Differential and integrated rate laws

Consider A → B: **a) 0^{th} Order**

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

Differential rate law

$$d[A] = -k\,dt \Rightarrow \int_{[A]_0}^{[A](t)} d[A] = -k\int_0^t dt$$

$$\Rightarrow [A](t) - [A]_0 = -kt$$

$$\boxed{[A](t) = [A]_0 - kt}$$

Integrated rate law

b) 1st Order

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

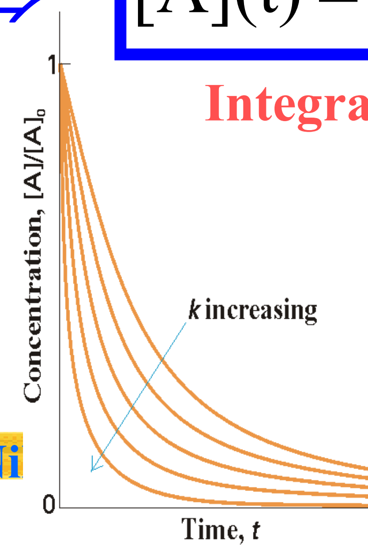
Differential rate law

$$\int_{[A]_0}^{[A](t)} \frac{d[A]}{[A]} = -k\int_0^t dt \Rightarrow$$

$$\boxed{[A](t) = [A]_0\, e^{-kt}}$$

Integrated rate law

$$\Rightarrow \ln[A](t) - \ln[A]_0 = \ln\left(\frac{[A](t)}{[A]_0}\right) = -kt$$



Differential and integrated rate laws of a second order reaction

c) 2nd Order

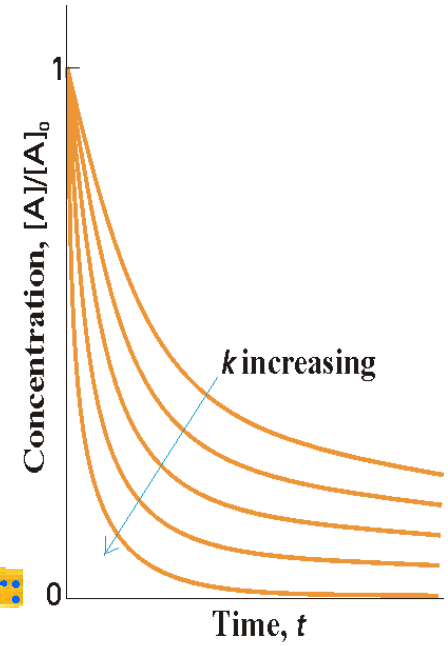
$$\boxed{-\frac{d[A]}{dt} = k[A]^2} \qquad \int_{[A]_0}^{[A](t)} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

Differential rate law

$$\Rightarrow \quad -\frac{1}{[A]}\Bigg|_{[A]_0}^{[A](t)} = -\left(\frac{1}{[A](t)} - \frac{1}{[A]_0}\right) = -kt$$

$$\Rightarrow \quad \boxed{\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}} \quad \Rightarrow \quad \boxed{[A](t) = \frac{[A]_0}{1+kt[A]_0}}$$

Integrated rate law



Nils Walter:

The half-life of a reaction

Half-Life of a Reaction:

The time required for [A] to drop by a factor of two

0th Order: $[A](t) = -kt + [A]_0$

$[A]_0/2 = -kt_{1/2} + [A]_0$

$kt_{1/2} = [A]_0 - [A]_0/2$

$$\Rightarrow \boxed{t_{1/2} = \frac{[A]_0}{2k}}$$

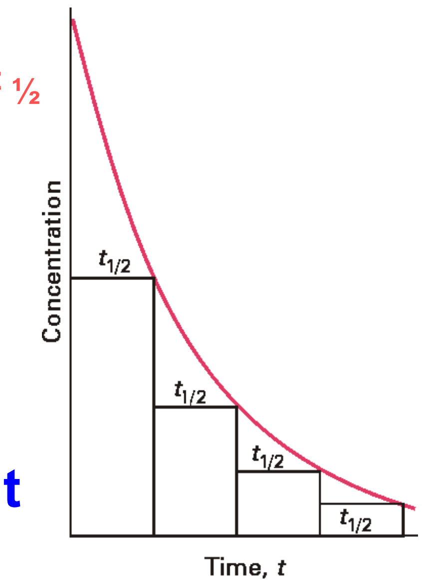
1st Order: $[A](t) = [A]_0\, e^{-kt}$

$[A]_0/2 = [A]_0\, e^{-kt_{1/2}}$

$e^{-kt_{1/2}} = 1/2$

$$\Rightarrow \boxed{t_{1/2} = \frac{\ln 2}{k}}$$

Independent of $[A]_0$!



