A quote of the week
(or camel of the week):

"The saddest aspect of life right now is that science gathers knowledge faster than society gathers wisdom."

Isaac Asimov

Relaxation

Relaxation means a return of the system to equilibrium (new) after shifting the original equilibrium by rapid change (shift) by some external stimulus (for example: concentration of a chosen reactant, pressure or temperature). Measuring the relaxation time is one of methods of determination of rate constants of equilibrium reactions.

Because the system returns (relaxes) to a new equilibrium, hence, the time required $t \rightarrow \infty$. Therefore, if we want to find the dependence between the relaxation time and characteristics of the system (also the stimulus size), we need to define the relaxation time more precisely.

Let’s look closer at the phenomenon, using as an example a thermal stimulus, (steplike increase in temperature), the system responding with increase of reactant A.

Relaxation (2)

In our system a reversible reaction, first order in both directions, occurs:

$$A \xrightleftharpoons{\text{T}^1} B$$

Relaxation time, $\tau_r$, or time of response of the system to the steplike stimulus is most frequently defined as time needed to $e$-times lowering the difference between the instantaneous (in the moment of application of the stimulus) and new equilibrium level of reactant concentration.

It is shown in the figure, where:

$$\Delta c = 1$$

$$\frac{\Delta c}{\Delta c_0} = e$$

$e$
Relaxation (3)

For reversible reactions we have:
\[
\frac{dc_A}{dt} = k_1 c_A - k_2 c_B
\]
What at equilibrium becomes:
\[
\frac{dc_A}{dt} = k_1 c_A - k_2 c_B = 0
\]
During relaxation \(\Delta c\) decreases:
\[
\frac{dc_A}{dt} = k_1(c_{Ae} - \Delta c) - k_2(c_{Be} + \Delta c) = \]
Because:
\[
\frac{dc_A}{dt} = -\frac{d\Delta c}{dt}
\]
we have:
\[
\frac{d\Delta c}{dt} = (k_1 + k_2) \Delta c
\]
what, after separation of variables and integration, yields:
\[
\ln \frac{\Delta c_0}{\Delta c} = (k_1 + k_2) t
\]

Relaxation (4)

\[
\ln \frac{\Delta c_0}{\Delta c} = (k_1 + k_2) t
\]
After insertion of the definition to the last equation:
\[
\frac{\Delta c}{\Delta c_0} = \frac{1}{e}
\]
The time becomes relaxation time \(\tau_r\):
\[
\tau_r = \frac{1}{(k_1 + k_2)}
\]
General equation (top) permits to determine times for different \(\Delta c_0/\Delta c\) ratios. Classic definition means that concentration closed to new equilibrium to 36.8\% (relaxation occurred in 63.2\%), but one can assume relaxation in 90\%, giving longer time as then \(\Delta c_0/\Delta c=10\).

Rate limiting (rate determining) step

Considering consecutive reactions, we got an equation describing concentration of the final product \(C\) after time \(t\):
\[
c_C = \left(1 + \frac{k_1 e^{-k_1 t} - k_2 e^{-k_2 t}}{k_2 - k_1}\right) c_{0A}
\]
If we assume, that \(k_2 >> k_1\), then:
\[
e^{-k_2 t} < < e^{-k_1 t}; \quad k_2 - k_1 \approx k_2
\]
And the original equation may be reduced to:
\[
c_C \approx \left(1 - e^{-k_2 t}\right) c_{0A}
\]
We see, therefore, that in such a case, the reaction rate depends exclusively on the rate of the slower of the two steps, which is then known as the step limiting (determining) the rate of the whole complex reaction.
**Steady State Approximation**  
**– SSA**

Steady state approximation (known as SSA) is an assumption that concentrations of all intermediate products, I, do not change during the reaction. From this assumption, a mathematical operation results, which permits, relatively easy determination of kinetics (writing the rate law) of reactions with complex mechanisms. These approximations have some physico-chemical justifications and give in many cases good (experimentally proven) results.

\[
\frac{dc_i}{dt} \approx 0
\]

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**Steady State Approximation**  
**– SSA (2)**

Given is mechanism of the following reaction: \(2A(g) \rightarrow 4B(g) + C(g)\):

- \(A \rightarrow B + D\) \(k_1\)
- \(B + D \rightarrow A\) \(k_1\)
- \(B + D \rightarrow C + E\) \(k_2\)
- \(E + A \rightarrow 3B\) \(k_2\)

