Reactivity 2.3

IB CHEMISTRY SL

Reactivity 2.3.1
Understandings:

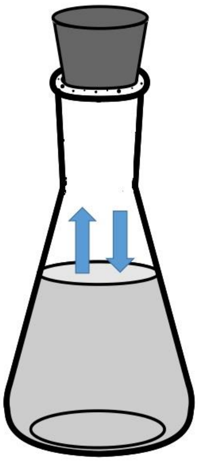
- A state of dynamic equilibrium is reached in a closed system when the rates of forward and backward reactions are equal.

Learning outcomes:

- Describe the characteristics of a physical and chemical system at equilibrium.

Physical equilibrium

- Physical equilibrium involves a change of state such as evaporation or condensation.
- Equilibrium requires a closed system in which no matter can escape.
- An example is a sealed flask containing water.



The processes of evaporation and condensation are still occurring; the liquid is evaporating and condensing at the same rate.
On a macroscopic level, there is no change in the level of the liquid.
At equilibrium, the rate of evaporation is equal to the rate of condensation.
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 equilibrium 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.

2) Compare the rates of evaporation and condensation when the system is at equilibrium.

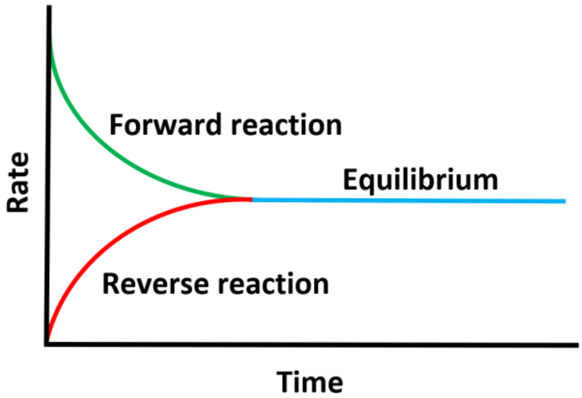
3) State one macroscopic properties that indicates the system is at equilibrium.

Chemical equilibrium

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

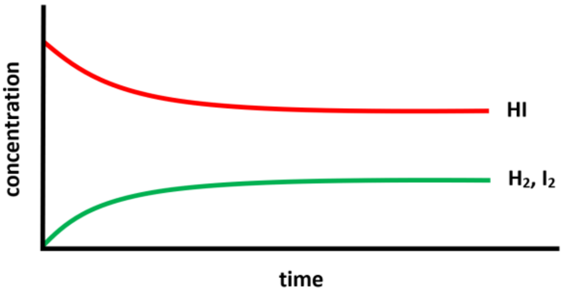
$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

- 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.

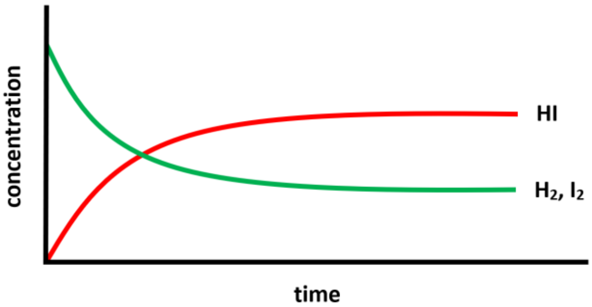


Equilibrium can be reached in either direction, as shown in the graphs below.

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



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



- When the concentrations of reactants and products are constant, the reaction is at equilibrium.

Summary:

1) Equilibrium is dynamic; the forward and reverse reactions are both occurring at the same rate.
2) Equilibrium is only achieved in a closed system.
3) At equilibrium the concentrations of reactants and products are constant.
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).

Exercise: Nitrogen and hydrogen react to produce ammonia as follows.

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

1) Comment on the rates of the forward and reverse reactions at equilibrium.

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

Reactivity 2.3.2 and 2.2.3
Understandings:

- The equilibrium law describes how the equilibrium constant, K, can be determined from the stoichiometry of a reaction (2.2.2).
- The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent (2.2.3).

Learning outcomes:

- Deduce the equilibrium constant expression from an equation for a homogeneous reaction (2.2.2).
- Determine the relationships between K values for reactions that are the reverse of each other at the same temperature (2.2.3).

Additional notes:

- Include the extent of reaction for: K<<1, K<1, K = 1, K>1, K>>1.

Linking questions:

- Reactivity 3.1 How does the value of K for the dissociation of an acid convey information about its strength?

Equilibrium constant K / Kc

- The K_c for a reaction is calculated using equilibrium concentrations of reactants and products.
- The concentrations of 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.

