

# Equilibrium SL

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IB CHEMISTRY SL

25 <b>Mn</b> Manganese 54.938045	16 <b>S</b> Sulfur 32.065	<b>J</b>	6 <b>C</b> Carbon 12.0107	2 <b>He</b> Helium 4.002602	25 <b>Mn</b> Manganese 54.938045
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## 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 amounts 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:

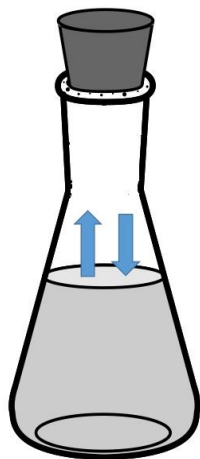
- Physical and chemical systems should be covered.
- Relationship between  $K_c$  values for reactions that are multiples or inverses of one another should be covered.
- Specific details of any industrial process are not required.

## Syllabus checklist

<b>Objective</b>	<b>I am confident with this</b>	<b>I need to review this</b>	<b>I need help with this</b>
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

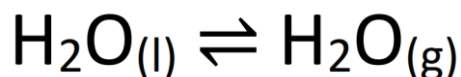
- Physical equilibrium involves a change of state.
- The flask below is a closed system (matter cannot escape).
- The rate of evaporation is equal to the rate of condensation (liquid level is constant).
- The system is at equilibrium.
- Note that in physical equilibrium, there is no chemical change occurring.



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.



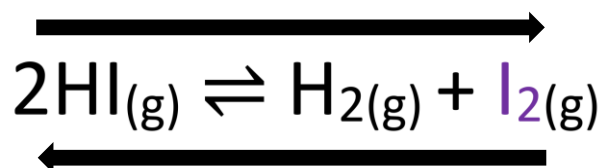
- The  $\rightleftharpoons$  sign is used to show that the system is at equilibrium.

### Exercises:

1. Bromine ( $\text{Br}_2$ ) 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.
2. What can you say about the rates of evaporation and condensation when the system is at equilibrium?
3. What other macroscopic properties would tell you the system is at equilibrium?

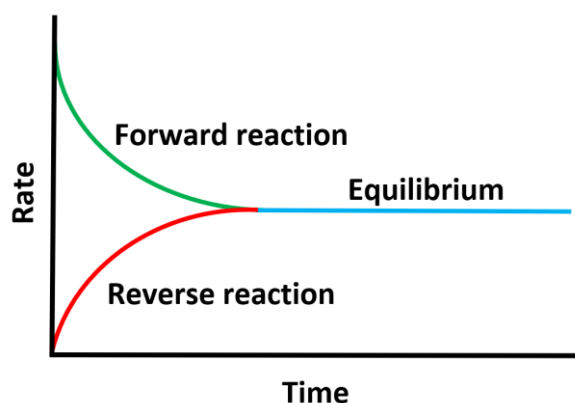
## Chemical equilibrium

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



- In the forward reaction, hydrogen iodide (HI) decomposes to form hydrogen (H<sub>2</sub>) and iodine (I<sub>2</sub>)
- In the reverse reaction, H<sub>2</sub> and I<sub>2</sub> react to form HI.

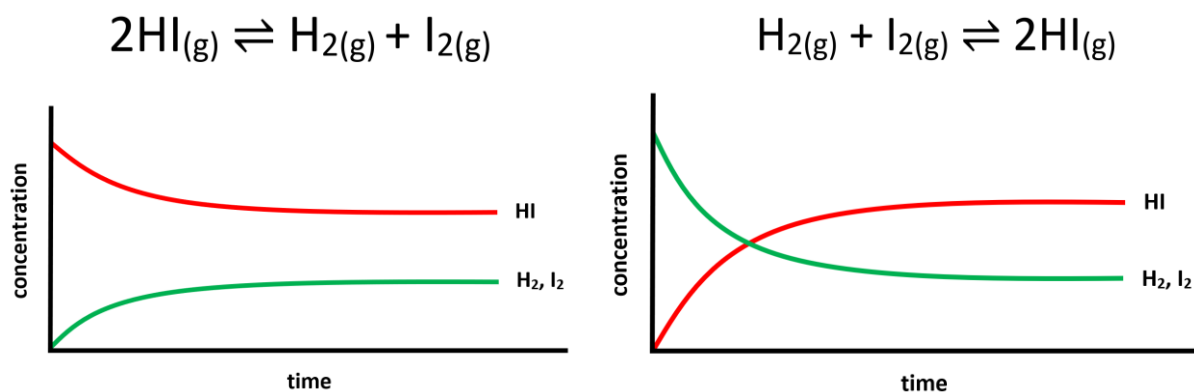
**At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.**



### 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.



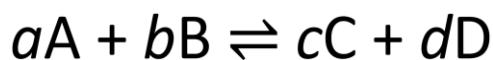
When the lines in the graphs are parallel, the reaction is at equilibrium. The concentrations of reactants and products are constant at equilibrium, **not equal**.

