7.1 CHEMICAL EQUILIBRIA

Learning outcomes
Candidates should be able to:

1. (a) understand what is meant by a reversible reaction

(b) understand what is meant by dynamic equilibrium in terms of the rate of forward and reverse reactions being equal and the concentration of reactants and products remaining constant

(c) understand the need for a closed system in order to establish dynamic equilibrium

2. define Le Chatelier's principle as: if a change is made to a system at dynamic equilibrium, the position of equilibrium moves to minimise this change

3. use Le Chatelier's principle to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration, pressure or presence of a catalyst on a system at equilibrium

4. deduce expressions for equilibrium constants in terms of concentrations, K_c

5 use the terms mole fraction and partial pressure

6 deduce expressions for equilibrium constants in terms of partial pressures, K_p (use of the relationship between K_p and K_c is not required)

7. use the K_c and K_p expressions to carry out calculations (such calculations will not require the solving of quadratic equations)

8. calculate the quantities present at equilibrium, given appropriate data

9. state whether changes in temperature, concentration or pressure or the presence of a catalyst affect the value of the equilibrium constant for a reaction

10. describe and explain the conditions used in the Haber process and the Contact process, as examples of the importance of an understanding of dynamic equilibrium in the chemical industry and the application of Le Chatelier's principle

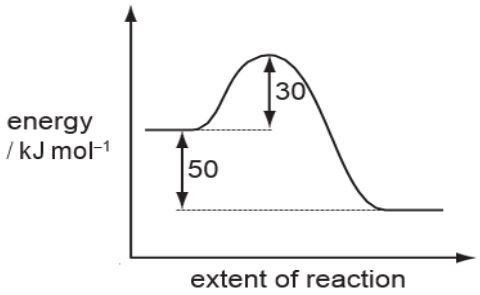
Introduction

Many chemical reactions do not go to completion. They stop at a point called the equilibrium position, where both reactants and products are present but there seems to be no further reaction.

Reversible reaction: a reaction in which products can be changed back to reactants by reversing the conditions.

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

1. The reaction pathway for a reversible reaction is shown below.



Which statement is correct?

A The activation energy of the reverse reaction is +80 kJ mol^{-1}.
B The enthalpy change for the forward reaction is +30 kJ mol^{-1}.
C The enthalpy change for the forward reaction is +50 kJ mol^{-1}.
D The enthalpy change for the reverse reaction is +30 kJ mol^{-1}.

2. For a particular reversible reaction the backward reaction is endothermic.
The activation energy of the backward reaction is 160 kJ mol^{-1}.
It can be assumed that the backward reaction proceeds by a mechanism that is the exact reverse of the mechanism for the forward reaction.
Which statement about the activation energy of the forward reaction is correct?

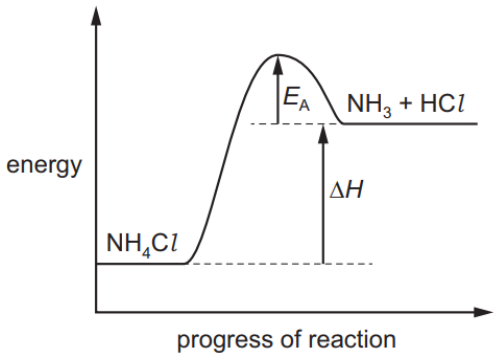
A The activation energy of the forward reaction is equal to -160 kJ mol^{-1}.
B The activation energy of the forward reaction is less than +160 kJ mol^{-1}.
C The activation energy of the forward reaction is equal to +160 kJ mol^{-1}.
D The activation energy of the forward reaction is greater than +160 kJ mol^{-1}.

3. The forward reaction of a reversible reaction is exothermic and has an activation energy of +30 kJ mol^{-1}.
The reverse reaction proceeds by a mechanism that is the exact reverse of the mechanism of the forward reaction.
Which statement about the activation energy of the reverse reaction is correct?

A The activation energy for the reverse reaction is equal to –30 kJ mol^{-1}.
B The activation energy for the reverse reaction is greater than 0 kJ mol^{-1} but less than +30 kJ mol^{-1}.
C The activation energy for the reverse reaction is equal to +30 kJ mol^{-1}.
D The activation energy for the reverse reaction is greater than +30 kJ mol^{-1}

4. The equation for the formation of ammonium chloride is shown.
$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)\ \Delta H = -314\ kJ\ mol^{-1}$
Which diagram shows the correctly labelled reaction pathway diagram for the **decomposition** of ammonium chloride?

A



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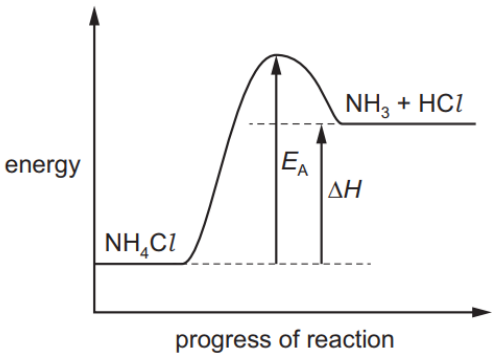

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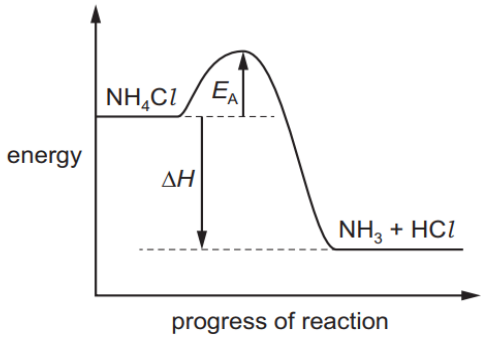

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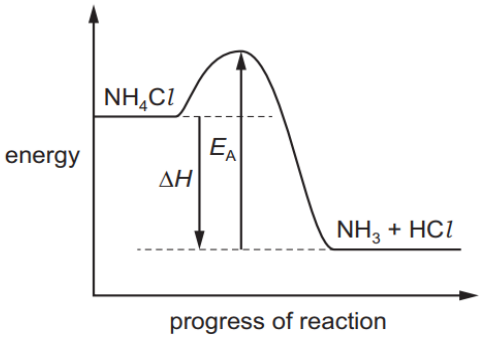
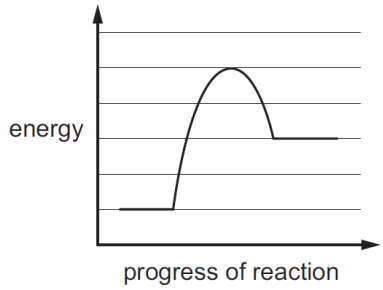


1. The reaction pathway diagram for a chemical reaction is shown.



Which statement is correct?

A The activation energy of the forward reaction and the enthalpy change of the backward reaction have the same sign.
B The activation energy of the forward reaction is more than twice the enthalpy change of the backward reaction and opposite in sign.
C The enthalpy change of the forward reaction and the activation energy of the backward reaction have the same sign.
D The enthalpy change of the forward reaction is more than twice the activation energy of the backward reaction.

In chemistry, **equilibrium** refers to chemical reactions that are in balance.
• In a reversible reaction at equilibrium, the rates of the forward and backward reactions are the same. In other words, the amount of reactants forming products in a given time is the same as the amount of products breaking down to give reactants in the same time. These are generally called **dynamic equilibria**.
An example of a dynamic equilibrium established in the gas phase is the reaction of nitrogen and hydrogen to form ammonia in the Haber process:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Dynamic equilibria can also happen in the liquid phase:
$2H^+(aq) + 2\ CrO_4^-(aq) \rightleftharpoons Cr_2O_7^{2-}(aq.) + H_2O(l)$
In dynamic equilibrium, the equilibrium compositions of the substances can be approached from either reactants or products.

Characteristics of equilibrium

- it is dynamic
- the forward and reverse reactions occur at the same rate
- the concentrations of reactants and products remain constant at equilibrium
- it requires a **closed system**.

