Medical Education

Chemical Equilibrium

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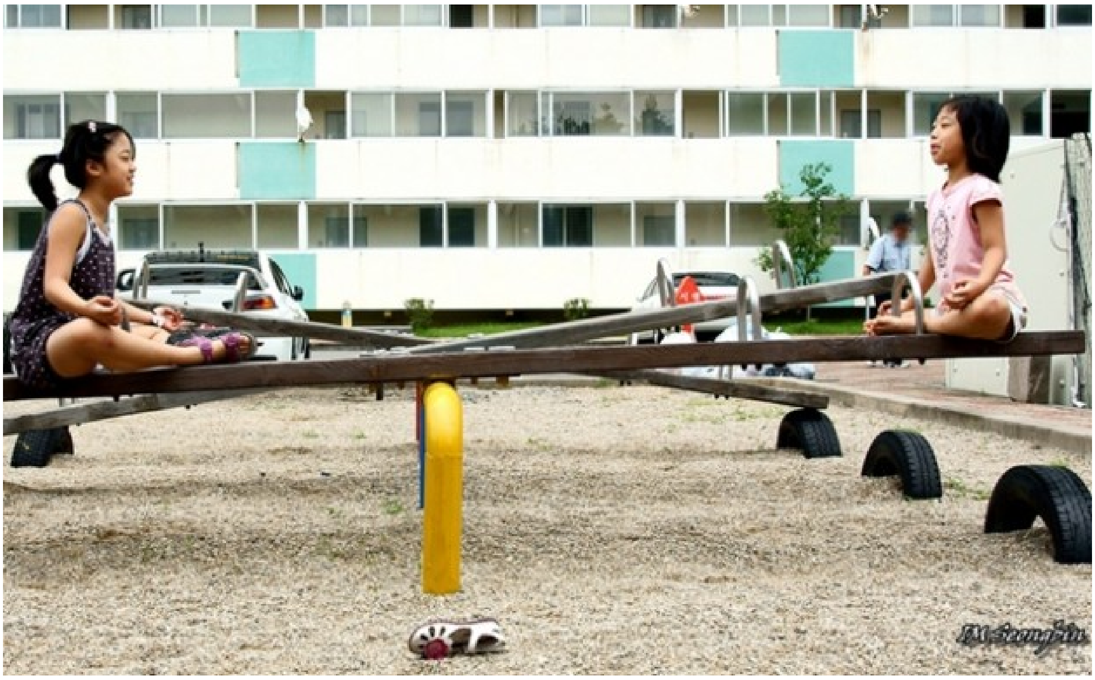
Chemical reactions occur as chemical compounds form and break apart. In a closed system, equilibrium results after a certain period of time. From this point forward, no changes in the concentration of the products and reagents can be observed anymore. In the following article, you learn which requirements are necessary for this state, what exactly characterizes this state, which meaning it has, and how one influences and uses it for certain purposes.



Nature of Chemical Equilibrium

Definition of chemical equilibrium

Chemical equilibrium is the state of a chemical system at which a **constant concentration of products and reagents** is present. Reactions, which take place in homogeneous solutions, seem to have come to rest because no changes in concentrations of the participating substances can be determined. Substance turnover occurs only on the particle level, which is why chemical equilibrium is also referred to as **dynamic equilibrium.**

For each reaction, the position of equilibrium, under certain surrounding conditions, is determined by a natural constant.

This form of reaction is also known as a **reversible reaction**, as it occurs in both directions and simultaneously. This condition results in the reaction equation for the reaction type of the **equilibrium reaction** to contain a double arrow. However, reversible reactions can take place only if none of the reaction partners leave the system.

Note: From a chemical standpoint, it is not correct to say that the same substance amounts of products and reagents are present. In the state of chemical equilibrium, the forward and backward reaction happens with the same velocity, which is why no changes in substance concentrations occur. Equalization of these facts must be absolutely avoided.

