Deriving Rate Laws

Example: Derive the rate law and \( k \) for

\[
\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g)
\]

from experimental data for rate of disappearance of

\( \text{CH}_3\text{CHO} \)

<table>
<thead>
<tr>
<th>Expt.</th>
<th>([\text{CH}_3\text{CHO}] ) (mol/L)</th>
<th>Rate of disappearance of ( \text{CH}_3\text{CHO} ) (mol/L•sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.020</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.081</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.182</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.318</td>
</tr>
</tbody>
</table>

Concentration / Time Relations

What is the concentration of reactant as a function of time?

Consider FIRST ORDER REACTIONS

The rate law is

\[
\text{Rate} = -\frac{\Delta [A]}{\Delta \text{time}} = k[A]
\]

Integrated Rate Laws

For a reaction with Reactant R becoming a Product P

\( R \rightarrow P \)

<table>
<thead>
<tr>
<th>Rate Equation</th>
<th>Integrated Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Order</td>
<td>(-\frac{\Delta [R]}{\Delta t} = k[R]), (\ln \frac{[R]}{[R]_0} = -kt)</td>
</tr>
<tr>
<td>Second Order</td>
<td>(-\frac{\Delta [R]}{\Delta t} = k[R]^2), (\frac{1}{[R]} - \frac{1}{[R]_0} = kt)</td>
</tr>
<tr>
<td>Zero Order</td>
<td>(-\frac{\Delta [R]}{\Delta t} = k[R]^3), ([R]_0 - [R] = kt)</td>
</tr>
</tbody>
</table>

Concentration / Time Relations

Integrating \(-\frac{\Delta [A]}{\Delta \text{time}} = k[A]\), we get

\[\ln \frac{[A]_0}{[A]_t} = -kt\]

\([A]_t = \text{fraction remaining after time } t \text{ has elapsed.}\]

This is the integrated first-order rate law.

Concentration / Time Relations

Sucrose decomposes to simpler sugars like glucose

Rate of disappearance of sucrose = \( k \) [sucrose]

If \( k = 0.21 \text{ hr}^{-1} \) and [sucrose] = 0.010 M

How long to drop 90% (to 0.0010 M)?
Chapter 15 — Kinetics - 1

Concentration / Time Relations

Rate of disappearance of sucrose = $k \cdot [\text{sucrose}]$, $k = 0.21 \text{ hr}^{-1}$. If initial $[\text{sucrose}] = 0.010 \text{ M}$, how long to drop 90% or to 0.0010 M?

Use the first order integrated rate law

$$\ln \left( \frac{0.0010 \text{ M}}{0.010 \text{ M}} \right) = -(0.21 \text{ hr}^{-1}) \cdot t$$

$$\ln (0.100) = -2.3 = -(0.21 \text{ hr}^{-1}) \cdot \text{time}$$

time = 11 hours