Reaction Rate Constant

1 Reaction Rate

1.1 Global Reaction Rate

The global reaction rate represents the overall rate of a series of chemical reactions that are combined into a single simplified reaction equation. Combustion reactions typically involve a fuel and an oxidizer, often releasing heat and resulting in the formation of reaction products such as carbon dioxide and water.

Take hydrogen combustion as an example:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1}$$

This reaction is a combination of a series elementary reactions, the global reaction rate is expressed as $d[H_2O]/dt$. Here, $[H_2O]$ represents the concentration of H_2O, which has unit as $molec/cm^3$, so the unit of reaction rate is $molec/cm^3/sec$.

1.2 Elementary Reaction Rate

As in all chemical reactions, an elementary reaction is a reaction in which reactants directly become products in a single kinetic step, with a single transition state. In contrast to the global reaction rate which provides a broad, simplified picture of a combustion process, the rate of an elementary reaction provides insight into the specific, individual steps within a larger, complex reaction mechanism.

1.3 Reaction Rate Expression

General elementary reaction can be expressed as:

$$\sum_{i=1}^{n} v_i' M_i \rightarrow \sum_{i=1}^{n} v_i'' M_i \tag{2}$$

Therefore, the reaction rate (RR) could be expressed as:

$$\frac{d[M_i]}{dt} = RR(v_i'' - v_i') \tag{3}$$

Notice that here M_i include both reactants and products, for example:

$$N + N + O \rightarrow NO + N \tag{4}$$

$$d[N]/dt = RR(1-2) = -RR \tag{5}$$

$$d[NO]/dt = RR \tag{6}$$

1.4 Reaction Rate Constant

Based on the kinetic theory, the reaction rate should be **proportional to amount of each reactant**:

$$RR = k\prod_i [M_i]^{v_i'} \tag{7}$$

Notice that here k is the reaction rate constant, and we are using reactants' coefficients for calculation. Example:

$$N + N + O \rightarrow NO + N \tag{8}$$

$$RR = k[N]^2[O] \tag{9}$$

In general, an elementary reaction can proceed in either direction:

$$\sum\nolimits_{\mathrm{i}}^{\mathrm{n}} v_{\mathrm{i}}' M_{\mathrm{i}} \xrightleftharpoons[\mathrm{k_r}]{\mathrm{k_f}} \sum\nolimits_{\mathrm{i}}^{\mathrm{n}} v_{\mathrm{i}}'' M_{\mathrm{i}}$$

Then the general form of concentration change rate (notice that this is not reaction rate) could be expressed as:

$$\frac{d[M_i]}{dt} = k_f \prod_i [M_i]^{v_i'}(v_i'' - v_i') + k_r \prod_i [M_i]^{v_i''}(v_i' - v_i'') \tag{10}$$

An example:

$$\mathrm{N + N + O} \xrightleftharpoons[\mathrm{k_r}]{\mathrm{k_f}} \mathrm{No + N}$$

$$\frac{dN}{dt} = -k_f[N]^2[O] + k_r[NO][N] \tag{11}$$

1.5 Equilibrium Constant

Consider result at thermodynamic equilibrium, then the concentration should be constant. Therefore:

$$\cancelto{0}{\frac{d[N]_{eq}}{dt}} = -k_f[N]_{eq}^2[O]_{eq} + k_r[NO]_{eq}[N]_{eq} \tag{12}$$

$$k_f[N]_{eq}^2[O]_{eq} = k_r[NO]_{eq}[N]_{eq} \tag{13}$$

Then, we define the **equilibrium constant (concentration form)** as:

$$K_c(T) = \frac{k_f}{k_r} = \frac{[NO]_{eq}[N]_{eq}}{[N]_{eq}^2[O]_{eq}} \tag{14}$$

2 Molecularity and Order

2.1 Molecularity

The molecularity of a reaction refers to the number of molecules, atoms, or ions that participate in the elementary (single step) reaction as reactants.

