III. Irreversible 2nd-Order Reaction

A. Given:

\[ A + A \xrightarrow{k} P \]

B. Rate Equation:

\[ -d[A]/dt = 2d[P]/dt = k[A]^2 \]

Integrate... (CRC #7)

\[ 1/[A] = 1/[A_0] + kt \]  \hspace{1cm} (1)

- Some treatments that include stoichiometric coefficients will show the rate constant as “2kt” rather than “kt”.
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C. Graphics:

1. Zeroth-Order Plot:

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[A] vs t (sec)

2nd order (sharper curvature)

1st order
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For a 2nd-order reaction, rearranging eq (1) provides...

\[ [A] = \frac{[A_0]}{1+([A_0]kt)} \]

with the fitting function written as...

\[ f(x) = \frac{a}{1+bx} \]

such that...

\[ a = [A_0] \quad b = [A_0]k \]

- The sharper curvature of a second-order reaction compared to a 1st-order reaction is not readily detected by the naked eye.
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2. 1st-Order Plot:

- Upward curvature (i.e., anomalous slowing) relative to 1st order.
- Curvature will not be obvious in 1st half-life.
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3. 2nd-Order Plot:

Since

\[ \frac{1}{[A]} - \frac{1}{[A_0]} = kt \]

Let...

\[ f(x) = ax \]

such that...

\[ f(x) = \frac{1}{[A]} - \frac{1}{[A_0]} \quad a = k \text{ (M}^{-1}\text{sec}^{-1}) \]
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Alternatively...

\[
\frac{1}{[A]} = \frac{1}{[A_0]} + kt
\]

Let...

\[ f(x) = b + ax \]

such that...

\[ f(x) = \frac{1}{[A]} \quad a = k (M^{-1}\text{sec}^{-1}) \quad b = \frac{1}{[A_0]} \]

The latter treatment is important if \([A_0]\) (i.e., the monitored property of \(A\) at \(t = 0\)) is not known.