Equilibrium SL (answers)

IB CHEMISTRY SL

7.1 Equilibrium

Understandings:

- A state of equilibrium is reached in a closed system when the rates of the forward and reverse reactions are equal.
- The equilibrium law describes how the equilibrium constant (K_c) can be determined for a particular chemical reaction.
- The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.
- The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time. Q is the equilibrium expression with non-equilibrium concentrations.
- The position of the equilibrium changes with changes in concentration, pressure, and temperature.
- A catalyst has no effect on the position of equilibrium or the equilibrium constant.

Applications and skills:

- The characteristics of chemical and physical systems in a state of equilibrium.
- Deduction of the equilibrium constant expression (K_c) from an equation for a homogeneous reaction.
- Determination of the relationship between different equilibrium constants (K_c) for the same reaction at the same temperature.
- Application of Le Châtelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant.

Guidance:

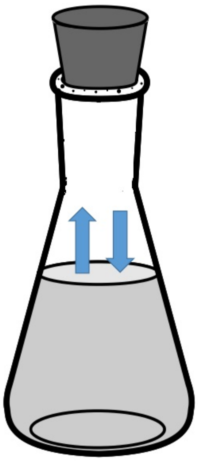
- Physical and chemical systems should be covered.
- Relationship between K_c values for reactions that are multiples or inverses of one another should be covered.
- Specific details of any industrial process are not required.

Syllabus checklist

Objective	I am confident with this	I need to review this	I need help with this
Outline the features of physical and chemical equilibrium			
Write expressions for the equilibrium constant K_c for a reaction			
Calculate the value of the equilibrium constant K_c			
Outline the difference between the equilibrium constant K_c and the reaction quotient Q			
Determine, when given the values of Q and K_c, in which direction the reaction will proceed.			
Outline how the value of K_c changes when changes are made to the reaction at constant temperature.			
Apply Le Chatelier's principle to predict the changes in the position of equilibrium for changes in concentration, temperature and pressure.			
Outline the effect of a catalyst on the position of equilibrium.			

Physical equilibrium

- Physical equilibrium involves a change of state.
- The flask below is a closed system (matter cannot escape).
- The rate of evaporation is equal to the rate of condensation (liquid level is constant).
- The system is at equilibrium.
- Note that in physical equilibrium, there is no chemical change occurring.



On a macroscopic level, there is no change in the level of the liquid. However, the processes of evaporation and condensation are still occurring; the liquid is evaporating and condensing at the same rate. Therefore, we say the system is at dynamic equilibrium.
What will happen if the stopper is removed from the top of the flask? Will the system reach equilibrium? Why/why not?

- The equation below represents the physical process occurring in the flask.

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

- The $\rightleftharpoons$ sign is used to show that the system is at equilibrium.

Exercises:

1. Bromine (Br_2) is a brown liquid that evaporates easily at room temperature. A sample of bromine is placed in a sealed flask. Write an equation to show the system is at equilibrium.

   $Br_{2(l)} \rightleftharpoons Br_{2(g)}$

2. What can you say about the rates of evaporation and condensation when the system is at equilibrium?
   The rate of evaporation is equal to the rate of condensation.

3. What other macroscopic properties would tell you the system is at equilibrium?

   Liquid level remains constant, no change in colour.

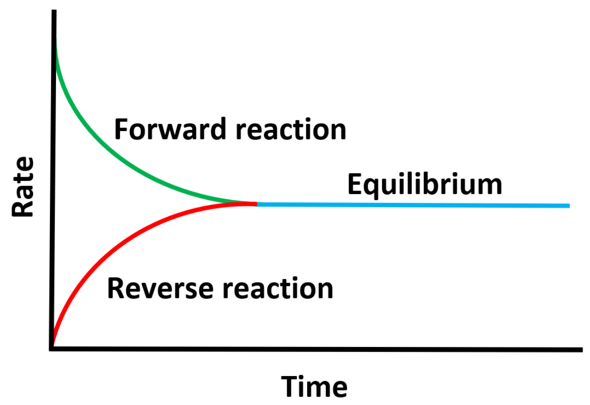
Chemical equilibrium

- Unlike physical equilibrium, which only involves a change of state, chemical equilibrium involves a chemical reaction.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

- In the forward reaction, hydrogen iodide (HI) decomposes to form hydrogen (H_2) and iodine (I_2)
- In the reverse reaction, H_2 and I_2 react to form HI.