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

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

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

Example: The following reaction is carried out at 440 ^oC.

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

Write the K_c expression for the reaction.

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

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 equilibrium position 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 is a higher concentration of products than reactants (the equilibrium position lies to the right).
- A low value of K_c means at equilibrium, there is 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 (reaction 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?

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 1.8×10^{-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 ^oC.

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

	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.

Manipulating K_c for different reaction equations

	Effect on K_c
Reversing the reaction	$\frac{1}{K_c}$
Doubling the reaction coefficients	K_c^2
Halving the reaction coefficients	$\sqrt{K_c}$
Adding together two reactions	$K_c^1 \times K_c^2$

Exercise: The equilibrium constant, K_c, 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?

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

Reactivity 2.3.4

Understandings:

- Le Châtelier’s principle enables the prediction of the qualitative effects of changes in concentration, temperature and pressure to a system at equilibrium.

Learning outcomes:

- Apply Le Châtelier’s principle to predict and explain responses to changes of systems at equilibrium.

Additional notes:

- Include the effects on the value of K and on the equilibrium composition.
- Le Châtelier’s principle can be applied to heterogeneous equilibria such as: $X(g) \rightleftharpoons X(aq)$.

Linking questions:

- Reactivity 2.2 Why do catalysts have no effect on the value of K or on the equilibrium composition?

Le Châtelier's principle

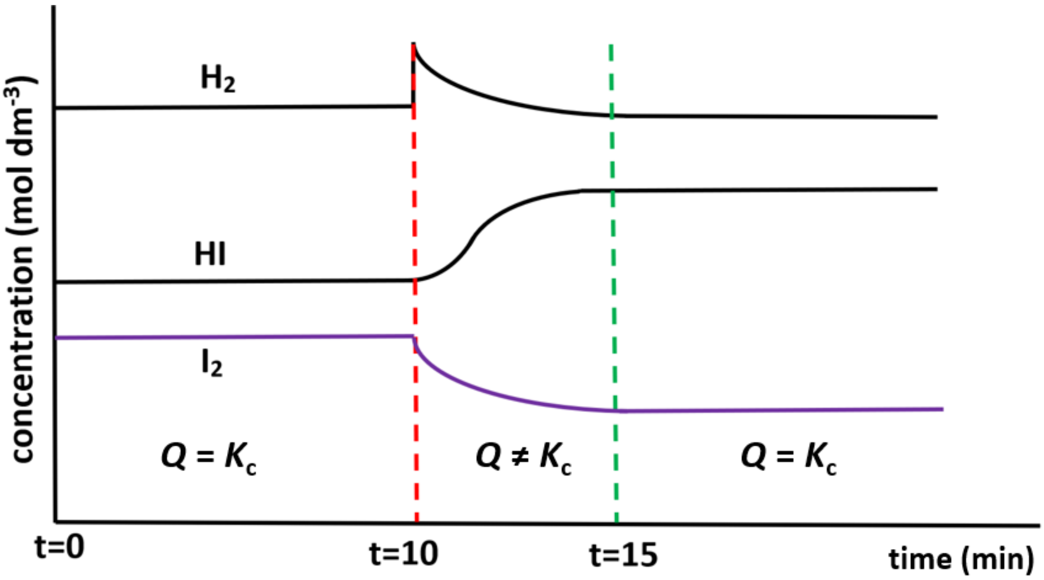
- When a system at equilibrium is subjected to a change, the system will respond to minimise the effect of the change.

Changes in concentration

- If changes are made to the concentration of the reactants or products or the pressure of the system, the equilibrium position 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?
- What happens at t=15 min?



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 equilibrium position 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 or by changing the volume of the reaction vessel.
- Boyle's law states pressure and volume are inversely proportional (at constant temperature).
- Changes in pressure only have an effect on the equilibrium position if there are different amounts of gaseous molecules in the reactants and products.
- The direction to which the equilibrium position shifts depends on the number of moles of gas in the reactants and products.

Example 1: Predict the direction in which the equilibrium position will shift when pressure is increased. State and explain the effect on the value of K_c.

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

Example 2: Predict the direction in which the equilibrium position will shift when pressure is decreased. State and explain the effect on the value of K_c.

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:

1) The pressure is increased.

2) The pressure is decreased.

Changes 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.

Example 1: Predict the direction in which the equilibrium position will shift when the temperature is increased in the reaction and explain your answer.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = \text{negative}$$

Example 2: Predict the direction in which the equilibrium position will shift in the 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.

Exercise: 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.

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

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

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: State and explain the effect of a catalyst on the equilibrium position and on the value of the K_c.