KINETICS
3: TIME DEPENDANCE OF CONCENTRATION

Dr. Sapna Gupta

TIME DEPENDENCE OF CONCENTRATION

As the reaction proceeds the concentration of the reactants decrease; one can figure out what the new concentrations will be over time.

- Integration of rate law is done via calculus.
- This is done via integrating the rate laws. The rate laws are different for first, second and third order reactions.
- Note: *ln* is natural log.

Order	Rate Law	Integrated Rate Law
0	Rate = k	$[A]_t = -kt + [A]_0$
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

EXAMPLE 1: CONC. OVER TIME

Cyclopropane is used as an anesthetic. The isomerization of cyclopropane to propene has a rate constant of 9.2/s. If an initial sample of cyclopropane has a concentration of 6.00 *M*, what will the cyclopropane concentration be after 1.00 s?

Answer:

Rate = k[cyclopropane]

k = 9.2/s; [A]0 = 6.00 M; t = 1.00 s, [A]t = ?

The reaction is first order (look at the units for k)

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

$$\ln \frac{[A]_t}{[A]_0} = -\frac{9.2}{s} \times 1.00\ s = -9.2$$

Take inverse *ln*

$$\frac{[A]_t}{[A]_0} = e^{-9.2} = 1.01 \times 10^{-4}$$

$$[A]_t = 1.01 \times 10^{-4}(6.00\ M) = \boxed{\mathbf{6.1 \times 10^{-4}\ M}}$$

HALF LIFE OF REACTION

Half life, $t_{1/2}$, of a reaction is when half the reactants are consumed.

- By substituting $\frac{1}{2}[A]_0$ for $[A]_t$, we solve the integrated rate law for the special case of $t = t_{1/2}$.

Order	Rate Law	Integrated Rate Law	Half life
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{0.693}{k}$
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

EXAMPLE 2: HALF LIFE

Ammonium nitrite is unstable because ammonium ion reacts with nitrite ion to produce nitrogen: $NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)}$. In a solution that is 10.0 *M* in NH_4^+, the reaction is first order in nitrite ion (at low concentrations), and the rate constant at 25°C is 3.0×10^3/s. What is the half-life of the reaction?

Answer:

The rate is first order in nitrite, NO_2^-: $k = 3.0 \times 10^{-3}$/s

For first-order reactions: $t_{½} = 0.693/k$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{\frac{3.0 \times 10^{-3}}{s}}$$