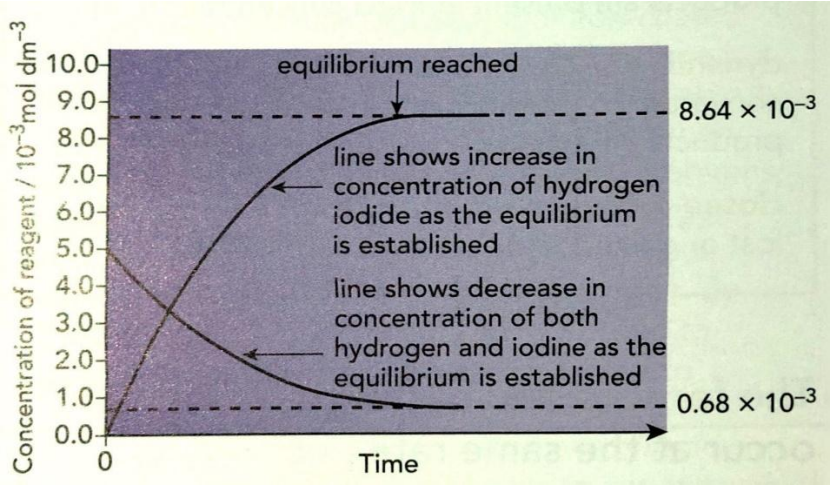
Closed system: where matter cannot be lost or gained.

Open system: where matter can be lost or gained.

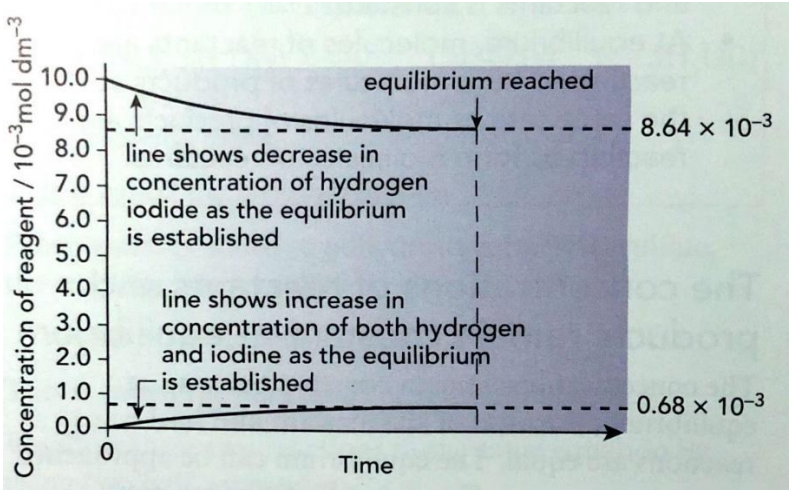
The following figure shows what happens when 5.00×10^{-3} mol of hydrogen molecules and 5.00×10^{-3} mol of iodine molecules react at 500 K in a vessel of volume 1 dm^3.

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

As time passes, the purple colour of the iodine vapour fades until equilibrium is reached. At equilibrium the mixture contains 0.68×10^{-3} mol of iodine, 0.68×10^{-3} mol of hydrogen and 8.64×10^{-3} mol of hydrogen iodide.



The following figure shows that the same equilibrium can be achieved when 10.00×10^{-3} mol of hydrogen iodide molecules decompose to iodine and hydrogen. You can see that the same equilibrium concentrations of all three molecules are achieved.



2. Describe what is meant by dynamic equilibrium. [2]

3. Magnesium oxide reacts reversibly with chlorine according to the following equation.
   $2MgO(s) + 2Cl_2(g) \rightleftharpoons 2MgCl_2(s) + O_2(g)$
   Under certain conditions, a dynamic equilibrium is established.
   State two features of a reaction that is in dynamic equilibrium. [2]

4. 0.025mol of H**I**(g) is added to a closed vessel and left to reach dynamic equilibrium. The total pressure of the vessel is 100kPa.
   equation 1 $2H\mathbf{I}(g) \rightleftharpoons H_2(g) + \mathbf{I}_2(g)$
   (i) Explain what is meant by dynamic equilibrium. [2]
   (ii) Describe **one difference** in the initial appearance of the reaction mixture compared to the mixture at equilibrium. [1]

5. NO and NO_2 react at 25°C to give N_2O_3 as shown in the equation.
   $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$ $\Delta H = -7.2 kJmol^{-1}$
   The reaction is reversible and reaches equilibrium in a closed system.
   Fig. 2.1 shows how the rate of the forward reaction changes with time.
   Initially, the rate of the reverse reaction is zero.
   Complete Fig. 2.1 to sketch how the rate of the *reverse* reaction changes with time.

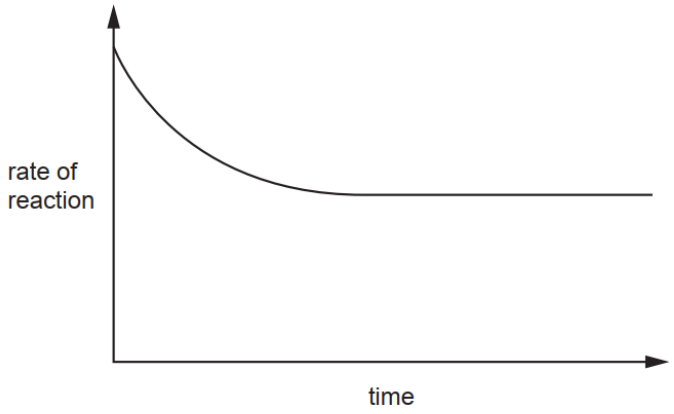


Fig. 2.1

6. A student heats equal amounts of $I_2(g)$ and $H_2(g)$ in a sealed flask. The student leaves the contents to cool.
   State what you would observe during the reaction.

   ..... [1]

Le-Chatelier's principle

The French chemist Henri le Chatelier studied many dynamic equilibria and suggested a general rule, **Le Chatelier's principle**, to help predict the changes in the position of equilibrium as different factors are changed.

Position of equilibrium

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

If a system in equilibrium is disturbed (e.g., by a change in temperature) and the concentration of products increases relative to the reactants, we say that the position of equilibrium has shifted to the right.

If the concentration of products decreases relative to the reactants, we say that the position of equilibrium has shifted to the left.

Le Chatelier's principle **states that if a closed system at equilibrium is subject to a change, then the system will adjust in such a way so as to minimise the effect of the change.**

» Increasing the concentration of a reactant moves the position of equilibrium to the right.

» Increasing the pressure in a gaseous reaction moves the equilibrium in the direction that has fewer gas molecules.

» Increasing the temperature moves the position of equilibrium in the endothermic direction.

Do catalysts have any effect on the position of equilibrium?

A catalyst is a substance that increases the rate of a chemical reaction. Catalysts reduce the time taken to reach equilibrium, but they have no effect on the position of equilibrium once this is reached. This is because they increase the rate of the forward and reverse reactions equally.

7. Define Le Chatelier's principle. [2]

8. The reaction of ethene, C_2H_4, with a 1:1 mixture of CO and H_2 is shown in equation 1.
   equation 1 $C_2H_4(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CHO(g)$
   At atmospheric pressure a cobalt-based catalyst is used in this reaction.
   Explain why the yield of $CH_3CH_2CHO(g)$ increases when the overall pressure of the reaction mixture is increased. [1]

9. In industry, ethanol is made by reacting ethene with steam in the presence of H_3PO_4.
   reaction 1 $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$
   Reaction 1 reaches equilibrium at constant temperature and pressure.
   Deduce what effect increasing the pressure will have on the amount of ethanol in the new equilibrium mixture.
   Use Le Chatelier's principle to explain your answer. [2]

10. State the effect of a decrease in pressure on the position of equilibrium in reaction **2**.

reaction **2**	$S_2Cl_2(l) + Cl_2(g) \rightleftharpoons 2\,SCl_2(l)$	$\Delta H_r = -40.6 kJmol^{-1}$

Explain your answer. [1]

5. In which equilibrium will an increase in pressure at constant temperature increase the yield of the products on the right-hand side of the equation?

