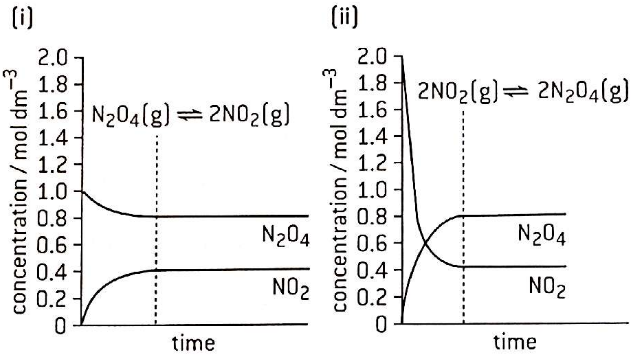
The equilibrium law

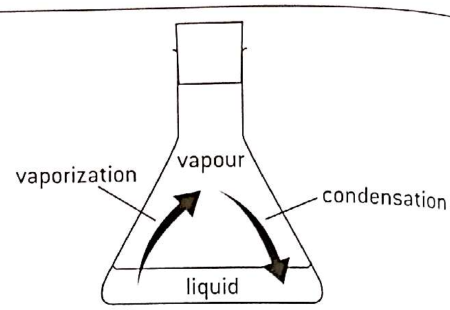
DYNAMIC EQUILIBRIUM

$$A + B \underset{\text{reverse reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} C + D$$

Most chemical reactions do not go to completion. Once some products are formed the reverse reaction can take place to reform the reactants. In a closed system the concentrations of all the reactants and products will eventually become constant. Such a system is said to be in a state of **dynamic equilibrium**. The forward and reverse reactions continue to occur, but at equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction.



Graph(i) shows the decomposition of N_2O_4. Graph(ii) shows the reverse reaction starting with NO_2. Once equilibrium is reached (shown by the dotted line), the composition of the mixture remains constant and is independent of the starting materials.



Dynamic equilibrium also occurs when physical changes take place. In a closed flask, containing some water, equilibrium will be reached between the liquid water and the water vapour. The faster moving molecules in the liquid will escape from the surface to become vapour and the slower moving molecules in the vapour will condense back into liquid. Equilibrium will be established when the rate of vaporization equals the rate of condensation.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

CLOSED SYSTEM

A closed system is one in which neither matter nor energy can be lost or gained from the system, that is, the macroscopic properties remain constant. If the system is open some of the products from the reaction could escape and equilibrium would never be reached.

REACTION QUOTIENT AND EQUILIBRIUM CONSTANT

Consider the following general reversible reaction in which w moles of A react with x moles of B to produce y moles of C and z moles of D.

$$wA + xB \rightleftharpoons yC + zD$$

At any particular point in time the concentrations of A, B, C and D can be written as [A], [B], [C] and [D] respectively. The reaction quotient, Q, is defined as being

$$Q = \frac{[C]^y \times [D]^z}{[A]^w \times [B]^x}$$

As the reaction proceeds, the reaction quotient will change until the point of equilibrium is reached. At that point the concentrations of A, B, C and D remain constant and the reaction quotient is known as the equilibrium constant, K_c.

The equilibrium law states that for this reaction at a particular temperature

$$K_c = \frac{[C]^y_{eqm} \times [D]^z_{eqm}}{[A]^w_{eqm} \times [B]^x_{eqm}}$$

Examples

Formation of sulfur trioxide in the Contact process

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

$$K_c = \frac{[SO_3]^2_{eqm}}{[SO_2]^2_{eqm} \times [O_2]_{eqm}}$$

Formation of an ester from ethanol and ethanoic acid

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

$$K_c = \frac{[CH_3COOC_2H_5]_{eqm} \times [H_2O]_{eqm}}{[C_2H_5OH]_{eqm} \times [CH_3COOH]_{eqm}}$$

In both of these examples all the reactants and products are in the same phase. In the first example they are all in the gaseous phase and in the second example they are all in the liquid phase. Such reactions are known as *homogeneous reactions*. Another example of a homogeneous system would be where all the reactants and products are in the aqueous phase.

