(V) oxide catalyst to form sulphur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -198 \text{ kJ mol}^{-1}$$

40.9 Chemical equilibrium systems in industry (p.59)

- Applying Le Chatelier's principle to this reaction system, you can predict that the maximum yield of sulphur trioxide can be produced with
  - excess air, which shifts the position of equilibrium to the right to reduce the concentration of oxygen;
  - a high pressure, which shifts the position of equilibrium to the right, i.e. to the side with fewer number of moles of gas;
  - a low temperature, which shifts the position of equilibrium to the right, i.e. in the exothermic.



The percentage yield of sulphur trioxide against temperature at a pressure of 1 atm

40.9 Chemical equilibrium systems in industry (p.59)

- In industry, the operating conditions chosen are a compromise between the need to maximise the yield of the product and the need to produce the product fast enough.
- In practice, 450 °C and 1 atmospheric pressure are used to achieve a 97% yield of sulphur trioxide. Given this high yield, it is unnecessary to use a high pressure to increase the yield of sulphur trioxide.

40.9 Chemical equilibrium systems in industry (p.59)

Practice 40.4

An important reaction in the manufacture of nitric acid is the catalytic oxidation of ammonia.

$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -910 \text{ kJ mol}^{-1}$

a) Use Le Chatelier's principle to state whether a high or low temperature should be used to obtain the highest possible yield of NO(g). Explain your answer.

A low temperature should be used.
A temperature decrease shifts the position of equilibrium to the right, i.e. the exothermic direction.

b) Le Chatelier's principle predicts that a high pressure will produce a low yield of NO(g). Explain why a high operating pressure is used in industry.

To increase the rate of reaction / of attainment of equilibrium.

Key terms (p.62)

position of equilibrium	平衡位置	Contact process	接觸法
Le Chatelier's principle	勒沙得利爾原理		

Summary (p.63)

1 Le Chatelier's principle states that when the condition of a chemical equilibrium system is changed, the position of equilibrium shifts so as to reduce the change.

2 In general, if the concentration of one of the substances in an equilibrium mixture is increased, the position of equilibrium shifts to the opposite side to reduce the concentration of this substance.

Summary (p.63)

3 The following is a summary of effect of concentration changes on a chemical equilibrium system.

reactants $\rightleftharpoons$ products

Action on equilibrium system	Rates of forward and backward reactions	Direction of net reaction	Shift of position of equilibrium	Value of K_c
Increasing the concentration of a reactant	rate of forward reaction increases	a net forward reaction occurs	to the right	unchanged
Decreasing the concentration of a reactant	rate of forward reaction decreases	a net backward reaction occurs	to the left	
Increasing the concentration of a product	rate of backward reaction increases	a net backward reaction occurs	to the left	
Decreasing the concentration of a product	rate of backward reaction decreases	a net forward reaction occurs	to the right	

Summary (p.63)

4 The following is a summary of effect of pressure changes on a chemical equilibrium system.

Number of moles of reactants	Number of moles of products	A pressure increase (rates of both forward and backward reactions increase)		A pressure decrease (rates of both forward and backward reactions decrease)		Value of K_c
		Direction of net reaction	Shift of position of equilibrium	Direction of net reaction	Shift of position of equilibrium	
more	fewer	a net forward reaction occurs	to the right	a net backward reaction occurs	to the left	unchanged
fewer	more	a net backward reaction occurs	to the left	a net forward reaction occurs	to the right	
same	same	no net reaction	no change	no net reaction	no change	

Summary (p.63)

5 The following is a summary of effect of temperature changes on a chemical equilibrium system.

Forward reaction	A temperature increase (rates of both forward and backward reactions increase, but not to the same extent)			A temperature decrease (rates of both forward and backward reactions decrease, but not to the same extent)		
	Direction of net reaction	Shift of position of equilibrium	Value of K_c	Direction of net reaction	Shift of position of equilibrium	Value of K_c
Exothermic (ΔH is negative)	a net backward reaction occurs	to the left	decreases	a net forward reaction occurs	to the right	increases
Endothermic (ΔH is positive)	a net forward reaction occurs	to the right	increases	a net backward reaction occurs	to the left	decreases

Summary (p.63)

6 a) The Contact process involves the oxidation of sulphur dioxide into sulphur trioxide:

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

The percentage of sulphur trioxide in the equilibrium mixture can be increased by using

- excess air;
- a high pressure; and
- a low temperature.

b) 'Compromise' sets of operating conditions that manufacturers use for the Contact process:

Temperature (°C)	Pressure (atm)	Catalyst
450	1	solid vanadium(V) oxide

Unit Exercise (p.65)

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;**

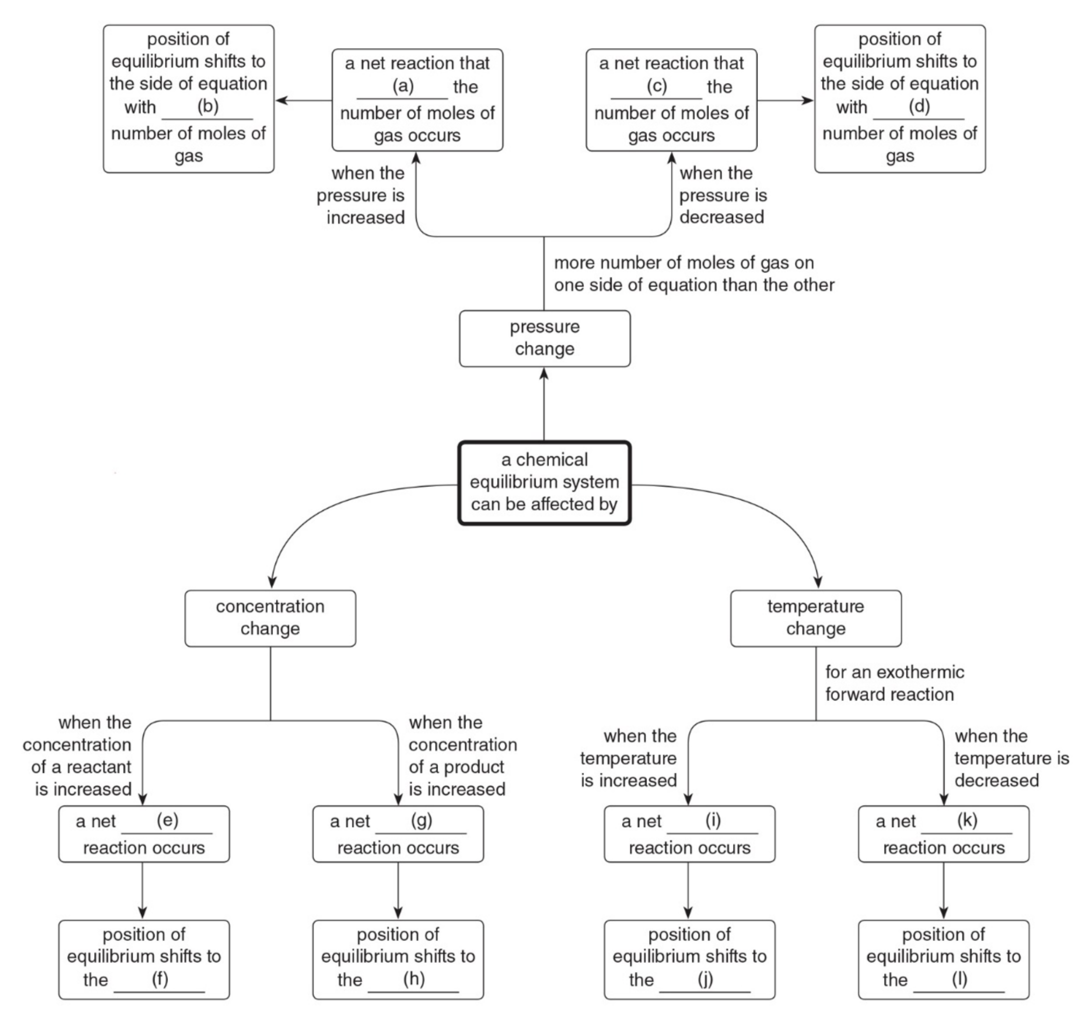
 **question targeted at level 5.**

‘ * ’ indicates 1 mark is given for effective communication.

Unit Exercise (p.65)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.



(a) decreases
(b) fewer
(c) increases
(d) more
(e) forward
(f) right
(g) backward
(h) left
(i) backward
(j) left
(k) forward
(l) right

Unit Exercise (p.65)

PART II MULTIPLE CHOICE QUESTIONS

2 NO(g), H_2(g), N_2(g) and H_2O(g) exist in equilibrium:

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

At room temperature and pressure, the equilibrium lies well to the right-hand side.

Which of the following could be the equilibrium constant for this equilibrium?

A 1.54×10^{-3} mol dm^{-3}

B 6.50×10^{2} mol dm^{-3}

C 1.54×10^{-3} dm^{3} mol^{-1}

D 6.50×10^{2} dm^{3} mol^{-1}

Answer: D

(OCR Advanced Level, Chem. A, H432/01, Sample Question Paper, 2016,12)

Unit Exercise (p.65)

2 (continued)

Explanation:

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

Units of K_c are given by $\frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})^2}$, i.e. $\text{dm}^3 \text{ mol}^{-1}$

Unit Exercise (p.65)

3 Consider the following equilibrium system:

$$Br_2(aq) + H_2O(l) \rightleftharpoons HOBr(aq) + H^+(aq) + Br^-(aq)$$

Which of the following can turn the colour of the system paler?

A Passing HCl(g) into the system
B Passing HBr(g) into the system
C Adding NaBr(s) to the system
D Adding NaOH(s) to the system

Answer: D

(HKDSE, Paper 1A, 2016, 27)

Unit Exercise (p.65)

4 In which of the following chemical equilibrium systems would the position of equilibrium NOT be affected by a pressure change at constant temperature?