A $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
B $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
C $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
D $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

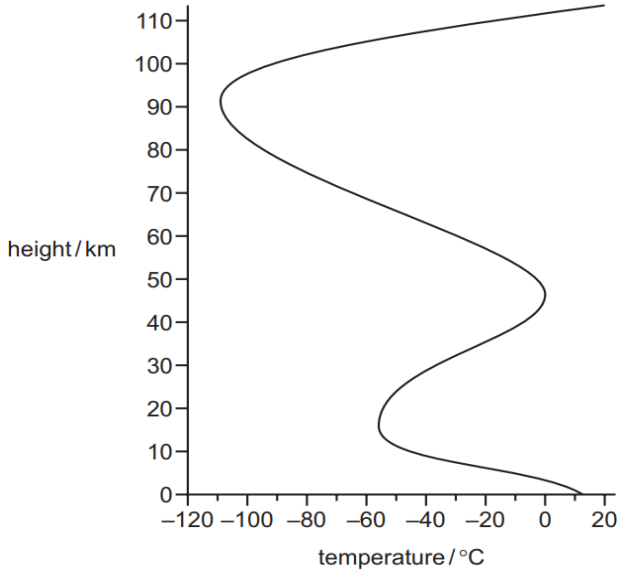
6. SO_3 is manufactured from SO_2 and O_2 in the Contact process.
The reaction is exothermic.
Which row shows the effect on the equilibrium yield obtained in the Contact process of increasing the temperature and of adding a vanadium(V) oxide catalyst?

	increasing the temperature	adding vanadium(V) oxide as catalyst
A	equilibrium yield decreases	equilibrium yield increases
B	equilibrium yield decreases	equilibrium yield unchanged
C	equilibrium yield increases	equilibrium yield unchanged
D	equilibrium yield increases	equilibrium yield increases

11. In the gas phase, $AlCl_3(g)$ exists at equilibrium with $Al_2Cl_6(g)$ as shown.
equation 1 $2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$ $\Delta H_r = -63\ kJmol^{-1}$
State the effect of an increase in temperature on the equilibrium mixture in equation **1**.
Explain your answer. [2]

12. NO and NO_2 react at 25°C to give N_2O_3 as shown in the equation.
$NO(g) + NO_2(g) \rightarrow N_2O_3(g)$ $\Delta H = -7.2 kJmol^{-1}$
The reaction is reversible and reaches equilibrium in a closed system.
State how the position of equilibrium changes, if at all, when the reaction takes place at 100°C.
Explain your answer.
Assume the pressure remains constant. [2]

13. Fig. 2.2 shows how the temperature of the atmosphere varies with height from the ground.



The equilibrium reaction in equation 1 has $\Delta H_r = -168 kJmol^{-1}$.
equation 1 $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
Suggest how the position of this equilibrium differs at a height of 20km compared with a height of 50km from the ground.
Explain your answer. [2]

7. Methanol is manufactured by reacting carbon dioxide and hydrogen together.
$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$ $\Delta H = -49$ kJ mol^{-1}
What increases the equilibrium yield of methanol in this process?

A increasing the pressure
B adding an excess of steam
C adding a catalyst
D increasing the temperature

8. A synthesis for methanol is shown.
$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta H = -49$ kJ mol^{-1}
Which conditions would produce the greatest yield of methanol at equilibrium?

	pressure	temperature / °C
A	high	80
B	high	20
C	low	80
D	low	20

9. Nitrogen dioxide, NO_2, exists in equilibrium with dinitrogen tetroxide, N_2O_4.
$2NO_2(g) \rightleftharpoons N_2O_4(g)$ $H = -57$ kJ mol^{-1}
Which conditions give the greatest percentage of $N_2O_4(g)$ at equilibrium?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

10. Nitric acid is produced by oxidising ammonia. The first step is to react ammonia with oxygen in the presence of a catalyst to form nitrogen monoxide.

$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -1636$ kJ mol^{-1}

Which set of conditions will produce the greatest yield of nitrogen monoxide at equilibrium?

	temperature	pressure
A	High	low
B	High	High
C	Low	High
D	Low	low

12. Hydrogen is produced industrially from methane as shown in the equation.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H^{\circ} = +205$ kJ mol^{-1}

Which conditions give the highest yield of hydrogen at equilibrium?

	pressure	Temperature
A	low	high
B	high	low
C	high	high
D	low	low

13. Ethene can be oxidised to form epoxyethane, C_2H_4O.

$C_2H_4(g) + \frac{1}{2} O_2(g) \rightleftharpoons C_2H_4O(g)$ $\Delta H^{o} = -107$ kJ mol^{-1}

Which set of conditions gives the greatest yield of epoxyethane at equilibrium?

	pressure	Temperature / °C
A	High	100
B	high	200
C	Low	100
D	low	200

14. The main stage in the Contact process is an equilibrium reaction.

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

Which row describes the effect of the named condition on the equilibrium yield?

	presence of catalyst	high pressure	high temperature
A	no effect on yield	decreases yield	increases yield
B	no effect on yield	increases yield	decreases yield
C	increases yield	decreases yield	increases yield
D	increases yield	increases yield	decreases yield

14. $Cl_2O_6(g)$ is produced by the reaction of $ClO_2(g)$ with $O_3(g)$.

$2ClO_2(g) + 2O_3(g) \rightleftharpoons Cl_2O_6(g) + 2O_2(g)$ $\Delta H = -216$ kJ mol^{-1}

The reaction takes place at 500 K and 100 kPa.

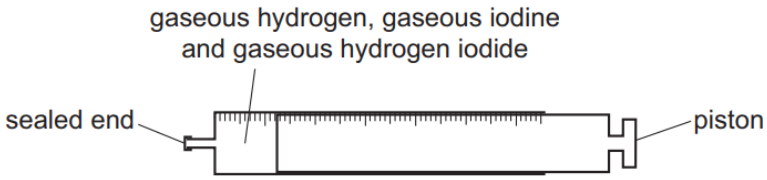
State and explain the effect on the yield of $Cl_2O_6(g)$ when the experiment is carried out:

- at 1000 K and 100 kPa
- at 500 K and 500 kPa. [4]

15. In which equilibrium reaction is the position of equilibrium moved to the right-hand side by increasing the temperature and also by decreasing the pressure?

A $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$	$\Delta H = 40$ kJ mol^{-1}
B $N_2O_4(g) \rightleftharpoons 2NO2(g)$	$\Delta H = 58$ kJ mol^{-1}
C $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$\Delta H = -197$ kJ mol^{-1}
D $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$	$\Delta H = -10$ kJ mol^{-1}

16. The diagram shows a gas syringe with a free-moving piston. The syringe contains gaseous hydrogen, gaseous iodine and gaseous hydrogen iodide at equilibrium.



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

Three changes are listed.
1 increasing the total pressure by adding an inert gas and keeping the volume constant
2 increasing the pressure by adding more gaseous hydrogen iodide and keeping the volume constant
3 decreasing the volume by pushing the piston to the left
Which changes will result in an equilibrium position at which the rate of the forward reaction has increased?

A 2 only **B** 1 and 2 **C** 1 and 3 **D** 2 and 3

15. $N_2(g)$ reacts with H_2 (g) in the Haber process, as shown in reaction 1.
reaction 1 N_2 (g) + $3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -x$ kJ mol^{-1}
Table 2.1 shows the different conditions used to produce three equilibrium mixtures, A, B and C.

	A	B	C
initial molar ratio of N_2 : H_2 added	1 : 3	1 : 3	1 : 3
temperature / °C	500	500	1000
pressure / atm	1000	1000	1000
iron present in mixture	no	yes	no
percentage yield of $NH_3(g)$ at equilibrium	58	x	y

(a) Describe and explain the change, if any, to the percentage yield of $NH_3(g)$ produced in B compared to A. [1]

(b) (i) Describe and explain the change, if any, to the percentage yield of $NH_3(g)$ produced in C compared to A. [1]

(ii) Describe and explain the change to the rate of the forward reaction that occurs to establish the equilibrium in C compared to A.
You do not need to refer to the Boltzmann distribution in your answer. [2]

16. $S_2Cl_2(l)$ reacts with $Cl_2(g)$ in a reversible reaction to form $SCl_2(l)$. Under certain conditions, a dynamic equilibrium is established.

$S_2Cl_2(l) + Cl_2(g)$ $2SCl_2(l)$ $\Delta H = -41$ kJ mol–1

(i) State what is meant by dynamic equilibrium.

.....

..... [1]

(ii) Identify the condition necessary to establish dynamic equilibrium.

..... [1]

(iii) $S_2Cl_2(l)$ is yellow and $SCl_2(l)$ is red.

$S_2Cl_2(l) + Cl_2(g)$ $2SCl_2(l)$ $\Delta H = -41$ kJ mol–1

State what is observed when the following changes are made to an equilibrium mixture of $S_2Cl_2(l)$ and $SCl_2(l)$. Explain your answers.

• The equilibrium mixture is warmed gently.

observation .....

explanation .....

.....

.....

• The overall pressure of the equilibrium mixture is increased.

observation .....

