

Chemical Kinetics

1 Truth of Chemical Reaction

In chemical reaction, the initial substances, or reactants, have a certain configuration of atoms held together by chemical bonds. During the reaction, these bonds are disrupted, releasing the atoms. Now we introduce a concept, **activation energy**. It is the minimum amount of energy that reactant molecules must possess in order to undergo a chemical reaction.

In a collision between atoms or molecules, the kinetic energy from the collision can be used to overcome this activation energy barrier. If the kinetic energy from the collision is less than the activation energy, the atoms or molecules will just bounce off each other and no reaction will occur. But if the kinetic energy from the collision is equal to or greater than the activation energy, the reaction can proceed. The atoms essentially get rearranged into new patterns. This process often involves changes in energy, as energy is needed to break bonds and energy is released when new bonds are formed.

2 Truth of Chemical Kinetics

Chemical kinetics is the study of the rates at which chemical reactions occur and the factors that influence these rates. From a molecular perspective, this involves looking at how reactant molecules interact to form products and what affects the frequency and effectiveness of these interactions.

3 Chemical Reaction Rates

3.1 Characteristic Time

The characteristic time in a chemical reaction, also known as the time constant, is a measure of the time scale on which the reaction occurs.

There are several kinds of characteristics:

1. τ_{chem} : measure of the time scale on which the chemical reactions in the combustion process occur.
2. τ_{flow} : measure of the time scale on which physical transport processes, such as the flow of gases or the mixing of reactants, occur.

3. $\tau_{diffusion}$: time scale associated with the diffusion or spreading of particles, such as molecules of fuel or oxidizer, through the reaction medium.
4. τ_{mixing} : time scale on which the reactants, typically fuel and oxidizer, are mixed together.

3.2 Damköhler Number

The Damköhler number (Da) in combustion is a dimensionless quantity that provides a ratio of the characteristic chemical reaction time to a characteristic flow or transport time. In essence, it's a measure of the relative importance of chemical reaction rates versus convective and diffusive transport rates in a combustion process. It is expressed as:

$$Da = \frac{\tau_{flow}}{\tau_{chem}} \quad (1)$$

1. $Da \ll 1$: it means that the reaction time scale is much smaller than the transport time scale, implying that the system is reaction-limited. The rate of chemical reaction is faster than the rate at which reactants can be brought together, which could lead to instabilities or detonation.
2. $Da \gg 1$: it means that the reaction time scale is much larger than the transport time scale, implying that the system is transport-limited. The rate at which reactants are being mixed together (through convection or diffusion) is faster than the rate at which they can react, potentially leading to incomplete combustion.

Based on this, we normally define:

1. **Fast Kinetics:** $\tau_{chem} \ll \tau_{other}$
2. **Chemically Frozen:** $\tau_{chem} \gg \tau_{other}$

3.3 Collision Rate

To study the chemical reaction rates, we actually study the molecules collision rate and frequency. So what will affect them? Based on **Gas Kinetic Theory**, the bi-molecular collision rate could be expressed as:

$$\zeta_{AB} = n_A n_B \int_0^\infty \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\frac{\mu g^2}{2kT}} \sigma_{AB} 4\pi g^3 dg \quad (2)$$

Here, the unit of collision rate is *molec/cm³/sec*. From the equation, we know that the collision rate is affected by:

1. n_A : mole density of A. The larger the density is, the easier the collision will happen.

2. μ : reduced mass. The equation is:

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (3)$$

3. g : relative speed. The faster the molecules move, the easier for them to collide.

4. σ : cross section, which can also refer to the area of force field.

Here is a detailed explanation of cross section. It represents the distance over which intermolecular forces act. For elastic sphere model, represents area of cylinder swept out by the two molecules.

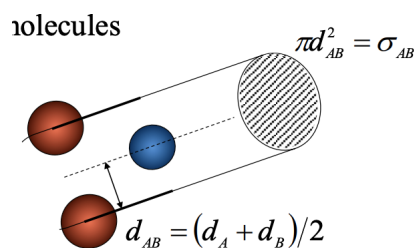


Figure 1: Cross Section.

The simplified elastic sphere model is:

$$\zeta_{AB} = n_A n_B \pi d_{AB}^2 \bar{g} \quad (4)$$

Here, \bar{g} is the mean relative speed:

$$\bar{g} = \sqrt{8kT/\pi\mu} \quad (5)$$

However, in real cases the collisions are not elastic. They involve conversion of kinetic energy to/from internal/chemical energy. We define:

1. **Endothermic:** Kinetic energy to chemical energy, breaking strong chemical bonds.
2. **Exothermic:** Chemical energy to kinetic energy, stronger chemical bonds formed.

Both endothermic and exothermic reactions need to pass the energy barrier, which is also called **activation energy**, during the process. It can be interpreted as the limit on which collisions have sufficient relative kinetic energy to cause internal energy change. With this consideration, the inelastic bimolecular rate is expressed as:

$$\zeta_{AB} = n_A n_B \bar{g} \sigma e^{\frac{-\epsilon_a}{kT}} \quad (6)$$

The larger the energy barrier is, the harder the chemical reaction can occur.