KINETICS -2
RATE LAW AND HALF LIFE

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RATE LAW

- Rate of reaction is dependent on the concentration of reactants.

- Rate of reaction is then given by the rate law. This is an equation that relates rate of reaction to the concentration of a reactant raised to various powers. The proportionality constant, k, is the rate constant.

For the generic reaction

$$a\text{A} + b\text{B} + c\text{C} \rightarrow d\text{D} + e\text{E}$$

the rate law is

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y[\text{C}]^z$$

- Where k = rate constant (specific for the reaction at a particular temp.)

- xyz are integers and called order of reaction (calculated experimentally)

- $x+y+z$ is the overall order of reaction.

ORDER OF REACTION

- **0 order -** changing the conc. of reactants does not affect rate of reaction.

- **1st order -** rate directly proportional to concentration – i.e. if you double the conc. you double the rate of reaction.

- **2nd order -** exponential relationship – i.e. if you double the conc. you quadruple the rate of reaction.

- Sum of exponents (order) indicates overall reaction order

For example, for the reaction below:

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$
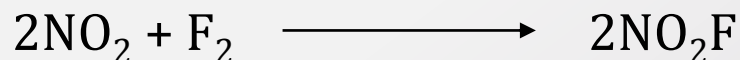
Rate = k $[NO_2][F_2]$

Order of reactions are 1 for both NO_2 and F_2 (we can write either 1 or no integer to represent 1)

Overall order is 2.

DETERMINING ORDER OF REACTION

- To obtain order of reaction, a series of reactions have to be performed.

- Depending on the number of reactants, one has to keep one reactant constant and change the concentration of the other and observe what happens to the rate of reaction.

- The process is then reversed i.e., keep the second one constant and change the first one and observe for change of rate of reaction.

- Once data is obtained calculate the order of reaction.

- The value of "k" can also be calculated after obtaining the orders of reaction.

EXAMPLE: ORDER OF REACTION

For a reaction between F_2 and ClO_2, reaction rate data was collected as given in the table below. Calculate the order of reaction.

Experiment	$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

- Find order (exponents) by comparing data Exp. 1 and 2: $[F_2]$ is held constant

$$\frac{[ClO_2]_2}{[ClO_2]_1} = \frac{0.040\ M}{0.010\ M} = 4 \qquad \frac{[rate]_2}{[rate]_1} = \frac{4.8 \times 10^{-3}\ M/s}{1.2 \times 10^{-3}\ M/s} = 4$$

Rate increases 4 times when conc. increases by a factor of 4 – 1st order with respect to ClO_2.

- Find order (exponents) by comparing data Exp. 1 and 3: $[ClO_2]$ is held constant

$$\frac{[F_2]_3}{[F_2]_1} = \frac{0.20\ M}{0.10\ M} = 2 \qquad \frac{[rate]_3}{[rate]_1} = \frac{2.4 \times 10^{-3}\ M/s}{1.2 \times 10^{-3}\ M/s} = 2$$

Rate increases 2 times when conc. increases by a factor of 2 – 1st order with respect to F_2.

- **Rate = $k[F_2]^1[ClO_2]^1$ overall order = 2**

- k = Rate/$[F_2]^1[ClO_2]^1$ = 1.2 x 10^{-3} /(0.1)(0.01) = **1.2 M^{-1}s^{-1}**

EXAMPLE: ORDER OF REACTION

- Lets do this one without detailed calculations.

Exp	[A]	[B]	Initial Rate (M/s)
1	0.10	0.015	2.1×10^{-4}
2	0.20	0.015	4.2×10^{-4}
3	0.10	0.030	8.4×10^{-2}

- In experiment 1 and 2; [B] is constant; [A] doubles and rate doubles - the reaction is 1st order with respect to [A]

- In experiment 1 and 3; [A] is constant; [B] doubles but the rate quadruples! This means that the reaction is 2nd order with respect to [B]

- Rate = k[A] [B]^2

$$k = \frac{[\text{rate}]}{[\text{A}][\text{B}]^2} = \frac{2.1 \times 10^{-4}\ M/\text{s}}{(0.10\ \text{M})\ (0.015\ M)^2} = 9.3\ M^{-2} \bullet \text{s}^{-1}$$

UNITS OF RATE CONSTANT

Note that the units on the rate constant are specific to the overall order of the reaction.

- For a zero-order reaction, the unit is M/s or mol/(L·s).

- For a first-order reaction, the unit is 1/s or s^{-1}.

- For a second-order reaction, the unit is 1/(M·s) or L/(mol·s).

If you know the rate constant, you can deduce the overall rate of reaction

DEPENDENCE OF REACTANT CONC. OVER TIME

- 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.

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

EXAMPLE: 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?

Solution:

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)

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

(Note: ln is natural log)

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

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

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

$$[A]_t = 6.1 \times 10^{-4}\,M$$

HALF LIFE OF REACTION

- Half life, $t_{\frac{1}{2}}$, 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 $t = t_{\frac{1}{2}}$.

