

# Chemical equilibrium

The vast majority of chemical reactions do not proceed until the complete conversion of reactants into products, but also proceed backwards. For all of them, however, an equilibrium is established after a certain time, and in the equilibrium state the concentrations of the individual substances are independent of time, i.e. they are constant. "**Chemical equilibrium**" is thus a state of the system in which **its composition "does not change"**, even though chemical processes are constantly taking place in it (the effects of the processes cancel out, they proceed at the same speed in both directions).

The original assumption was based on the erroneous hypothesis that the chemical reaction proceeds in the direction of ``starting substances → products. *Today it is proven that the reaction can proceed **in both directions** (i.e. starting substances ↔ products).*

## Theoretical assumptions

First of all, the law of conservation of chemical equilibrium applies, i.e. that the value of the equilibrium constant of a certain system is always constant. A chemical equilibrium is also called dynamic because the products are still formed by the forward reaction, but at the same time they are consumed by the reverse reaction at the same rate.

## Derivation of equilibrium constant

The expression of chemical equilibrium can be achieved using the so-called equilibrium constant  $K$ , while the relation for the equilibrium constant is independent of the reaction mechanism.

According to the Gulberg-Waag law, the rate of a chemical reaction is directly proportional to the product of the concentration of the reactants at a particular temperature.

**Failed to parse (syntax error):  $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$**

**Failed to parse (syntax error):  $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$**

The first step to establish chemical equilibrium is to equalize the rate of forward and reverse reactions, i.e.:

$$[I_2] = [H_2]$$

equilibrium **Failed to parse (syntax error):  $v = v'$**

**Failed to parse (syntax error):  $v = k \cdot [H_2] \cdot [I_2]$**

**Failed to parse (syntax error):  $v' = k' \cdot [HI]^2$**

Furthermore, according to the Gulberg-Waag law for some reactions (where the partial orders of the chemical reaction are identical to the stoichiometric coefficients), the relationship for the dependence of the reaction rate on the concentration of the reactants:

**Failed to parse (syntax error):  $k_1 \cdot [A]^a \cdot [B]^b = k_2 \cdot [C]^c \cdot [D]^d$**

$$K = \frac{k_1}{k_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$K_c$  - equilibrium constant expressed using substance concentrations

$K_p$  - equilibrium constant expressed using partial pressure

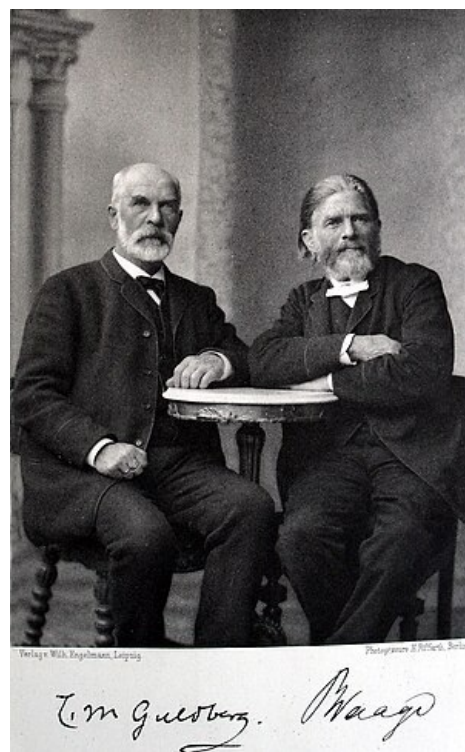
$K_c$  and  $K_p$  - change only when the temperature changes

**From the numerical value of  $K_c$  and  $K_p$  we can derive:**

- in which direction the reaction will proceed:

' $K_c$  (or  $K_p$ )  $> 1$  = there will be more products' (the reaction will proceed in the direction of the products)

$K_c$  (or  $K_p$ )  $< 1$  = there will be more starting substances (the reaction will proceed in the direction of the starting substances)



Messrs Gulberg and Waage in a historical photograph.

- to what extent the reaction will take place:

$K_c > 10^6$  = there are mainly **products in the equilibrium mixture**

$K_c > 10^{-6}$  = in the equilibrium mixture there are mostly **starting substances**

- influence of reaction conditions (*pressure, temperature, catalysts*):

The Gibbs energy (G) can be used to determine the feasibility of an event, it is a quantity determining the equilibrium constant:

**Failed to parse (syntax error):  $\Delta G < 0$**  = reaction runs spontaneously **from left to right**

**Failed to parse (syntax error):  $\Delta G = 0$**  = the reaction system is in **equilibrium**

**Failed to parse (syntax error):  $\Delta G > 0$**  = **a reverse reaction is in progress**

Gibbs energy change is only calculated for chemically pure substances.

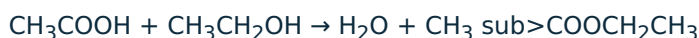
## Factors affecting chemical equilibrium

By changing the reaction conditions, there will be a **violation of the original equilibrium**. Over time, a new equilibrium will be established. This is characterized **by new (different)** concentration values of starting substances and products.

## Le Chatelier's principle of action and reaction

Violation of the chemical balance by an external intervention (*action*) causes an event (*reaction*) which aims to cancel the effect of this external intervention.