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

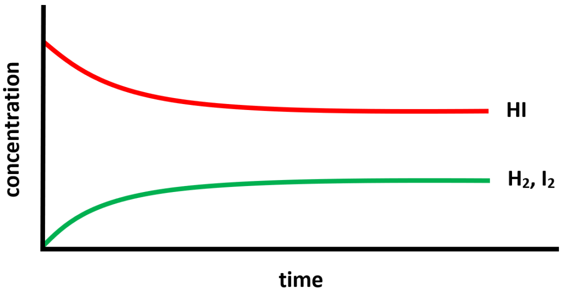


Important points about a reaction at equilibrium:

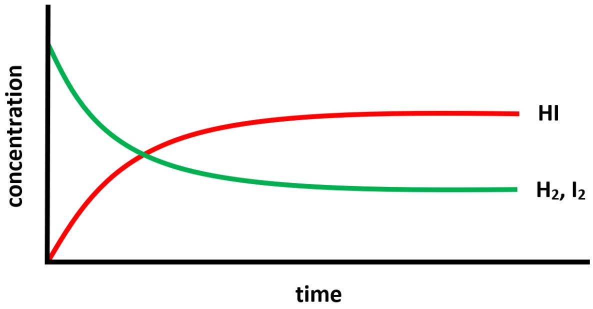
1. Equilibrium is dynamic; the reaction has not stopped and both forward and reverse reactions are still happening (at the same rate).
2. Equilibrium is achieved in a closed system.
3. The concentrations of reactants and products at equilibrium are constant (**NOT EQUAL**).
4. At equilibrium, there is no change in macroscopic properties such as colour.
5. Equilibrium can be reached from either direction (from reactants to products or from products to reactants).

Equilibrium can be reached in either direction, as shown in the graphs below.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$



$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$



When the lines in the graphs are parallel, the reaction is at equilibrium. The concentrations of reactants and products are constant at equilibrium, **not equal**.

Exercise:

1. Ammonia (NH_3) is made in the reaction of N_2 and H_2. The reaction reaches equilibrium. Write an equation for the forward reaction (with all species in the gaseous state).

   $$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

2. What can you say about the rates of the forward and backward reactions at equilibrium?

   The rate of the forward reaction is equal to the rate of the reverse reaction.

3. Are the concentrations of reactants and products equal at equilibrium? Explain your answer.

   The concentrations of reactants and products are constant but not equal.

Equilibrium constant K_c

- K_c is calculated using **equilibrium concentrations** of reactants and products.
- The products go in the numerator and the reactants in the dominator.
- The concentrations are raised to the powers of the coefficients in the balanced equation.

$$aA + bB \rightleftharpoons cC + dD$$

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

- The equilibrium constant K_c has a fixed value for a reaction at a specific temperature (it is temperature dependent).

Example: The following reaction is carried out at 440°C.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Write the expression for the K_c

Exercises:

1) Write expressions for the equilibrium constant K_c for the following reactions:

a) $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$

b) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$

c) $CH_3OH_{(g)} \rightleftharpoons CO_{(g)} + 2H_{2(g)}$

d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

e) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Note that state symbols are not required in equilibrium expressions.

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

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

c. $K_c = \frac{[CO(g)][H_2(g)]^2}{[CH_3OH(g)]}$

d. $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

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

Calculating the value of the equilibrium constant K_c

Calculate the equilibrium constant, K_c, for the reaction shown, if 0.0954 mol of CO_2, 0.0454 mol of H_2, 0.0046 mol of CO, and 0.0046 mol of H_2O vapor were present in a 1.00 dm^3 reaction vessel at equilibrium (at 440°C).

$$CO_{2\,(g)} + H_{2\,(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

Species	Equilibrium concentrations (mol dm^{-3})
CO_2	0.0954 / 1.00 = 0.0954
H_2	0.0454 / 1.00 = 0.0454
CO	0.0046 / 1.00 = 0.0046
H_2O	0.0046 / 1.00 = 0.0046

Magnitude of K_c and extent of reaction

- The position of equilibrium of a reaction can lie to the left or to the right.
- If a reaction mixture at equilibrium contains mostly reactants, we say the equilibrium position lies to the left.
- If a reaction mixture at equilibrium contains mostly products, we say the equilibrium position lies to the right.
- A high value of K_c means at equilibrium, there are a higher concentration of products than reactants (the equilibrium position lies to the right).
- A low value of K_c means at equilibrium, there are a higher concentration of reactants than products (the equilibrium position lies to the left).