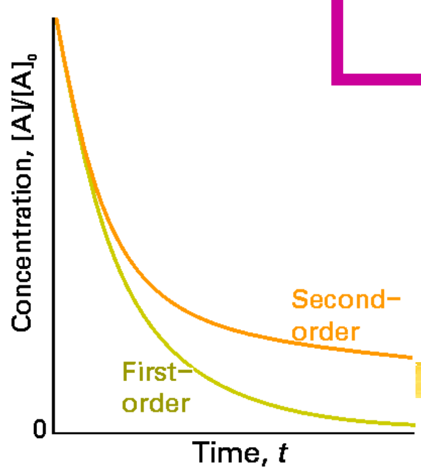
2nd Order: $$\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0} \Rightarrow \boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

Summary of rate laws

	Differential Rate Law	Integral Rate Law	Half-Life
0^{th} Order:	$-\frac{d[A]}{dt} = k$	$[A](t) = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1^{st} Order:	$-\frac{d[A]}{dt} = k[A]$	$[A](t) = [A]_0 e^{-kt}$	$t_{1/2} = \frac{\ln 2}{k}$
2^{nd} Order:	$-\frac{d[A]}{dt} = k[A]^2$	$\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$	$t_{1/2} = \frac{1}{k[A]_0}$



Tricks to determine rate laws

Consider A → B:

0th Order: $[A](t) = -kt + [A]_0$

1st Order: $\ln[A](t) = -kt + \ln[A]_0$

2nd Order: $\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$

Linear regression y = mx + b

Consider A + B → C :

2nd Order: $-\frac{d[A]}{dt} = k[A][B]$

BUT by

a) choosing $[A]_0 = [B]_0$

$\Rightarrow$ [A] = [B] !

$\Rightarrow -\frac{d[A]}{dt} = k[A]^2$

b) choosing $[A]_0 << [B]_0 \Rightarrow [B] \approx$ constant !

$\Rightarrow -\frac{d[A]}{dt} = k'[A];\; k' = k[B]_0$

Sample Problem:

Consider: $CH_3CH_2NO_2 + OH^- \rightarrow CH_3CHNO_2^- + H_2O$

Initially $[CH_3CH_2NO_2] = [OH^-] = 5.00\times10^{-3}$ M. The concentration of hydroxide was then measured by monitoring the pH with the following result. What is the order of the reaction? What is k?

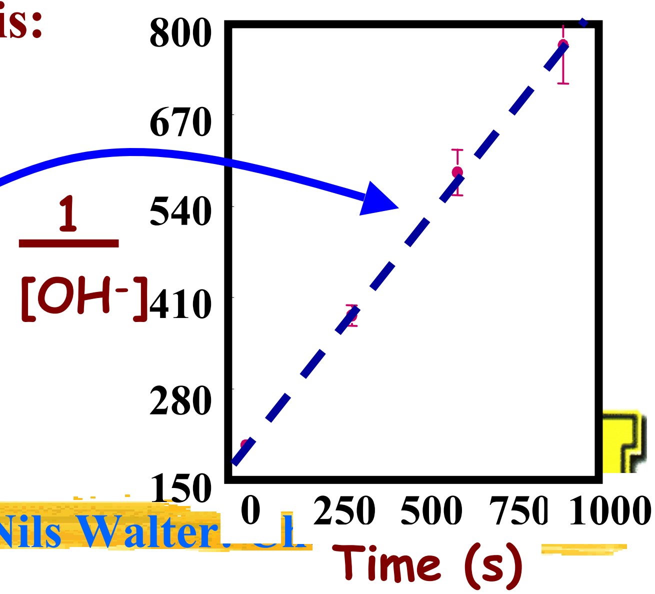
t (min)	0	5	10	15
$[OH^-]$ (M)	5.00×10^{-3}	2.6×10^{-3}	1.7×10^{-3}	1.3×10^{-3}
$[OH^-]^{-1}$	200	385	588	769

The most reasonable initial guess for this reaction is:

$$\frac{-d[OH^-]}{dt} = k\,[OH^-][CH_3CH_2NO_2] = k\,[OH^-]^2$$

Good line (r = 0.9998) ⇒ correct rate law

$$\boxed{\text{slope} = k = 0.637\ M^{-1}\ s^{-1}}$$



$$\Rightarrow \frac{1}{[OH^-]} = kt + \frac{1}{[OH^-]_0}$$

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