

First Order Reaction

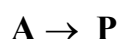
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Computer-aided Experiments - Chemical Kinetics

- Hydrolysis of Tertiary Butyl Chloride

A reaction



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:

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

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

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:

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

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:

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

Therefore

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

Substituting (5) into (4) leads to:

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

Plotting $\ln [\mathbf{A}]$ or $\ln [\mathbf{A}] / [\mathbf{A}]_0$ 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:

$$[\mathbf{A}] = [\mathbf{A}]_0 e^{-k t} \quad (7)$$

This means that the concentration of \mathbf{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:

$$k t_{1/2} = \ln \frac{[\mathbf{A}]_0}{[\mathbf{A}]_0 / 2} \quad \text{or} \quad k = \frac{\ln 2}{t_{1/2}} \quad (8)$$