Examples of equilibrium reactions

- Pure water: H_2O dissociates into H^+ and OH^-. In pure water, there is an equilibrium between H_2O and the dissociated ions. The position is very far on the side of $H_{2,}$ and this results in a pH value of 7.
- If glucose is dissolved in water at room temperature, a stable concentration relation results in 63 % β-glucose and 37 % α-glucose.

Requirements of chemical equilibrium

- **Closed or concluded system:** Reversible reactions can occur only if none of the participating substances can escape.
- **Reversible reaction:** If a reaction has begun and the first products have formed, an instant and the immediate backward reaction take place so that the products are decomposed to their original substances again. The reaction velocities of the reaction partners adjust due to the back and forth swinging of the reactions until a constant relation has developed after a certain period of time.

Features of chemical equilibrium

- Forward and the backward reaction happens simultaneously: dynamic equilibrium.
- Identical reaction velocities ($v_{forth} = v_{back}$)
- Adjustable from both sides
- Original substances and reaction products are present simultaneously and in a constant concentration relation.
- Incomplete substance turnover
- Substance conversion is observable only on the particle level due to constant substance concentration.
- This applies: C_{RP} / C_{OS} = constant.
- Catalyzers do not influence the location of the equilibrium.
- Catalyzers shorten the time until equilibrium is reached.

Development of chemical equilibrium

In order to explain the equilibration of a reaction, be conscious of the meaning of the term **reaction velocity**. Many reactions can go backward, as well as forward. Reaction velocity is the **change in substance concentration during a certain period of time**. If forward and backward reactions occur simultaneously, which is typical for an equilibrium reaction, the following applies:

$$\mathbf{A + B \Leftrightarrow C + D}$$
$$\mathbf{V_{forward} = k_1 \bullet c_A \bullet c_B}$$

$$V_{backward} = k_2 \cdot c_C \cdot c_D$$

(k= proportionality factor, c = concentration)

Thus, the following applies in chemical equilibrium:

$$V_{forward} = v_{backward}, \text{ and } k_1 \cdot c_A \cdot c_B = k_2 \cdot c_C \cdot c_D$$

If a reaction takes place incompletely in a closed system and is also reversible (equilibrium reaction), the reaction initially has a **high reaction velocity**, as the concentrations of the original substances are high. The reaction velocity of the forward reaction gradually decreases because the substance concentrations of the reagents constantly decrease, while the backward reaction gains velocity because the substance concentrations of the products increase in the course of the reaction.

This process swings back and forth until a state is reached at which the same amount of products and reagents is formed. In this state, the **velocities of the forward and backward reactions are equal**. This is why the reaction seems to have halted. Macroscopically, no changes can be observed as the chemical transitions occur only on the particle level.

Note: The greater the activity of the original substances, the greater the velocity of the chemical reaction. In other words, the reaction velocity is directly proportional to the activity of the reagents.
The position of the chemical equilibrium is specific for each reaction and corresponds to a natural constant, which means that it cannot be changed. However, the **time for equilibration** can be shortened with the help of catalyzers.

Equilibration time is also specific for each reaction, but only at constant temperature conditions. Shortening of the time can be explained by the ability of catalyzers to cause more ‘effective collisions’ in their active state so that the chemical reaction is accelerated.

Law of Mass Action

The law of mass action, or **LMA**, offers the mathematical instrument to **quantitatively describe the position of chemical equilibrium**.

If more than 50% of the original substances react to products, the equilibrium is rather on the right side of the overall picture, referred to as **equilibrium located on the right side.**

Requirements of the law of mass action

- Closed system
- Equilibrated state

Calculation of the law of mass action

$$a \times A + b \times B \rightleftarrows c \times C + d \times D$$

$$K_c = \frac{c^c(C) \times c^d(D)}{c^a(A) \times c^b(B)}$$

k = equilibrium or mass action constant
c = substance concentration
A, B, C, D = reaction partners or their substance concentrations
a, b, c, d = stoichiometric numbers; can be taken from the reaction equation

Explanation of the law of mass action

One main statement of the LMA is that the relation k of the multiplied product concentrations to the multiplied reagent concentrations is **constant** for certain reactions under determined conditions. Thus, the quotient K of this equation is also referred to as **equilibrium** or **mass action constant.**

However, one must consider that the LMA can be applied only to dilute solutions. In more concentrated solutions, there are deviations between the particles due to interactions. For example, OH ions cannot move in strong bases, as there is not enough solvent present for the ions. This makes one conclude that the position of the equilibrium fluctuates, depending on the concentration. Yet, the same concentrations develop in the equilibrium according to the LMA, which is why one always considers diluted solutions as 'reference'.

