Concept of chemical equilibrium

Total or non-total

A chemical reaction is not always complete. In this case, none of the reactants have completely disappeared when the system stops changing. Such a reaction is said to be limited.
The final yield, x_f, of a chemical reaction is the progress of the reaction at the final state. This value is obtained experimentally.
The maximum yield, x_{max}, of a chemical reaction is the progress of the reaction when it is considered complete. This value is a theoretical value, obtained from the initial quantities of material and the progress table.

If $x_f = x_{max}$, the reaction is total. If $x_f < x_{max}$, the reaction is limited.

A system evolving in both directions

A chemical transformation of a given system is a transformation of that system between an initial state and a final state. At the microscopic level, this transformation consists of collisions between entities present within the reaction mixture.
These collisions are random and can occur between reactants, but also between products.
There are then two reactions taking place simultaneously within the system:

- The reactants interact to form the products. This is called a direct reaction.
- The products interact to form the reactants. This is called a reverse reaction.

A steady-state equilibrium

The concentration of reactants decreases during the transformation, which leads to a decrease in the forward reaction. The concentration of products increases during the transformation, which leads to an increase in the rate of the reverse reaction. The system evolves in this way until the two reaction rates equalize. The final state has been reached. In the final state, the reactants and products may coexist, remaining in constant proportions. Such a state, with no apparent macroscopic change, is called a state of equilibrium.
A state of chemical equilibrium is not static. In fact, on a microscopic scale, both reactions continue to take place. We therefore refer to a state of dynamic equilibrium, a steady-state equilibrium

Quantitative approach of equilibrium

1. Equilibrium constant.

Each reaction equation is associated with a constant called the equilibrium constant, K. Consider a chemical transformation summarized by the reaction equation:

$$aA_{(aq)} + bB_{(aq)} \leftrightarrows cC_{(aq)} + dD_{(aq)}$$

The equilibrium constant associated with this chemical transformation is written as:

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

Notes:

- *K is a number without units and characterises the reaction equation.*
- *Its value depends on the temperature.*
- ***Equilibrium constant is thermodynamical: it is linked to the Gibbs energy***

$$\Delta G = -RT\ln(K) \Leftrightarrow K = e^{-\frac{\Delta G}{RT}}$$

2. Rigor is fundamental!!!

a. Physical state of the chemicals involved.

Only chemicals in solution are involved in the building of the equilibrium constant. The contribution of non aqueous chemicals is set to 1.

Ex: $aA_{(aq)} + bB_{(aq)} + nH_2O_{(l)} \leftrightarrows cC_{(g)} + dD_{(s)}$ $\qquad K' = \frac{1}{[A]_{eq}{}^{a}[B]_{eq}{}^{b}}$

Note: An exception can be made for reactions fully in gaseous state: A concentration for each gas can then also be defined: $[gas] = \frac{n_{gas}}{V_{space}}$

b. Stoichiometric coefficients.

A reaction equation should always be written with the lowest possible values for the stoichiometric coefficients.

Ex: $2aA_{(aq)} + 2bB_{(aq)} \leftrightarrows 2cC_{(aq)} + 2dD_{(aq)}$ $\quad K' = \frac{[C]_{eq}{}^{2c}[D]_{eq}{}^{2d}}{[A]_{eq}{}^{2a}[B]_{eq}{}^{2b}} = K^2$

c. Reactants and products are defined a bit differently.

Even if the system can evolve in both directions, the vocabulary used remains the same, with a slight change in the definitions: Reactants are not anymore the chemicals present at the beginning, but the ones written on the left of the equation. Products are not anymore the chemicals formed during the reaction, but the ones written on the right of the equation.
Therefore, the way the equation is written will have an influence on the equilibrium constant.

Ex: $cC_{(aq)} + dD_{(aq)} \leftrightarrows aA_{(aq)} + bB_{(aq)}$ $K' = \frac{[A]_{eq}{}^{a}[B]_{eq}{}^{b}}{[C]_{eq}{}^{c}[D]_{eq}{}^{d}} = \frac{1}{K}$

3. Equilibrium constant and evolution of a chemical system.

a. Reaction quotient.

Following the same principles than for the equilibrium constant, a reaction quotient can be defined at any time during the reaction:

$$Q_{r,t} = \frac{[C]_t{}^{c}[D]_t{}^{d}}{[A]_t{}^{a}[B]_t{}^{b}}$$

Note: The reaction quotient is mainly used at the initial state (just before the reaction starts) or at equilibrium:

$Q_{r,i} = \frac{[C]_i{}^{c}[D]_i{}^{d}}{[A]_i{}^{a}[B]_i{}^{b}}$ $\qquad Q_{r,eq} = \frac{[C]_{eq}{}^{c}[D]_{eq}{}^{d}}{[A]_{eq}{}^{a}[B]_{eq}{}^{b}} = K$

b. Reaction quotient vs. Equilibrium constant.

A spontaneous chemical reaction always follows **Le Chatelier's Principle : the system evolves from initial state towards its equilibrium state defined by the equilibrium constant**.
The reaction quotient therefore evolves from its initial value to a value equal to the equilibrium constant.

- $Q_{r,i} < K$: The reaction quotient increases until reaching K. The system evolves in the direct direction (« from left to right »), with a decrease in the concentration of reactants and the increase in the concentration of products.
- $Q_{r,i} > K$: The reaction quotient decreases until reaching K. The system evolves in the inverse direction (« from right to left »), with an increase in the concentration of reactants and a decrease in the concentration of products.
- $Q_{r,i} = K$: The system is already at its equilibrium state, and therefore doesn't evolve anymore at the macroscopic scale: the concentrations of the reactants and the products do not change anymore.

Progression rate of a chemical reaction

The progression rate of a chemical reaction is defined as $\tau = \frac{x_f}{x_{max}}$

It is a number without units, between 0 and 1. It is used to define if a chemical reaction can be considered as total or not.

If $\tau = 0$, no reaction has taken place.
If $\tau = 1$, the reaction is total.
If $\tau < 1$, the reaction is non-total.

Note : The progression rate of a reaction depends on the initial state and the equilibrium constante linked to the equation of the reaction.