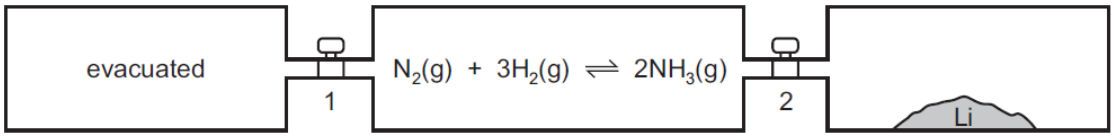
explanation .....

.....

..... [4]

17. Lithium reacts with nitrogen at room temperature to form solid Li_3N.

Three vessels of equal volume are connected by taps 1 and 2 as shown.



At the start, taps 1 and 2 are closed, the left-hand vessel is evacuated, the middle vessel has the indicated reaction at equilibrium and the right-hand vessel contains lithium only.

Which action would allow the equilibrium mixture to contain the most ammonia?

A Keep both taps 1 and 2 closed.
B Open both taps 1 and 2.
C Open tap 1 only.
D Open tap 2 only.

17. In acidic conditions, a dynamic equilibrium is established between $CrO_4^{2-}(aq)$ and $Cr_2O_7^{2-}(aq)$.
$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$ $\Delta H > 0$

(i) $CrO_4^{2-}(aq)$ ions are yellow and $Cr_2O_7^{2-}(aq)$ ions are orange.
State what is observed when the following changes are made to an equilibrium mixture of acidified $CrO_4^{2-}(aq)$ and Cr_2O_7 –(aq) ions.
Explain your answers.
• The equilibrium mixture is warmed gently.

observation .....

explanation .....

.....

.....

• Dilute HCl (aq) is added to the equilibrium mixture.

observation .....

explanation .....

.....

..... [4]

18. A 5.00 dm^3 sealed flask contains 0.400 mol of CO(g) and 0.800 mol of $H_2(g)$ and an Al_2O_3 catalyst. The flask is heated to a temperature of 290 °C and allowed to reach equilibrium.
Equation 1 shows the reaction.
equation 1 $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

The equilibrium constant, Kc, of equation 1 is given.

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$$

(i) State the units of Kc.

..... [1]

(ii) The equilibrium mixture contains 0.280 mol of $CH_3OH(g)$.
Calculate the value of Kc.
Give your answer to three significant figures.

value of Kc = ... [3]

(iii) State and explain the effect, if any, on the value of Kc when the overall pressure in the sealed flask is increased.

.....

..... [1]

Mole fraction

The mole fraction of a species (given the symbol χ) is given by the expression

mole fraction of A = $\left(\frac{number\ of\ moles\ of\ A}{total\ number\ of\ gaseous\ moles}\right)$

or $\chi_A = \left(\frac{nA}{nA+nB+nC}\right)$

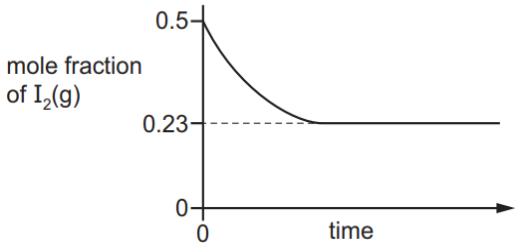
1. A mixture of gases consists of 12.0g of hydrogen, 42.0g of nitrogen and 4.0g of helium.
What is the mole fraction of hydrogen in the mixture?

A 0.21 **B** 0.60 **C** 0.71 **D** 0.75

2. The equation shows that $H_2(g)$ and $I_2(g)$ react to form an equilibrium mixture.

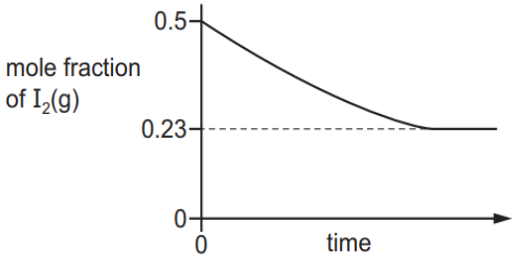
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -9.6\ kJ\ mol^{-1}$$

A mixture containing equal amounts of $H_2(g)$ and $I_2(g)$ is made at temperature T_1 and the composition of the mixture is monitored. A graph of the results is shown.

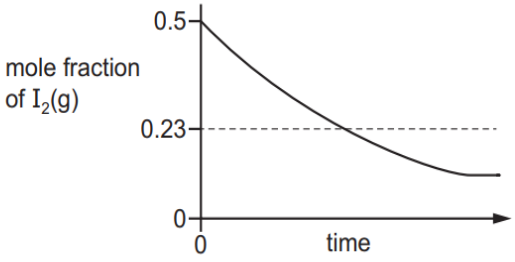


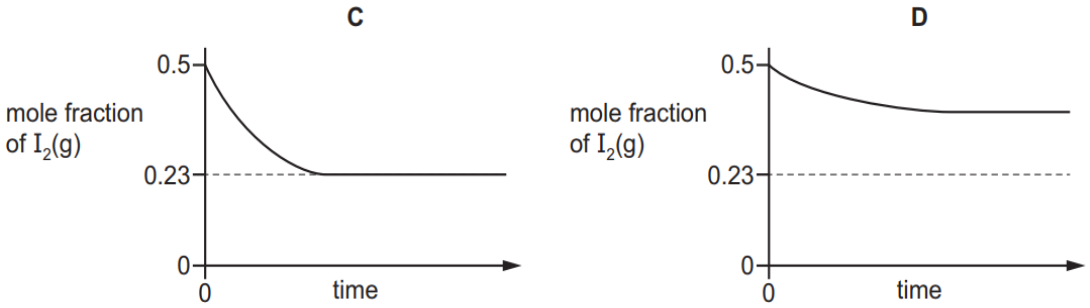
The experiment is repeated at a lower temperature, T_2.
Which new graph would be obtained?

A



B





19. Equilibrium mixture D is made when 1.0 mol of $N_2(g)$ and 3.0 mol of $H_2(g)$ are added to a sealed container at 750 °C and 1000 atm and left to reach equilibrium. This mixture contains 1.16 mol of $NH_3(g)$.
reaction 1 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -x$ kJ mol^{-1}
Calculate the mole fraction of $NH_3(g)$ in D. [2]

Expression of equilibrium constant, K_C

For any equilibrium in the liquid state an equilibrium constant, **K**c, can be defined in terms of concentration. For our general equation:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

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

The quantities in square brackets represent the concentrations of the different species at equilibrium, in mol dm^{-3} unit. It is also important to remember that equilibrium constants depend on temperature.

The equilibrium constant, *Kc* or *Kp*, remains the same value even when we change the concentration or pressure or add a catalyst.
Only change in temperature affects the value of the equilibrium constant *Kc* or *Kp*.

IMPORTANT
- ✓ **Remember that the concentrations of products go at the top of an equilibrium expression and the concentrations of the reactants go at the bottom.**
- ✓ **Solids and liquids that appear in the balanced equation are NOT included in the equilibrium expression.**

units of K_c

20. When **G**, $C_4H_{10}O$, is heated in a sealed container, an equilibrium mixture is produced.
$C_4H_{10}O(g) \rightleftharpoons C_2H_6(g) + CO(g) + CH_4(g)$
Complete the expression for the equilibrium constant, K_c, for this reaction.
State the units of K_c.

K_c= units = ...[2]

3. The equation for the reaction between silver chloride and aqueous ammonia is shown.
$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$
What are the units of K_c for this reaction?

A no units **B** $mol^{-1}dm^3$ **C** $mol\ dm^{-3}$ **D** mol^2dm^{-6}

21. Thermal decomposition of **G**($C_4H_{10}O$) in the presence of I_2 affects the activation energy, E_a, for the reaction. Table 3.2 shows E_a for the thermal decomposition of **G** with and without I_2.

reaction	E_a (with I_2) /kJmol^{-1}	E_a /kJmol^{-1}
$C_4H_{10}O(g) \rightleftharpoons C_2H_6(g) + CO(g) + CH_4(g)$	143	224

State what effect adding I_2 to the reaction mixture has on the value of K_c.
Explain your answer. [2]

4. Sulfur dioxide reacts with oxygen as shown.
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^{\ominus} = -197\ kJ\ mol^{-1}$
Which change will move the equilibrium position to the right side and change the value of the equilibrium constant, Kc?