A $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$
B $I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$
C $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
D $CH_2ClCH_2Cl(g) \rightleftharpoons CH_2{=}CHCl(g) + HCl(g)$

Answer: B

Explanation:

$I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$

There is no change in the number of moles of gas during the course of the reaction. Changes in pressure have NO effect on the position of equilibrium of the chemical equilibrium system at a given temperature.

Unit Exercise (p.65)

5 An acid-alkali indicator is a weak acid and may be represented by the formula HIn(aq). The equation for its dissociation is shown below.

$$\underset{\text{red}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\text{yellow}}{In^-(aq)}$$

Under certain conditions, at equilibrium, a solution of HIn has a yellow colour.

Unit Exercise (p.65)

5 (continued)

What would be the effect on the colour of the solution if five drops of dilute sodium hydroxide solution are added?

A No observable change
B From yellow to orange
C From yellow to red
D From yellow to orange and then to red

Answer: A

Explanation:

The OH^-(aq) ions from dilute sodium hydroxide solution added react with H^+(aq) ions to form H_2O(l). The position of equilibrium shifts to the right to produce more H^+(aq) ions. The solution remains yellow in colour.

Unit Exercise (p.65)

6 The following system has attained equilibrium at a certain temperature:

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

The volume of the system is decreased while the temperature remains unchanged.

Which of the following statements is INCORRECT?

A The value of K_c increases.

B The position of equilibrium shifts to the right.

C The rate of decomposition of $PCl_5(g)$ increases.

D The amount of $PCl_5(g)$ increases.

Explanation:
The value of K_c does NOT change as the temperature remains unchanged.

Answer: A

Unit Exercise (p.65)

7 Consider the following chemical equilibrium system:
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Increasing the pressure of the system

A has no effect on the rate and the position of equilibrium.

B increases the rate and shifts the position of equilibrium to the left.

C increases the rate and shifts the position of equilibrium to the right.

D increases the rate but does not affect the position of equilibrium.

Answer: D

Explanation:
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
There is no change in the number of moles of gas during the course of the reaction. Changes in pressure have NO effect on the position of equilibrium of the chemical equilibrium system at a given temperature.

Unit Exercise (p.65)

8 A mixture of $CO(g)$, $Cl_2(g)$ and $COCl_2(g)$ is allowed to attain equilibrium in a closed container.

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \quad \Delta H < 0$

Answer: D

The chemical equilibrium system is suddenly heated at constant volume. Which of the following changes would result?

A The concentration of $CO(g)$ would decrease.
B The equilibrium constant for the reaction would increase.
C The rate of the forward reaction would decrease.
D The total number of gas molecules in the container would increase.

Explanation:
A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the left. More $CO(g)$ and $Cl_2(g)$ would form.

Unit Exercise (p.65)

9 Refer to the production of hydrogen by the reaction of methane with steam. The reaction mixture reaches a state of dynamic equilibrium.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

Which of the following shows how the equilibrium yield of hydrogen and the value of the equilibrium constant are affected by the changes shown?

	Change	Effect on equilibrium yield of $H_2(g)$	Effect on value of K_c
A	increase pressure	decrease	decrease
B	add a catalyst	increase	no effect
C	increase temperature	increase	increase
D	remove CO(g) as formed	increase	increase

Answer: C

(AQA Advanced Subsidiary, Paper 2, Jun. 2016, 21)

Explanation:
A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the right.
$[CO(g)]$ and $[H_2(g)]$ increase, while $[CH_4(g)]$ and $[H_2O(g)]$ decrease.
Hence the value of K_c increases.

Unit Exercise (p.65)

10 Consider the following equilibrium system in a certain liquid medium at 25 °C:

$$CH_3COCH_3 + HCN \rightleftharpoons (CH_3)_2C(OH)CN \qquad \Delta H > 0$$

Which of the following statements is correct (assuming the total volume of the system remains unchanged)?

A Adding $(CH_3)_2C(OH)CN$ would increase the equilibrium constant K_c.
B Increasing the temperature would increase the concentration of $(CH_3)_2C(OH)CN$.
C The concentration of CH_3COCH_3 must be equal to the concentration of $(CH_3)_2C(OH)CN$.
D After adding HCN and when a new equilibrium is attained, the concentration of HCN would be restored to the value before the addition of HCN.

Answer: B

(HKDSE, Paper 1A, 2018, 26)

Unit Exercise (p.65)

11 Sulphur trioxide can be manufactured from the reaction between sulphur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198 \text{ kJ mol}^{-1}$$

What would happen when a catalyst is added to this chemical equilibrium system?

A The rate of the forward reaction increases and that of the backward reaction decreases.
B The rates of both the forward and backward reactions increase.
C The value of ΔH increases.
D The yield of sulphur trioxide increases.

Answer: B

Unit Exercise (p.65)

12 Consider the following chemical equilibrium system in a closed container kept at 350 °C.

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g) \qquad \Delta H = -85 \text{ kJ mol}^{-1}$$

Which of the following statements is correct?

Answer: A

A Increasing the temperature will increase the rate of formation of $SO_2Cl_2(g)$.

B Increasing the volume of the container will increase the amount of $SO_2Cl_2(g)$.

C Increasing the temperature will increase the amount of $SO_2Cl_2(g)$.

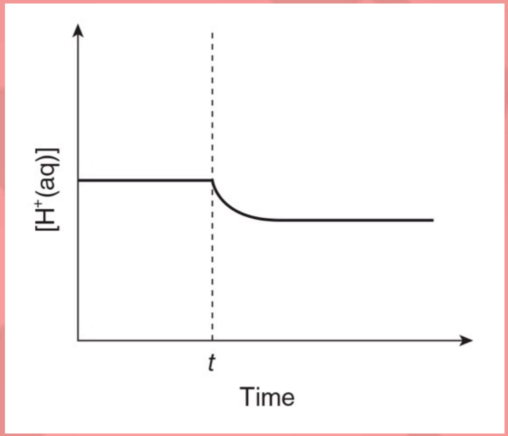
D Adding a catalyst will increase the amount of $SO_2Cl_2(g)$.

Unit Exercise (p.65)

13 Consider the following chemical equilibrium system:

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ $\Delta H < 0$

A change was applied at time t and the concentration of $H^+(aq)$ ion was shown in the plot below.



The change that was applied at time t was

A the addition of HCl(aq).

B decreasing the temperature.

C the addition of $CH_3COONa(aq)$.

D increasing the volume of the container.

Answer: C

Explanation:

Adding $CH_3COONa(aq)$ (i.e. $CH_3COO^-(aq)$ ion) makes the position of equilibrium shift to the left.

Hence $[H^+(aq)]$ decreases.

Unit Exercise (p.65)

Directions: Questions 14 and 15 refer to the following process. The Ostwald Process is a method for making nitric acid. The equation for the first stage of this process is

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -905 \text{ kJ mol}^{-1}$$

14 The equilibrium yield of nitrogen monoxide, NO, is increased by

A increasing both the pressure and the temperature.
B decreasing both the pressure and the temperature.
C decreasing the pressure and increasing the temperature.
D increasing the pressure and decreasing the temperature.

Answer: B

(Edexcel Advanced Level GCE, Unit 4, Jun. 2016, 10(a))

Unit Exercise (p.65)

14 (continued)

Explanation:

A pressure decrease shifts the position of equilibrium to the side with more number of moles of gas, i.e. to the right.

A temperature decrease shifts the position of equilibrium in exothermic direction, i.e. to the right.

Unit Exercise (p.65)

15 For this stage of the process, the catalyst is an alloy of platinum and rhodium. A pressure of between 4 and 10 atm and a temperature of 1 150 K are used. Unreacted reactants are recycled.

Which one of the following changes will affect the value of the equilibrium constant, K_c?

A Changing the composition of the platinum-rhodium catalyst
B Increasing the pressure above 10 atm
C Decreasing the temperature below 1 150 K
D Not recycling unreacted reactants

Answer: C

(Edexcel Advanced Level GCE, Unit 4, Jun. 2016, 10(b))

Unit Exercise (p.65)

16 The following system attains equilibrium at a certain temperature:

$O_2(g) + 2HF(g) \rightleftharpoons OF_2(g) + H_2O(g)$ $\Delta H = +318$ kJ mol^{-1}

Which of the following statements is / are correct when some extra $O_2(g)$ is added to the system while the temperature remains unchanged?

(1) The value of K_c increases.
(2) The position of equilibrium shifts to the right.
(3) The rate of formation of $OF_2(g)$ increases.

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

Answer: D

Explanation:
(1) The value of K_c does NOT change as the temperature remains unchanged.

Unit Exercise (p.65)

17 The following system has attained equilibrium in a closed container kept at a certain temperature:

$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$

Answer: D

Which of the following changes will shift the position of equilibrium to the right?

(1) Adding a suitable catalyst
(2) Decreasing the concentration of oxygen
(3) Increasing the volume of the container

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

Explanation:

(3) Increasing the volume of the container shifts the position of equilibrium to the side with more number of moles of gas, i.e. to the right.

Unit Exercise (p.65)

18 A mixture of $N_2O_4(g)$ and $NO_2(g)$ is allowed to attain equilibrium in a fixed volume container at room temperature.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57 \text{ kJ mol}^{-1}$

pale yellow dark brown

Answer: D

Which of the following are correct when the temperature is increased?

(1) The equilibrium constant, K_c, increases.
(2) The colour of the mixture becomes darker.
(3) Both the rates of forward and backward reactions increase.

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

Explanation:
A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the right.
$[NO_2(g)]$ increases while $[N_2O_4(g)]$ decreases.
Hence the value of K_c increases.

Unit Exercise (p.65)

PART III STRUCTURED QUESTIONS

19 The oxidation of sulphur dioxide to sulphur trioxide is a key reaction in the manufacture of sulphuric acid by the Contact process.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H < 0$

In industry, conditions for the reaction between sulphur dioxide and oxygen can be chosen to increase the rate of the reaction and the yield.

Which conditions increases the rate only, which increases the yield only and which increases both?

Put a tick (✓) in one box of each row.