Order	Rate Law	Integrated Rate Law	Half-Life
0	$\text{Rate} = k$	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$
1	$\text{Rate} = k[A]$	$\ln\dfrac{[A]_t}{[A]_0} = -kt$	$0.693/k$
2	$\text{Rate} = k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$1/(k[A]_0)$

EXAMPLE: HALF LIFE

Ammonium nitrite is unstable because ammonium ion reacts with nitrite ion to produce nitrogen: $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$. 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?

Solution:

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

For first-order reactions: $kt_{½} = 0.693$

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

$$t_{½} = 2.3 \times 10^2 \text{ s} = 3.9 \text{ min}$$

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.
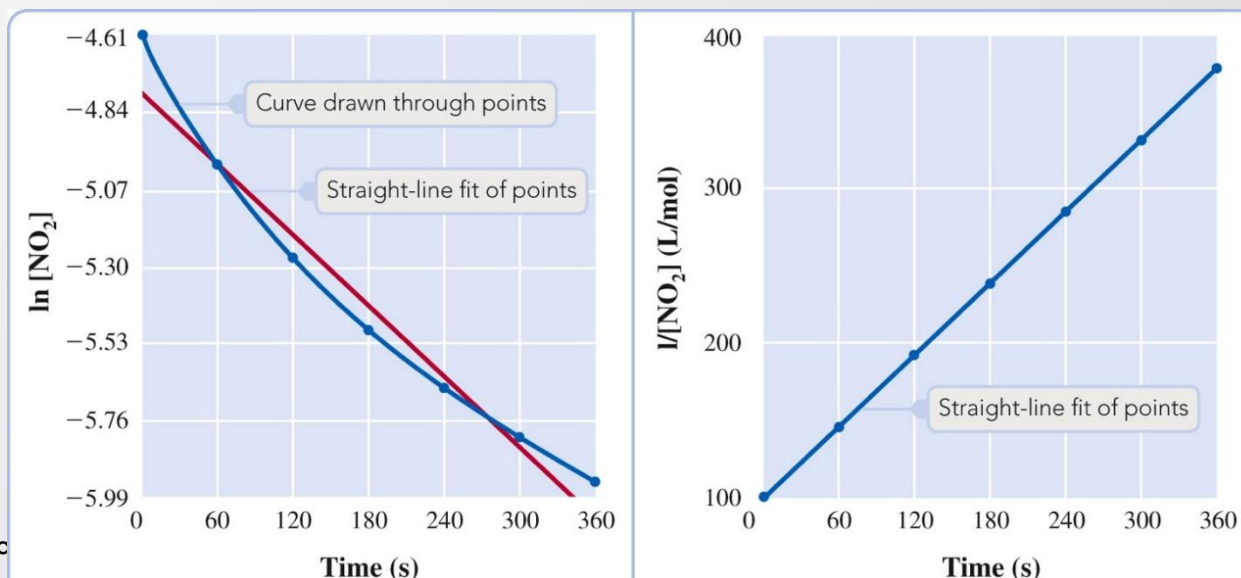
MORE ON GRAPHING

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

Table 13.2	Relationships for Zero-Order, First-Order, and Second-Order Reactions			
Order	Rate Law	Integrated Rate Law	Half-Life	Straight-Line Plot
0	$Rate = k$	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$	$[A]$ vs t
1	$Rate = k[A]$	$\ln\dfrac{[A]_t}{[A]_0} = -kt$	$0.693/k$	$\ln[A]$ vs t
2	$Rate = k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$1/(k[A]_0)$	$\dfrac{1}{[A]}$ vs t

The y-intercept is $[A]_0$.

The graph crosses the origin (0).

The y-intercept is $1/[A]_0$.

EXAMPLE: CALCULATING CONC. 1

The rate constant for the reaction $2A \rightarrow B$ is 7.5×10^{-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?

Solution:

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

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

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

EXAMPLE: CALCULATING CONC. 2

The following reaction is second order and has a rate constant of 7.0×10^9 M^{-1} s^{-1} at 23°C: $I(g) + I(g) \rightarrow I_2(g)$.

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

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

Solution:

a)   Using 2nd order rate eq.

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

$$\frac{1}{[A]} = (7.0 \times 10^9 \ M^{-1} s^{-1}) \ 120s + \frac{1}{[0.086 \ M]}$$

$$= 8.4 \times 10^{11} \ M^{-1}$$

$$[A] = \frac{1}{8.4 \times 10^{11} \ M^{-1}} = 1.2 \times 10^{-12} \ M$$

b)   Use the half-life eq.

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

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

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

KEY CONCEPTS

- Calculate order of reactions

- Calculating concentrations of reactants/products at different times

- Calculating half life
  - Here are ALL the formulas:

Order	Rate Law	Integrated Rate Law	Half-Life	Straight-Line Plot
0	Rate = k	$[A]_t = -kt + [A]_0$	$\dfrac{[A]_0}{2k}$	$[A]$ vs t
1	Rate = $k[A]$	$\ln\dfrac{[A]_t}{[A]_0} = -kt$	$0.693/k$	$\ln[A]$ vs t
2	Rate = $k[A]^2$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$1/(k[A]_0)$	$\dfrac{1}{[A]}$ vs t