A the addition of a catalyst
B increasing the pressure of the reaction
C decreasing the temperature of the reaction
D decreasing the concentration of product

5. A reversible reaction is shown.
$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)\ \Delta H = +77.0\ kJ\ mol^{-1}$
Which change in conditions will move the position of equilibrium to the right and increase the value of the equilibrium constant?

A a decrease in pressure
B a decrease in temperature
C an increase in pressure
D an increase in temperature

22. Reaction 1 describes the reversible reaction between yellow $Fe^{3+}(aq)$ and colourless $SCN^{-}(aq)$ to produce red $FeSCN^{2+}(aq)$.

reaction 1 $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$ $\Delta H = -x$ kJ mol^{-1}

yellow colourless red

A mixture of $Fe^{3+}(aq)$, $SCN^{-}(aq)$ and $FeSCN^{2+}(aq)$ is at equilibrium at 20 °C.
The temperature of this mixture is then increased to 50 °C and allowed to reach equilibrium.
Deduce the changes that occur, if any, in the equilibrium mixture at 50 °C compared to the equilibrium mixture at 20 °C.

• change in appearance.....

• change in relative concentration of $FeSCN^{2+}(aq)$

.....

• change in value of the equilibrium constant, K_c

…… [3]

23. Reaction 4 describes the reversible reaction between yellow $Fe^{3+}(aq)$ and colourless $SCN^{-}(aq)$ to produce red $FeSCN^{2+}(aq)$.

reaction 4 $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$ $\Delta H = -x$ kJ mol^{-1}

yellow colourless red

An equilibrium mixture contains $Fe^{3+}(aq)$, $SCN^{-}(aq)$ and $FeSCN^{2+}(aq)$. A few colourless crystals of soluble KSCN(s) are added. The mixture is then left until it reaches equilibrium again. The temperature of both equilibrium mixtures is the same.
(i) Deduce the changes that occur, if any, in the equilibrium mixture after KSCN(s) is added compared to the original equilibrium mixture.

• change in appearance …….....

• change in relative concentration of $Fe^{3+}(aq)$ .....

• change in value of the equilibrium constant, Kc..... [3]

6. 0.200 mol of sulfur dioxide and 0.200 mol of oxygen are placed in a 1.00 dm^3 sealed container. The gases are allowed to react until equilibrium is reached.

$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$

At equilibrium, there is 0.100 mol of SO_3 in the container.
What is the value of **Kc**?

A 0.150 mol dm^{-3} ***B*** 0.800 mol dm^{-3} ***C*** 1.25 mol^{-1} dm^3 ***D*** 6.67 mol^{-1} dm^3

7. Hydrogen and iodine can react reversibly to produce hydrogen iodide. The equation is shown.

$H_2(g) + \mathbf{I}_2(g) \rightleftharpoons 2H\mathbf{I}(g)$

4.00 mol of hydrogen gas and X mol of iodine vapour are mixed in a sealed container of volume 1.00 dm^3 at a temperature of 460 K. The system is allowed to reach equilibrium.
The equilibrium mixture contains 2.00 mol of hydrogen iodide. The equilibrium constant, Kc, for the reaction at 460 K is

4.0.
What is the value of X?

A 0.50 mol *B* 1.17 mol *C* 1.33 mol *D* 2.50 mol

8. Nitrogen reacts with hydrogen to produce ammonia.

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

A mixture of 2.00 mol of nitrogen, 6.00 mol of hydrogen and 2.40 mol of ammonia is allowed to reach equilibrium in a sealed vessel of volume 1 dm^3. It is found that 2.32 mol of nitrogen were present in the equilibrium mixture.
Which expression will give the value of K_c?

A $\frac{(1.76)^2}{(2.32)(6.96)^3}$ **B** $\frac{(1.76)^2}{(2.32)(6.32)^3}$ **C** $\frac{(2.08)^2}{(2.32)(6.32)^3}$ **D** $\frac{(2.40)^2}{(2.32)(6.00)^3}$

9. When 0.20 mol of hydrogen gas and 0.15 mol of iodine gas are heated at 723 K until equilibrium is established, the equilibrium mixture contains 0.26 mol of hydrogen iodide.
The equation for the reaction is as follows.

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

What is the correct expression for the equilibrium constant K_c?

A $\frac{2 \times 0.26}{0.20 \times 0.15}$ **B** $\frac{(2 \times 0.26)^2}{0.20 \times 0.15}$ **C** $\frac{(0.26)^2}{0.07 \times 0.02}$ **D** $\frac{(0.26)^2}{0.13 \times 0.13}$

10. Gaseous hydrogen and gaseous iodine react to form gaseous hydrogen iodide.

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

In an experiment, 2.0 mol of hydrogen and 2.0 mol of iodine are placed in a sealed container of volume 1.0 dm^3.
The K_c value for this reaction under the conditions used is 9.0.
How many moles of hydrogen iodide are present at equilibrium?

A 0.57 mol **B** 1.2 mol **C** 1.5 mol **D** 2.4 mol

11. The reaction between sulfur dioxide and oxygen is reversible.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ Kc = 280 mol^{-1} dm^3 at 1000 K

In an equilibrium mixture at 1000 K the sulfur trioxide concentration is 6.00 mol dm^{-3}.
The sulfur dioxide concentration is twice the oxygen concentration.
What is the sulfur dioxide concentration?

A 0.175 mol dm^{-3} **B** 0.252 mol dm^{-3} **C** 0.318 mol dm^{-3} **D** 0.636 mol dm^{-3}

12. In aqueous solution, sulfuric acid dissociates as shown.

$H_2SO_4 \rightarrow HSO_4^- + H^+$ This reaction goes to completion.

$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$ This reaction reaches equilibrium with constant K_c.

Analysis of a 2.00 mol dm^{-3} solution of H_2SO_4 found the HSO_4^- concentration to be 1.988 mol dm^{-3}.
What is K_c?

A 1.381×10^5 dm^3 mol^{-1} **B** 82.34 dm^3 mol^{-1} **C** 1.214×10^{-2} mol dm^{-3} **D** 7.244×10^{-5}mol dm^{-3}

13. An alcohol, ROH, reacts reversibly with ethanoic acid to produce an ester.

$ROH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOR(l) + H_2O(l)$

3.0 mol of ROH, 2.0 mol of ethanoic acid and 1.0 mol of water are mixed together. At equilibrium, 1.5 mol of CH_3COOR is present.
What is the value of the equilibrium constant, Kc, for this reaction?

A 0.20 B 0.25 C 2.00 D 5.00

Solution: $ROH(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COOR(aq) + H_2O(l)$

Initially	*3.0/x*	*2.0/x*	*0/x*	*1.0/x*
At equilibrium	*1.5/x*	*0.5/x*	*1.5/x*	*2.5/x*

$K_c = \frac{[CH3COOR][H2O]}{[ROH][CH3COOH]} = \frac{\frac{1.5}{x} X \frac{2.5}{x}}{\frac{1.5}{x} X \frac{0.5}{x}} = 5$

24. The expression for the equilibrium constant, Kc, for reaction 4 is shown.

reaction 4: $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$ $\Delta H = -x$ kJ mol^{-1}

$K_c = ([FeSCN^{2+}(aq)])/([Fe^{3+}(aq)] \times [SCN^-(aq)])$

5.00×10^{-5} mol of $Fe^{3+}(aq)$ and 5.00×10^{-5} mol of $SCN^-(aq)$ are added together and allowed to reach equilibrium. The total volume of the mixture is 25.0 cm^3.
At equilibrium the concentration of $FeSCN^{2+}(aq)$ is 4.23×10^{-4} mol dm^{-3}.
Calculate the equilibrium constant, Kc, for reaction 4.
Include the units in your answer.

