First Order Reaction

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Computer-aided Experiments - Chemical Kinetics

- **Hydrolysis of Tertiary Butyl Chloride**

A reaction

A → P

where **A** is a reactant and **P** is a product is called a first-order reaction. The rate is proportional to the concentration of a single reactant raised to the first power

The decrease in the concentration of **A** over time can be written as:

$$v = -\frac{d[A]}{dt} = k[A] \qquad (1)$$

$$-\frac{d[A]}{[A]} = k\,dt \qquad (2)$$

Equation **(2)** represents the differential form of the rate law. Integration of this equation and determination of the integration constant **C** produces the corresponding integrated law.

Integrating equation **(2)** yields:

$$\ln[A] = -kt + C \qquad (3)$$

The constant of integration **C** can be evaluated by using boundary conditions.

When $t = 0$, $[A] = [A]_0$. $[A]_0$ is the original concentration of **A**.

Substituting into equation **(3)** gives:

$$\ln[A]_0 = -k(0) + C \qquad (4)$$

Therefore

$$C = \ln[A]_0 \qquad (5)$$

Substituting **(5)** into **(4)** leads to:

$$\ln \frac{[\mathbf{A}]}{[\mathbf{A}]_0} = -\mathbf{k\,t} \qquad \textbf{(6)}$$

Plotting ln [A] or ln [A] / $[A]_0$ against time gives a straight line with slope of –k. The plot should be linear up to a 80-90% conversion, that is up to the point at which 80-90% of the concentration of the limiting reactant is consumed.

Equation **(6)** can also be written as:

$$[\mathbf{A}] = [\mathbf{A}]_\mathbf{0}\,\mathbf{e}^{-\mathbf{kt}} \qquad \textbf{(7)}$$

This means that the concentration of **A** decreases exponentially as a function of time.

The rate constant **k** can also be determined from the half-life $t_{1/2}$. Half-life is the time it takes for the concentration to fall from $\mathbf{[A]_0}$ to $\mathbf{[A]_0 / 2}$.

According to equation **(6)** is obtained:

$$\mathbf{k\,t_{1/2}} = \mathbf{ln}\frac{[\mathbf{A}]_\mathbf{0}}{[\mathbf{A}]_\mathbf{0}/\mathbf{2}} \qquad \text{or} \qquad \mathbf{k} = \frac{\mathbf{ln2}}{\mathbf{t}_{1/2}} \qquad \textbf{(8)}$$