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 \(10^1\) 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:

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

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

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

but

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

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.

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

\[
[A + B \rightleftharpoons C + Q \label{5}
\]

at new higher temperature.
k_f, k_r, [A]_{eq}, [B]_{eq}, [C]_{eq} are the values at the 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:

\[ X_t = X_0 e^{(-t/T)} \] \( \text{label}(6) \)

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 \( \langle T \rangle \) is the relaxation time. When \( \tau = t \),

\[ X_t = \frac{X_0}{e} = \frac{X_0}{2.718} \] \( \text{label}(7) \)

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.

\[ X_t = X_0 e^{(-t/T)} \] \( \text{label}(8) \)

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.

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### Derivation the equation

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

\[ A + B \rightleftharpoons C + Q \] \( \text{label}(10) \)

and

\[ H^+ + OH^- \rightleftharpoons H_2O + Q \] \( \text{label}(10) \)

Both new equilibrium in \( k_f \) and \( k_r \) at higher temperature with \( \langle [A]_{eq} \rangle, \langle [B]_{eq} \rangle, \langle [C]_{eq} \rangle \). 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 \( \langle [A]_{eq} \rangle, \langle [B]_{eq} \rangle, \langle [C]_{eq} \rangle \) 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:
\( \frac{d[C]}{dt} = k_f[A]_t[B]_t - k_r[C]_t \label{11} \)

From the diagram, we have:

\( [A]_t = [A]_{\text{eq}} - X_t \label{12a} \)

\( [B]_t = [B]_{\text{eq}} - X_t \label{12b} \)

\( [C]_t = [C]_{\text{eq}} + X_t \label{12c} \)

Substituted:

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

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

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

Since:

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

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

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

\( \frac{dX_t}{X_t} = -L(dt) \label{18} \)

\( \int_{X_o}^{X_t} \frac{dX_t}{dt} = -L \int_0^t dt \label{19} \)

\( \rightarrow (\ln X_t - \ln X_o = -Lt) \rightarrow \)

\( \frac{d}{dt} \ln(X_t) = -L \rightarrow e^{(-Lt)} = \frac{d}{dt} \ln(X_o) \label{20} \)

\( [X_t = X_o(e^{(-Lt)}) \label{21} \)

From equation 1 & 3,

\( [X_o(e^{(-t/T)}) = X_o(e^{(-Lt)}) \rightarrow \frac{d}{dt}T = -L \rightarrow T = 1/L \)

We get:

\( T = \frac{k_f[A]_{\text{eq}} + k_f[B]_{\text{eq}} + k_r}{k_f[A]_{\text{eq}}[B]_{\text{eq}} - k_r[C]_{\text{eq}} + k_fX_t^2 - X_t(k_f[B]_{\text{eq}}X_t + k_f[A]_{\text{eq}} + k_r)} \label{22} \)

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


Contributors

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