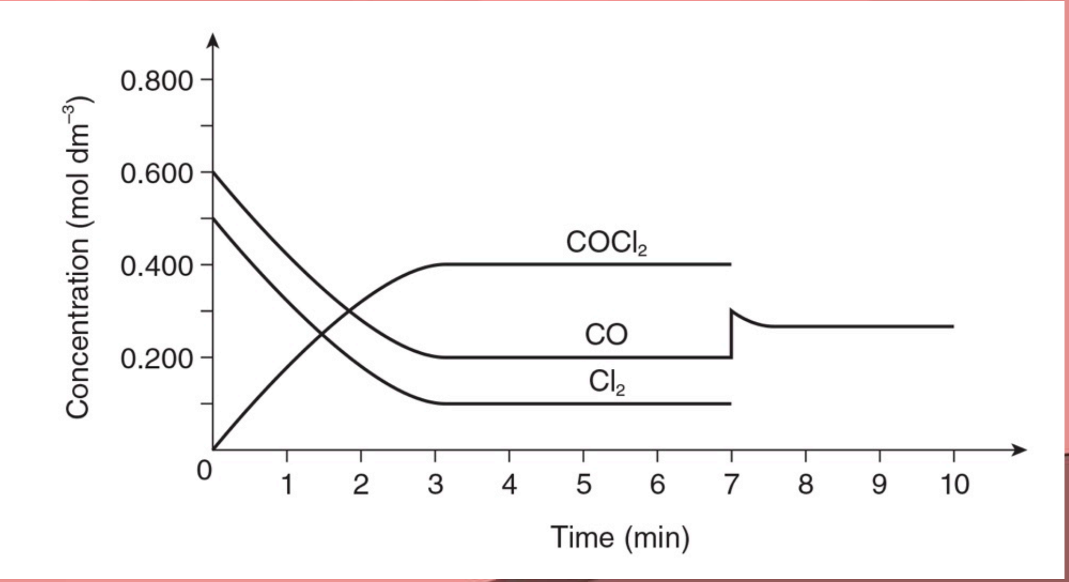
Condition	Increases the rate only	Increases the yield only	Increases both the rate and the yield
High temperature	✓ (1)		
High pressure			✓ (1)
The use of a catalyst	✓ (1)		

Unit Exercise (p.65)

20 $CO(g)$ and $Cl_2(g)$ react to form $COCl_2(g)$ according to the equation below.

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

$CO(g)$ and $Cl_2(g)$ were mixed in the presence of a catalyst. The concentrations of the three gases changed according to the graph below.



Unit Exercise (p.65)

20 (continued)

a) Calculate the equilibrium constant, K_c, for the reaction.

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

$$= \frac{0.400 \text{ mol dm}^{-3}}{(0.200 \text{ mol dm}^{-3})(0.100 \text{ mol dm}^{-3})} \quad (1)$$

$= 20.0 \text{ dm}^3 \text{ mol}^{-1}$ (1)

b) A change was made to the mixture at the 7th minute.

i) What was the change made?

Some CO(g) was added. (1)

ii) Explain the effect of this change on the concentrations of $Cl_2(g)$ and $COCl_2(g)$ respectively. Calculations are NOT required.

The position of equilibrium shifted so as to decrease the concentration of CO(g), i.e. to the right. (1)

$[COCl_2(g)]$ increased.
$[Cl_2(g)]$ decreased. } (1)

Unit Exercise (p.65)

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

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

Under certain conditions, the equilibrium constant, K_c, for this reaction is 0.160 $dm^3\ mol^{-1}$.

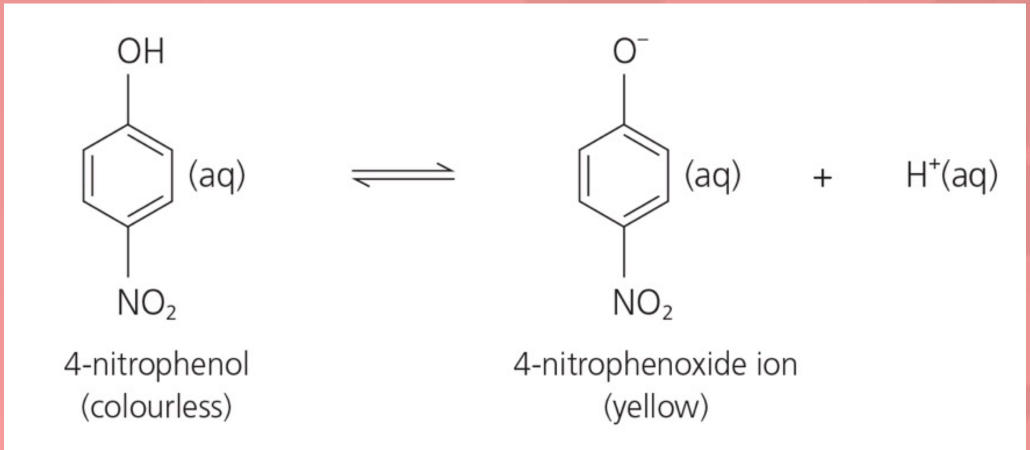
Using the value of K_c, explain whether the position of equilibrium lies towards the product or reactant side under such conditions.

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

There are more reactants than product at equilibrium.
Thus, the position of equilibrium lies towards the reactant side. (1)

Unit Exercise (p.65)

22 The equation below shows the ionisation of 4-nitrophenol in water:



At 25 °C, the equilibrium constant K_c for the ionisation is 8.0×10^{-8} mol dm^{-3}.

a) Write an expression for K_c.
(You may use HA to represent 4-nitrophenol and A^- to represent 4-nitrophenoxide ion.)

Unit Exercise (p.65)

22 (continued) Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

b) When the above ionisation attains equilibrium at 25 °C, the pH of an aqueous solution of 4-nitrophenol is 2.4. Calculate the ratio of the concentration of 4-nitrophenol to the concentration of 4-nitrophenoxide ions in this solution.

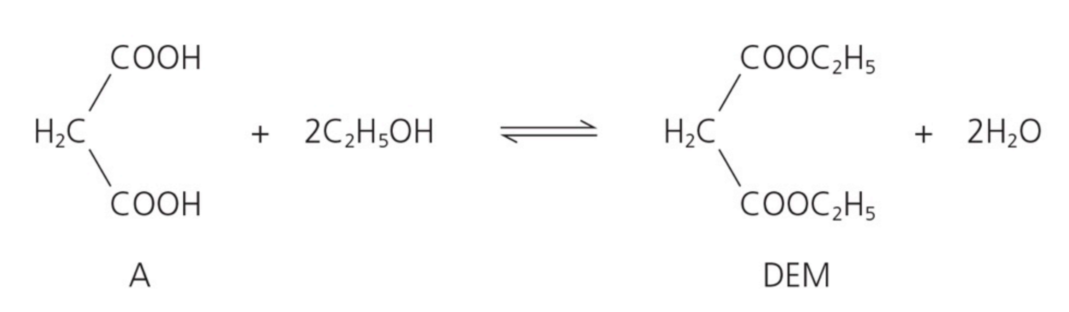
c) Suggest if there is any colour change when NaOH(aq) is added gradually into the solution in (b). Explain your nswer.

d) Suggest ONE possible use of 4-nitrophenol in acid-base titration experiments.

(HKDSE, Paper 1B, 2017,11)

Unit Exercise (p.65)

23 The ester commonly known as diethyl malonate (DEM) occurs in strawberries and grapes. It can be prepared from acid A according to the following equilibrium.



A mixture of 2.40 moles of A and 9.60 moles of ethanol was left to reach equilibrium in an inert solvent in the presence of a small amount of concentrated sulphuric acid. The equilibrium mixture formed contained 1.60 moles of DEM in a total volume, *V* dm^3, of solution.

a) What is the IUPAC name of acid A?

Propanedioic (1)

Unit Exercise (p.65)

23 (continued)

b) Calculate the equilibrium constant, K_c, for the reaction.

	A	+	$2C_2H_5OH$	⇌	DEM	+	$2H_2O$	
Initial concentration ($mol\ dm^{-3}$)	$\frac{2.40}{V}$		$\frac{9.60}{V}$		0		0	
Equilibrium concentration ($mol\ dm^{-3}$)	$\frac{2.40 - 1.60}{V} = \frac{0.80}{V}$		$\frac{9.60 - 3.20}{V} = \frac{6.40}{V}$		$\frac{1.60}{V}$		$\frac{3.20}{V}$	(1)

$$K_c = \frac{[DEM][H_2O]^2}{[A][C_2H_5OH]^2}$$

$$= \frac{\left(\frac{1.60}{V}\ mol\ dm^{-3}\right)\left(\frac{3.20}{V}\ mol\ dm^{-3}\right)^2}{\left(\frac{0.80}{V}\ mol\ dm^{-3}\right)\left(\frac{6.40}{V}\ mol\ dm^{-3}\right)^2} \quad (1)$$

$= 0.50$ (1)

Unit Exercise (p.65)

23 (continued)

c) The total volume of the mixture was doubled by the addition of more of the inert solvent.
State and explain the effect of this addition on the equilibrium yield of DEM.

No effect

Equal number of moles of chemical species on each side of equation / reaction quotient does not change. (1)

Unit Exercise (p.65)

24 The table below lists the equilibrium constant, K_c, for the following reversible reaction at three different temperatures.

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

Temperature (K)	298	373	448
K_c	1.0×10^{-2}	2.0	67.8

Deduce whether the forward reaction is exothermic or endothermic.

The values of K_c increase with increasing temperature. It can be deduced that the forward reaction is endothermic.

The increase in value of K_c means [C(aq)] and [D(aq)] increase but [A(aq)] and [B(aq)] decrease. It can be deduced that the position of equilibrium shifts to the right when the temperature increases. (1)

According to Le Chatelier's principle, a system adjusts in order to bring the temperature down when the temperature is increased. Hence the forward reaction should be endothermic. (1)

Unit Exercise (p.65)

25 Consider the following system:

$$X_2(g) + 2Y_2(g) \rightleftharpoons 2XY_2(g) \qquad \Delta H = +50 \text{ kJ mol}^{-1}$$

A mixture of 3.00 moles of $X_2(g)$ and 2.00 moles of $Y_2(g)$ in a 1.50 dm^3 closed container attained equilibrium at temperature T_1. The equilibrium concentration of $XY_2(g)$ was found to be 0.560 mol dm^{-3}.

