Under certain conditions, the 2nd order kinetics can be well approximated as first order kinetics. These Pseudo-1st-order reactions greatly simplify quantifying the reaction dynamics.

**Introduction**

A 2nd-order reaction can be challenging to follow mostly because the two reactants involved must be measured simultaneously. There can be additional complications because certain amounts of each reactant are required to determine the reaction rate, for example, which can make the cost of one's experiment high if one or both of the needed reactants are expensive. To avoid more complicated, expensive experiments and calculations, we can use the pseudo-1st-order reaction, which involves treating a 2nd order reaction like a 1st order reaction.

In second order reactions with two reactant species, the rate of disappearance of \([A]\) is

\[
\frac{d[A]}{dt} = k[A][B]
\]

The integrated form is

\[
\frac{1}{[B]_0-[A]_0} \ln \frac{[B][A]_0}{[B]_0[A]} = kt \tag{2nd}
\]

when \([B]_0>[A]_0\).

When \([B]_0>>[A]_0\), then \([B]_0 \approx [B]\) and Equation \((\text{ref}(2nd))\) becomes

\[
\frac{1}{[B]_0-[A]_0} \ln \frac{[B][A]_0}{[B]_0[A]} \approx \frac{1}{[B]} \ln \frac{[A]_0}{[A]} = kt
\]

or

\[
[A] = [A]_0 e^{-[B]kt}
\]

This functional form of the decay kinetics is similar to the first order kinetics and the system is said to operate under pseudo-first order kinetics. In a pseudo-1st-order reaction, we can manipulate the initial concentrations of the reactants. One of the reactants, \([A]\), for example, would have a significantly high concentration, while the other reactant, \([B]\), would have a significantly low concentration. We can then assume that reactant \([A]\) concentration effectively remains constant during the reaction because its consumption is so small that the change in concentration becomes negligible. Because of this assumption, we can multiply the reaction rate, \((k)\), with the reactant with assumed constant concentration, \([A]\), to create a new rate constant \((k'=k[A])\) that will be used in the new rate equation,

\[
\text{Rate} = k'[B]
\]

as the new rate constant so we can treat the 2nd order reaction as a 1st order reaction.

One way to create a pseudo-1st-order reaction is to manipulate the physical amounts of the reactants. For example, if one were to dump a liter of 5 M HCl into a 55 M ocean, the concentration of the mixture would be closer or equal to that of the ocean because there is so much water physically compared to the HCl and also because 55 M is relatively larger
compared to 5 M.

In theory, if we have an instance where there are more than two reactants involved in a reaction, all we would have to do is make the reaction appear like it is first order. If there were three reactants, for example, we would make two of the three reactants be in excess (whether in amount or in concentration) and then monitor the dependency of the third reactant.

We can also write the pseudo\textsuperscript{st}-order reaction equation as:

or

where

- \([A]_o\) is the initial concentration of \(A\),
- \([B]_o\) is the initial concentration of \(B\),
- \(k\) is the pseudo-1\textsuperscript{st}-order reaction rate constant,
- \(k'\) is the 2\textsuperscript{nd} order reaction rate constant, and
- \([A]\) is the concentration of \(A\) at time \(t\).

By using natural log to both sides of the pseudo-1\textsuperscript{st}-order equation we get:

or

\textit{1}\textsuperscript{st} order reaction mechanisms and additional information can be found in this link.

Example 1

Consider the reaction between cyanide and bromopropane:

\[
\text{[C}_H3\text{CH}_2\text{CH}_2\text{Br}_{(aq)} + \text{CN}^\text{-}_{(l)} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CN}_{(aq)} + \text{Br}^\text{-}_{(aq)}]
\]

The reaction involves two reactants, so it is a 2\textsuperscript{nd} order reaction:

\[
\text{rate}=k[C_H3CH_2CH_2Br_{(aq)}][CN^-_{(l)}]
\]

In this case, the concentration of cyanide equals 100 M, which is significantly higher than the concentration of bromopropane. Because the concentration of cyanide is significantly higher than the concentration of bromopropane, we can assume cyanide’s concentration will stay constant in the reaction.