Kc = ... units ..... [4]

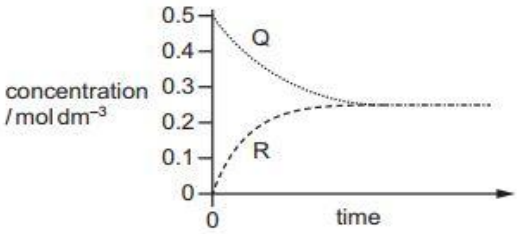
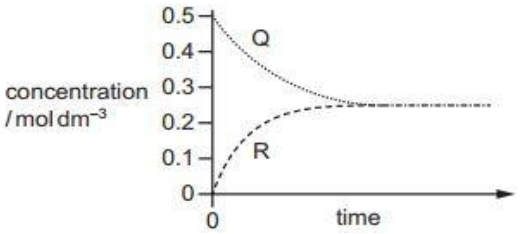
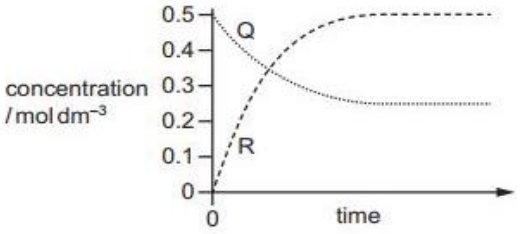
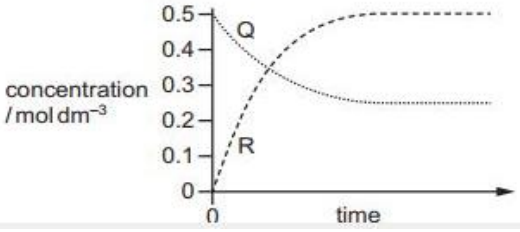
14. A dimer, Q, is stable when solid but a dynamic equilibrium is set up in solution.

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

A solution of Q has an initial concentration of 0.50 mol dm^{-3}. When equilibrium has been reached, [Q(aq)] has fallen to 0.25 mol dm^{-3}.

The changes in [Q(aq)] and [R(aq)] are plotted against time until equilibrium is reached. The value of Kc is then calculated.

Which graph and value for Kc are correct?

	graph	K_c / mol dm^{-3}
A		1
B		0.25
C		1
D		2

25. (a) A sample of HI(g) is added to a 2.00 dm^3 sealed vessel at 764K and allowed to reach equilibrium.

reaction 1 $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $K_c = 0.0217$ at 764K

At equilibrium the mixture contains 1.70mol of HI(g).

(i) State *one* difference in the appearance of the initial reaction mixture compared to the mixture at equilibrium.[1]

(ii) Deduce the expression for equilibrium constant K_c for reaction 1. [1]

(iii) Calculate the concentration of I_2 present in the reaction mixture at equilibrium.
Show your working.

concentration of $\mathbf{I}_2$ = ….*(ans = 0.125)*.... mol dm^{-3} [3]

(b) The experiment is repeated at 500K. The value of K_c under these conditions is 0.00625.

(i) Describe the difference in the composition of the equilibrium mixture at 500K compared to 764K. [1]

(ii) Use Le Chatelier's principle to deduce whether the decomposition of H*I*(g) is endothermic or exothermic. Explain your answer. [1]

Partial Pressure

For reactions involving mixtures of gases, it is easier to measure the pressure than to measure concentrations. The total pressure in a mixture of gases is due to each molecule bombarding the walls of the container. At constant temperature, each gas in the mixture contributes to the total pressure in proportion to the number of moles present. The pressure exerted by any one gas in the mixture is called its **partial pressure**.

The partial pressure of a gas in a mixture of gases in a vessel is defined as the pressure exerted by that gas if it were occupying the whole volume alone.

26. $NCl_3(l)$ decomposes according to the equation shown.

$2NCl_3(l) \rightarrow N_2(g) + 3Cl_2(g)$

A sealed container of volume 250 cm^3 contains an unreactive gas at a pressure of 1.00×10^5 Pa.

0.241 g of $NCl_3(l)$ was injected into the sealed container.

The sealed container was heated to make the $NCl_3(l)$ decompose fully and then cooled to 20 ° C.

Calculate the final total pressure inside the sealed container at 20 ° C after the $NCl_3(l)$ has fully decomposed.

final total pressure = ... Pa [4]

15. A mixture of the three gases, oxygen, nitrogen and argon, is at a total pressure of 500 kPa. There is a total of 1.2 moles of gas in the mixture.
If the oxygen gas alone occupied the entire volume of the mixture, it would exert a pressure of 150 kPa.
At room conditions the amount of nitrogen gas in the mixture would occupy a volume of 5.76 dm^3.
What is the partial pressure of the argon gas in the mixture?

A 150 kPa B 200 kPa C 250 kPa D 300 kPa

Partial pressure and mole fractions

These are related with following relation.

partial pressure = mole fraction × total pressure

27. The mole fraction of $N_2(g)$ is 0.625 in a new equilibrium mixture, **E**.
Calculate the partial pressure of $N_2(g)$ in **E** when the total pressure is 1000 atm.

partial pressure of $N_2(g)$ = ... atm [1]

Expression of K_p

From the ideal gas equation, at a given temperature, and if the volume is fixed, then

$$p \propto n$$

the mole fraction of A equals the ratio of its partial pressure to the overall (total) pressure.

$$\chi \text{ A} = \frac{pA}{pT}$$

Thus, the equilibrium constant can be written in terms of the partial pressures of the different components rather than their molecular concentrations.

For a following hypothetical equilibrium

$$\text{p A(g)} + \text{q B(g)} \rightleftharpoons \text{r C(g)} + \text{s D(g)}$$

the expression of K_p is expressed as

$$K_p = \frac{P_C^r P_D^s}{P_A^p P_B^q}$$

16. Methanol can be produced from hydrogen and carbon monoxide.
$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
What is the expression for Kp for this reaction?

A $K_p = \frac{2p_{H_2}^2 \times p_{CO}}{p_{CH_3OH}}$ **C** $K_p = \frac{p_{CH_3OH}}{p_{H_2}^2 \times p_{CO}}$

B $K_p = \frac{p_{H_2}^2 \times p_{CO}}{p_{CH_3OH}}$ **D** $K_p = \frac{p_{CH_3OH}}{2p_{H_2}^2 \times p_{CO}}$

28. Write an expression for the equilibrium constant, Kp, for reaction 1. State the units.
reaction 1 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -x$ kJ mol^{-1}

Kp = …….. units ..... [2]

29. Methanol is made by reacting carbon monoxide with hydrogen.
$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$
Carbon monoxide and hydrogen react at 1.0×10^7Pa and 200°C. Eventually, the reaction mixture reaches dynamic equilibrium.
Write an expression for the equilibrium constant, $\mathbf{K}_p$, for this reaction. State the units in your answer. [2]

17. What are the units of K_p for the reaction shown?
$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$

A Pa^{-1} **B** Pa **C** Pa^2 **D** no units

18. Which reaction has an equilibrium constant, Kp, that has no units?

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
B $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
C $2NO_2(g) \rightleftharpoons N_2O_4(g)$
D $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

19. The table shows the partial pressures in an equilibrium mixture formed by the Haber process.

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

substance	partial pressure / kPa
nitrogen	7000
hydrogen	8000
ammonia	4000

What is the numerical value of the equilibrium constant, Kp, for this reaction?

A 4.46×10^{-9} B 4.76×10^{-5} C 7.14×10^{-5} D 2.24×10^{8}

20. Hydrogen and iodine react to form hydrogen iodide in an exothermic reaction. The equation is shown.
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
A 1 m^3 reaction vessel contains H_2, I_2 and HI gases at equilibrium. The temperature is changed such that the total pressure in the 1 m^3 vessel doubles.
What is the effect on the value of K_p and on the position of equilibrium?

	effect on the value of K_p	effect on the position of equilibrium
A	decreases	moves left
B	increases	moves right
C	no change	moves left
D	no change	no change

21. For which equilibrium do both of the equilibrium constants K**c** and K**p** have no units?
A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ B $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ D $SO_2(g) + O_2(g) \rightleftharpoons SO_3(g)$

22. Hydrogen iodide is added to an evacuated reaction vessel. The vessel is sealed and warmed. A decomposition reaction occurs. Hydrogen and iodine are formed. Some hydrogen iodide remains.
When equilibrium is established, the total pressure is 1.20×10^5Pa. The partial pressure of hydrogen is 4.00×10^3Pa.
Hydrogen iodide, hydrogen and iodine are all gaseous under the conditions used.
What is the value of Kp for the equilibrium at this temperature, assuming the decomposition is the forward reaction?

A $1.19X10^{-3}$ B $1.28X10^{-3}$ C $1.38X10^{-3}$ D $1.43X10^{-3}$

23. Nitrogen and hydrogen are mixed in a reaction vessel. The reaction reaches equilibrium giving a mixture of nitrogen, hydrogen and ammonia gases.
$N_2 + 3H_2 \rightleftharpoons 2NH_3$
The mixture of gases present at equilibrium at a total pressure of 300 atm is shown.

gas	Number of moles in mixture
nitrogen	180
hydrogen	590
ammonia	160

What is the equilibrium constant, K_p, for the forward reaction?