Unit Exercise (p.65)

25 (continued)

a) Calculate the equilibrium constant, K_c, for this reaction at temperature T_1.

Number of moles of $XY_2(g)$ at equilibrium = 0.560 mol dm^{-3} x 1.50 dm^3
= 0.840 mol

Number of moles of $X_2(g)$ consumed at equilibrium = $\frac{0.840}{2}$ mol
= 0.420 mol

Number of moles of $Y_2(g)$ consumed at equilibrium = 0.840 mol

	$X_2(g)$	+	$2Y_2(g)$	$\rightleftharpoons$	$2XY_2(g)$	
Equilibrium concentration (mol dm^{-3})	$\frac{3.00 - 0.420}{1.50}$ = 1.72		$\frac{2.00 - 0.840}{1.50}$ = 0.773		0.560	(1)

$$K_c = \frac{[XY_2(g)]^2}{[X_2(g)]\,[Y_2(g)]^2}$$

$$= \frac{(0.560 \text{ mol dm}^{-3})^2}{(1.72 \text{ mol dm}^{-3})\,(0.773 \text{ mol dm}^{-3})^2} \quad (1)$$

$$= 0.305 \text{ dm}^3 \text{ mol}^{-1} \quad (1)$$

Unit Exercise (p.65)

25 (continued)

b) The mixture was allowed to attain equilibrium at temperature T_2 in the 1.50 dm^3 closed container. The value of K_c was found to have decreased. State and explain whether T_1 or T_2 is the higher temperature.

T_1 is the higher temperature.
As the forward reaction is endothermic, the value of K_c decreases with decreasing temperature. (1)

c) The mixture was allowed to attain equilibrium at temperature T_1 in a different closed container of volume 3.00 dm^3. Predict and explain whether the amount of XY_2(g) in the equilibrium mixture would increase, decrease or remain the same.

The amount of XY_2(g) would decrease.
When the volume of the container is increased, the position of equilibrium shifts to the side with more number of moles of gas, i.e. to the left. (1)

Unit Exercise (p.65)

26 The dissociation of water is shown below.

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

Under fixed conditions, $[H_2O(l)]$ can be considered as a constant. In consideration of the definition of K_c, $[H^+(aq)][OH^-(aq)]$ would also be a constant.

At 25 °C, $[H^+(aq)][OH^-(aq)]$ is 1.00×10^{-14} $mol^2\ dm^{-6}$.
At 60 °C, $[H^+(aq)][OH^-(aq)]$ is 9.31×10^{-14} $mol^2\ dm^{-6}$.

Unit Exercise (p.65)

26 (continued)

a) Explain whether the dissociation of water is an exothermic or endothermic process.

The values of K_c increase with increasing temperature. It can be deduced that the dissociation of water is endothermic.

The increase in value of K_c means $[H^+(aq)][OH^-(aq)]$ increase. It can be deduced that the position of equilibrium shifts to the right when the temperature increases. (1)

According to Le Chatelier's principle, a system adjusts in order to bring the temperature down when the temperature is increased. Hence the dissociation of water should be endothermic. (1)

Unit Exercise (p.65)

26 (continued)

b) Predict, using a calculation, whether a pH of 7 at 60 °C is neutral, acidic or alkaline.

pH 7 i.e. $[H^+(aq)] = 10^{-7}$ mol dm^{-3}

$$[OH^-(aq)] = \frac{9.31 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{10^{-7} \text{ mol dm}^{-3}}$$

$$= 9.31 \times 10^{-7} \text{ mol dm}^{-3} \ (1)$$

As $[OH^-(aq)] > [H^+(aq)]$, thus a pH of 7 at 60 °C is alkaline. (1)

Unit Exercise (p.65)

27 A solution contains an equilibrium mixture of two types of cobalt(II) ion.

$$Co^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons CoCl_4^{2-}(aq) \qquad \Delta H > 0$$

pink blue

The solution contains pink $Co^{2+}(aq)$ ions and blue $CoCl_4^{2-}(aq)$ ions, and the solution has a purple colour. 10 cm^3 of the purple solution were poured into each of three test tubes labelled X, Y and Z.

The test tubes were placed in separate water baths, each having a different temperature. The resulting colour changes of the equilibrium mixtures were observed.

Unit Exercise (p.65)

27 (continued)

The results were shown in the following table.

Test tube	Water bath temperature	Observation
X	20 °C	solution remained purple
Y	80 °C	solution turned blue
Z	0 °C	solution turned pink

a) Compared with test tube X, explain the colour change of the mixture in each test tube.

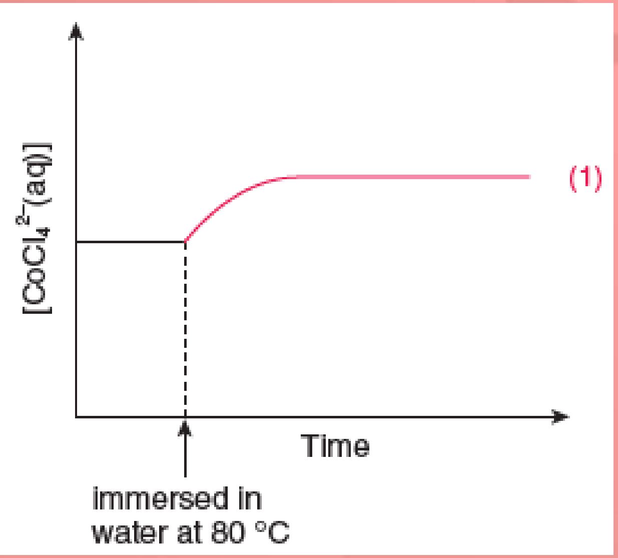
When the temperature is increased, the position of equilibrium shifts in the endothermic direction, i.e. to the right. (1)
The concentration of blue $CoCl_4^{2-}(aq)$ ions increases.
When the temperature is decreased, the position of equilibrium shifts in the exothermic direction, i.e. to the left. (1)
The concentration of pink $Co^{2+}(aq)$ ions increases.

Unit Exercise (p.65)

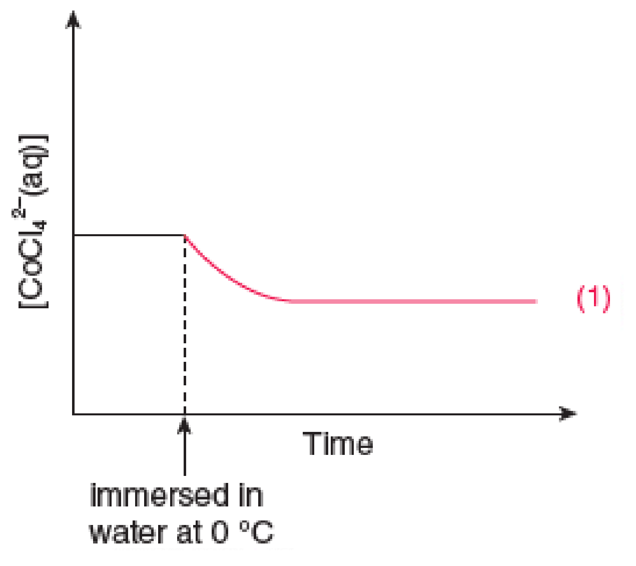
27 (continued)

b) Sketch on each graph given below to show the expected variation in the concentration of $CoCl_4^{2-}(aq)$ ions in the mixture until the attainment of a new equilibrium.

i) Test tube Y



ii) Test tube Z



Unit Exercise (p.65)

28 The first step in the manufacture of nitric acid from ammonia involves the reaction of ammonia with oxygen.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -910 \text{ kJ mol}^{-1}$$

An equilibrium mixture of the four substances is subjected to each of the following changes. Will the number of moles of NO(g) obtained increase, decrease or remain unchanged? Explain your answer in each case.

a) Increasing the pressure

Decrease

A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the left. (1)

Unit Exercise (p.65)

28 (Continued)

b) Increasing the temperature

Decrease

A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the left. (1)

c) Adding a suitable catalyst

Remain unchanged

A catalyst has NO effect on the position of equilibrium. (1)

Unit Exercise (p.65)

29 Hydrogen is produced in industry from methane and steam in a two-stage process.

a) In the first stage, carbon monoxide and hydrogen are formed.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +206 \text{ kJ mol}^{-1}$$

i) Make a prediction of the conditions of temperature and pressure that would produce the maximum yield of $H_2(g)$. Explain your answers.

High temperature and low pressure

A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the right. (1)

A pressure decrease shifts the position of equilibrium to the side with more number of moles of gas, i.e. to the right. (1)

Unit Exercise (p.65)

29 (Continued)

a) ii) A nickel oxide catalyst is used in the first stage. State why a catalyst is used, and give its effect on K_c.

To increase the rate of reaction / of attainment of equilibrium. (1)

No effect on K_c. (1)

b) The second stage is carried out in a separate reactor. Carbon monoxide is converted into carbon dioxide and more hydrogen is formed.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H = -41 \text{ kJ mol}^{-1}$

Predict the effect of an increase in the total pressure on the yield of hydrogen in this second stage. Explain your answer.

No effect

There is no change in the number of moles of gas during the course of the reaction. (1)

Unit Exercise (p.65)

30 Nitrogen reacts with hydrogen to form ammonia.

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

a) The minimum volumes of nitrogen and hydrogen that must react completely to form 5 000 dm^3 of ammonia are calculated.
These volumes are mixed and left, under appropriate conditions, until the reaction reaches equilibrium.
Explain which gas or gases will be present when equilibrium is reached.
All the three gases are present.
The reaction is reversible. / Ammonia decomposes to form nitrogen and hydrogen. (1)

Unit Exercise (p.65)

30 (Continued)

b) The Haber process is carried out under a pressure of about 200 atm. Explain the effect on the equilibrium yield of ammonia, if the process is carried out at a pressure higher than 200 atm.

