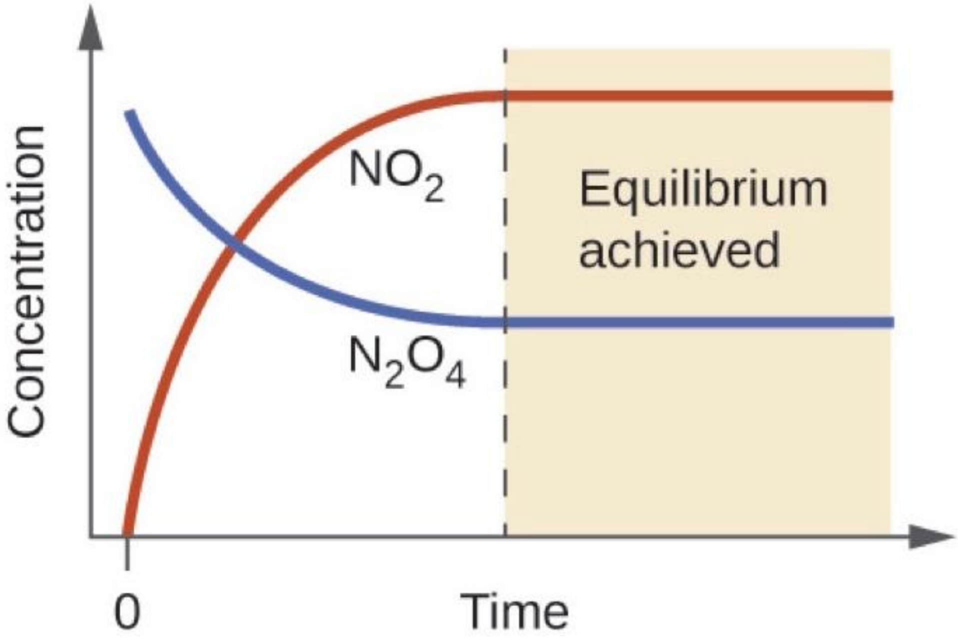
UNIT 4

INTRODUCTION TO PHYSICAL CHEMISTRY

PART 3 – CHEMICAL EQUILIBRIUM



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Key words: dynamic equilibrium, equilibrium constant, Le Chatelier's Principle

Units which must be completed before this unit can be attempted:
Unit 1 – Atomic Structure and the Periodic Table
Unit 2 – Particles, Structure and Bonding
Unit 3 – Amount of Substance

1. Dynamic Equilibrium

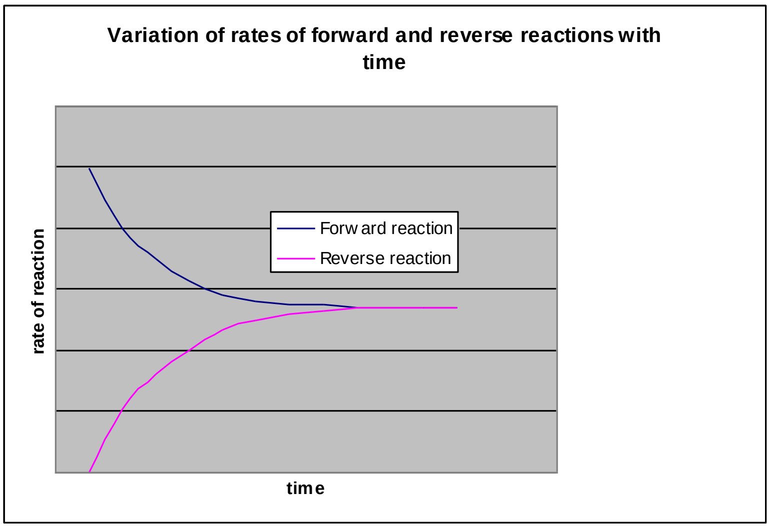
(a) Reversible reactions and equilibrium

A reversible reaction is a reaction which can proceed in both directions at the same time. Reversible reactions are represented by the $\rightleftharpoons$ sign instead of by a regular arrow $\rightarrow$.