We want to find an expression describing reaction rate defined as \(dc_1/dt\). First, according to SSA, we compare to zero both \(dc_2/dt\) and \(dc_3/dt\):

\[
\begin{align*}
\frac{dc_1}{dt} &= k_1c_A - k_1c_Bc_D - k_2c_Bc_D \Rightarrow \frac{dc_D}{dt} = \frac{k_1c_A}{(k_1 + k_2)c_B} \\
\frac{dc_2}{dt} &= k_2c_Bc_D - k_2c_Ec_A \Rightarrow \frac{dc_E}{dt} = \frac{k_2c_B}{k_3c_A} = \frac{k_1k_2}{k_3(k_1 + k_2)}
\end{align*}
\]

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**Steady State Approximation**  
**– SSA (3)**

Equations describing the values of intermediate products D and E we substitute to the expression describing \(dc_3/dt\) we have:

\[
\begin{align*}
\frac{dc_A}{dt} &= (k_1 + k_2)c_B - k_1c_Bc_D - k_2c_Ac_E \\
\frac{dc_D}{dt} &= k_1c_A - k_2c_Bc_D \\
\frac{dc_E}{dt} &= k_2c_D - k_3c_A
\end{align*}
\]

This, after rearrangements, yields a first order rate law, with a complex rate constant being a combination of rate constants of elementary reactions:

\[
\frac{dc_A}{dt} = -\frac{k_1 + k_2}{(k_1 + k_2)}c_A = -\frac{k_1k_2}{(k_1 + k_2)}c_A
\]

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*Physical Chemistry GTM 16*
Reactions with preliminary equilibrium

Frequently, a mechanism known as a preliminary equilibrium (pre-equilibrium) may be found in practice, that may be written as:

\[ A + B \xrightarrow{k_1} C \xrightarrow{k_2} D \]

or:

\[ A + B \rightarrow C; \quad C \rightarrow A + B; \quad C \rightarrow D; \quad k_2 \]

Using SSA we reach:

\[ \frac{dc_C}{dt} = k_1 c_A c_B - k_2 c_C \approx 0 \Rightarrow c_C = \frac{k_1 c_A c_B}{(k_{-1} + k_2)} \]

And the final rate law of 2nd order:

\[ \frac{dc_D}{dt} = k_2 c_C = \frac{k_1 k_2}{(k_{-1} + k_2)} c_A c_B \]

Reactions with preliminary equilibrium (2)

Frequently, if transformation of the intermediate product C into the final one, D, is sufficiently slow to not disturb the pre-equilibrium:

\[ A + B \xrightarrow{k_1} C \xrightarrow{k_2} D \]

we can simplify the obtained equation into:

\[ \frac{dc_D}{dt} = \frac{k_1 k_2}{k_{-1}} c_A c_B = k_2 K c_A c_B \]

That also gives the second order rate law, where \( K \) means the equilibrium constant of the pre-equilibrium.

Mechanism with pre-equilibrium is frequently confirmed in practice.

Lindemann-Hinshelwood Mechanism

Rate laws of many reactions in gaseous phase were difficult to explain. Among them, one should mention the monomolecular reactions, e.g., isomerisation:

\[ \Delta \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 \]

Generally, first order rate laws described their kinetics quite properly, yet in some cases second order could be observed. On the other hand, molecules gain energy needed for a reaction to occur, thank to collisions with other molecules, and this is a two-molecule act. First effective explanation was given by L. and H. (1921-25).

Their fundamental statement was that these reactions were not elementary (true monomolecular) reactions, but complex reactions.
They suggested the following mechanism of $A \rightarrow B$ reaction:

- $A + A \rightarrow A^* + A$ \quad $k_1$ \quad molecule $A$ gains energy
- $A^* + A \rightarrow A + A$ \quad $k_{-1}$ \quad while excited $A^*$ can lose it as well
- $A^* \rightarrow B$ \quad $k_2$ \quad or undergo transformation to $B$.

Applying SSA with respect to $A^*$:

$$\frac{dc_A}{dt} = k_1 c_A^2 - k_{-1} c_A c_{A^*} - k_2 c_{A^*} \Rightarrow c_{A^*} = \frac{k_1 c_A^2}{k_{-1} c_A + k_2}$$

$$\frac{dc_B}{dt} = k_2 c_A^2 \quad \frac{k_1 k_2 c_A^2}{k_{-1} c_A + k_2}$$

However, if pressure is low, when $c_A$ is smaller: $k_{-1} c_A \ll k_2$

Then we get a second order rate law:

$$\frac{dc_B}{dt} \approx k_1 c_A^2$$

At low pressure, therefore, the limiting step is two molecular formation of $A^*$, while at high pressures, it was the decomposition $A^* \rightarrow B$. 
**Lindemann-Hinshelwood Mechanism (5)**