**Exercise:**

1. Ammonia ( $\text{NH}_3$ ) is made in the reaction of  $\text{N}_2$  and  $\text{H}_2$ . The reaction reaches equilibrium. Write an equation for the forward reaction (with all species in the gaseous state).
2. What can you say about the rates of the forward and reverse reactions at equilibrium?
3. Are the concentrations of reactants and products equal at equilibrium? Explain your answer.

### Equilibrium constant $K_c$

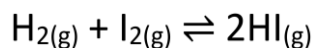
- $K_c$  is calculated using **equilibrium concentrations** of reactants and products.
- The products go in the numerator and the reactants in the denominator.
- The concentrations are raised to the powers of the coefficients in the balanced equation.



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

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

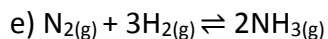
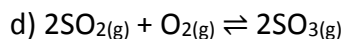
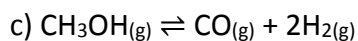
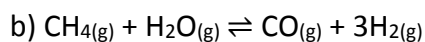
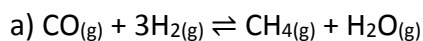
**Example:** The following reaction is carried out at 440°C.



Write the expression for the  $K_c$

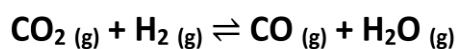
### Exercises:

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



### Calculating the value of the equilibrium constant $K_c$

Calculate the equilibrium constant,  $K_c$ , for the reaction shown, if 0.0954 mol of  $\text{CO}_2$ , 0.0454 mol of  $\text{H}_2$ , 0.0046 mol of  $\text{CO}$ , and 0.0046 mol of  $\text{H}_2\text{O}$  vapor were present in a  $1.00 \text{ dm}^3$  reaction vessel at equilibrium (at  $440^\circ\text{C}$ ).



Species	Equilibrium concentrations ( $\text{mol dm}^{-3}$ )
$\text{CO}_2$	$0.0954 / 1.00 = 0.0954$
$\text{H}_2$	$0.0454 / 1.00 = 0.0454$
$\text{CO}$	$0.0046 / 1.00 = 0.0046$
$\text{H}_2\text{O}$	$0.0046 / 1.00 = 0.0046$



### 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).

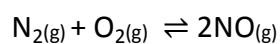
Reaction	$K_c$ value (at 298 K)	Equilibrium position
$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$	$1.9 \times 10^{-23}$	Lies to the left (forward reaction hardly proceeds)
$2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)}$	$3.2 \times 10^{81}$	Lies to the right (goes to completion)
$\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$	$4.61 \times 10^{-3}$	Lies to the left – reaction mixture contains mostly reactants
$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$	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?
2. Which is present in greater concentrations if the equilibrium position lies to the right, reactants or 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?

4. A reaction has a  $K_c$  of  $1.8 \times 10^{-5}$ . What can be said about the equilibrium position and the concentration of reactants and products at equilibrium?

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



	Equilibrium concentrations (mol dm <sup>-3</sup> )
$\text{N}_{2(\text{g})}$	0.81
$\text{O}_{2(\text{g})}$	0.75
$\text{NO}_{(\text{g})}$	0.030

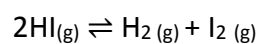
From the above data, calculate the equilibrium constant  $K_c$ . Comment on the magnitude of  $K_c$  with respect to the composition of the reaction mixture at equilibrium.

### Manipulating $K_c$ for different reaction equations

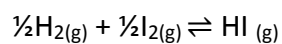
	Effect on equilibrium expression	Effect on $K_c$
Reversing the reaction		
Doubling the reaction coefficients		
Halving the reaction coefficients		
Adding together 2 reactions		

#### Example:

The equilibrium constant,  $K_c$ , for the following reaction is 0.04.

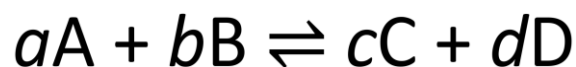


What would be the value of the equilibrium constant for the following reaction at the same temperature?



### 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**.



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

- At equilibrium, the concentrations of A, B, C and D are constant, and the reaction quotient is known as  $K_c$

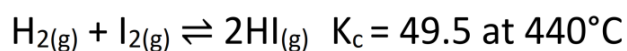
**Exercise:** Outline the difference between the reaction quotient  $Q$  and the equilibrium constant  $K_c$

### $Q$ , $K_c$ 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).

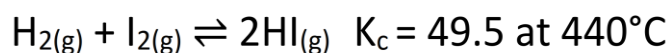
### Relationship between reaction quotient $Q$ and $K_c$

- 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:**

Calculate the value of  $Q$  when the concentration of HI is  $0.100 \text{ mol dm}^{-3}$  and the concentrations of  $\text{H}_2$  and  $\text{I}_2$  are both  $0.0500 \text{ mol dm}^{-3}$

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

**Example 2:**

Calculate the value of  $Q$  when the concentration of HI is  $0.300 \text{ mol dm}^{-3}$  and the concentration of  $\text{H}_2$  is  $0.0250 \text{ mol dm}^{-3}$  and the concentration of  $\text{I}_2$  is  $0.0350 \text{ mol dm}^{-3}$

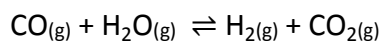
Based on your calculation, predict in which direction the reaction will proceed and explain your answer.

