

CH 117 - Kinetics Notes

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Kinetics

- Kinetics tells how quickly a reaction occurs, which equals the rate.
- Thermodynamics tells whether a reaction will occur or not.
- The order is determined experimentally; can't use the balanced equation to find the exponents.

Rate Law

Methods

1. Initial Rate
 - Depends on initial concentration of reactants and products
 - Determine rate at beginning of reaction
2. Integrated Rate Law
 - Concentration vs. Time
 - Only study one reactant at a time

Order

- Use units for rate constant (k)

Zero order = M/s

First order = s⁻¹

Second order = M⁻¹s⁻¹

Third order = M⁻²s⁻¹

Steps

- 1) Observe Data Table
- 2) Determine Order
- 3) Use Order to Get Integrated Rate Law
- 4) Using the table below determine the rate law and calculate the rate constant.

Trial	[A]	[B]	Initial Rate
1	0.20M	0.20M	0.4 M/min
2	0.20M	0.40M	1.6 M/min
3	0.40M	0.20M	0.8 M/min

$$\text{rate} = k[A][B]^2$$

$$1.6 = k[0.2][0.4]^2$$

$$1.6 = k(0.2)(1.6)$$

$$1.6 = k(0.32)$$

$$k = \frac{0.16}{0.32} = \frac{1}{2} \text{ M}^{-2} \text{ s}^{-1}$$

3rd Order

- 2) Find the rate law expression for the following reaction, then solve for the rate constant (use appropriate units).

THE RATE LAW EXPRESSION

The word **rate** should be read as rate of reaction.

Commonly has units of M/s

Order (the exponents)

- Commonly 0, 1, or 2 (but can be negative or fractions)
- Sum is the "overall order"
- Determined experimentally

$\text{rate} = k[A]^x[B]^y$

The rate constant

- For a specific reaction
- Varies with temperature
- Presence of a catalyst changes value

The brackets indicate molar concentration (M).

INTEGRATED RATE LAW EQUATIONS

Order	Rate equals	Integrated rate law*	Straight-line plot	Slope of plot
0	$k[A]^0 = k$	$[A]_t = -kt + [A]_0$	$[A]_t$ vs t	$-k$
1	$k[A]$	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]_t$ vs t	$-k$
2	$k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]_t}$ vs t	k

*In the table, $[A]_0$ indicates the initial concentration of substance A, that is, the concentration of A at $t = 0$, the time when the reaction begins.

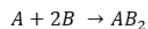
Zero-order reaction

First-order reaction

Second-order reaction

To find order of each substance

- 1) Find A or B
- 2) Find trials that are the same for substance that we are not reviewing
- 3) Find how substance and initial rate changes (does it double, quadruple, etc?)
- 4) Set up and equation



Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	.05	.13	2.2×10^{-4}
2	.06	.19	2.2×10^{-4}
3	.05	.26	8.7×10^{-4}
4	.12	.19	4.4×10^{-4}

- Write out the rate law equation: $\text{rate} = k [A]^x [B]^y$
- Solve for the order of [A] by keeping the [B] constant or the same
 - Pick trials 2 and 4 because the [B] is the same
 - Since [A] goes up by a factor of 2^x and the initial rate doubles $\times 2$
 - Set the factors equal to each other so: $2^x = 2$ and solve for x which will be one
 - So now, $\text{rate} = k [A]^1 [B]^y$ which is formally written as $\text{rate} = k [A][B]^y$
- Solve for the order of [B] by keeping the [A] constant or the same
 - Pick trials 1 and 3 because the [A] is the same
 - Since [B] goes up by a factor of 2^y and the initial rate quadruples $\times 4$
 - Set the factors equal to each other so: $2^y = 4$ and solve for Y which will be two
 - So now, $\text{rate} = k [A]^1 [B]^2$ which is formally written as **$\text{rate} = k [A][B]^2$**

Now we can plug and chug some numbers, so pick any trial (I will do trial 1)

$$2.2E-4 \text{ M/s} = k[0.05][0.13]^2$$

$$2.2E-4 \text{ M/s} = k [0.05] [0.0169]$$

$$\frac{2.2E-4 \text{ M/s}}{[0.05][0.0169]} = k$$

- 3) Find the units on the rate constant for the following rate law expression.

$$\text{Rate} = k[A]^2[B]^2$$

Handwritten:

$$= 4^{\text{th}} \text{ Order}$$

$$2(\text{order of A}) + 2(\text{order of B})$$

$$\text{Answer} = M^{-3} s^{-1}$$