MAGNITUDE OF THE EQUILIBRIUM CONSTANT

Since the equilibrium expression has the concentration of products on the top and the concentration of reactants on the bottom it follows that the magnitude of the equilibrium constant is related to the position of equilibrium. When the reaction goes nearly to completion $K_c \gg 1$. If the reaction hardly proceeds then $K_c \ll 1$. If the value for K_c lies between about 10^{-2} and 10^2 then both reactants and products will be present in the system in noticeable amounts. The value for K_c in the esterification reaction above is 4 at 100 °C. From this it can be inferred that the concentration of the products present in the equilibrium mixture is roughly twice that of the reactants.

Le Chatelier's principle and factors affecting the position of equilibrium

LE CHATELIER'S PRINCIPLE

Provided the temperature remains constant the value for K_c must remain constant. If the concentration of the reactants is increased, or one of the products is removed from the equilibrium mixture then more of the reactants must react in order to keep K_c constant, i.e. the position of equilibrium will shift to the right (towards more products). This is the explanation for Le Chatelier's principle, which states that if a system at equilibrium is subjected to a small change the equilibrium tends to shift so as to minimize the effect of the change.

2. equilibrium shifts to minimize effect

$$A + B \rightleftharpoons C + D$$

1. remove product

FACTORS AFFECTING THE POSITION OF EQUILIBRIUM

CHANGE IN CONCENTRATION

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

If more ethanoic acid is added the concentration of ethanoic acid increases so that at the point of addition:

$$K_c \neq \frac{[\text{ester}] \times [\text{water}]}{[\text{acid}] \times [\text{alcohol}]}$$

To restore the system so that the equilibrium law is obeyed the equilibrium will move to the right, so that the concentration of ester and water increases and the concentration of the acid and alcohol decreases.

CHANGE IN PRESSURE

If there is an overall volume change in a gaseous reaction then increasing the pressure will move the equilibrium towards the side with less volume. This shift reduces the total number of molecules in the equilibrium system and so tends to minimize the pressure.

$$\underset{\substack{\text{brown} \\ (2\text{ vols})}}{2NO_2(g)} \rightleftharpoons \underset{\substack{\text{colourless} \\ (1\text{ vol})}}{N_2O_4(g)}$$

If the pressure is increased the mixture will initially go darker as the concentration of NO_2 increases then become lighter as the position of equilibrium is re-established with a greater proportion of N_2O_4.

CHANGE IN TEMPERATURE

In exothermic reactions heat is also a product. Taking the heat away will move the equilibrium towards the right, so more products are formed. The forward reaction in exothermic reactions is therefore increased by lowering the temperature

$$\underset{\text{brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4(g)} \qquad \Delta H^\ominus = -24 \text{ kJ mol}^{-1}$$

Lowering the temperature will cause the mixture to become lighter as the equilibrium shifts to the right.

For an endothermic reaction the opposite will be true.

Unlike changing the concentration or pressure, a change in temperature will also change the value of K_c. For an exothermic reaction the concentration of the products in the equilibrium mixture decreases as the temperature increases, so the value of K_c will decrease. The opposite will be true for endothermic reactions.

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

T / K	K_c
298	1.00×10^{-5}
500	7.76×10^{-3}
700	1.23×10^{-1}
900	6.01×10^{-1}

increase

ADDING A CATALYST

A catalyst will increase the rate at which equilibrium is reached, as it will speed up both the forward and reverse reactions equally, but it will have no effect on the position of equilibrium and hence on the value of K_c.

MANIPULATING EQUILIBRIUM CONSTANTS

When a reaction is reversed the equilibrium constant for the reverse reaction will be the reciprocal of the equilibrium constant for the forward reaction, K_c. For example, for the reverse reaction of the Haber process, $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

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

If there are multiple steps in a reaction, each with its own equilibrium constant, then the equilibrium constants are multiplied to give the overall value of K_c. For example,

For the step $A + B \rightleftharpoons C$ $\qquad K_c^1 = \dfrac{[C]}{[A] \times [B]}$

For the step $C + D \rightleftharpoons X + Y$ $\qquad K_c^2 = \dfrac{[X] \times [Y]}{[C] \times [D]}$

For the overall reaction $A + B + D \rightleftharpoons X + Y$ $\qquad K_c = \dfrac{[X] \times [Y]}{[A] \times [B] \times [D]} = K_c^1 \times K_c^2$

HL Equilibrium calculations

EQUILIBRIUM CALCULATIONS

The equilibrium law can be used either to find the value for the equilibrium constant, or to find the value of an unknown equilibrium concentration.

a) 23.0 g (0.50 mol) of ethanol was reacted with 60.0 g (1.0 mol) of ethanoic acid and the reaction allowed to reach equilibrium at 373 K. 37.0 g (0.42 mol) of ethyl ethanoate was found to be present in the equilibrium mixture. Calculate K_c to the nearest integer at 373 K.