$t½ = 2.3 \times 10^2$ s = **3.9 min**

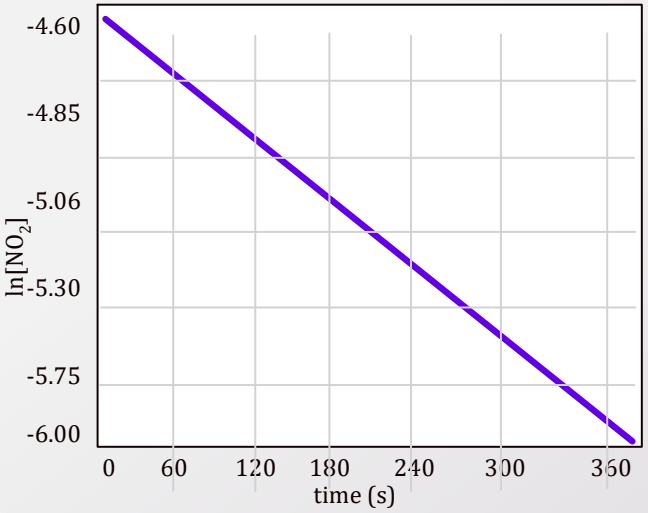
GRAPHING RATE OF REACTION DATA

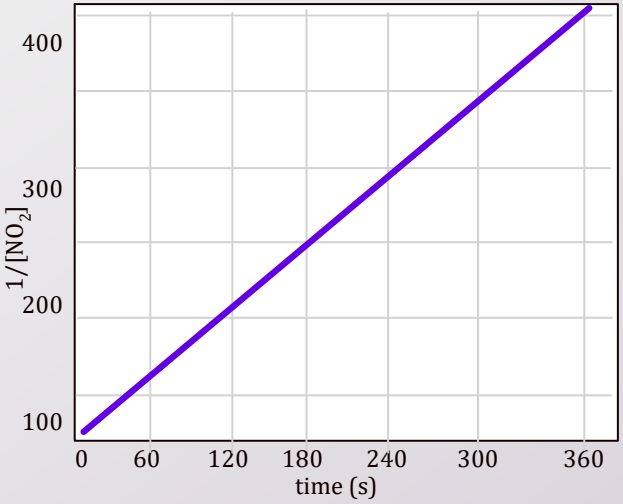
A reaction is followed in a number of ways, however, one way of telling the rate of reaction without doing detailed calculations is by graphing the data or the change of concentration over time.

- For zero-order reactions, [A] versus *t* is linear.
- For first-order reactions, ln[A] versus *t* is linear.
- For second order reactions, 1/[A] versus *t* is linear.

Left: Plot of ln[NO_2] versus *t* is not linear, so the reaction is not first order.

Right: Plot of 1/[NO_2] versus *t* is linear, so the reaction is second order in NO_2.





MORE ON GRAPHING

In each case, the rate law is in the form of y = mx + b, which lets us to use the slope and intercept to find the values.

y = mx + b

Order	Rate Law	Integrated Rate Law	Half life	Straight-Line Plot
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$	[A] vs t The y-intercept is $[A]_0$
1	Rate = k[A]	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{0.693}{k}$	ln[A] vs t The graph crosses the origin (0)
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$	$\frac{1}{[A]_0}$ vs t The y-intercept is $1/[A]_0$

EXAMPLE 3: CALCULATING CONC. 1

The rate constant for the reaction $2A \longrightarrow B$ is $7.5 \times 10^{-3}\ s^{-1}$ at 110°C. The reaction is 1st order in A. How long (in seconds) will it take for [A] to decrease from 1.25 *M* to 0.71 *M*?

Answer:

For 1st order - $\ln\frac{[A]_t}{[A]_0} = -kt$

$$\ln\frac{(0.71\text{M})}{(1.25\text{M})} = -7.5 \times 10^{-3}\text{s}^{-1}(t)$$

$$\boldsymbol{t = 75\text{s}}$$

EXAMPLE 4: CALCULATING CONC. 2

The reaction, $A_{(g)} + B_{(g)} \longrightarrow AB_{(g)}$ is second order and has a rate constant of $7.0 \times 10^9\ M^{-1}\ s^{-1}$ at 23°C.

a) If the initial [A] is 0.086 *M*, calculate the concentration after 2.0 min.

b) Calculate the half-life of the reaction when the initial [A] is 0.60 *M* and when the [A] is 0.42 *M*.

Answer:

a) Using 2nd order rate eq.

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

$$\frac{1}{[\mathrm{A}]_t} = \left(7.0 \times 10^9 \mathrm{M}^{-1}\mathrm{s}^{-1}\right)120\mathrm{s} + \frac{1}{[0.086\mathrm{M}]} = 8.4 \times 10^{11}\mathrm{M}^{-1}$$

$$[\mathrm{A}]_t = \frac{1}{8.4 \times 10^{11}\mathrm{M}^{-1}} = \boxed{\mathbf{1.2 \times 10^{-12}}\boldsymbol{M}}$$

b) Use the half-life eq.

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

$$t_{1/2} = \frac{1}{(7.0 \times 10^9 \mathrm{M}^{-1}\mathrm{s}^{-1})(\mathbf{0.60}\boldsymbol{M})} = \boxed{\mathbf{2.4 \times 10^{-10}\,s}}$$

$$t_{1/2} = \frac{1}{(7.0 \times 10^9 \mathrm{M}^{-1}\mathrm{s}^{-1})(\mathbf{0.42}\boldsymbol{M})} = \boxed{\mathbf{3.4 \times 10^{-10}\,s}}$$

KEY CONCEPTS

- Calculating concentrations of reactants/products at different times
- Calculating half life
  - Here are ALL the formulas:

Order	Rate Law	Integrated Rate Law	Half life
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{0.693}{k}$
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$