# 4 Simple Reactions

## 4.1 Reversible reaction approaching to equilibrium

Let us consider a reversible reaction between A and B

$$\mathrm{A} \overset{k_f, k_b}{\rightleftharpoons} \mathrm{B} \tag{36}$$

If we start with pure A, i.e., $[\mathrm{A}]_0 \neq 0$ and $[\mathrm{B}]_0 = 0$, part of A will be converted to B until they reach the equilibrium state in which the concentrations are $[\mathrm{A}]_\infty$ and $[\mathrm{B}]_\infty$. (These are $[\mathrm{A}]_t$ and $[\mathrm{B}]_t$ at time $t = \infty$. Although we use the symbol for infinity, $\infty$, this practically means a sufficiently long time compared to the time scale of the reaction.) The ratio between these two is the equilibrium constant of this reaction.

$$K = \frac{[\mathrm{B}]_\infty}{[\mathrm{A}]_\infty} \tag{37}$$

Note the difference from the reactions treated in the previous section

$$\mathrm{A} \longrightarrow \mathrm{P}$$

with no backward reaction. In this case, [A] will decay to zero, i.e., $[\mathrm{A}]_\infty = 0$. This is in contrast with the reversible reaction (36), in which finite amount of A will be restored due to the existence of the backward reaction and hence $[\mathrm{A}]_\infty \neq 0$ and the equilibrium constant $K$ is finite.

We will assume that both the forward and backward rate constants $k_f$ and $k_b$ are first order. Therefore, the forward reaction contributes to the loss of A and gain of B as

$$-\frac{d[\mathrm{A}]}{dt} = +\frac{d[\mathrm{B}]}{dt} = k_f[\mathrm{A}] \tag{38}$$

Similarly, the backward reaction contributes to the gain of A and loss of B as

$$+\frac{d[\mathrm{A}]}{dt} = -\frac{d[\mathrm{B}]}{dt} = k_b[\mathrm{B}] \tag{39}$$

Overall, the rate of the change of [A] is a combination of these two contributions such as

$$\frac{d[\mathrm{A}]}{dt} = -k_f[\mathrm{A}] + k_b[\mathrm{B}] \tag{40}$$

In sufficiently long time $t = \infty$, the system will relax to the equilibrium state in which the concentrations do not change any more. That is, $d[\mathrm{A}]/dt = 0$ at $t = \infty$.
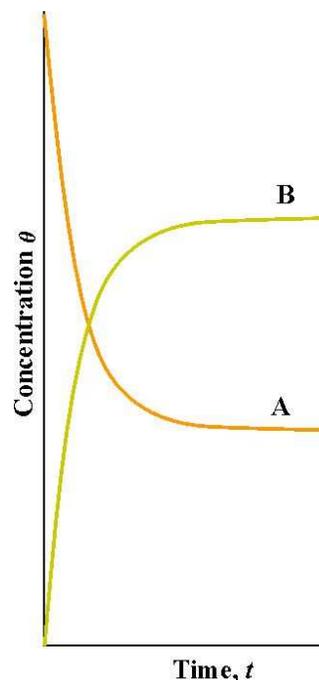
Then, Eq (40) will be[††]

$$0 = -k_f[\text{A}]_\infty + k_b[\text{B}]_\infty \quad \Rightarrow \quad \frac{[\text{B}]_\infty}{[\text{A}]_\infty} = \frac{k_f}{k_b} \tag{41}$$

As seen in Eq (37), the left hand side of the last equation is equal to the equilibrium constant $K$. We therefore find a relation

$$K = \frac{[\text{B}]_\infty}{[\text{A}]_\infty} = \frac{k_f}{k_b} \tag{42}$$

Although this might appear a simple equation, it is conceptually remarkable because it finds a relation between the **equilibrium** property $K$ and the **kinetic** quantities $k_f$ and $k_b$.

## 4.2   Pre-equilibrium

Now we introduce, in addition to the reversible process A $\rightleftharpoons$ B just considered, a reactive process from B to a final product P.

$$\text{A} \overset{k_f, k_b}{\rightleftharpoons} \text{B} \overset{k_r}{\rightarrow} \text{P} \tag{43}$$

This last process will disturb, or even destroy, the equilibrium between A and B. However, we will assume that this process is very slow such that the equilibrium between A and B is well maintained. In other words, we will consider situations where the ratio [B]/[A] is approximately kept constant. Let us denote this constant by $K$.

$$\frac{[\text{B}]}{[\text{A}]} \simeq K = \frac{k_f}{k_b} \tag{44}$$

The last equality has been found in the previous section in Eq (42). We call this the '**pre-equilibrium**' assumption: the equilibrium A $\rightleftharpoons$ B prior to the reactive process B $\rightarrow$ P is approximately well maintained throuout the reaction.