	$C_2H_5OH(l)$	+	$CH_3COOH(l)$	$\rightleftharpoons$	$CH_3COOC_2H_5(l)$	+	$H_2O(l)$
Initial amount / mol	0.50		1.00		–		–
Equilibrium amount / mol	(0.50 – 0.42)		(1.00 – 0.42)		0.42		0.42
Equilibrium concentration / mol dm^{-3}	$\frac{(0.50 - 0.42)}{V}$		$\frac{(1.00 - 0.42)}{V}$		$\frac{0.42}{V}$		$\frac{0.42}{V}$

(where V = total volume)

$$K_c = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]} = \frac{(0.42/V) \times (0.42/V)}{(0.08/V) \times (0.58/V)} = 4 \text{ (to the nearest integer)}$$

b) What mass of ester will be formed at equilibrium if 2.0 moles of ethanoic acid and 1.0 moles of ethanol are reacted under the same conditions?

Let x moles of ester be formed and let the total volume be V dm^3.

$$K_c = 4 = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]} = \frac{x^2/V^2}{(1.0 - x)/V \times (2.0 - x)/V} = \frac{x^2}{(x^2 - 3x + 2)}$$

$\Rightarrow 3x^2 - 12x + 8 = 0$

solve by substituting into the quadratic expression $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \Rightarrow x = \frac{12 \pm \sqrt{144 - 96}}{6}$

$x = 0.845$ or ~~3.15~~ (it can not be 3.15 as only 1.0 mol of ethanol was taken)

Mass of ester = 0.845 × 88.08 = 74.4 g (Note: IB Diploma Programme chemistry does not examine the use of the quadratic expression.)

c) 1.60 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium at a temperature of 704 K in a 4.00 dm^3 flask, the amount of hydrogen iodide formed in the equilibrium mixture is 1.80 mol. Determine the value of the equilibrium constant at this temperature.

	$H_2(g)$	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial amount / mol	1.60	1.00		0
Equilibrium amount / mol	0.70	0.10		1.80
Equilibrium concentration / mol dm^{-3}	0.175	0.025		0.450

$$K_c = \frac{[HI(g)]^2}{[H_2(g)] \times [I_2(g)]} = \frac{0.450^2}{0.175 \times 0.025} = 46.3 \text{ at } 704 \text{ K}$$

RELATIONSHIP BETWEEN FREE ENERGY CHANGE AND THE EQUILIBRIUM CONSTANT

The position of equilibrium corresponds to a maximum value of entropy and a minimum in the value of the Gibbs free energy change. This means that the equilibrium constant, K_c and the Gibbs free energy change, $\Delta G^\ominus$ can both be used to measure the position of equilibrium in a reaction. They are related by the equation

$\Delta G = -RT\ lnK$

This can be illustrated by the dissociation of water according to the equation

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad \Delta H^\ominus = +55.8$ kJ mol^{-1}

The relevant entropy values are:

	$H_2O(l)$	$H^+(aq)$	$OH^-(aq)$
$S^\ominus$ / J K^{-1} mol^{-1}	+70.0	0	– 10.9

The change in entropy, $\Delta S^\ominus = (\Sigma S^\ominus \textit{products}) - (\Sigma S^\ominus \textit{reactants}) = (-10.9) - (+70.0) = -80.8$ J K^{-1} mol^{-1}

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = 55.8 \times 1000 - (298 \times -80.8) = +79900$ J mol^{-1}

Using the expression $\Delta G = -RT\ lnK$

$$\ln K = \frac{-79900}{8.314 \times 298} = -32.2$$

$K = e^{-32.2} = 1.00 \times 10^{-14}$ at 298 K

This is the value for the equilibrium constant of water at 298 K, known as the ionic product constant for water (K_w), given in Section 2 of the IB data booklet.

MULTIPLE CHOICE QUESTIONS – EQUILIBRIUM

1. Which statement is true about a chemical reaction at equilibrium?
   A. The reaction has completely stopped.
   B. The concentrations of the products are equal to the concentrations of the reactants.
   C. The rate of the forward reaction is equal to the rate of the reverse reaction.
   D. The concentrations of the products and reactants are constantly changing.