All reactions are reversible in theory; although in practice many reactions are considered irreversible, either because the reverse reaction is insignificant or because the reverse reaction is not allowed to take place.

Consider a reversible reaction $A + B \rightleftharpoons C + D$

As the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases. Eventually, the reaction will reach a stage where both forward and backward reactions are proceeding at the same rate:



At this stage, a **dynamic equilibrium** has been reached. “Dynamic” means that the reaction has not stopped; it is simply moving in both directions at the same rate. “Equilibrium” means that the amount of reactants and products in the system is staying the same.

A dynamic equilibrium is reached when the forward and reverse reactions are taking place at the same rate, which means that the concentrations or reactants and products are not changing.

(b) open and closed systems

A **closed system** is one from which reactants and products cannot escape. In closed systems the forward and reverse reactions continue until dynamic equilibrium is reached. All reactions in a closed system are thus reversible in theory, although they are only considered as such if both forward and reverse reactions occur to a significant extent.

Eg $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
In this case the reverse reaction is not significant so the reaction is represented by single arrow.
Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
In this case the reverse reaction is significant, so the reaction is represented by an equilibrium sign.

An **open system** is one from which reactants and products can escape. The open air or a fume cupboard is an example of an open system. In an open system, the products are removed as soon as they are formed, so the reverse reaction is not allowed to take place. Such reactions clearly never reach equilibrium, but proceed until all the reactions have been converted into products. Reactions which proceed under these conditions are clearly irreversible.

Eg $H_2O(l) \rightarrow H_2O(g)$
This reaction would not be expected to proceed significantly under normal conditions, since water is more stable than steam at normal temperatures. However puddles will disappear completely if left for long enough. This is because the water vapour is removed by wind currents as soon as it is produced, and so the reverse reaction is not allowed to take place. Thus the system never reaches equilibrium and the reaction is irreversible.

Thus if a reaction is represented by an equilibrium sign, it means that:
- **the system is closed**
- **the reverse reaction is significant**

2. Equilibrium Constants

In a closed system, all reactions will reach equilibrium eventually.

In some cases, the equilibrium mixture mostly consists of products, with only a small number of reactant particles still remaining. For example, consider the following reversible reaction:

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

The equilibrium mixture formed when this reaction reaches equilibrium contains mostly SO_3, with not much SO_2 or O_2. In such cases, it is said that the **position of equilibrium** lies to the right-hand side of the reaction.

Now consider the following reversible reaction:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The equilibrium mixture formed when this reaction reaches equilibrium contains mostly CH_3COOH, with not much CH_3COO^- or H^+. In such cases, it is said that the **position of equilibrium** lies to the left-hand side of the reaction.

The position of equilibrium can be expressed mathematically using the concentrations of reactants and products. It has been proved that product of the product concentrations raised to their stoichiometric coefficients divided by the product of the reactant concentrations raised to their stoichiometric coefficients is always a fixed value, at a given temperature. This value is known as the **equilibrium constant** of the reaction at that temperature.

Consider the reversible reaction:

$$A + 3B \rightleftharpoons C + 2D$$

The equilibrium constant (K_c) $= \dfrac{[C][D]^2}{[A][B]^3}$

The square brackets [] are used to represent the concentration of that reactant, so [A] means the concentration of A in $moldm^{-3}$.

This value is always the same at a particular temperature, no matter what amounts of reactants and products are present at the start of the reaction.

