

11 • Kinetics

Graphical Methods of Determining Reaction Order and the Rate Constant

First-Order Reactions: (rate is directly proportional to the concentration)

$$\text{Rate} = - \frac{\Delta[R]}{\Delta t} = k[R]$$

using calculus, as the Δt approaches 0, the Rate equation becomes

$$\ln\left(\frac{[R]_o}{[R]_t}\right) = kt$$

which can be rearranged into the “y = mx + b” format

$$\ln[R]_t = -kt + \ln[R]_o$$

so... IF the reaction is **first-order** with respect to R,
plotting $\ln[R]_t$ versus time results in a straight line with **k = -slope**

Summary:

Order	Rate Equation	Integrated Rate Equation	Straight Line Plot	Slope	k Units
0	Rate = $k[R]^0$	$[R]_o - [R]_t = kt$	$[R]_t$ vs. t	$-k$	mol/L·s
1	Rate = $k[R]^1$	$\ln([R]_o/[R]_t) = kt$	$\ln[R]_t$ vs. t	$-k$	s ⁻¹
2	Rate = $k[R]^2$	$(1/[R]_t) - (1/[R]_o) = kt$	$1/[R]_t$ vs. t	k	L/mol·s
memorize this!					

Second-Order Reactions	Zero-Order Reactions:
Rate = $-\frac{\Delta[R]}{\Delta t} = k[R]^2$	Rate = $-\frac{\Delta[R]}{\Delta t} = k[R]^0$
$\frac{1}{[R]_t} - \frac{1}{[R]_o} = kt$	$[R]_o - [R]_t = kt$
$1/[R]_t = kt - (1/[R]_o)$	$[R]_t = -kt + [R]_o$

Half-Life and First-Order Reactions: (radioactivity is a first-order reaction)

Recall (from the Nuclear Chemistry chapter) the special case of half-life ($t_{1/2}$)

$$\ln\left(\frac{[R]_o}{[R]_t}\right) = kt \text{ becomes } \ln(2) = kt_{1/2}$$

$$\ln(2) = 0.693$$

$$\text{so... } k = 0.693/t_{1/2} \text{ and } t_{1/2} = 0.693/k$$

Practice Problem: Data for the decomposition of N_2O_5 in a particular solvent at 45°C are as follows:

$[N_2O_5]$ (mol/L)	t (min)	$\ln[N_2O_5]$	$1/[N_2O_5]$
2.08	3.07		
1.67	8.77		
1.36	14.45		
0.72	31.28		

Plot $[N_2O_5]$, $\ln[N_2O_5]$, and $1/[N_2O_5]$ versus time, t .

What is the order of the reaction? What is the rate constant, k , for the reaction?