2. What is the equilibrium constant expression, K_c, for the following reaction?
   $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$
   A. $K_c = \dfrac{[NO][Br_2]}{[NOBr]}$
   B. $K_c = \dfrac{[NO]^2[Br_2]}{[NOBr]^2}$
   C. $K_c = \dfrac{2[NO] + [Br_2]}{[2NOBr]}$
   D. $K_c = \dfrac{[NOBr]^2}{[NO]^2[Br_2]}$

3. The following are K_c values for a reaction, with the same starting conditions, carried out at different temperatures. Which equilibrium mixture has the highest concentration of products?
   A. 1×10^{-2}
   B. 1
   C. 1×10^{1}
   D. 1×10^{2}

4. What effect will an increase in temperature have on the K_c value and the position of equilibrium in the following reaction?
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92\,kJ$

	K_c	Equilibrium position
A.	increases	shifts to the right
B.	decreases	shifts to the left
C.	increases	shifts to the left
D.	decreases	shifts to the right

5. Consider the following equilibrium reaction.
   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^{\ominus} = -197\,kJ$
   Which change in conditions will increase the amount of SO_3 present when equilibrium is re-established?
   A. Decreasing the concentration of SO_2
   B. Increasing the volume
   C. Decreasing the temperature
   D. Adding a catalyst

6. The Haber process uses an iron catalyst to convert hydrogen gas, $H_2(g)$, and nitrogen gas, $N_2(g)$, to ammonia gas, $NH_3(g)$.
   $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$
   Which statements are correct for this equilibrium system?
   I. The iron catalyst increases rates of the forward and reverse reactions equally.
   II. The iron catalyst does not affect the value of the equilibrium constant, K_c.
   III. The iron catalyst increases the yield for ammonia gas, $NH_3(g)$.
   A. I and II only
   B. I and III only
   C. II and III only
   D. I, II and III

7. The formation of nitric acid, $HNO_3(aq)$, from nitrogen dioxide, $NO_2(g)$, is exothermic and is a reversible reaction.
   $4NO_2(g) + O_2(g) + 2H_2O(l) \rightleftharpoons 4HNO_3(aq)$
   What is the effect of a catalyst on this reaction?
   A. It increases the yield of nitric acid.
   B. It increases the rate of the forward reaction only.
   C. It increases the equilibrium constant.
   D. It has no effect on the equilibrium position.

8. The value of K_c for the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ is 4.0×10^{-2}. What is the value of the equilibrium constant for the reaction $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$ at the same temperature?
   A. 4.0×10^{-2} C. 25
   B. 2.0×10^{-1} D. 400

HL

9. 0.50 mol of $I_2(g)$ and 0.50 mol of $Br_2(g)$ are placed in a closed flask. The following equilibrium is established.
   $I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$
   The equilibrium mixture contains 0.80 mol of IBr(g). What is the value of K_c?
   A. 0.64 C. 2.6
   B. 1.3 D. 64

10. A 2.0 dm^3 reaction vessel initially contains 4.0 mol of P and 5.0 mol of Q. At equilibrium 3 mol of R is present. What is the value of K_c for the following reaction?
   $P(g) + Q(g) \rightleftharpoons R(g) + S(g)$
   A. $\frac{2}{9}$ C. 4.5
   B. $\frac{9}{20}$ D. 9

11. At 35 °C $K_c = 1.6 \times 10^{-5}\,mol\,dm^{-3}$ for the reaction
   $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
   Which relationship must be correct at equilibrium?
   A. [NO] = [NOCl] C. [NOCl] < $[Cl_2]$
   B. 2[NO] = $[Cl_2]$ D. [NO] < [NOCl]

12. Free energy change and the equilibrium constant are related by the equation $\Delta G = -RT\ln K_c$. Which combination is most likely for a reaction to go to completion at all temperatures?

	$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	K_c
A	–	+	> 1
B	+	+	> 1
C	–	–	< 1
D	–	–	> 1

SHORT ANSWER QUESTIONS – EQUILIBRIUM

1. Ethanol is manufactured by the hydration of ethene according to the equation below.

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

   a) State the expression for the equilibrium constant, K_c, for this reaction. [1]

   b) Under certain conditions, the value of K_c for this reaction is 3.7×10^{-3}. When the temperature is increased the value is 4.9×10^{-4}.