Thus:

If we measure the the \(k\) and \([CN^-]\) at different concentrations of \([CN^-]\) (still in excess compared to \([CH_3CH_2CH_2Br]\)) and plot out a graph of \(k\) vs. \([CN^-]\) the slope will equal \(k'\).
Half-Life in a Pseudo-1st Order reaction

Half-life refers to the time required to decrease the concentration of a reactant by half, so we must solve for t. Here, \([B]\) will be the reactant in excess, and its concentration will stay constant. \([A_0]\) is the initial concentration of \(A\); thus the half-life concentration of \(A\) is \((0.5[A_0])\).

The pseudo-1\textsuperscript{st}-order reaction equation can be written as:

or

By using natural log to both sides of the pseudo-1\textsuperscript{st}-order equation, we get:

or

Because the half-life concentration of \(A\) is \((0.5[A_0])\) at half-life time \((t_{(1/2)})\):

or

\[\ln(0.5[A_0]) - \ln[A_0] = -kt_{(1/2)}\]

or

\[\ln(0.5[A_0]) - \ln[A_0] = -k'B_0 t_{(1/2)}\]

Recall that \((\ln(A) - \ln(B))\) equals \((\ln(frac(A))(B)))\):

\[\ln(0.5[A_0]) - \ln[A_0] = -kt\]

or

\[\ln(0.5[A_0]) - \ln[A_0] = -k'B_0 t\]

The \([A_0]\) cancels out:

\[\ln(0.5) = -kt_{(1/2)}\]

or

\[\ln(0.5) = -k'B_0 t_{(1/2)}\]

\[t_{(1/2)} = \frac{\ln 0.5}{-k} \]

or

\[t_{(1/2)} = \frac{\ln 0.5}{-k'B_0} \]
Questions

1. If a 2\textsuperscript{nd} order reaction has the rate equation $R = \textit{k}[A][B]$, and the rate constant, $\textit{k}$, is $3.67\text{M}^{-1}\text{s}^{-1}$, $[A]$ is 4.5M and $[B]$ is 99M, what is the rate constant of its pseudo-1\textsuperscript{st}-order reaction?

2. What is the half-life of a reaction with $[A]_o = 109\text{M}$, $[B]_o = 1\text{M}$, $\textit{k}' = 45\text{M}^{-1}\text{s}^{-1}$?

3. If $[A] = 55\text{M}$ at 39s, $[A]_o = 99\text{M}$, and $[B]_o = 1000\text{M}$, what is the 2\textsuperscript{nd} order reaction rate constant?

4. What is the concentration of $A$ at time 45s if $[A]_o = 1\text{M}$, $[B]_o = 45\text{M}$, and 2\textsuperscript{nd} order rate constant is $0.6\text{M}^{-1}\text{s}^{-1}$?

5. What is the rate of a reaction if $[A]_o = 560\text{M}$, $[B]_o = 0.2\text{M}$, and 2\textsuperscript{nd} order rate constant is $0.1\text{M}^{-1}\text{s}^{-1}$?

Solutions

1. Because $[B]$ is in excess we multiply 99M with $3.67\text{M}^{-1}\text{s}^{-1}$

$(99\text{M})(3.67\text{M}^{-1}\text{s}^{-1}) = 363.33\text{s}^{-1}$

2. Because $[A]$ is in excess we can multiply the $\textit{k}'$ with $[A]_o$ to find $\textit{k}$

$(109\text{M})(45\text{M}^{-1}\text{s}^{-1}) = 4905\text{s}^{-1}$

$t_{1/2} = (\ln0.5 / -\textit{k})$

$t_{1/2} = 1.41 \times 10^{-4} \text{s}$

3. Use the equation $[A] = [A]_o e^{-\textit{k}'[B]_o t}$

$(55\text{M}) = (99\text{M})e^{-\textit{k}'(1000\text{M})(39\text{s})}$

$\textit{k}' = 1.507 \times 10^{-5} \text{M}^{-1}\text{s}^{-1}$

4. Use the equation $[A] = [A]_o e^{-\textit{k}'[B]_o t}$

$[A] = (1)e^{-\textit{(0.6 M^{-1}s^{-1})}(45)}$

$[A] = 1.88 \times 10^{-12}\text{M}$

5. Use the equation $R = \textit{k}'[A][B]$

$R = (0.1\text{M}^{-1}\text{s}^{-1})(560\text{M})(0.2\text{M})$

Rate = 11.2\text{Ms}^{-1}$
References


Contributors

- Kan, Chin Fung Kelvin, Masako Le