Method of initial rates

→ measure rates when different concentrations of reactants are mixed, immediately after the reaction starts.

\[
\text{N}_2\text{O}_5(g) + \text{NO}_2(g) \rightarrow \text{N}_2 + 2\text{H}_2\text{O(l)}
\]

<table>
<thead>
<tr>
<th>Exp</th>
<th>[HNO\textsubscript{3}]</th>
<th>[NO\textsubscript{2}]</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 M</td>
<td>0.005 M</td>
<td>1.35 \times 10^{-7} (mol L\textsuperscript{-1}s\textsuperscript{-1})</td>
</tr>
<tr>
<td>2</td>
<td>0.1 M</td>
<td>0.01 M</td>
<td>2.70 \times 10^{-7}</td>
</tr>
<tr>
<td>3</td>
<td>0.2 M</td>
<td>0.01 M</td>
<td>5.4 \times 10^{-7}</td>
</tr>
</tbody>
</table>

rate = -\frac{d[\text{HNO}_3]}{dt} = k [\text{HNO}_3]^n [\text{NO}_2]^m

n = 1 \quad \& \quad m = 1

rate = k [\text{HNO}_3][\text{NO}_2]
Integrated rate laws

\[-\frac{d[A]}{dt} = k[A]^n\] is a differential equation.

We wish to find the value of \([A]\) at time \(t = t\).

We need to integrate
Order

\[ \frac{\text{d} (\text{A}_1)}{\text{d} t} = k (\text{A}_1^0) = k \]

\[ \int -\text{d} (\text{A}_1) = \int k \text{d} t \]

\[ 0 = 0 \]

\[ -\text{A}_1 + \text{A}_1^0 = k (t-0) = k t \]

\[ \text{A}_1 = -k t + \text{A}_1^0 \]

Half life of a reaction:

\[ t = t_{1/2} \quad \text{when} \quad \text{A}_1^0 = \frac{\text{A}_1^0}{2} \]

\[ \int -\text{d} (\text{A}_1) = -k t_{1/2} + \text{A}_1^0 \]
1st order

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

\[\int_{A_0}^{A} \frac{d[A]}{[A]} = \int_{0}^{t} k \, dt\]

\[-\ln(A) + \ln(A_0) = kt\]

\[\ln|A| = -kt + \ln(A_0)\]

at \( t = t_{1/2} \) ; \( \frac{[A]}{[A_0]} = \frac{1}{2} \)

\[\ln\left(\frac{[A_0]}{[A_0]/2}\right) = k t_{1/2} : \ln\left(2\right) = k \frac{t_{1/2}}{k} \]

\[t_{1/2} = \frac{0.693}{k}\]
Second order

\[-\frac{d}{dt} \frac{\Delta A}{\Delta N^2} = k \frac{\Delta A}{\Delta N^2} \]

\[-\int_0^t \frac{d\Delta A}{\Delta N^2} = \int_0^t k \, dt \]

\[\frac{\Delta A}{\Delta N_0} \]

\[+ \frac{1}{\Delta N} - \frac{1}{\Delta N_0} = k \, t \]

or

\[\frac{1}{\Delta N} = \frac{1}{\Delta N_0} + k \, t \]

when \( t = t_{1/2} \); \( \Delta A = \Delta A_{1/2} \)

\[\frac{\Delta A_0}{\Delta N_0} = \frac{1}{\Delta N_0} + k \, t \Rightarrow \]

\[t_{1/2} = \frac{1}{k \, \Delta N_0} \]
Newton's Law of Cooling

\[-\frac{dT}{dt} = k(T - T_{env})\]

The rate of cooling is proportional to the temperature difference.

\[-\int \frac{dT}{dt} = \int k(T - T_{env}) dt\]

\[-\int \frac{dT}{dT} = \int k dt\]

\[\Delta T(t) = \Delta T(0)e^{-kt}\]

[diff at time 0]
Compound interest

\[ A = P \left(1 + \frac{r}{n}\right)^{nt} \]

\[ \text{accumulated value (including principal P)} \]

\[ r \] is the annual interest rate

\[ n \] is the compounding frequency (e.g. 1 time per year)

\[ t \] is time

\$1,500 at 4% compounded annually over 20 years

\[ t = 20, \ r = 0.04, \ n = 1 \]

\[ A = \$3,286.68 \text{ cents} \]
If the compounding is instantaneous (continuous compounding) at

$$P(t) = P_0 e^{rt}$$

$P_0 = \$1,500$

$r = 4\% = 0.04$

$t = 20$ years

$$P(20 \text{ years}) = \$3338.51$$

$\$1,800 \text{ in 40 years at } 10\% \text{ annually is } \$100,000.$