Many chemical reactions are complete in less than a few seconds, which makes the rate of reaction difficult to determine. In these cases, the relaxation methods can be used to determine the rate of the reaction.

## Introduction

The term **relaxation** is used to describe a reaction's return to equilibrium. An equilibrium system is subjected to an external perturbation, such as a temperature change. When the change is applied suddenly, the lagging time it takes the system to reach the new equilibrium position is related to the $k_f$ and $k_r$ constants and is called **relaxation time**, $\tau$. To determine the relaxation method can be utilized by reactions with half-lives of 1 s to $10^{10}$ s. There are three different techniques (each are different processes that suddenly disturbs a reaction), that are used to witness the relaxation time. They are:

- Pressure Jump
- Electric Field Jump
- Temperature Jump

It can be found that:

$$ \tau = \frac{1}{k_f([A]_{eq}+[B]_{eq}) + k_r} \tag{1} $$

where $([A]_{eq})$ and $([B]_{eq})$ are the values at the new equilibrium at the final temperature. These values can be measured in separate experiments. Thus $K$, the equilibrium constant, can also be calculated from

$$ K = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \tag{2} $$

but

$$ K = \frac{k_f}{k_r} = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \tag{3} $$

Hence, we can find $k_f$ and $k_r$.

The relaxation time, $\tau$ is a function of the rate constants $k_f$ and $k_r$ of a chemical system at equilibrium with equilibrium concentrations $[A]_{eq}$ and $[B]_{eq}$

## Temperature-jump

$([A]_{eq})$ and $([B]_{eq})$ are the new equilibrium concentrations which resulted after the system was subjected to a temperature-jump while it was under rest at same other equilibrium state.

$$ \tau = \frac{1}{k_f([A]_{eq}+[B]_{eq}) + k_r} \tag{4} $$

$$ [A + B \rightleftharpoons C + Q \tag{5} $$

at new higher temperature.
The new conditions (higher temperature) can be applied so rapidly that movement of even very responsive systems (very fast moving to new equilibrium) to a new state of equilibrium can be followed. A temperature jump of as much as 10 °C for example can be produced in an aqueous solution by an electric discharge that lasts no more than 1 μs. If the properties of the system can be recorded following such a change, the rates of reaction that produce a new state of equilibrium, even within a few microseconds eg. 35 μs, can be measured.

It has been found that the restoration is always the first order for small displacements from equilibrium, giving:

\[ X_t = X_0 e^{(-t/T)} \]  
\( X_t \) and \( X_0 \) are the values of the linear property at time \( t = t \) and \( t = 0 \), respectively, and \( T \) is the relaxation time. When \( T = t \),

\[ X_t = \frac{X_0}{e} = \frac{X_0}{2.718} \]  
Thus, the relaxation time can be determined, by measuring the time it takes for \( X_0 \) to decrease to \( X_0/2.718 \). In other words, it is the time in which the relaxation process carries the system a fraction 1/e toward the equilibrium position. Thus, \( T \) is a time interval like the half-life \( t_{1/2} \).

Because the property \( X \) is proportional to the extent of the reaction eg. to the concentration of the reacting species at time \( t \). We can write the same equation with \( X_t \) and \( X_0 \) representing concentration instead conductance or absorbance.

\[ X_t = X_0 e^{(-t/T)} \]

Thus relaxation time is the time it takes for the concentration of \( C \) in this case to be decreased to 1/e of its initial value.

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**Derivation the equation**

\[ \tau = \frac{1}{k_f[A]_{eq} + k_r} \]

\[ A + B \rightleftharpoons C + Q \]

\[ H^+ + OH^- \rightleftharpoons H_2O + Q \]

Both new equilibrium in \( k_f \) and \( k_r \) at higher temperature with \( [A]_{eq}, [B]_{eq}, [C]_{eq} \). Of course, before the temperature-jump experiment, there was the old equilibrium, \( k_f' \) and \( k_r' \) different from \( k_f \) and \( k_r \), with \( [A]_o, [B]_o, [C]_o \) at the initial temperature.

After the temperature-jump, system is at the higher temperature and also the rate constants. The rate equation for \( C \) will be:
\[ \frac{d[C]}{dt} = k_f[A]_t[B]_t - k_r[C]_t \quad \text{(11)} \]

From the diagram, we have:

\[ [A]_t = [A]_{eq} - X_t \quad \text{(12a)} \]
\[ [B]_t = [B]_{eq} - X_t \quad \text{(12b)} \]
\[ [C]_t = [C]_{eq} + X_t \quad \text{(12c)} \]

Substituted:

\[ \frac{d([C]_{eq} + X_t)}{dt} = \frac{dX_t}{dt} = k_f([A]_{eq} - X_t)([B]_{eq} - X_t) - k_r([C]_{eq} + X_t) \quad \text{(13)} \]

\[ \frac{dX_t}{dt} = k_f[A]_{eq}[B]_{eq} - k_f[A]_{eq}X_t - k_f[B]_{eq}X_t + k_fX_t^2 - k_r[C]_{eq} - k_rX_t \quad \text{(14)} \]

\[ = k_f[A]_{eq}[B]_{eq} - k_f[A]_{eq}X_t - k_r[C]_{eq} + k_fX_t^2 - X_t(k_f[B]_{eq}X_t + k_f[A]_{eq} + k_r) \quad \text{(15)} \]

Since:

\[ \frac{d[C]}{dt} = 0 = k_f[A]_{eq}[B]_{eq} - k_r[C]_{eq} \quad \text{(16)} \]

\( k_fX_t^2 \) can be neglected for a small extent of reaction. Hence,

\[ \frac{dX_t}{dt} = -X_t(k_f[B]_{eq}X_t + k_f[A]_{eq} + k_r) = -L(X_t) \quad \text{(17)} \]

\[ \frac{dX_t}{X_t} = -L(dt) \quad \text{(18)} \]

\[ \int_{X_o}^{X_t} \frac{dX_t}{dt} = -L \int_0^t dt \quad \text{(19)} \]

\[ \Rightarrow \ln X_t - \ln X_o = -Lt \rightarrow e^{-Lt} = \frac{X_t}{X_o} \quad \text{(20)} \]

\[ X_t = X_o(e^{-Lt}) \quad \text{(21)} \]

From equation 1 & 3,

\[ X_o(e^{-t/T}) = X_o(e^{-Lt}) \rightarrow \frac{-t}{T} = -L \rightarrow T = \frac{1}{L} \quad \text{(22)} \]

We get:

\[ T = \frac{1}{k_f[A]_{eq} + k_f[B]_{eq} + k_r} \quad \text{(23)} \]

Overall, the rate constants of a reversible reaction can be determined by using relaxation method.
References


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