Test Your Progress: Topic 4 Part 3 Exercise 1

1. For each of the following equilibria, write the expression for the equilibrium constant K_c:

(a) $2NO_2(g) == N_2O_4(g)$

(b) $CH_3CH_2CO_2H(l) + CH_3CH_2OH(l) == CH_3CH_2CO_2CH_2CH_3(l) + H_2O(l)$

(c) $H_2(g) + I_2(g) == 2HI(g)$

(d) $2SO_2(g) + O_2(g) == 2SO_3(g)$

(e) $N_2(g) + 3H_2(g) == 2NH_3(g)$

2. For the equilibrium $PCl_5(g) == PCl_3(g) + Cl_2(g)$
   the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 are 1.0, 0.205 and 0.205 $moldm^{-3}$ respectively. Calculate the value of K_c.
3. For the equilibrium $2N_2O_5(g) == 2N_2O_4(g) + O_2(g)$
   The equilibrium concentrations are $[N_2O_5] = 1.0$ $moldm^{-3}$, $[N_2O_4] = 0.11$ $moldm^{-3}$, $[O_2] = 0.11$ $moldm^{-3}$. Calculate the value of K_c.

3. Le Chatelier's Principle

If the conditions are changed after equilibrium has been established, the system may no longer be at equilbrium and may move in one direction or another to re-establish equilibrium. The direction in which the system will move to re-establish equilibrium can be predicted by **Le Chatelier's principle**:

"If a constraint is imposed on a system at equilibrium, then the system will respond in such a way as to opposed the effect of that constraint."

The constraints imposed could be the addition or removal of one of the reactants or products, a change in pressure, a change in temperature or the addition or removal of a catalyst. Each must be treated separately:

(a) Changing the concentration of one of the reactants

Le Chatelier's principle predicts that **if a reactant's concentration in a system is increased, the equilibrium position will move to the right in order to decrease the concentration of that reactant. If the reactant's concentration is decreased, the equilibrium position will move to the left in order to replace that reactant**. Similarly, if a product's concentration is increased then the equilibrium position will move to the left and if a product's concentration is decreased then the equilibrium position will move to the right.

Changing the concentrations of reactants and products has no effect on the equilibrium constant.

Given that K_c does not change, the effect of changing the concentration of one of the species can be shown with reference to K_c:

Consider the reaction: $aA + bB \rightleftharpoons cC + dD$

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

If the concentration of A is increased, then [C] and [D] must increase and [B] must decrease to maintain K_c.
If the concentration of C is increased, then [D] must decrease and [A] and [B] must increase to maintain K_c.

(b) Changing the pressure

The pressure in a system depends on the number of gas molecules in the system. Le Chatelier's principle therefore predicts that **if the pressure of the system is increased, the system will move towards the side which has fewer gas molecules in order to decrease the pressure. If the pressure of the system is decreased, the system will move towards the side which has more gas molecules in order to increase th pressure**. If the number of gas moles on both sides in the same, then pressure has no effect on the equilibrium position.

Eg $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
In this equation there is one gas molecule on the left and two on the right.
If the pressure is increased, the equilibrium position will move to the left, where there are fewer gas molecules, in order to decrease the pressure.
If the pressure is decreased, the equilibrium position will move to the right, where there are more gas molecules, in order to increase the pressure.

Eg $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
In this equation there are three gas molecules on the left and two on the right.
If the pressure is increased, the equilibrium position will move to the right, where there are fewer gas molecules, in order to decrease the pressure.
If the pressure is decreased, the equilibrium position will move to the left, where there are more gas molecules, in order to increase the pressure.

Eg $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
In this equation there are the same number of gas molecules on both sides.
Changing the pressure will have no effect on the position of this equilibrium.

Changing the pressure has no effect on the equilibrium constant.

(c) Changing the temperature

If the forward reaction is exothermic, then the temperature of the system will rise if the forward reaction takes place. The reverse reaction will therefore be endothermic, and the temperature of the system will fall if the reverse reaction takes place.

