V. Irreversible Mixed 2nd-Order Reaction

A. Given:

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

B. Rate Equation:

1. If \([A_0] = [B_0]\):

Since...

\[-d[A]/dt = -d[B]/dt = d[P]/dt = k[A][B] \quad (1)\]

The rate expression reduces to...

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

• Described in Section III.
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2. If $[A_0] \neq [B_0]$:

$$[A_0] - [A] = [B_0] - [B]$$

Consequently...

$$[B] = [A] - [A_0] + [B_0] \quad (2)$$

Substituting $[B]$ from eq (2) into eq (1)...

$$-d[A]/dt = k[A]([A] - [A_0] + [B_0]) \quad (3)$$

Integrate... (CRC #37)

$$\frac{1}{[B_0] - [A_0]} \ln \left( \frac{[A_0][B_0] - [A_0] + [A]}{[A][B_0]} \right) = kt \quad (4)$$

• This expression is undefined at $[A_0] = [B_0]$. 
C. Graphics:

\[ f(x) = ax \]

\[ \text{linear, slope} = k \]

Let...

\[ f(x) = ax \]

such that...

\[
 f(x) = \frac{1}{[B_0] - [A_0]} \ln \left( \frac{[A_0][B_0] - [A_0] + [A]}{[A][B_0]} \right) \quad x = t \quad a = k
\]

• \([A_0]\) and \([B_0]\) are known, and we measure \([A]\) vs. \(t\). Problems arise (particularly at high conversions) from a hypersensitivity of the rates to the accuracy in measuring \([A_0]\) and \([B_0]\).
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D. Flooding Techniques:

1. Let \([B_0] >> [A_0]\)

Then \([B] \approx [B_0]\) and eq (4) reduces to...

\[
\frac{1}{[B_0]} \ln \frac{[A_0]}{[A]} = kt
\]

Rearranging...

\[
\ln \frac{[A]}{[A_0]} = -k[B_0]t = -k_{\text{obsd}}t
\]

such that...

\[
k_{\text{obsd}} = k[B_0] = \text{constant}
\]

• "pseudo-first-order" conditions.

2. Note: Ideally...

\[
[B_0] \geq 20[A_0]
\]

If the reaction is high order in \([B]\), even a 10% consumption of \(B\) can distort the data.