A $6.65 \times 10^{-6} atm^{-2}$ **B** $7.13 \times 10^{-5} atm^{-2}$ **C** $0.599\ atm^{-2}$ **D** $1.50 \times 10^{5}\ atm^{2}$

30. (i) Write an expression for the equilibrium constant, Kp, for reaction 1. State the units.
reaction 1 N_2 (g) + $3H_2$(g) ⇌ $2NH_3$(g) $\Delta H = -x$ kJ mol^{-1}

Kp = …….. units ..... [2]

(ii) Equilibrium mixture D is made when 1.0 mol of N_2(g) and 3.0 mol of H_2(g) are added to a sealed container at 750 °C and 1000 atm and left to reach equilibrium. This mixture contains 1.16 mol of NH_3(g).
Calculate the mole fraction of NH_3(g) in D. [2]

(iii) The mole fraction of N_2(g) is 0.625 in a new equilibrium mixture, E.
Calculate the partial pressure of N_2(g) in E when the total pressure is 1000 atm. [1]

31. (a) The standard enthalpy change of formation, of HI(g) is +26.5kJmol^{-1}.
Define the term *standard enthalpy change of formation*.
(b) HI(g) can be formed by reacting H_2(g) with I_2(g). The reaction is reversible, and an equilibrium forms quickly at high temperatures.
H_2(g) + I_2(g) ⇌ 2HI(g)
(i) The equilibrium partial pressures of the gases at 200 ° C are as follows.
p_{H2}(g) = 895 Pa
p_{I2}(g) = 895 Pa
p_{HI}(g) = 4800 Pa
Calculate K_p for this reaction. [1]

(ii) State how the value of K_p would change, if at all, if the reaction were carried out at 100 ° C rather than 200 ° C.
Explain your answer. [2]

24. Ethanol is produced industrially by reacting ethene and steam.

$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$

$\mathbf{K_p}$ has a value of 1.8×10^{-5} and the partial pressures of the reactants at equilibrium are shown.

reactant	partial pressure / kPa
ethene	4.8×10^3
steam	2.8×10^3

Which row is correct?

	partial pressure of ethanol at equilibrium / kPa	units of K_p
A	2.42×10^2	kPa^{-1}
B	2.42×10^2	kPa
C	7.47×10^{11}	kPa^{-1}
D	7.47×10^{11}	kPa

32. NO and NO_2 react at 25°C to give N_2O_3 as shown in the equation.

$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g) \quad \Delta H = -7.2 kJmol^{-1}$

The reaction is reversible and reaches equilibrium in a closed system.

The following table shows the composition of an equilibrium mixture of NO(g), $NO_2(g)$ and $N_2O_3(g)$ at 101kPa.

gas	number of moles at equilibrium/mol
NO	0.605
NO_2	0.605
N_2O_3	0.390

Calculate K_p, the equilibrium constant with respect to partial pressures.

Deduce the units of K_p.

33. Methanol is made by reacting carbon monoxide with hydrogen.

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

Carbon monoxide and hydrogen react at 1.0×10^7Pa and 200°C. Eventually, the reaction mixture reaches dynamic equilibrium.

The table shows the amounts of each species present in the mixture.

	CO(g)	$H_2(g)$	$CH_3OH(g)$
initial amount/mol	1.0	2.0	0
equilibrium amount/mol	0.030	0.060	0.97

Calculate the partial pressure of methanol vapour at equilibrium under these conditions.

Show your working. *(ans = 9.15 x 10^6 Pa)* [2]

25. When an equimolar mixture of H_2 and I_2 react, the mole fraction of HI in the final mixture is x.
What is the equilibrium constant, Kp, for the reaction?

A $\dfrac{x^2}{(1-x)^2}$ **C** $\dfrac{4x^2}{(1-x)^2}$

B $\dfrac{x^2}{(1-2x)^2}$ **D** $\dfrac{4x^2}{(1-2x)^2}$

34. 0.025mol of H**I**(g) is added to a closed vessel and left to reach dynamic equilibrium. The total pressure of the vessel is 100kPa.
equation 1 $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(i) Write an expression for Kp for the reaction described in equation 1. [1]

(ii) At equilibrium the partial pressure of HI(g) is 86.4kPa.
Calculate the amount of HI(g) present in the mixture at equilibrium. Show your working. ….*(ans = 0.0216 moles)*…. [1]

(iii) Describe the effect of increasing pressure on the value of $\mathbf{K_p}$ for the decomposition of HI(g). [1]

35. Magnesium oxide reacts reversibly with chlorine according to the following equation.
$2MgO(s) + 2Cl_2(g) \rightleftharpoons 2MgCl_2(s) + O_2(g)$
Under certain conditions, a dynamic equilibrium is established.
The equilibrium constant, K_p, is given by the following expression.
$K_p = P_{O_2}/(P_{Cl_2})^2$

At 1.00×10^5 Pa and 500K, 70% of the initial amount of $Cl_2(g)$ has reacted.
Calculate K_p and state its units.

K_p= .....(ans = 2.52×10^{-5})
units = ... [3]

26. Two reactions are shown.
reaction 1 $X_2(g) + Y_2(g) \rightleftharpoons 2XY(g)$
reaction 2 $XY(g) \rightleftharpoons 1/2\ X_2(g) + 1/2\ Y_2(g)$
The equilibrium constant, K_p, for reaction 1 is 0.0052.
What is K_p for reaction 2?

A $2.6 \cdot 10^{-3}$ **B** 13.9 **C** 192.3 **D** 384.6

27. 3.60 moles of hydrogen gas and 2.00 moles of iodine vapour are placed in a reaction vessel which is then sealed and maintained at a constant temperature.
The equation for the reaction is shown.
$H_2 + I_2 \rightleftharpoons 2HI$
At equilibrium, 3.20 moles of hydrogen remain. All reactants and products are gaseous.
What is the value of Kp under these conditions?

A 0.0313 **B** 0.125 **C** 0.156 **D** 8.00

28. Gas X dissociates on heating to set up the following equilibrium.
$X(g) \rightleftharpoons Y(g) + Z(g)$
A quantity of gas X is heated at constant pressure, p, at a certain temperature. The equilibrium partial pressure of gas X is found to be p/7.
What is the equilibrium constant, Kp, at this temperature?

A 6/7 p B 9/7 p C 36/7 p D 9p

29. A mixture of hydrogen gas and iodine gas is placed in a reaction vessel of volume V at temperature T.
The reaction $H_2 + I_2 \rightleftharpoons 2HI$ is allowed to come to equilibrium.
All substances remain in the gaseous state.
Argon gas is then pumped into the reaction vessel. The temperature in the vessel is maintained at T.
How are the rate of the forward reaction and the partial pressure of HI at equilibrium affected?

	rate of	partial pressure of

	forward reaction	HI at equilibrium
A	increased	increased
B	increased	unaffected
C	unaffected	increased
D	unaffected	unaffected

30. Silver chloride and silver iodide form equilibria when added to water.
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $K_c = K_1$
$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ $K_c = K_2$
Each equilibrium position lies well to the **left**.
Silver iodide will not dissolve in aqueous ammonia. Silver chloride will dissolve in aqueous ammonia. Another equilibrium is formed.
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{2+}(aq)$ $K_c = K_3$
The position of this equilibrium lies to the **right**.
What is the order of magnitude for these three equilibrium constants?