Reaction	K_c value (at 298 K)	Equilibrium position
$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$	1.9×10^{-23}	Lies to the left (forward reaction hardly proceeds)
$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$	3.2×10^{81}	Lies to the right (goes to completion)
$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$	4.61×10^{-3}	Lies to the left – reaction mixture contains mostly reactants
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	640	Lies to the right – reaction mixture contains mostly products

Exercises:

1. Which is present in greater concentrations if the equilibrium position lies to the left, reactants or products?
   Reactants.

2. Which is present in greater concentrations if the equilibrium position lies to the right, reactants or products?
   Products.

3. A reaction has a K_c of 2. What can be said about the equilibrium position and the concentration of reactants and products at equilibrium?
   Equilibrium position lies to the right and equilibrium mixture contains mostly products.

4. A reaction has a K_c of 1.8×10^{-5}. What can be said about the equilibrium position and the concentration of reactants and products at equilibrium?
   Equilibrium position lies to the left and equilibrium mixture contains mostly reactants.

5. The table below shows equilibrium concentrations of reactants and products for the following reaction at 2130 °C

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

	Equilibrium concentrations (mol dm^{-3})
$N_{2(g)}$	0.81
$O_{2(g)}$	0.75
$NO_{(g)}$	0.030

From the above data, calculate the equilibrium constant K_c. Comment on the magnitude of K_c with respect to the composition of the reaction mixture at equilibrium.

Write the expression for the K_c

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

Input values into the expression (products in numerator, reactants in denominator)

$$K_c = \frac{[0.030]^2}{[0.81][0.75]} = 1.5 \times 10^{-3}$$

K_c is small, therefore, equilibrium mixture will contain higher concentration of reactants than products (equilibrium lies to the left).

Manipulating K_c for different reaction equations

	Effect on equilibrium expression	**Effect on K_c**
Reversing the reaction	Inverts the expression	$1/K_c$
Doubling the reaction coefficients	Squares the expression	K_c^2
Halving the reaction coefficients	Square root the expression	$\sqrt{Kc}$
Adding together 2 reactions	Multiplies the expressions	$K_c \times K_c$

Exercise:

The equilibrium constant for the following reaction is 0.04.

$$2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$$

What would be the value of the equilibrium constant for the following reaction at the same temperature?

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$$

K_c for reaction = 5

Reaction quotient *Q*

- The reaction quotient *Q* measures the relative amounts of reactants and products at a point in time.
- It is expressed with **non-equilibrium concentrations**.

$$aA + bB \rightleftharpoons cC + dD$$

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

- At equilibrium, the concentrations of A, B, C and D are constant, and the reaction quotient is equal to the K_c

Exercise: Outline the difference between the reaction quotient *Q* and the equilibrium constant K_c

The reaction quotient *Q* uses non-equilibrium concentrations of reactants and products. The equilibrium constant K_c uses equilibrium concentrations of reactants and products.

Q, K_c and direction of reaction

- Let's start with a quick explanation of what is meant by the following terms:
- *Reaction proceeds to the right* – the reaction proceeds to the products side (more products will be produced).
- *Reaction proceeds to the left* – the reaction proceeds to the reactants side (more reactants will be produced).

Relationship between reaction quotient *Q* and K_c

- When the value of *Q* is equal to the value of the K_c the reaction is at equilibrium.
- What happens if the value of *Q* is lower or higher than the value of K_c?
- If the value of *Q* is lower than the value of K_c, the reaction will proceed to the right to increase the value of *Q*.
- If the value of *Q* is higher than the value of K_c, the reaction will proceed to the left to lower the value of *Q*.

Example 1:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \quad K_c = 49.5 \text{ at } 440°C$$

Calculate the value of *Q* when the concentration of HI is 0.100 mol dm^{-3} and the concentrations of H_2 and I_2 are both 0.0500 mol dm^{-3}

Based on your calculation, predict in which direction the reaction will proceed and explain your answer.