Furthermore, the location of equilibrium depends on temperature and, possibly, on pressure relations. The section below discussing disturbances of chemical equilibrium will provide further explanation.

The calculated **equilibrium constant Kc** has great importance for further calculations. On the bases of the value of Kc, one can calculate the transformed amount of reagents or the exploit of reaction products. Kc can be determined from experimental values.

Disturbances or Influencing the Equilibrium

If a chemical equilibrium is disturbed, an **acceleration of the reaction** occurs, which then eliminates or reverses the disturbance. This rule is also known as the **principle of least constraint**, or Le Châtelier's principle. The "constraint" refers to the disturbance of the equilibrium, which leads to the reaction having to be compensated by acceleration.

> *If one applies a constraint to a system in equilibrium, the system shifts in the direction of a new equilibrium level so that the effect of the constraint becomes minimal. That is the smallest.*

A disturbance can be triggered by different factors. As mentioned previously, the position of the equilibrium can be changed by **the deviation of temperature and pressure conditions**. Also, **participating in substance amounts** also have an influence.

The following section examined other factors to illustrate the way changes can be triggered by different factors.

Energy input

Energy input (e.g., via heating) results in a reinforced ‘uphill’ reaction. An increase in the formation of reagents occurs, which actually forms products, which store their energy there, under ‘normal’ conditions.

This means that an increase in temperature promotes an endothermic reaction and that the value of the equilibrium constant decreases. Analogously, the opposite happens in the event of a decrease in energy or temperature: The location of the equilibrium shifts in the direction of the products and the exothermic reaction is promoted.

Changes in the amount of substance

For the sake of ‘rescue’, the following reactions occur with the adding or removal of reaction partners: [reaction: A + B → C + D].

1. Adding of original substances A or B → increased formation of the reaction products C and D
2. Adding of the products C or D → increased formation of the reagents A and B
3. Removal of A or B → increased formation of A or B
4. Removal of C or D → increased product formation (C, D)

An **increase in the concentration of a substance promotes its consumption** and a **decrease in concentration promotes its reproduction**.

Note: If 1 wants to reach 100% product formation, 1 of the reaction products has to be removed from the reaction mixture completely and steadily. This also results in the fact that a change in substance concentration also always changes the concentrations of the other substances.
Via adding of acids, bases, or precipitants, the concentration of reaction partners can, however, also be disturbed. In such a case, 2 coupled equilibrium reactions often occur parallel.

Changes in pressure conditions

If the participating substances in an equilibrium reaction in a closed system are gasses, a change in pressure results in a change in the location of the chemical equilibrium. If the reaction partners have another aggregate phase than gaseous, the equilibrium is not affected or changed. The background of this phenomenon is that changes in volume at reactions with non-gaseous substances are so small that the dependency of the location of the equilibrium on the pressure can be neglected.

If an **increase in pressure** occurs during a reaction that takes place under a **decrease in volume**, the chemical equilibrium shifts to the side of the products. An increase in pressure during a reaction that takes place under an increase in volume leads to the location of the equilibrium to be shifted to the reagents.

A **decrease in pressure** promotes the reaction, which occurs under **an increase in volume**.

References

Cardulla, F., & TMW Media Group. (2004). *Chemistry the complete course: Lesson twenty-one*. Venice, CA: TMW Media Group.

Donbigh, K., &Donbigh, K. (1973). *Principles of Chemical Equillibrium*. Cambridge: University Press.

Notes