Increased / higher yield of ammonia (1)

A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the right. (1)

c) Explain the effect on the rate of attainment of equilibrium, if the process is carried out at a pressure higher than 200 atm.

The rate of attainment of equilibrium increases.

The gas molecules are closer. / The concentrations of all substances increase.

The chance of collision of molecules increases, so there are more effective collisions in a unit volume per unit time. (1)

(Edexcel GCSE (Higher Tier), Unit C3, Jun. 2015, 4(b)(ii)–(iv))

Unit Exercise (p.65)

31 Sulphur trioxide, SO^3, is used for the industrial manufacture of sulphuric acid.

SO_3 is produced by reacting sulphur dioxide, SO_2, and oxygen, O_2, as shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$

Le Chatelier's principle can be used to predict how different conditions affect the equilibrium position.

- Using Le Chatelier's principle, show that a low temperature and a high pressure should be used to obtain a maximum equilibrium yield of SO_3.
- Explain why the actual conditions used in industry may be different from the conditions needed for a maximum equilibrium yield.

(OCR Advanced Subsidiary Level, Chem. A, H032/01, Jun. 2016, 25(a))

Unit Exercise (p.65)

31 (Continued)

A low temperature shifts the position of equilibrium in the exothermic reaction, i.e. to the right. (1)

A high pressure shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the right. (1)

However, a low temperature gives a low reaction rate. A high pressure is expensive to generate / produces a safety risk. (1)

The actual conditions used in industry are a compromise between the need to maximise the yield of the product, the need to produce the product fast enough, the cost and safety risk. (1)

Unit Exercise (p.65)

32 Ethanol can be made by the hydration of ethene.

$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \quad \Delta H = -42\ kJ\ mol^{-1}$

In a simulation of study of the reaction, identical mixtures of $C_2H_4(g)$ + $H_2O(g)$ were allowed to attain equilibrium under different reaction conditions, and the percentage yield of $C_2H_5OH(g)$ were recorded. The table below listed the results obtained.

Trial	Reaction conditions			Percentage yield of $C_2H_5OH(g)$ (%)
	Temperature (°C)	Pressure (atm)	Catalyst	
1	200	40	phosphoric acid	15
2	200	80	phosphoric acid	50
3	400	40	phosphoric acid	x
4	400	80	—	y
5	200	40	—	z

(No catalyst was used in trials 4 and 5.)

Unit Exercise (p.65)

32 (Continued)

a) In which TWO trials are the percentage yield of $C_2H_5OH(g)$ the same? Explain your answer.

Trials 1 and 5

For identical mixtures, the position of equilibrium is affected by temperature and pressure only. In trials 1 and 5, both the temperature and pressure are the same, thus they have the same percentage yield of $C_2H_5OH(g)$. (1)

b) In which trial is the percentage yield of $C_2H_5OH(g)$ the highest? Explain your answer.

Trial 2

A temperature decrease shifts the position of equilibrium in the exothermic direction, i.e. to the right. (1)

A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the right. (1)

In trial 2, the temperature is the lowest while the pressure is the highest.

Unit Exercise (p.65)

32 (Continued)

*c) Typical conditions used for the reaction are as follows:

Temperature	300 °C
Pressure	60 atm
Catalyst	phosphoric acid

Explain why this set of reaction conditions is used.

Temperature at 300 °C is high enough to increase the reaction rate, but low enough to give a reasonable yield. (1)
Pressure at 60 atm is high enough to increase the rate and yield, but low enough to minimise the maintenance cost of pipelines (the cost of building and running the plant is not high). (1)
Phosphoric acid catalyses the reaction / speeds up the reaction. (1)
Communication mark (1)

Topic Exercise (p.75)

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.

Topic Exercise (p.75)

PART I MULTIPLE CHOICE QUESTIONS

Directions: Questions 1 and 2 refer to the information below.
Approximate values of the equilibrium constant for the Haber process reaction are given in the table.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

Temperature (K)	K_c
298	10^4
1 100	10^{-8}

1 Which of the following statements about this reaction is correct?

A At 298 K the equilibrium position is towards the reactants.

B There will be no temperature between 298 K and 1 100 K where K_c = 1.

C As the temperature is raised, more ammonia is formed.

D At 1 100 K the position of equilibrium lies to the left.

Answer: D

(OCR Advanced Subsidiary Level, Chem. B (Salters), H033/01, Sample Question Paper, 2014, 10(a))

Topic Exercise (p.75)

2 In a pilot plant making ammonia, NH_3, 200 cm^3 of nitrogen are mixed with 300 cm^3 of hydrogen.

What would be the final volume (at the same temperature and pressure) if complete reaction occurs?

A 200 cm^3
B 250 cm^3
C 300 cm^3
D 400 cm^3

Answer: C

(OCR Advanced Subsidiary Level, Chem. B (Salters), H033/01, Sample Question Paper, 2014, 10(b))

Unit Exercise (p.65)

2 (continued)

Explanation:

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

200 cm³ 300 cm³

1 mole of N_2 reacts with 3 moles of H_2 to make 2 moles of NH_3.

In this reaction, 100 cm^3 of N_2 react with 300 cm^3 of H_2 to make 200 cm^3 of NH_3.

Volume of N_2 remaining = (200 – 100) cm^3
= 100 cm^3

Final volume of gas = (100 + 200) cm^3
= 300 cm^3

Topic Exercise (p.75)

3 Consider the following chemical equilibrium system:

$$CH_3Cl(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Cl^-(aq)$$

Adding which of the following substances will shift the position of equilibrium to the left?

A $HNO_3(aq)$
B $KNO_3(aq)$
C $NaOH(aq)$
D $CH_3Cl(aq)$

Explanation:
$H^+(aq)$ ions from $HNO_3(aq)$ react with $OH^-(aq)$ ions to form water. The position of equilibrium shifts to the left to produce more $OH^-(aq)$ ions.

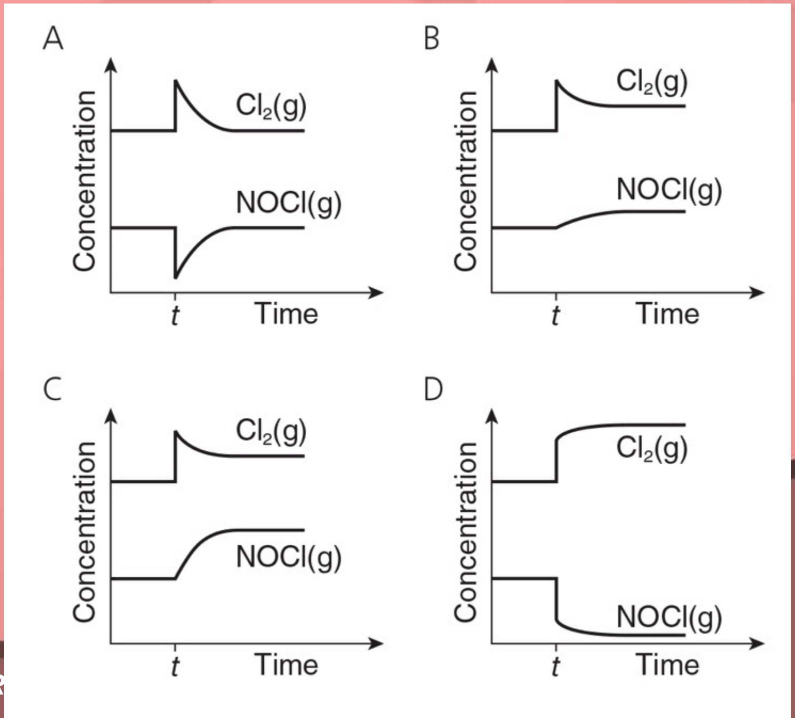
Answer: A

Topic Exercise (p.75)

4 NOCl(g) decomposes to give NO(g) and Cl_2(g) according to the equation below.

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

A sample of NOCl(g) was placed in a closed container and allowed to attain equilibrium. At time *t* after equilibrium, some extra Cl_2(g) was added to the equilibrium mixture. A new equilibrium was attained. Which of the following graphs best represents the changes in concentrations of NOCl(g) and Cl_2(g)?



Answer: C

Topic Exercise (p.75)

4 (continued)

Explanation:

When some extra Cl_2(g) was added, the position of equilibrium shifted to the left. Some of the extra Cl_2(g) was consumed and more NOCl(g) was formed.

Topic Exercise (p.75)

5 The following reaction has attained equilibrium in a fixed volume container:

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad \Delta H = -41.1 \text{ kJ mol}^{-1}$

Which of the following is correct if the temperature of the system is increased?

A The pressure of the system remains unchanged.
B Both the rates of forward and backward reaction increase.
C The equilibrium constant of the reaction remains unchanged.
D The respective yields of $CO_2(g)$ and $H_2(g)$ increase to the same extent.

Answer: B

(HKDSE, Paper 1A, 2016, 26)

Topic Exercise (p.75)

6 The following system attained equilibrium at a certain temperature:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad \Delta H = -111 \text{ kJ mol}^{-1}$$

Which of the following changes would affect both the value of the equilibrium constant, K_c, and the proportion of $PCl_5(g)$ in an equilibrium mixture of the three gases?

A Adding a catalyst
B Changing the temperature
C Increasing the concentration of $PCl_3(g)$
D Increasing the pressure

Answer: B

Topic Exercise (p.75)

7 The industrial production of hydrogen involves the reaction below.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +206 \text{ kJ mol}^{-1}$

Under which set of conditions would the highest yield of $H_2(g)$ be obtained?

	Pressure (atm)	Temperature (K)
A	100	200
B	200	200
C	100	500
D	200	500

Explanation:
A pressure decrease shifts the position of equilibrium to the side with more number of moles of gas, i.e. to the right.
A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the right.
Thus, a low pressure and a high temperature would give the highest yield of $H_2(g)$.

