14.3 Rate Laws

Determining Rate Law Using the Method of Initial Rates

$2\ ICl + H_2 = I_2 + 2\ HCl$

a) What is the overall order of the reaction? 3

Exp	$[ICl]_o$, M	$[H_2]_o$, M	Initial Rate, Ms^{-1}
1	0.309	0.114	7.07e-3
2	0.618	0.114	1.41e-2
3	0.309	0.228	2.83e-2
4	0.618	0.228	5.65e-2

Previously we did this the long way, this time we will short cut it!

Initial Rate $= k[ICl]^x[H_2]^y$

Exp 1 & 3 : $[ICl]$ is held constant while the $[H_2]$ increases by a factor of 2

$$\frac{3}{1} : \frac{2.83\times10^{-2}}{7.07\times10^{-3}} = 4$$

$$2^y = 4$$
$$y = 2$$

Exp 1 & 2 : $[H_2]$ is held constant while the $[ICl]$ increases by a factor of 2.

$$\frac{2}{1} : \frac{1.41\times10^{-2}}{7.07\times10^{-3}} = 2$$

$$2^x = 2$$
$$x = 1$$

Overall Order $= x + y$
$= 1 + 2$
$= 3$

14.4 Concentration Changes over Time

Integrated Rate Laws

Integrated Rate Laws for Reactions of Type A → Products

Reaction Order	Rate Law	Integrated Rate Law
Zero order	rate = $k\,[A]^0 = k$	$[A]_t = [A]_0 - kt$
First order *	rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$
Second order	rate = $k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$

t : time.
$[A]_0$: initial concentration at t = 0.
$[A]_t$: concentration at t = t.

A = Products

$-\frac{\Delta[A]}{\Delta t} = k[A]$

$\frac{d[A]}{dt} = -k[A]$ ... if Δ is very small

$\left(\frac{1}{[A]}\right) d[A] = -k\,dt$

$\int_{t=0}^{t=t} (1/[A])\, d[A] = -k \int_{t=0}^{t=t} dt$

$\ln [A]_t - \ln [A]_0 = -kt$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

14.4 Concentration Changes over Time

Integrated Rate Laws

The decomposition of nitrous oxide

$$N_2O(g) = N_2(g) + \tfrac{1}{2} O_2(g)$$

is **second order in N_2O** with a rate constant of $1.20 \times 10^{-3}\ M^{-1}s^{-1}$.
If the initial concentration of N_2O is 1.79 M, the concentration of N_2O will be 0.187 M after how many seconds. ~?,000 s

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$[A]_0$ = 1.79 M
$[A]_t$ = 0.187 M
k = $1.20 \times 10^{-3}\ M.s^{-1}$
t = ?

$$\frac{1}{0.187} = \frac{1}{1.79} + 1.20 \times 10^{-3} t$$

$$5.348 = 0.5587 + 1.20 \times 10^{-3} t$$

$$1.20 \times 10^{-3} t = 5.348 - 0.5587$$

$$t = \frac{4.7893}{1.20 \times 10^{-3}} = 3,991\ s$$

14.4 Concentration Changes over Time

Graphical Determination of Reaction Order

Determining the Rate Equation: Graphical Method

Description

The rate law for reactions involving a single reactant can be determined using the graphical method. This method involves constructing a series of plots of concentration vs. time data and analyzing the plots to extract the reaction order and the rate constant.

The general reaction used for this tutor is:

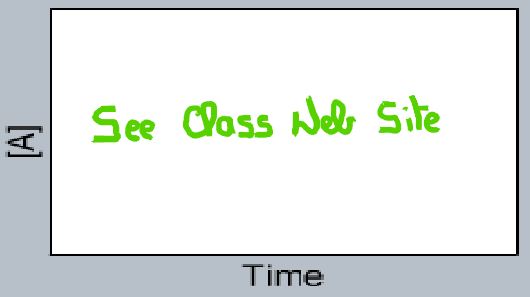
$$A \longrightarrow C$$

The concentration vs. time data at right were collected by running the reaction at a constant temperature. These are data taken for a single trial of the reaction.