Example 2:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \quad K_c = 49.5 \text{ at } 440°C$$

Calculate the value of *Q* when the concentration of HI is 0.300 mol dm^{-3} and the concentration of H_2 is 0.0250 mol dm^{-3} and the concentration of I_2 is 0.0350 mol dm^{-3}

Based on your calculation, predict in which direction the reaction will proceed and explain your answer.

Summary:

Q vs K_c	**Direction of reaction**	**Change in *Q***
$Q > K_c$	To the left (reactants)	decrease
$Q < K_c$	To the right (products)	Increase
$Q = K_c$	No change (reaction is at equilibrium)	None

Exercises:

1. The table below show non-equilibrium concentrations of reactions and products for the following reaction at 527°C. The value of K_c for this reaction at 527 °C is 5.10.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

	Concentration at time t (mol dm^{-3})
$CO_{(g)}$	0.15
$H_2O_{(g)}$	0.25
$H_{2(g)}$	0.42
$CO_{2(g)}$	0.37

From the above data, calculate the reaction quotient *Q* and predict in which direction the reaction will proceed.

Write expression for *Q*

$$Q = \frac{[H_2][CO_2]}{[H_2O]\ [CO]}$$

Input values into the expression (products in numerator, reactants in denominator)

$$Q = \frac{(0.42)(0.37)}{(0.25)(0.15)} = 4.1$$

The value of the reaction quotient *Q* is less than the value of K_c so the reaction will proceed to the right (products side), increasing the value of *Q*.

2. The table below shows non-equilibrium concentrations of reactions and products for the following reaction at 1000°C. The value of K_c for this reaction at 1000°C is 1.00×10^{-13}

$$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$$

	Concentration at time t (mol dm^{-3})
$HF_{(g)}$	23.0
$H_{2(g)}$	0.540
$F_{2(g)}$	0.380

From the above data, calculate the reaction quotient *Q* and predict in which direction the reaction will proceed.

Write expression for *Q*

$$Q = \frac{[H_2]\,[F_2]}{[HF]^2}$$

Input values into the expression (products in numerator, reactants in denominator)

$$Q = \frac{(0.540)\,(0.380)}{(23.0)^2} = 3.88 \times 10^{-4}$$

The value of the reaction quotient Q is greater than the value of K_c so the reaction will proceed to the left (reactants side), decreasing the value of Q.

Le Chatelier's principle

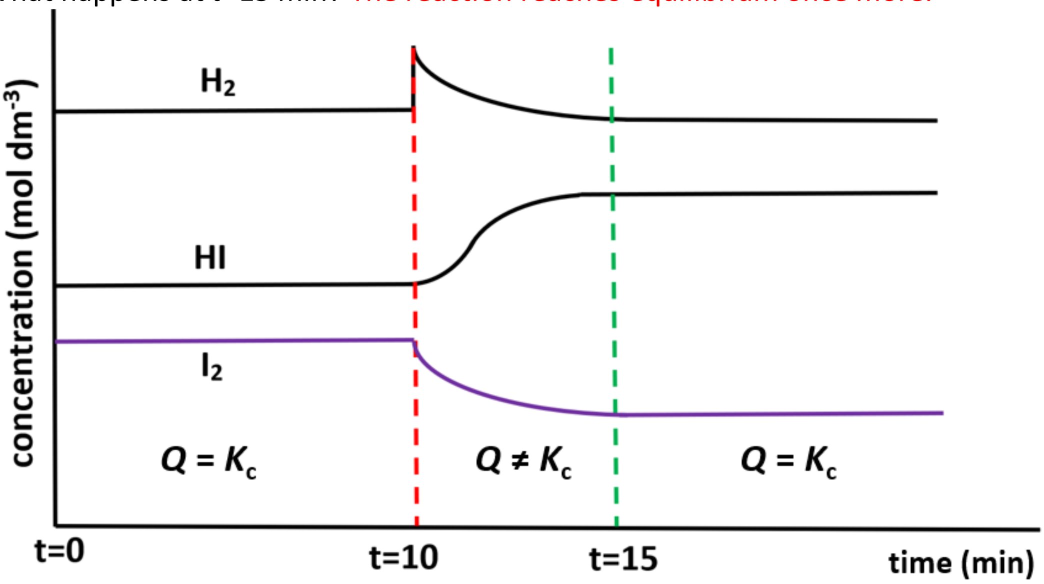
'When a system at equilibrium is subjected to a change, the system will respond to minimize the effect of the change.'