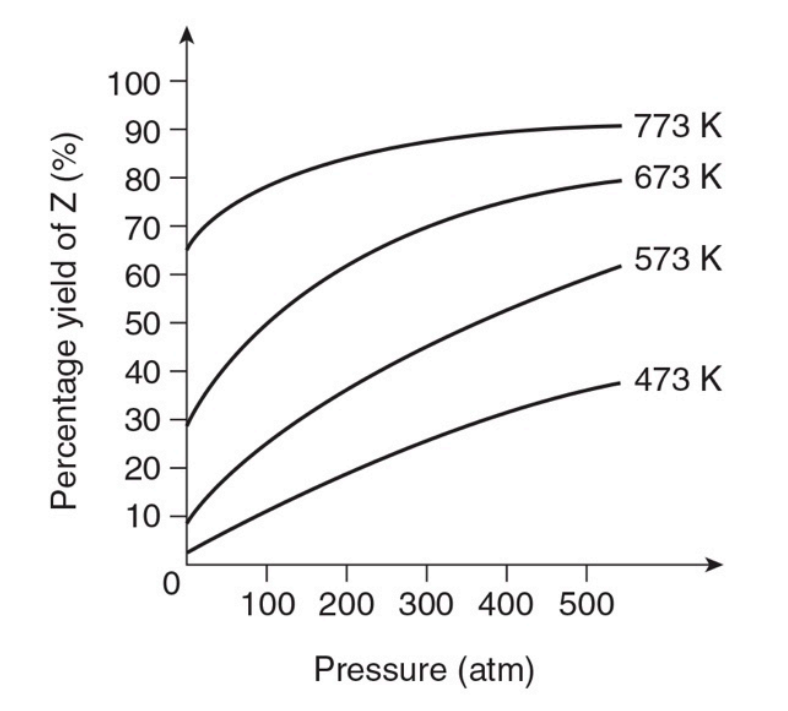
Answer: C

Topic Exercise (p.75)

8 In an industrial process, two gases X and Y react together to form a single gaseous product Z.

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

The percentage yield of product Z at equilibrium varies according to the pressure and the temperature as shown below:



Topic Exercise (p.75)

8 (continued)

Which of the following statements about this reaction is correct?

A Decreasing the temperature decreases the value of the equilibrium constant.

B Decreasing the temperature increases the rate of this reaction.

C Increasing the pressure increases the value of the equilibrium constant.

D The forward reaction is exothermic.

Answer: A

Explanation:

The yield of product Z decreases with decreasing temperature. It can be deduced that the value of K_c decreases with decreasing temperature.

Topic Exercise (p.75)

Directions: Questions 9 and 10 refer to the following reaction involving four miscible liquids.

$W(l) + X(l) \rightleftharpoons Y(l) + Z(l) \qquad \Delta H = +45\ kJ\ mol^{-1}$

At 25 °C, the equilibrium constant K_c for the reaction is 2.5. In an experiment, 1.0 mol of W(l) and 1.0 mol of X(l) are placed in a closed container keeping at 25 °C. When equilibrium is attained, the total volume of the reaction mixture is 0.20 dm^3.

9 Which of the following statements about this reaction is correct?

A 0.44
B 0.61
C 0.71
D 0.83

Answer: B

(HKDSE, Paper 1A, 2017, 31)

Topic Exercise (p.75)

10 When equilibrium is attained, which of the following would increase the number of moles of Y(l)?

(1) Removing Z(l) from the reaction mixture
(2) Increasing the volume of the container
(3) Increasing the temperature of the reaction mixture

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

Answer: C

(HKDSE, Paper 1A, 2017, 32)

Topic Exercise (p.75)

Directions: Questions 11 and 12 refer to the information below.

Ethanoic acid can be manufactured by reacting carbon monoxide with methanol in the presence of a catalyst.

$CO(g) + CH_3OH(g) \rightleftharpoons CH_3COOH(g) \quad \Delta H = -137 \text{ kJ mol}^{-1}$

The reaction is carried out at 200 °C and 30–60 atmospheres.

11 Which of the following combinations shows the effects of the catalyst on the rate of forward reaction, the rate of backward reaction and the yield of $CH_3COOH(g)$?

	Rate of forward reaction	Rate of backward reaction	Yield of $CH_3COOH(g)$
A	increases	decreases	no change
B	increases	increases	no change
C	no change	no change	increases
D	decreases	increases	decreases

Answer: B

Topic Exercise (p.75)

12 What would be the consequences of carrying out the reaction at the same temperature but at a pressure of 100 atmospheres?

(1) The manufacturing costs would increase.
(2) The yield of $CH_3COOH(g)$ would be higher.
(3) The reaction would proceed at a higher rate.

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

Explanation:
A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the right.

Answer: D

Unit Exercise (p.65)

13 In a closed container and at a certain temperature, the following equilibrium was attained:

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

Which of the following statements is / are correct?

(1) $CO(g)$ and $Cl_2(g)$ must be of the same concentration.

(2) The rate of decomposition of $COCl_2(g)$ is equal to the rate of formation of $CO(g)$.

(3) The equilibrium constant K_c for the reaction increases when the volume of the container increases.

A (1) only

B (2) only

C (1) and (3) only

D (2) and (3) only

Answer: B

(HKDSE, Paper 1A, 2015, 31)

Topic Exercise (p.75)

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

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$

When equilibrium is attained, which of the following would increase the yield of $NH_3(g)$?

(1) Increasing the pressure
(2) Decreasing the temperature
(3) Adding $H_2(g)$

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

Answer: D

Explanation:

(1) Increasing the pressure shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the right.

(2) Decreasing the temperature shifts the position of equilibrium in the exothermic direction, i.e. to the right.

(3) Adding $H_2(g)$ shifts the position of equilibrium to the right.

Topic Exercise (p.75)

Directions:
Each question (Questions 15–16) consists of two separate statements. Decide whether each of the two statements is true or false; if both are true, then decide whether or not the second statement is a correct explanation of the first statement. Then select one option from A to D according to the following table :

A	Both statements are true and the 2nd statement is a correct explanation of the 1st statement.
B	Both statements are true but the 2nd statement is NOT a correct explanation of the 1st statement.
C	The 1st statement is false but the 2nd statement is true.
D	Both statements are false.

Topic Exercise (p.75)

15 1st statement

At chemical equilibrium state, the forward reaction rate equals zero.

2nd statement

At chemical equilibrium state, the reactants would NOT react to give the products.

(HKDSE, Paper 1A, 2014, 35)

Answer: D

Topic Exercise (p.75)

16 1st statement

The addition of a catalyst increases the equilibrium yield of a reversible reaction.

2nd statement

A catalyst can increase the rate of the forward reaction.

Explanation:

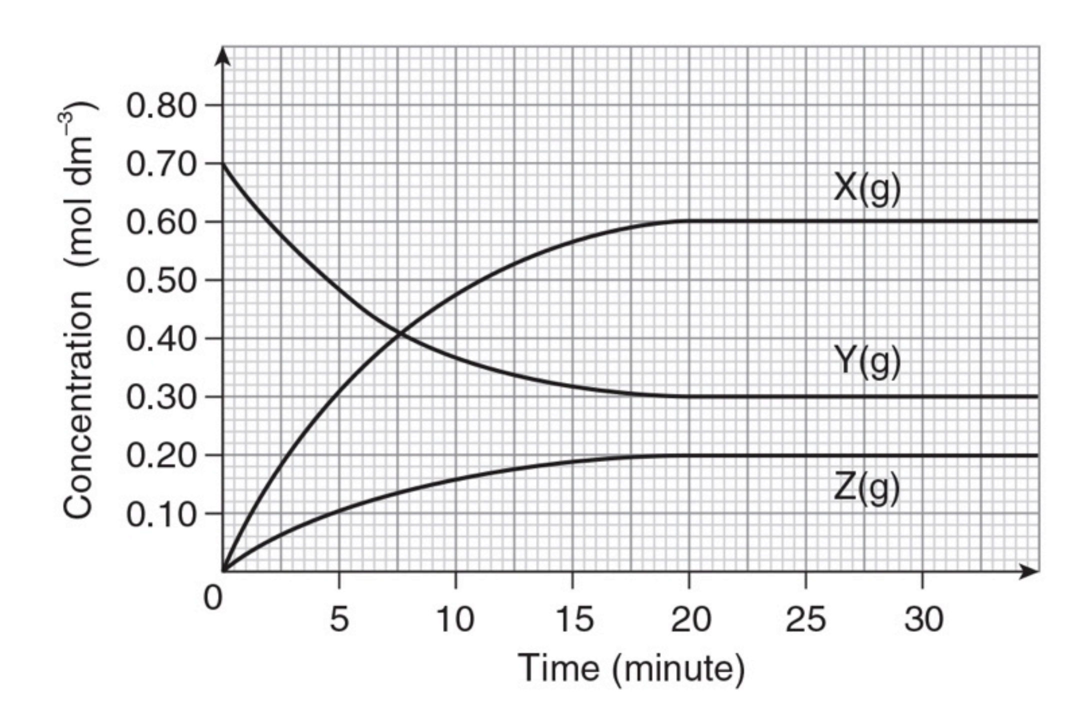
The addition of a catalyst has NO effect on the position of equilibrium, i.e. NO effect on the yield.

Answer: C

Topic Exercise (p.75)

PART II STRUCTURED QUESTIONS

17 An experiment was performed for a reversible reaction involving X(g), Y(g) and Z(g) in a closed container of 2.0 dm^3 at a constant temperature. The graph below shows the relevant experimental data.



Topic Exercise (p.75)

17 (continued)

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

b) Calculate the equilibrium constant *K*c for the reaction at the temperature of the experiment.

c) Comment on the following statement:
'The rate of the forward reaction is zero at the 25th minute after the start of the reaction.'

(HKDSE, Paper 1B, 2018, 13)

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Topic Exercise (p.75)

18 Consider the reaction represented by the equation below.

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

K_c = 1 078 $dm^3\ mol^{-1}$ at 25 °C

In an experiment, 25.0 cm^3 of 0.0100 mol dm^{-3} $Fe_2(SO_4)_3(aq)$ and 25.0 cm^3 of 0.0100 mol dm^{-3} KSCN(aq) were mixed in a conical flask kept at 25 °C.