Rate = [ ] [A][ ]

Submit

time, min	[A], mol/L	time, min	[A], mol/L
0	0.7245	5	0.4046
1	0.6605	6	0.3406
2	0.5965	7	0.2766
3	0.5325	8	0.2126
4	0.4686		



- (•) [A] vs. Time
- ( ) ln[A] vs. Time
- ( ) 1/[A] vs. Time
- [ ] Least Squares

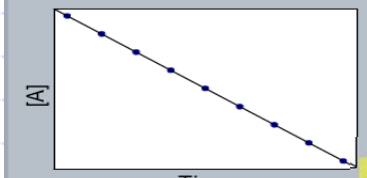
Plot

14.4 Concentration Changes over Time

Graphical Determination of Reaction Order

Reaction Order	Integrated Rate Law	Rearranged Rate Law	Straight-Line Plot
Zero order	$[A]_t = [A]_0 - kt$	$[A]_t = -kt + [A]_0$ $y = mx + b$	$y = [A]_t$ $x = t$ slope = $-k$
First order	$\ln\frac{[A]_t}{[A]_0} = -kt$	$\ln[A]_t = -kt + \ln[A]_0$ $y = mx + b$	$y = \ln[A]_t$ $x = t$ slope = $-k$
Second order	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ $y = mx + b$	$y = 1/[A]_t$ $x = t$ slope = k

time, min	[A], mol/L	time, min	[A], mol/L
0	0.7210	5	0.3978
1	0.6563	6	0.3331
2	0.5917	7	0.2685
3	0.5271	8	0.2038
4	0.4624		

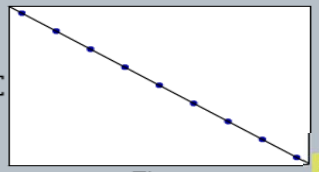


○ [A] vs. Time
○ ln[A] vs. Time
○ 1/[A] vs. Time
☑ Least Squares
Plot
slope = -0.065
intercept = 0.721

Rate = $k[A]^0$
= k
= 0.065

Slope = $-k$

time, min	[A], mol/L	time, min	[A], mol/L
0	0.8466	5	0.0058
1	0.3121	6	0.0021
2	0.1151	7	0.0008
3	0.0424	8	0.0003
4	0.0156		

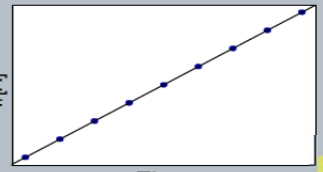


○ [A] vs. Time
● ln[A] vs. Time
○ 1/[A] vs. Time
☑ Least Squares
Plot
slope = -0.998
intercept = -0.167

Rate = $k[A]$
= 0.998 [A]

Slope = $-k$

time, min	[A], mol/L	time, min	[A], mol/L
0	0.8126	5	0.1807
1	0.4782	6	0.1564
2	0.3387	7	0.1378
3	0.2623	8	0.1232
4	0.2140		



○ [A] vs. Time
○ ln[A] vs. Time
● 1/[A] vs. Time
☑ Least Squares
Plot
slope = 0.861
intercept = 1.231

Rate = $k[A]^2$
= 0.861 $[A]^2$

Slope = k

14.4 Concentration Changes over Time

Reaction Half-Life

Zero Order	First Order	Second Order
$t_{1/2} = \frac{[A]_o}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_o}$
Directly proportional to $[A]_o$	Constant	Inversely proportional to $[A]_o$

$\ln[A]_t = -kt + \ln[A]_o$: @ $t_{1/2}$, $[A]_t = \frac{1}{2}[A]_o$

$\ln(\frac{1}{2}[A]_o) = -kt_{1/2} + \ln[A]_o$

$-kt_{1/2} = \ln(\frac{1}{2}[A]_o) - \ln[A]_o$

$= \ln\frac{1}{2} + \ln[A]_o - \ln[A]_o$

$= \ln\frac{1}{2}$

$= \ln 1 - \ln 2$

$= 0 - \ln 2$

$-kt_{1/2} = -\ln 2$

$kt_{1/2} = \ln 2$

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

14.4 Concentration Changes over Time

Reaction Half-Life

Nitrogen-13 is used in tracers injected into the bloodstream for positron emission tomography (PET). The **half-life of nitrogen-13 is 10.0 minutes**. **How much time** is required for the mass of a sample of nitrogen-13 to fall to **6.25 percent** of its original value? Since the **decomposition is a radioactive decay** reaction, it is **first order**.

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad ; \quad t_{1/2} = 10 \text{ min} \quad ; \quad \frac{[A]_t}{[A]_0} = 0.0625$$

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

$$10 = \frac{\ln 2}{k}$$

$$10k = \ln 2$$

$$k = \frac{\ln 2}{10} = 6.930 \times 10^{-2} \text{ min}^{-1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln (0.0625) = -6.930 \times 10^{-2} t$$

$$t = \frac{\ln (0.0625)}{-6.930 \times 10^{-2}}$$

$$= 40 \text{ minutes}$$