Changes in concentration

- If changes are made to the concentration of the reactants or products or the pressure of the system, then the position of equilibrium will shift to keep the value of K_c the same.

The following questions refer to the graph below.

- From *t*=0 min to *t*=10 min, the reaction is at equilibrium.
- At *t*=10 min, hydrogen gas, H_2, is added to the system.
- What effect does this have on the equilibrium position and the concentrations of I_2 and HI? $[I_2]$ decreases and [HI] increases.
- What happens at *t*=15 min? The reaction reaches equilibrium once more.



Example 1

Predict the effect of adding extra $H_{2(g)}$ to the equilibrium mixture below:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

In which direction will the position of equilibrium shift and what is the effect on the value of K_c?

Equilibrium shifts to the right to use up extra H_2. Value of K_c does not change.

Example 2

Predict the effect of adding $HI_{(g)}$ to the equilibrium mixture above:

Equilibrium shifts to the left to use up extra HI. Value of K_c does not change.

Changes in pressure (gaseous reactions)

- The direction to which the equilibrium shifts in gaseous reactions depends on the number of moles of gas in the reactants and products.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Example 1:

Predict the direction in which the equilibrium will shift when pressure is increased. State and explain the effect on the value of K_c.

Equilibrium shifts to the right because there are a fewer number of gaseous molecules in the products. Value of K_c does not change as K_c is temperature dependent.

Example 2:

Predict the direction in which the equilibrium will shift when pressure is decreased. State and explain the effect on the value of K_c

Equilibrium shifts to the left because there are a greater number of gaseous molecules in the reactants. Value of K_c does not change as K_c is temperature dependent.

Exercise:

Consider the following reaction:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$

Explain the effects on the position of equilibrium on the above reaction when:

a) The pressure is increased.

Equilibrium shifts to the right because there are a fewer number of gaseous molecules in the products. Value of K_c does not change as K_c is temperature dependent.

b) The pressure is decreased.

Equilibrium shifts to the left because there are a greater number of gaseous molecules in the reactants. Value of K_c does not change as K_c is temperature dependent.

Changes in temperature

- Important point about a change in temperature:

A change in temperature will change the value of K_c

- If the temperature of the reaction changes, the value of K_c will also change.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Predict the direction in which the equilibrium will shift when the temperature is increased in the above reaction and explain your answer.

Equilibrium position will shift to the left as forward reaction is exothermic. Value of K_c will decrease.

Predict the direction in which the equilibrium will shift in the above reaction when the temperature is decreased and explain your answer.

Equilibrium position will shift to the right as forward reaction is exothermic. Value of K_c will increase.

The effect of temperature on the value of K_c

- For an exothermic reaction, increasing the temperature shifts the equilibrium to the left (reactants side) and decreases the value of K_c
- For an endothermic reaction, increasing the temperature shifts the equilibrium to the right (products side) and increases the value of K_c

Exercises:

Predict and explain the effect of **decreasing the temperature** on each of the following reactions at equilibrium and the effect on the value of K_c.

a $X_2(g) + AB_3(g) \rightleftharpoons 2BX(g) + AB(g)$ $\Delta H = -50\ \text{kJ mol}^{-1}$

Equilibrium position will shift to the right as forward reaction is exothermic. Value of K_c will increase.

b $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $\Delta H = -200\ \text{kJ mol}^{-1}$

Equilibrium position will shift to the right as forward reaction is exothermic. Value of K_c will increase.

c $N_2O_5(g) + NO(g) \rightleftharpoons 3NO_2(g)$ $\Delta H = +51\ \text{kJ mol}^{-1}$

Equilibrium position will shift to the left as forward reaction is endothermic. Value of K_c will decrease.

Catalysts and equilibrium

- A catalyst increases the rate of the forward and reverse reactions by the same amount.
- Catalysts do not change the position of equilibrium or the value of K_c
- Catalysts allow equilibrium to be reached more quickly.

Exercise:

Many reversible reactions in industry use a catalyst. State and explain the effect of a catalyst on the position of equilibrium and on the value of the K_c.

A catalyst does not change the position of equilibrium or the value of the K_c

A catalyst increases the rate of the forward and reverse reactions by the same amount.

A catalyst allows equilibrium to be reached more quickly.