Calculate the concentration of $Fe(SCN)^{2+}(aq)$ when equilibrium was attained.

Topic Exercise (p.75)

18 (continued)

Suppose the equilibrium concentration of $Fe(SCN)^{2+}(aq)$ is x mol dm^{-3}.

	$Fe^{3+}(aq)$ +	$SCN^{-}(aq)$ $\rightleftharpoons$	$Fe(SCN)^{2+}(aq)$	
Initial concentration (mol dm^{-3})	$2 \times \frac{0.0100}{2}$	$\frac{0.0100}{2}$	0	
Equilibrium concentration (mol dm^{-3})	$0.0100 - x$	$0.00500 - x$	x	(1)

$$K_c = 1\,078 \text{ dm}^3 \text{ mol}^{-1} = \frac{[Fe(SCN)^{2+}(aq)]}{[Fe^{3+}(aq)]\,[SCN^{-}(aq)]}$$

$$= \frac{x \text{ mol dm}^{-3}}{(0.0100 - x) \text{ mol dm}^{-3}\,(0.00500 - x) \text{ mol dm}^{-3}} \quad (1)$$

Rearranging the equation gives

$1\,078(0.0100 - x)(0.00500 - x) = x$

$0.0539 - 16.17x + 1\,078x^2 = x$

$1\,078x^2 - 17.17x + 0.0539 = 0$

$x = 4.30 \times 10^{-3}$ or 0.0116 (rejected) (1)

$\therefore$ the equilibrium concentration of $Fe(SCN)^{2+}(aq)$ is 4.30×10^{-3} mol dm^{-3}.

Topic Exercise (p.75)

19 Ammonia is manufactured by the reaction between nitrogen and hydrogen at 723 K.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ K_c = 0.134 $dm^6\ mol^{-2}$ at 723 K

In a simulation of the process, a mixture of nitrogen and hydrogen was placed in a closed container. The initial concentrations of nitrogen and hydrogen were 0.500 mol dm^{-3} and 1.50 mol dm^{-3} respectively.

Topic Exercise (p.75)

19 (continued)

a) Calculate the percentage of nitrogen consumed when equilibrium was attained.

Suppose the equilibrium concentration of $NH_3(aq)$ is $2x$ mol dm^{-3}.

	$N_2(g)$ +	$3H_2(g)$ ⇌	$2NH_3(g)$	
Equilibrium concentration (mol dm^{-3})	$0.500 - x$	$1.50 - 3x$	$2x$	(1)

$$K_c = 0.134 \text{ dm}^6 \text{ mol}^{-2} = \frac{[NH_3(g)]^2}{[N_2(g)]\,[H_2(g)]^3}$$

$$= \frac{(2x \text{ mol dm}^{-3})^2}{(0.500 - x) \text{ mol dm}^{-3}\,(1.50 - 3x)^3 \text{ mol}^3 \text{ dm}^{-9}} \quad (1)$$

Rearranging the equation gives

$$0.134 = \frac{(2x)^2}{(0.500 - x)27(0.500 - 3x)^3}$$

$$0.134 \times 27 = \frac{(2x)^2}{(0.500 - x)^4}$$

$$1.90 = \frac{2x}{(0.500 - x)^2}$$

$$1.90(0.500 - x)^2 = 2x$$

$$0.475 - 1.9x + 1.9x^2 = 2x$$

$$1.9x^2 - 3.9x + 0.475 = 0$$

$x = 0.130$ or 1.92 (rejected) (1)

$$\% \text{ of nitrogen consumed} = \frac{0.130}{0.500} \times 100\%$$

$= 26.0\%$ (1)

∴ 26.0% of nitrogen were consumed.

Topic Exercise (p.75)

19 (continued)

b) Explain why the process is NOT operated at temperatures much higher or much lower than 723 K.

The forward reaction is exothermic.

Operating at a much higher temperature shifts the position of equilibrium in the endothermic direction, i.e. to the left. This lowers the yield of ammonia. (1)

Operating at a much lower temperature makes the reaction very slow. It takes a long time to attain equilibrium. (1)

Topic Exercise (p.75)

20 Ethene gas and bromine gas react according to the equation below.

$$C_2H_4(g) + Br_2(g) \rightleftharpoons C_2H_4Br_2(g)$$

K_c = 0.600 dm^3 mol^{-1} at temperature T

2.00 moles of C_2H_4(g), 1.20 moles of Br_2(g) and 1.00 mole of $C_2H_4Br_2$(g) were mixed in a 2.00 dm^3 closed container kept at temperature T.

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

$$Q_c = \frac{\frac{1.00}{2.00}\text{ mol dm}^{-3}}{\left(\frac{2.00}{2.00}\text{ mol dm}^{-3}\right)\left(\frac{1.20}{2.00}\text{ mol dm}^{-3}\right)}$$

$= 0.833$ dm^3 mol^{-1} (1)

Topic Exercise (p.75)

20 (continued)

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

As $Q_c > K_c$, $[C_2H_4(g)]$ and $[Br_2(g)]$ must increase while $[C_2H_4Br_2(g)]$ must decrease until $Q_c = K_c$.

A net backward reaction occurred, i.e. the backward reaction rate was greater than the forward reaction rate. (1)

Topic Exercise (p.75)

20 (continued)

b) Calculate the concentration of $C_2H_4Br_2(g)$ when the system attained equilibrium.

Suppose x mole of $C_2H_4Br_2(g)$ was consumed when the system attained equilibrium.

$$C_2H_4(g) + Br_2(g) \rightleftharpoons C_2H_4Br_2(g)$$

Equilibrium concentration (mol dm^{-3}) $\frac{2.00 + x}{2.00}$ $\quad \frac{1.20 + x}{2.00}$ $\quad \frac{1.00 - x}{2.00}$

$$K_c = 0.600 \text{ dm}^3 \text{ mol}^{-1} = \frac{[C_2H_4Br_2(g)]}{[C_2H_4(g)]\,[Br_2(g)]}$$

$$= \frac{\frac{1.00 - x}{2.00} \text{ mol dm}^{-3}}{\left(\frac{2.00 + x}{2.00} \text{ mol dm}^{-3}\right)\left(\frac{1.20 + x}{2.00} \text{ mol dm}^{-3}\right)}$$

Rearranging the equation gives

$0.600(2.00 + x)(1.20 + x) = 2.00(1.00 - x)$

$1.44 + 1.92x + 0.6x^2 = 2.00 - 2x$

$0.6x^2 + 3.92x - 0.560 = 0$

$x = 0.140$ or -6.67 (rejected) (1)

Equilibrium concentration of $C_2H_4Br_2(g)$ = $\frac{1.00 - 0.140}{2.00}$ mol dm^{-3}

= 0.430 mol dm^{-3} (1)

∴ the equilibrium concentration of $C_2H_4Br_2(g)$ is 0.430 mol dm^{-3}.

Topic Exercise (p.75)

*21 You are provided with common laboratory apparatus, and the following chemicals:

- ethanoic acid;
- ethanol;
- concentrated sulphuric acid;
- standard sodium hydroxide solution.

Outline how you would perform an experiment to determine the equilibrium constant (K_c) for the esterification reaction below:

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

Topic Exercise (p.75)

*21 (continued)

Procedure

Step 1 Place an equal amount of ethanoic acid and ethanol in a pear-shaped flask. Withdraw 1.00 cm^3 of the mixture and add to a conical flask containing 25 cm^3 of deionised water. Titrate the contents of the conical flask against standard sodium hydroxide solution. (1)

Step 2 Add a few drops of concentrated sulphuric acid to the acid-alcohol mixture in the pear-shaped flask. Withdraw 1.00 cm^3 of the mixture and add to a conical flask containing 25 cm^3 of deionised water. Titrate the contents of the conical flask against standard sodium hydroxide solution as in *Step 1*.(1)

Step 3 Heat the contents of the pear-shaped flask under reflux for two hours. After cooling, withdraw 1.00 cm^3 of the mixture and add to a conical flask containing 25 cm^3 of deionised water. Titrate the contents of the conical flask against standard sodium hydroxide solution as in *Step 1*. (1)

Topic Exercise (p.75)

*21 (continued)

Calculations

Determine the concentration of ethanoic acid in the original mixture from the titration result in *Step 1*.
Determine the concentration of ethanoic acid in the equilibrium mixture from titration results in *Steps 2* and *3*. (1)

Determine the concentration of other chemical species and calculate the equilibrium constant (K_c) for the esterification reaction by using the expression below:

$$K_c = \frac{[CH_3COOCH_2CH_3(l)]\,[H_2O(l)]}{[CH_3COOH(l)]\,[CH_3CH_2OH(l)]} \quad (1)$$

Communication mark (1)

Topic Exercise (p.75)