General equation: \[ \frac{dc_A}{dt} = \frac{k_1 k_2 c_A^2}{k_3 c_A + k_2} \]

may be written as:

\[ \frac{dc_A}{dt} = k c_A \quad \text{where} \quad k = \frac{k_1 k_2 c_A}{k_3 c_A + k_2} \]

And the last expression (expressing the effective rate constant) one can transform into:

\[ \frac{1}{k} = \frac{k_1}{k_1 k_2} + \frac{1}{k_1 c_A} \]

**Michaelis-Menten Mechanism**

This mechanism describes enzymatic reactions (E is an enzyme). \[ E + A \xrightarrow{k_{-1}} EA \xrightarrow{k_2} B + E \]

M&M suggested the following mechanism of the reaction \( A \rightarrow B \):

- \( E + A \rightarrow EA \) \( k_1 \) formation of a complex of enzyme with the reactant
- \( EA \rightarrow A + E \) \( k_{-1} \) which may be decomposed back to the reactant
- \( EA \rightarrow B + E \) \( k_2 \) or may be transformed into product B

Enzymes are biochemical catalysts, highly specific. The do not influence (like all the catalysts) on the equilibrium constant of this reaction, but only on the rate of approaching this equilibrium. Summarily and apparently they do not participate in the reaction, yet they take part in the mechanism (usually changing it and thus influencing the reaction rate).

**Michaelis-Menten Mechanism (2)**

Applying SSA to \( EA \):

\[ E + A \xrightarrow{k_{-1}} EA \xrightarrow{k_2} B + E \]

\[ \frac{dc_{EA}}{dt} = k c_A c_E - k_{EA} c_{EA} - k_2 c_{EA} \approx 0 \Rightarrow c_{EA} = \frac{k c_A c_E}{k_{-1} + k_2} \]

If we denote the total concentration of enzyme as \( c_{E0} \), then \( c_{E0} = c_E + c_{EA} \)

and:

\[ c_{EA} = \frac{k c_A (c_{E0} - c_{EA})}{k_{-1} + k_2} \quad \text{as well} \quad c_{EA} = \frac{k c_A c_{E0}}{k_{-1} + k_2 + k_c A} \]

\[ \frac{dc_{EA}}{dt} = k_{-1} c_{EA} = k_{-1} c_{E0} \quad \text{where} \quad k = \frac{k c_A}{k_M + c_A} \quad \text{a} \quad k_M = \frac{k_{-1} + k_2}{k_1} \]
One can observe, that at these conditions the reaction is of zeroth order with respect to A, and that this is the maximum rate of enzymolysis. Constant $k_2$ is known as the maximum molecular activity of the enzyme.

If $k_M \ll c_A$ then $k = k_2$, and reaction rate is:

$$\frac{dc_B}{dt} = k_2 c_A$$

One can show, that at these conditions the reaction is of zeroth order with respect to A, and that this is the maximum rate of enzymolysis. Constant $k_2$ is known as the maximum molecular activity of the enzyme.

IF $k_M >> c_A$ then:

$$\frac{dc_B}{dt} = \frac{k_2}{k_M} c_A$$

That may be shown on a plot:

**Michaelis-Menten Mechanism (4)**

From the equation: $k = \frac{k_2 c_A}{k_M + c_A}$ it results, that:

$$\frac{1}{k} = \frac{1}{k_2} + \frac{k_M}{k_2 c_A}$$

That may be shown on a plot:

**Rate of complex reactions and temperature**

If a complex rate constant of a reaction occurring via a pre-equilibrium mechanism is given as:

$$k = \frac{k_1 \cdot k_2}{k_{-1}}$$

Then:

$$k = \frac{A_1 e^{-E_{a1}/RT} \cdot A_2 e^{-E_{a2}/RT}}{A_{-1} e^{-E_{a-1}/RT}} = \frac{A_1 \cdot A_2}{A_{-1}} e^{-(E_{a1} + E_{a2} - E_{a-1})/RT}$$

Then activation energy of such a complex reaction must be equal to:

$$E_a = E_{a1} + E_{a2} - E_{a-1}$$
Rate of complex reactions and temperature (2)

Let’s consider two cases:

$E_{a1} + E_{a2} > E_{a-1}$; $E_a > 0$

The rate of the complex reaction increases with temperature.

$E_{a1} + E_{a2} < E_{a-1}$; $E_a < 0$

The rate of the complex reaction decreases with temperature !!!