**Summary:**

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

**Exercises:**

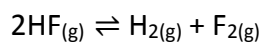
1) The table below show non-equilibrium concentrations of reactions and products for the following reaction at 527°C. The value of  $K_c$  for this reaction at 527 °C is 5.10.



	Concentration at time t (mol dm <sup>-3</sup> )
CO <sub>(g)</sub>	0.15
H <sub>2</sub> O <sub>(g)</sub>	0.25
H <sub>2(g)</sub>	0.42
CO <sub>2(g)</sub>	0.37

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

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  $1.00 \times 10^{-13}$



	Concentration at time t (mol dm <sup>-3</sup> )
HF <sub>(g)</sub>	23.0
H <sub>2(g)</sub>	0.540
F <sub>2(g)</sub>	0.380

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

## Le Chatelier's principle

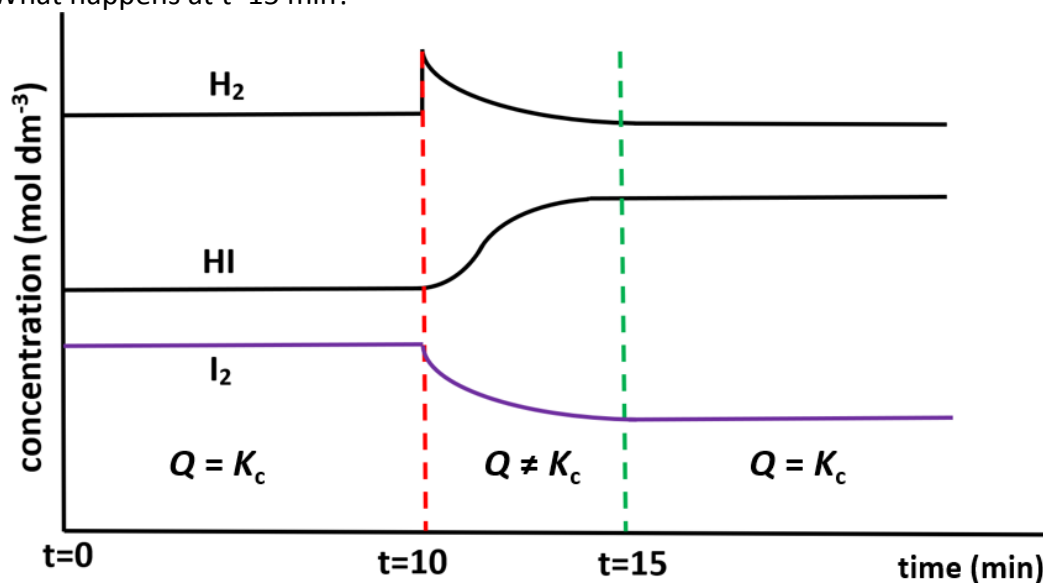
'When a system at equilibrium is subjected to a change, the system will respond to minimize the effect of the change.'

### 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.

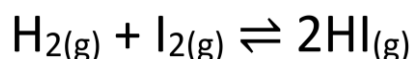
The following questions refer to the graph below.

- From  $t=0$  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  $HI$ ?
- What happens at  $t=15$  min?



### Example 1

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



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

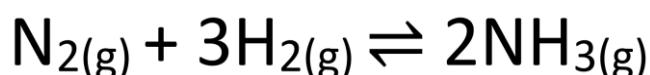
### Example 2

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

### Changes in pressure (gaseous reactions)

The pressure of a system can be changed by:

- Adding or removing a reactant or product
  - Changing the volume of the reaction vessel
  - Boyle's law: pressure and volume are inversely proportional (at constant temperature).
  - Changes in pressure only have an effect on the equilibrium position when there are different amounts of gaseous molecules in the reactants and products.
- 
- The direction to which the equilibrium shifts in gaseous reactions depends on the number of moles of gas in the reactants and products.



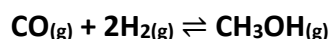
#### Example 1:

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

#### Example 2:

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

**Exercise:** Consider the following reaction:



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

a) The pressure is increased.

b) The pressure is decreased.

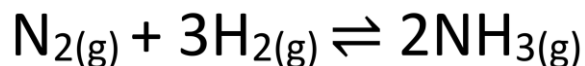


### Changes in temperature

- 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.



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

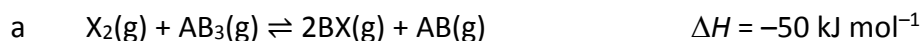
Predict the direction in which the equilibrium will shift in the above reaction when the temperature is decreased and explain your answer.

### 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  $K_c$ .



### **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  $K_c$ .