Le Chatelier's principle therefore predicts that **an increase in temperature will favour the endothermic reaction in order to reduce the temperature, and that a decrease in temperature will favour the exothermic reaction in order to increase the temperature**. If the forward reaction is exothermic, an increase in temperature will cause the equilibrium position to shift to the left, in the endothermic direction, to decrease the temperature, and a decrease in temperature will cause the equilibrium position to shift to the right, in the exothermic direction, to increase the temperature. If the forward reaction is endothermic, an increase in temperature will cause the equilibrium position to shift to the right, in the endothermic direction, to decrease the temperature and a decrease in temperature will cause the equilibrium position to shift to the left, in the exothermic direction, to increase the temperature. If $\Delta H = 0$, then a change in temperature will have no effect on the position of equilibrium.

Eg $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, ΔH = -ve
The forward reaction is exothermic.
An increase in temperature will cause the reaction to decrease the temperature by moving in the endothermic direction, which in this case is the reverse direction, so an increase in temperature will cause the equilibrium position to move to the left.
A decrease in temperature will cause the reaction to increase the temperature by moving in the exothermic direction, which in this case is the forward direction, so a decrease in temperature will cause the equilibrium position to move to the right.

Eg $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, ΔH = +ve
The forward reaction is endothermic.
An increase in temperature will cause the reaction to decrease the temperature by moving in the endothermic direction, which in this case is the forward direction, so an increase in temperature will cause the equilibrium position to move to the right.
A decrease in temperature will cause the reaction to increase the temperature by moving in the exothermic direction, which in this case is reverse direction, so a decrease in temperature will cause the equilibrium position to move to the left.

A change in temperature does change the value of the equilibrium constant.
If the reaction is exothermic, then an increase in temperature will cause the value of K_c to decrease.
If the reaction is endothermic, then an increase in temperature will cause the value of K_c to increase.

(d) Adding or removing a catalyst

The addition or removal of a catalyst will have no effect on the position of equilibrium. It will change the rate of the forward and reverse reactions, but by the same amount. The position of equilibrium will thus be unchanged.

As the position of equilibrium is unchanged, it follows that **adding a catalyst has no effect on the equilibrium constant**.

(e) Effect of changing conditions on a system at equilibrium - summary

Change	Type of change	Effect on equilibrium position	Effect on equilibrium constant
Concentration	Add reactant or remove product	Moves to right	No effect
	Add product or remove reactant	Moves to left	No effect
Pressure (or volume)	Increase pressure or decrease volume	Moves towards side with fewer gas moles (right if Δn = -ve, left if Δn = +ve)	No effect
	Decrease pressure or increase volume	Moves towards side with more gas moles (left if Δn = -ve, right if Δn = +ve)	No effect
Temperature	Increase temperature	Moves in endothermic direction (right if ΔH = +ve, left if ΔH = -ve)	Increases (if ΔH = +ve) Decreases (if ΔH = -ve)
	Decrease temperature	Moves in exothermic direction (left if ΔH = +ve, right if ΔH = -ve)	Decreases (if ΔH = +ve) Increases (if ΔH = -ve)
Catalyst	Add or remove catalyst	No effect	No effect

Test Your Progress: Topic 4 Part 3 Exercise 2

1. Consider the following exothermic reaction: $4HCl(g) + O_2(g) == 2Cl_2(g) + 2H_2O(g)$
   State, with a reason, what would happen to the amounts of chlorine and hydrogen chloride in the system if the following changes were made after equilibrium had been established in a sealed container:
   a) water is removed from the system;
   b) extra oxygen is added to the system;
   c) the volume of the container was reduced;
   d) the temperature of the container was increased;
   e) a catalyst was added.
2. For each of the following reactions, state and explain whether a high or low temperature and a high or low pressure should be used to maximize the yield of product:
   a) $2SO_2(g) + O_2(g) == 2SO_3(g)$, ΔH = -ve
   b) $PCl_5(g) == PCl_3(g) + Cl_2(g)$, ΔH = +ve
   c) $H_2(g) + I_2(g) == 2HI(g)$, ΔH = -ve
   d) $HCOOH(l) + CH_3OH(l) == HCOOCH_3(l) + H_2O(l)$, $\Delta H = 0$