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 $1 \text{ s to } 10^{10} \text{ s}$. 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:

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

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

$$ K = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \quad \text{(2)} $$

but

$$ K = \frac{k_f}{k_r} = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \quad \text{(3)} $$

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.

$$ T = \frac{1}{k_f([A]_{eq} + [B]_{eq}) + k_r} \quad \text{(4)} $$

$$ [A + B \rightleftharpoons C + Q \quad \text{(5)} $$

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:

\[ X_t = X_0 e^{(-t/ \tau)} \]  \hspace{1cm} \text{(6)}

where \( \langle X \rangle \) is a property like electrical conductance or spectroscopic absorption proportional to the extent of the reaction. \( \langle X_t \rangle \) and \( \langle X_0 \rangle \) are the values of the linear property at time \( t = t \) and \( t = 0 \), respectively, and \( \langle \tau \rangle \) is the relaxation time. When \( \tau = t \),

\[ X_t = \frac{X_0}{e} = \frac{X_0}{2.718} \]  \hspace{1cm} \text{(7)}

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, \( \tau \) 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.

\[ X_t = X_0 e^{(-t/ \tau)} \]  \hspace{1cm} \text{(8)}

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.

**Derivation the equation**

\[ \tau = \frac{1}{k_f([A]_{eq}+[B]_{eq}) + k_r} \]  \hspace{1cm} \text{(9)}

\[ A + B \rightleftharpoons C + Q \]  \hspace{1cm} \text{(10)}

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 \( [A]_{eq}, [B]_{eq}, [C]_{eq} \) 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:

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

Substituted:

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

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

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,

\[\frac{dX_t}{dt} = -X_t( k_f[B]_{eq}X_t + k_f[A]_{eq} + k_r) = -L (X_t) \quad \text{(15)}\]

\[\int_{X_0}^{X_t} \frac{dX_t}{X_t} = -L \int_0^t dt \quad \text{(16)}\]

\[\ln X_t - \ln X_0 = -Lt \quad \Rightarrow \quad \frac{\ln X_t}{X_0} = -Lt \quad \Rightarrow \quad e^{-Lt} = \frac{X_t}{X_0} \quad \text{(17)}\]

\[X_t = X_o(e^{-Lt}) \quad \text{(18)}\]

From equation 1 & 3,

\[X_o(e^{-t/T}) = X_o(e^{-Lt}) \quad \Rightarrow \quad \frac{-t}{T} = -L \quad \Rightarrow \quad T = \frac{1}{k_f [A]_{eq}+k_f [B]_{eq}+ k_r} \quad \text{(19)}\]

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


Contributors and Attributions

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