	Smallest	→	largest
A	K_3	K_2	K_1
B	K_3	K_1	K_2
C	K_2	K_1	K_3
D	K_1	K_2	K_3

Haber's and Contact processes

In the Haber (or Haber–Bosch) process, ammonia is produced on a massive scale using nitrogen from the air and hydrogen from the reaction of methane, CH_4, with steam:

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

To make the process as economic as possible, the conditions needed are:

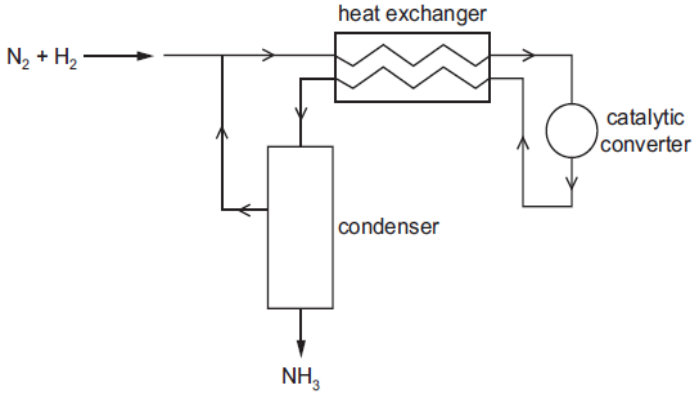
- a high equilibrium concentration of ammonia
- equilibrium to be reached in a short period of time

To understand the conditions chosen you need to know more about the reaction:

- At 298 K the equilibrium constant is very large, but only a tiny amount of ammonia is produced at this temperature because the rates of the forward and backward reactions are so low that equilibrium is never reached.
- Increasing the temperature increases the rates of both reactions but drastically reduces the equilibrium constant because the reaction is exothermic.
- Increasing the partial pressures of the reactants increases the equilibrium concentration of ammonia – for example, using 7500 kPa of hydrogen and 2500 kPa of nitrogen at 798 K gives a conversion with about 10% of ammonia at equilibrium.

The solution is to use an iron catalyst to increase the rate of attaining equilibrium, and then to use a compromise set of conditions – a relatively low temperature (around 750 K) and a moderately high pressure (20 000 kPa). The equilibrium mixture is then passed through a heat exchanger to cool and liquefy the ammonia, which is removed – the unreacted nitrogen and hydrogen are recycled.

36. The diagram represents the Haber process for the manufacture of ammonia from nitrogen and hydrogen.



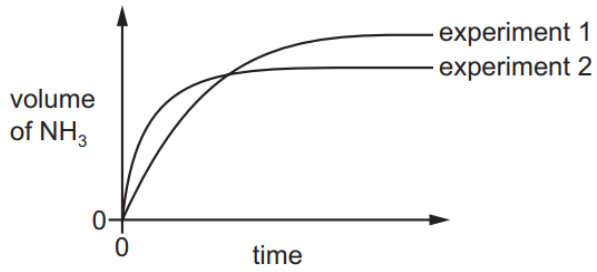
What is the purpose of the heat exchanger?

A to cool the incoming gas mixture to avoid overheating the catalyst
B to cool the reaction products and separate the NH_3 from unused N_2 and H_2
C to warm the incoming gas mixture and shift the equilibrium to give more NH_3
D to warm the incoming gas mixture and speed up the reaction

31. The Haber process is carried out with a nitrogen partial pressure of 50 kPa, a hydrogen partial pressure of 150 kPa, a temperature of 400 °C and an iron catalyst.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
If all other conditions are kept the same, which change will result in a raised activation energy?

A Both the nitrogen and hydrogen partial pressures are changed to 100 kPa.
B The iron is removed.
C The nitrogen partial pressure is increased to 150 kPa.
D The temperature is increased to 500 °C.

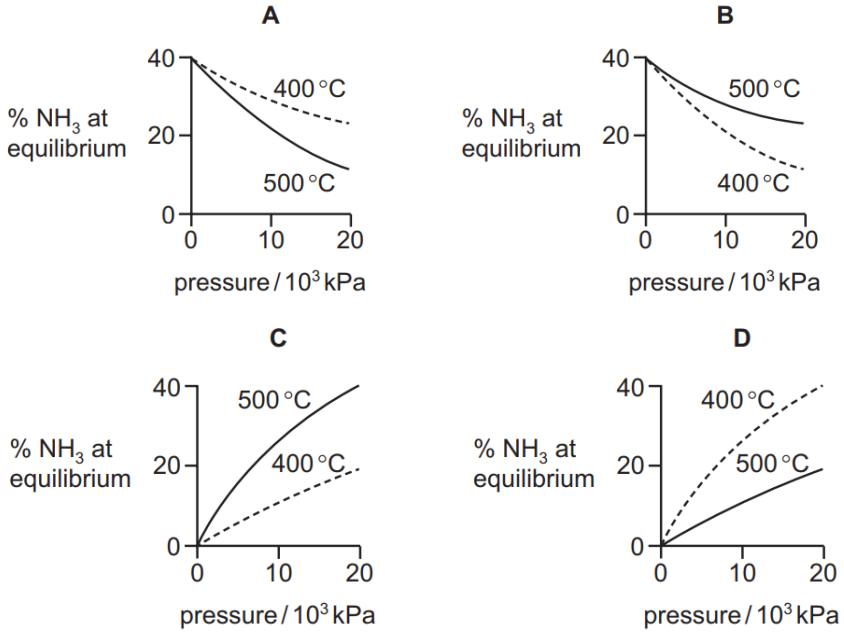
32. The volume of ammonia produced against time is measured in two experiments.
$N_2(g) + 3H_2(g)\ 2NH_3(g)\ \Delta\mathbf{H} = -92\ kJ\ mol^{-1}$
In experiment 1, 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ react together at 45°C and a pressure of 200 atm.
A graph showing the volume of ammonia produced against time is plotted.
Experiment 2 is then performed. Experiment 2 differs from experiment 1 in one condition only.



How does experiment 2 differ from experiment 1?

A An iron catalyst is present in experiment 2.
B 2 mol of helium gas is present in the reaction mixture in experiment 2.
C A pressure of 250 atm is used in experiment 2.
D A temperature of 600°C is used in experiment 2.

33. Graphs can be drawn to show the percentage of ammonia at equilibrium when nitrogen and hydrogen are mixed at different temperatures and pressures.
Which diagram correctly represents these two graphs?



The Contact process

The key stage in the production of sulfuric acid relies on an equilibrium reaction. In this process, sulfur dioxide is reacted with oxygen to form sulfur trioxide:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

The forward reaction is exothermic. Therefore, Le Chatelier's principle predicts that cooling the reaction mixture would give an increased yield.
However, as you saw in the Haber process, this reduces the rate of attaining equilibrium.
Because there is an overall reduction in the number of molecules moving from left to right, Le Chatelier's principle also predicts that increasing the pressure will drive the equilibrium to the right, increasing the yield of sulfur trioxide.
The conditions used mirror these principles. The gas mixture is passed over three catalyst beds and is cooled after each pass to try to force the equilibrium to the right. Although a higher pressure is predicted to push the equilibrium to the right, most chemical plants producing sulfuric acid operate at just above atmospheric pressure to reduce costs.

34. The Contact process takes place at a pressure between 100 000 Pa and 200 000 Pa. A catalyst is used.
Which statement is correct?

A V_2O_5 catalyst is added to increase the equilibrium yield of the reaction.
B Changes in pressure have no effect on the position of equilibrium.
C The equilibrium yield of the reaction is very high under the conditions used.
D An iron catalyst is added to increase the rate of reaction.

35. Ethanol combines with ethanoic acid to form ethyl ethanoate according to the following reaction.
$C_2H_5OH(l) + CH_3CO_2H(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$ $\Delta H_o = -6$ kJ mol^{-1}
9.2 g ethanol, 12 g ethanoic acid and 8.8 g ethyl ethanoate are mixed and allowed to stand at 298 K, until equilibrium is reached.
(M_r: C_2H_5OH, 46; CH_3CO_2H, 60; $CH_3CO_2C_2H_5$, 88)
The resulting equilibrium mixture is found to contain 4.8 g ethanoic acid.
The experiment is repeated at 323 K.

Which statements are correct?

1 There are 0.22 moles of ethyl ethanoate in the mixture at equilibrium at 298 K.

2 The equilibrium mixture at 323 K will contain more than 4.8 g of ethanoic acid.

3 If a small amount of water is added at the start of either experiment the value of K_c would not be affected.

37. In another experiment, equimolar amounts of $Fe^{3+}(aq)$ and $SCN^-(aq)$ are mixed together and allowed to reach equilibrium. The total volume of the mixture is 25.0 cm^3.

reaction 1 $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$

At equilibrium the mixture contains:

- $[SCN^-] = 1.30 \times 10^{-3}$ mol dm^{-3}
- $[FeSCN^{2+}] = 0.300 \times 10^{-3}$ mol dm^{-3}.

(i) Calculate the initial amount, in mol, of $Fe^{3+}(aq)$ added to $SCN^-(aq)$ to produce this mixture.

initial amount of $Fe^{3+}(aq)$ = ... mol [2]

(ii) Calculate *K*c for reaction 1 and state its units.

Show your working.

*K*c = ... units .....[2]

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****