### Change in concentration of c



If we increase the concentration of the starting substances, the concentration of the products will increase. Otherwise, if we take products from the mixture, we will get more products.

### Change in pressure

A change in pressure affects the chemical equilibrium only in reactions in which all reactants are in the gas phase and the number of moles of starting substances and products are different - it must therefore occur from a change in the amount of substances during the reaction.

When this condition is met, an **increase** in pressure results in a shift of the equilibrium **in the direction of a "smaller" number of moles of particles**. On the contrary, when the pressure is reduced, the equilibrium shifts **in the direction of a greater number of moles of particles**.

**Failed to parse (syntax error):  $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$**

= pressure will increase ( $3 + 1 > 2$ )

**Failed to parse (syntax error):  $2 \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})$**

= pressure decreases ( $2 < 2 + 1$ )

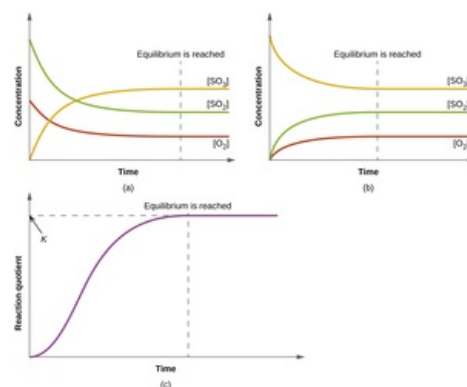
### Temperature change

u endothermic reaction - as T increases,  $K_c$  increases

u exothermic reaction - as T increases,  $K_c$  decreases

**Increasing** the temperature causes a shift in the equilibrium in the direction of the formation of *products* in an **endothermic reaction**.

**Decreasing** the temperature causes a shift in the equilibrium composition in the direction of the formation of *products* in an **exothermic reaction**.



Graphical representation of chemical equilibrium

This is an exothermic reaction → lower the temperature.



This is an endothermic reaction → increase the temperature.

## Effect of catalysts

Catalysts do not affect the composition of the equilibrium mixture, they only change **the time** in which equilibrium is established. An illustrative example is, for example, the notorious Haber-Bosch synthesis of ammonia.

## Summary

Action	Reaction
addition of reactants	increasing the concentration of products
adding products	increasing the concentration of reactants
pressure reduction	an increase in co-concentration in the direction of a greater number of moles of substances
pressure increase	increasing the concentration in the direction of fewer moles of substances
decrease in temperature	increasing the concentration of substances in the direction of the exothermic reaction
increase in temperature	increasing the concentration of substances in the direction of the endothermic reaction

## Reaction Types

The chemical equilibrium is established in the reactions "protolytic" (acid-base reactions), "redox", "precipitation", "complex-forming".

## Chemical equilibrium in precipitation reactions

There is a **heterogeneous equilibrium** in precipitation reactions.

$K_c$  – dependent *only on the concentration of liquid or gaseous* substances. However, in precipitation reactions it is called **solubility product** and is denoted by  $K_s$ .

The smaller the  $K_s$ , *the less soluble (more stable) the substance is*. E.g.  $\text{BaSO}_4$  has a small solubility product, which is why it is used in medicine to examine the digestive tract.

Precipitation reactions are used for the evidence and determination of certain ions *in analytical chemistry and to remove substances* from a reaction mixture (the solubility of a substance can be greatly reduced by adding an electrolyte *that has with a sparingly soluble salt identical ion*).

## Chemical equilibrium in complex reactions



$K_c$  in complex reactions is called **the dissociation constant of the complex** and is denoted by  $K_k$ .

## Chemical equilibrium in redox reactions



In redox reactions,  $K_c$  refers only to substances that are in aqueous solution.

## Chemical equilibrium in protolytic reactions

In protolytic reactions,  $K_c$  is distinguished into  $K_A$  (acid dissociation constant) and  $K_B$  (base dissociation constant). The strength of the acid (base) can be determined from the  $K_A$  ( $K_B$ ) values. The smaller the value of  $K_A$  ( $K_B$ ) → **the weaker** the acid (base) is.

- strong electrolyte:  $K_A(K_B) > 10^2$
- medium strength electrolyte:  $10^{-2} > K_A(K_B) > 10^{-4}$
- weak electrolyte:  $K_A(K_B) < 10^{-4}$

The electrolyte is **a class 1 conductor**. The charge in it carries the ions. It is a substance that dissociates into ions when dissolved.

- strong electrolyte – all molecules dissociate into ions (NaOH, H<sub>2</sub>SO<sub>4</sub>)
- weak electrolyte – only part of the molecules dissociate into ions, the greater part of the substance is in the form of whole molecules (NH<sub>3</sub>, CH<sub>3</sub>COOH)

## Links

### Related Articles

- Chemical Reactions
- Theory of acids and bases
- Enzymes
- What drives our cells

### References

- Lectures by RNDr. Alena Trávníčková
- Wikipedia. *Chemical equilibrium* [online]. Last revision 2013-03-09, [cit. 2015-03-19]. <[https://cs.wikipedia.org/wiki/Chemick%C3%A1\\_rovnov%C3%A1ha](https://cs.wikipedia.org/wiki/Chemick%C3%A1_rovnov%C3%A1ha)>
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