Unimolecular:

$$CO_2 \rightarrow CO + O \tag{15}$$

Bimolecular:

$$O + N_2 \rightarrow NO + N \tag{16}$$

Tremolecular:

$$H + H + H \rightarrow H_2 + H \tag{17}$$

2.2 Order

The order of a reaction refers to the power dependence of the rate of reaction on the concentration of each reactant. The overall order of the reaction is the sum of the powers of the concentrations of the reactants in the rate equation of the reaction. For example if:

$$RR = k[A]^2[B] \tag{18}$$

Then this reaction is third order, second order with respect to reactant A and first order with respect to reactant B.

3 Arrhenius Rate Law

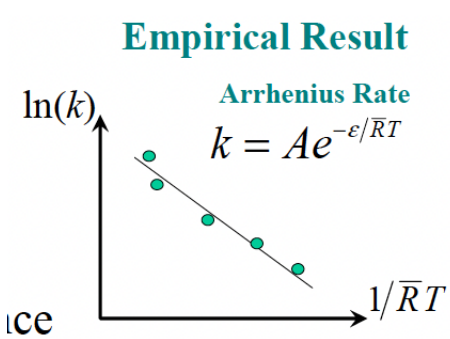

Figure 1: Arrhenius Law.

Recall the inelastic bimolecular collision rate:

$$\zeta_{AB} = n_A n_B \bar{g} \sigma e^{\frac{-\epsilon_a}{kT}} \tag{19}$$

Here, we take out the constant part as:

$$k = P_{steric} N_{Av} \sigma e^{\frac{-\epsilon_a}{RT}} \tag{20}$$

Here:

1. P_{steric} is the steric factor, which is a non-dimensional value. The steric effect refers to the influence on a chemical reaction rate that arises from the spatial arrangement and physical size of atoms or groups of atoms in a molecule. These factors can affect the ability of molecules to approach and react with each other.

2. N_{Av} is the Avogradro constant. It is a fundamental physical constant that signifies the number of particles (such as atoms, molecules, ions, electrons, or other particles) in one mole of a substance. Its value is defined as exactly $6.02214076 \times 10^{23}$ entities per mole

3. $\bar{g}$ is the mean relative speed.

$$\bar{g} = \sqrt{8 k_{Boltz} T / \pi \mu} \tag{21}$$

4. k_{Boltz} is the Boltzmann constant. It is a fundamental physical constant that describes the relationship between the temperature of a system in thermodynamic equilibrium and its energy. The Boltzmann constant has the dimension of energy per temperature, and its value is approximately 1.380649×10^{-23} joules per kelvin (J/K)

5. σ is the cross section, explained in last chapter.

6. μ is the reduced mass, explained in last chapter.

If we examine temperature dependence, based on empirical result, we can get the **Arrhenius Rate Law**:

$$k = A T^{1/2} e^{\frac{-\epsilon_a}{RT}} \tag{22}$$

We also have the modified Arrhenius Rate with more general T dependence:

$$k = A T^{b} e^{\frac{-\epsilon_a}{RT}} \tag{23}$$

Revisit k_f and k_r:

- If k_f known $\quad k_f = AT^n e^{-\varepsilon_a/\bar{R}T}$
- Get k_r from thermodynamics

$$k_r = \frac{K_c(T)}{k_f} = \frac{K_p(T)\Big/(\bar{R}T)^{\sum(\nu_i''-\nu_i')}}{k_f}$$

$$= \frac{e^{-\sum(\nu_i''-\nu_i')\bar{g}_i^o/\bar{R}T}\Big/(\bar{R}T)^{\sum(\nu_i''-\nu_i')}}{AT^n e^{-\varepsilon_a/\bar{R}T}}$$

$$= \frac{e^{\Delta s_R/\bar{R}} e^{-\Delta H_R/\bar{R}T}}{(\bar{R}T)^{\sum(\nu_i''-\nu_i')}} = \frac{A_f T^{b_f} e^{-E_{af}/\bar{R}T}}{A_r T^{b_r} e^{-E_{ar}/\bar{R}T}}$$

$$\frac{A_f T^{b_f}}{A_r T^{b_r}} \cong \frac{e^{\Delta s_R/\bar{R}}}{(\bar{R}T)^{\sum(\nu_i''-\nu_i')}}$$

&

$$\Delta H_R \cong E_{af} - E_{ar}$$

We can notice that the heat of reaction is actually the difference between the activation energy of forward and reverse reaction.