22 Hydrogen and iodine react together in a reversible reaction.

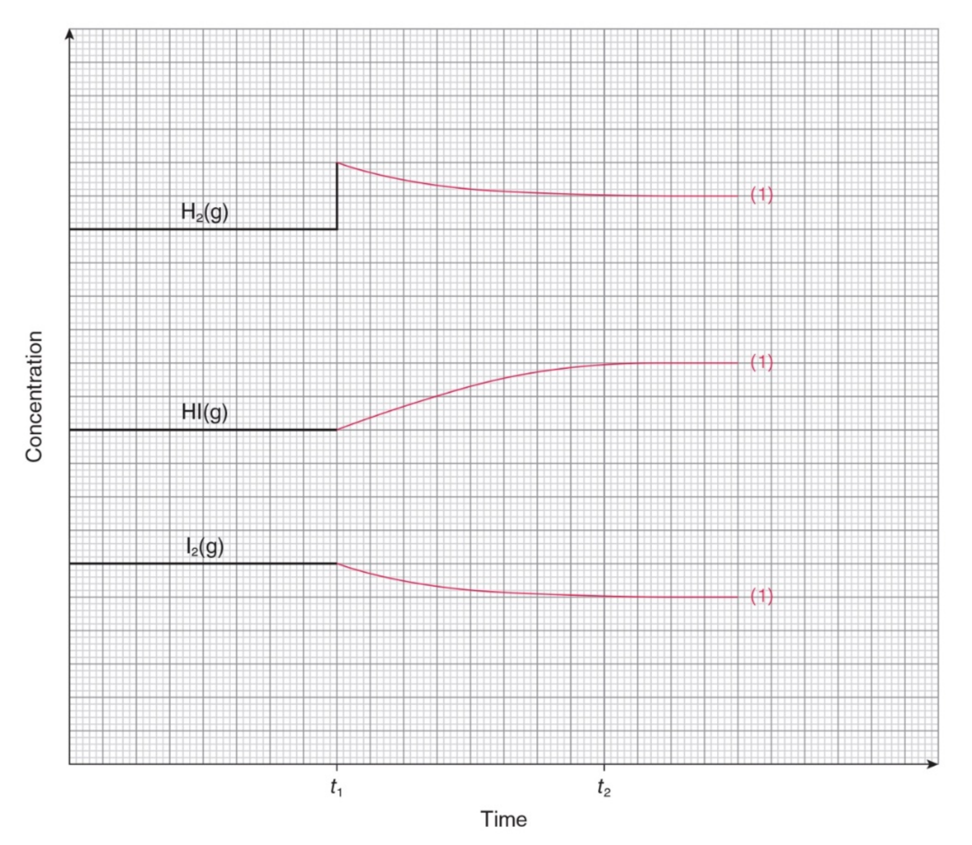
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -10.4\ kJ\ mol^{-1}$

$H_2(g)$, $I_2(g)$ and HI(g) were mixed together and allowed to attain equilibrium in a closed container. At time t_1, a small amount of $H_2(g)$ was added to the equilibrium system. The system attained a new equilibrium at time t_2.

Topic Exercise (p.75)

22 (continued)

a) Sketch, on the graph below, the variations of concentrations of the three gases with time until t_2. (Assume that the temperature of the system remained constant throughout the whole process.)



Topic Exercise (p.75)

22 (continued)

b) The volume of the container of the new equilibrium system was halved at constant temperature after t_2. Predict and explain the effect of this change on:

i) the position of equilibrium;

A volume decrease has NO effect on the position equilibrium because there is no change in the number of moles of gas during the course of the reaction. (1)

ii) the rate of decomposition of HI(g);

The rate of decomposition of HI(g) increases.

The gas molecules are closer. / The concentrations of all substances increase.

The chance of collision of molecules increases, so there are more effective collisions in a unit volume per unit time. (1)

iii) the value of K_c.

The value of K_c does NOT change because the temperature remains constant. (1)

Topic Exercise (p.75)

23 Bromomethane can be prepared via the reaction below.

$$CH_3OH(g) + HBr(g) \rightleftharpoons CH_3Br(g) + H_2O(g) \quad \Delta H = -37.2 \text{ kJ mol}^{-1}$$

a) The volume of the container of the chemical equilibrium system is decreased at constant temperature.
Predict and explain the effect of this change on:

i) the rate of formation of $CH_3Br(g)$;

The rate of formation of $CH_3Br(g)$ increases.
The gas molecules are closer. / The concentrations of all substances increase.
The chance of collision increases, so there are more effective collisions in a unit volume per unit time. (1)

Topic Exercise (p.75)

23 (continued)

a) ii) the yield of $CH_3Br(g)$;

The yield of $CH_3Br(g)$ does NOT change.

There is no change in the number of moles of gas during the course of the reaction. Changes in pressure have NO effect on the position of equilibrium. (1)

iii) the value of K_c.

The value of K_c does NOT change because the temperature remains constant. (1)

b) The product $CH_3Br(g)$ is removed continuously at constant pressure and temperature.

Predict and explain the effect of this change on the yield of $CH_3Br(g)$.

The yield of $CH_3Br(g)$ increases. (1)

Removing the product favours the forward reaction. (1)

Topic Exercise (p.75)

24 Refer to the following chemical equation:

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H > 0$

Under fixed conditions, $[H_2O(l)]$ is considered as a constant. In consideration of the definition of K_c, $[H^+(aq)][OH^-(aq)]$ would also be a constant.

a) The pH of an aqueous solution is defined as $-\log[H^+(aq)]$. The pH of water equals 7.0 at 298 K. Find, at this temperature, the:

i) $[H^+(aq)]$

ii) $[H^+(aq)]\ [OH^-(aq)]$

Topic Exercise (p.75)

24 (continued)

b) [$H_2O(l)$] equals 55.6 mol dm^{-3} at 298 K. Suggest why [$H_2O(l)$] is considered as a constant with reference to the values of [$H^+(aq)$] and [$OH^-(aq)$].

c) Explain whether the pH of water at 328 K would be less than 7.0, equal to 7.0, or greater than 7.0.

(HKDSE, Paper 1B, 2015, 11)

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Topic Exercise (p.75)

25 Dinitrogen tetroxide, $N_2O_4(g)$, dissociates to form nitrogen dioxide, $NO_2(g)$, according to the following equation.

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

0.280 mole of $N_2O_4(g)$ is placed in an empty 2.00 dm^3 flask and heated to 130 °C. When the system attains equilibrium, 0.302 mole of $NO_2(g)$ is present in the flask.

Topic Exercise (p.75)

25 (continued)

a) Calculate the equilibrium constant, K_c, for the reaction at 130 °C.

	$N_2O_4(g)$ $\rightleftharpoons$	$2NO_2(g)$
Equilibrium concentration ($mol\ dm^{-3}$)	$\dfrac{0.280 - \dfrac{0.302}{2}}{2.00}$ = 0.0645	$\dfrac{0.302}{2.00}$ = 0.151 (1)

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

$$= \frac{(0.151\ mol\ dm^{-3})^2}{0.0645\ mol\ dm^{-3}} \quad (1)$$

$$= 0.354\ mol\ dm^{-3} \quad (1)$$

Topic Exercise (p.75)

25 (continued)

b) At 25 °C, the numerical value of the equilibrium constant for this reaction is 0.120. Explain whether the forward reaction is endothermic or exothermic.

The values of K_c increase with increasing temperature. It can be deduced that the forward reaction is endothermic. The increase in value of K_c means $[NO_2(g)]$ increases but $[N_2O_4(g)]$ decreases. It can be deduced that the position of equilibrium shifts to the right when the temperature increases. (1)

According to Le Chatelier's principle, a system adjusts in order to bring the temperature down when the temperature is increased. Hence the forward reaction should be endothermic. (1)

Topic Exercise (p.75)

26 In an experiment, 2.0 mol of SO_2(g) and 2.0 mol of O_2(g) are allowed to react in a closed container maintained at 950 K. The chemical equation for the reaction is shown below:

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -198$ kJ mol^{-1}

When the reaction attains dynamic equilibrium, 1.8 mol of SO_3(g) is obtained.

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

b) At 950 K, the equilibrium constant Kc for the above reaction is 878 dm^3 mol^{-1}. Calculate the volume of the container.

c) If the above equilibrium mixture is subjected to each of the following changes, will the number of moles of SO_3(g) obtained increase, decrease or remain unchanged? Explain your answer in each case.

i) Increasing the temperature

ii) Adding a suitable catalyst

(HKDSE, Paper 1B, 2016,10)

Answers for the questions of the public examinations in Hong Kong are not provided (if applicable).

Topic Exercise (p.75)

27 Ethanol can be made industrially by reacting ethene with steam in the presence of a catalyst.

$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$ $\Delta H = -46\ kJ\ mol^{-1}$

a) Suggest the conditions of temperature and pressure that would produce the maximum yield of ethanol. Explain your answers.

Low temperature and high pressure

A temperature decrease shifts the position of equilibrium in the exothermic direction, i.e. to the right. (1)

A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas, i.e. to the right. (1)

b) Give a disadvantage of using a low temperature in the process.

The reaction is very slow. It takes a long time to attain equilibrium. (1)

c) The actual pressure used in the process is 65 atmospheres. Apart from safety issues, suggest a disadvantage of using a higher pressure.

High cost of container / more expensive to build container with thicker walls / high cost of generating high pressure (1)

Topic Exercise (p.75)

28 Carbon dioxide reacts with hydrogen to produce methanol.

carbon dioxide + hydrogen ⇌ methanol + steam

Identical mixtures of carbon dioxide and hydrogen were allowed to attain equilibrium under different pressures and temperatures.

The table below lists the percentage yield of methanol under different conditions.

Pressure (atm)	Temperature (°C)			
	100	200	300	400
20	90%	81%	52%	38%
40	93%	87%	70%	58%
60	96%	92%	83%	73%
80	98%	95%	90%	83%
100	99%	97%	94%	90%

Topic Exercise (p.75)

28 (continued)

a) A student predicts that the reaction between carbon dioxide and hydrogen is endothermic and involves a reduction in the number of moles of gas.
Explain whether the student's predictions are supported by the results in the table.

The yield of methanol decreases with increasing temperature. (1)
This means that the position of equilibrium shifts to the left when the temperature is increased.
A temperature increase shifts the position of equilibrium in the endothermic direction, i.e. to the left. (1)
Thus, the forward reaction, i.e. the reaction between carbon dioxide and hydrogen, should be exothermic.
The yield of methanol increases with increasing pressure. (1)
This means that the position of equilibrium shifts to the right when the pressure is increased.
A pressure increase shifts the position of equilibrium to the side with fewer number of moles of gas. (1)
Thus, the forward reaction, i.e. the reaction between carbon dioxide and hydrogen, involves a reduction in the number of moles of gas.

Topic Exercise (p.75)

28 (continued)

b) Describe and explain how the position of equilibrium would change when extra carbon dioxide is added to the equilibrium mixture.

When extra carbon dioxide is added, the position of equilibrium shifts to the right. Some of the extra carbon dioxide is consumed. (1)