**Question:**   Sketch (roughly) the changes of [A], [B] and [P] along time $t$. (Hint: Look at the graph in the previous page for A $\rightleftharpoons$ B, and consider what will happen by introducing the reactive step B $\rightarrow$ P.)

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[††] We can also derive Eq (41) by the following consideration. In equilibrium at $t = \infty$, the forward Eq (38) and backward Eq (39) processes will balance, such that

$$k_f[\text{A}]_\infty = k_b[\text{B}]_\infty$$

We further assume that the reactive step B $\to$ P is a 1st order process:

$$\frac{d[\text{P}]}{dt} = k_r[\text{B}]$$

The overall reaction rate is given by this rate of the product formation.

$$\text{Rate} = \frac{d[\text{P}]}{dt}$$

With the pre-equilibrium assumption, Eq (44), this is rewritten as

$$\text{Rate} = \frac{d[\text{P}]}{dt} = k_r[\text{B}] \simeq k_r K[\text{A}] = \frac{k_r k_f}{k_b}[\text{A}] \propto [\text{A}] \tag{45}$$

Therefore, the overall rate law turns out to be 1st order with respect to A.

Now, a question arises: How can we distinguish this from the straightforward 1st order reaction A $\to$ P when we have no way to detect the intermediate specie B? Sometimes, though not always, we can get some clue to this question by looking at the **temperature dependence** of the reaction rate. To this end, it is useful to look at the following specific example.

**Example:** Oxidation of nitrogen oxide

$$2\text{NO(g)} + \text{O}_2\text{(g)} \to 2\text{NO}_2\text{(g)}$$
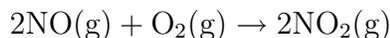
Experimental facts are:

1. Rate law is given by; Rate = $k\,[\text{NO}]^2[\text{O}_2]$ (overall 3rd order)

2. Reaction rate decreases as the temperature increases.

These observations cannot be explained by the simple bimolecular collision mechanism (which predicts a 2nd order rate law $k\,[\text{NO}][\text{O}_2]$). In particular, the second observation is unusual in view of the ordinary temperature dependence described by the Arrhenius equation (Section 2.3).

Let us assume a pre-equilibrium mechanism for this reaction:

$$\text{NO} + \text{NO} \overset{k_f,k_b}{\rightleftharpoons} \text{N}_2\text{O}_2 \tag{46}$$

$$\text{N}_2\text{O}_2 + \text{O}_2 \overset{k_r}{\to} 2\text{NO}_2 \tag{47}$$
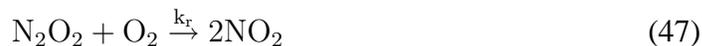
From the pre-equilibrium assumption we get

$$\frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \simeq K = \frac{k_f}{k_b} \quad \Rightarrow \quad [\text{N}_2\text{O}_2] \simeq K[\text{NO}]^2$$

Putting this into the rate expression derived from the reactive step EQ (47),

$$\text{Rate} \;=\; \frac{d[\text{NO}_2]}{dt} = k_r[\text{N}_2\text{O}_2][\text{O}_2]$$

we obtain

$$\text{Rate} \;=\; k_r K[\text{NO}]^2[\text{O}_2] \tag{48}$$

This immediately explains the first fact, the overall 3rd order rate law.

Now, let's see how this explains the second fact, the unusual temperature dependence of the rate. As seen in Eq (48), the overall rate constant is a product of two factors, $k = k_r K$. We can naturally assume that the rate constant of the reactive step $k_r$ has a normal temperature dependence such that it increases in higher temperatures. However, the behaviour of the equilibrium constant $K$ can be different. It may increase or decrease in higher temperatures depending on the sign [‡‡] of the free energy change $\Delta G^{\circ}$. For example, $\Delta G^{\circ} < 0$ means that the product state has lower $G$ than the reactant. Generally, by raising the temperature we increase the populations of the higher energy state. This means that, when $\Delta G^{\circ} < 0$, increase of the temperature will result in an increase of the reactant concentrations and hence a decrease of $K$.

In this way, the overall rate constant $k = k_r K$ may contain competing positive and negative factors of the temerature dependence. The obseved fact for this particular reaction suggests that the decrease of $K$ is the dominant factor to determine the overall temperature dependence.

## 4.3   Consecutive reaction

Let us next consider the following consecutive reaction

$$\text{A} \xrightarrow{k_a} \text{B} \xrightarrow{k_b} C$$

The behaviour of the intermediate [B] will depend on the difference between $k_a$ and $k_b$.

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[‡‡] This can be described more quantitatively by $K = e^{-\Delta G^{\circ}/RT}$.