   (i) State what can be deduced about the position of equilibrium at the higher temperature from these values of K_c. [1]

   (ii) State what can be deduced about the sign of ΔH for the reaction, explaining your choice. [3]

   c) The process used to manufacture ethanol is carried out at high pressure. State and explain two advantages of using high pressure. [4]

2. Ammonia is produced by the Haber process according to the following reaction

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H$ is negative

   a) State the equilibrium expression for the above reaction. [1]

   b) Predict, giving a reason, the effect on the position of equilibrium when the pressure in the reaction vessel is increased. [2]

   c) State and explain the effect on the value of K_c when the temperature is increased. [2]

   d) Explain why a catalyst has no effect on the position of equilibrium. [1]

3. Consider the following equilibrium:

   $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\quad \Delta H^{\ominus} = -909$ kJ

   a) Deduce the equilibrium constant expression, K_c, for the reaction. [1]

   b) Predict the direction in which the equilibrium will shift when the following changes occur. [4]

   (i) The volume increases.

   (ii) The temperature decreases.

   (iii) $H_2O(g)$ is removed from the system.

   (iv) A catalyst is added to the reaction mixture.

   c) Define the term *activation energy*. [1]

4. An example of a homogeneous reversible reaction is the reaction between hydrogen and iodine.

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

   a) Outline the characteristics of a homogeneous chemical system that is in a state of equilibrium. [2]

   b) Formulate the expression for the equilibrium constant, K_c. [1]

   c) Predict what would happen to the position of equilibrium and the value of K_c if the pressure is increased from 1 atm to 2 atm. [2]

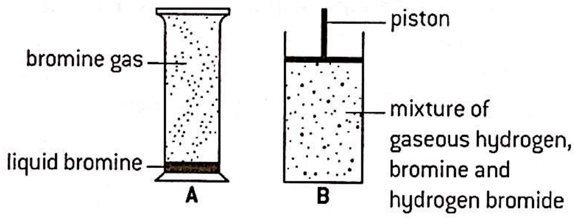
   d) The value of K_c at 500 K is 160 and the value of K_c at 700 K is 54. Deduce what this information tells us about the enthalpy change of the forward reaction. [1]

   (e) Deduce the value of the equilibrium constant, K_c' at 500 K for the reaction below: [1]

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

HL

5. Consider the two equilibrium systems involving bromine gas illustrated below.



   a) Formulate equations to represent the equilibria in A and B with $Br_2(g)$ on the left-hand side in both equilibria. [2]

   b) (i) Describe what you would observe if a small amount of liquid bromine is introduced into **A**. [1]

   (ii) Predict what happens to the position of equilibrium if a small amount of hydrogen is introduced into **B**. [1]

   (iii) State and explain the effect of increasing the pressure in **B** on the position of equilibrium. [2]

   c) (i) Deduce the equilibrium constant expression, K_c, for the equilibrium in **B**. [1]

   (ii) State the effect of increasing $[H_2]$ in **B** on the value of K_c. [1]

6. Ammonia production is important in industry.

   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H = -92$ kJ

   a) The standard entropy values, S, at 298 K for $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 193, 131 and 192 J K^{-1} mol^{-1} respectively. Calculate $\Delta S^{\ominus}$ for the reaction as shown by the equation above. [2]

   b) Determine $\Delta G^{\ominus}$ for the reaction at 298 K. [2]

   c) Describe and explain the effect of increasing temperature on the spontaneity of the reaction. [2]

   d) Determine the value of the equilibrium constant at 298 K by using the value of $\Delta G^{\ominus}$ that you obtained in b). [3]

   e) 0.20 mol of N(g) and 0.20 mol of $H_2(g)$ were allowed to reach equilibrium in a 1 dm^3 closed container at a temperature T_2 which is different to 298 K. At equilibrium the concentration of $NH_3(g)$ was found to be 0.060 mol dm^{-3}. Determine the value of K_c at temperature T_2. [3]

   f) Comment on the two different values for K_c that you have obtained. [2]

   g) Describe how increasing the pressure affects the yield of ammonia. [2]

   h) In practice, typical conditions used in the Haber process are a temperature of 500°C and a pressure of 200 atmospheres. Suggest why these conditions are used rather than those that give the highest yield. [2]

   i) Iron is used as a catalyst in this manufacturing process. A catalyst has no effect on the value of K_c or on the position of equilibrium. Suggest why a catalyst is used in this process. [1]