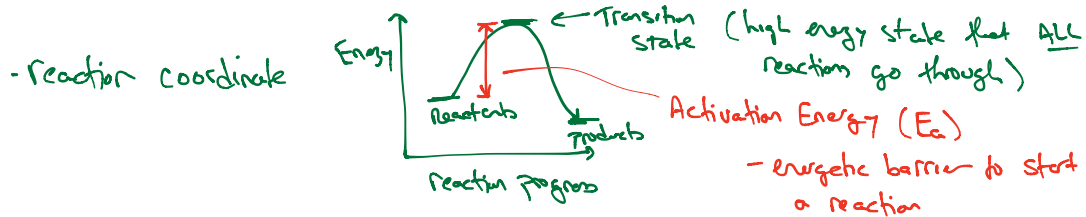


- Recall:
- Kinetics is the study of reaction rates
 - Reaction MAY occur when reactants collide
 - All reactions must overcome an energy barrier before products can form



- the larger the E_a , the slower a reaction

- predicted by the Arrhenius Equation:

$R \rightarrow$ gas constant (with different units)
 8.314 J/mol K

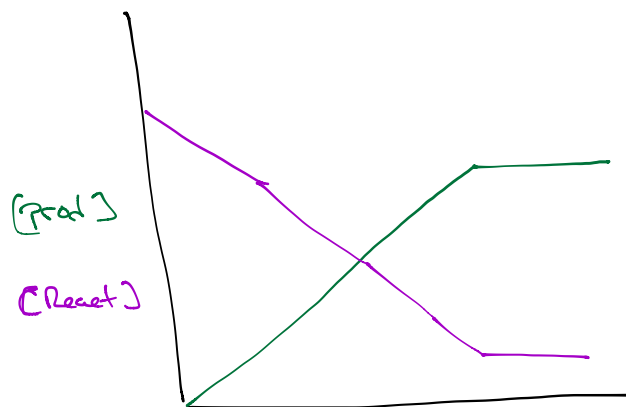
$$k = A e^{-E_a/RT}$$

rate constant (bigger = faster reaction)

Arrhenius constant (Ignore for this class)

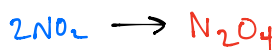
- reaction rate increases with rate constant (rate $\propto k$)
- k can \uparrow if Temp increases or E_a decreases

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

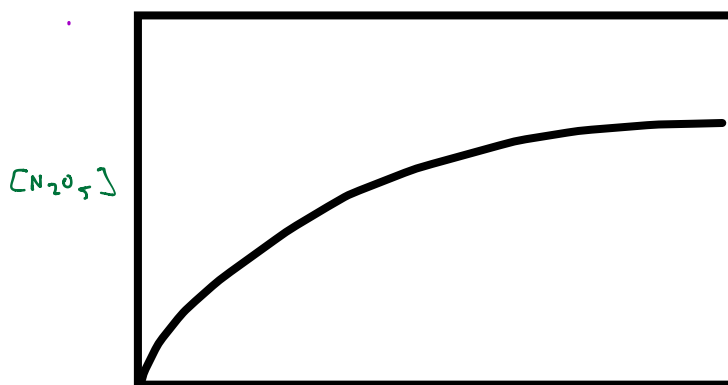


Kinetics is the study of reaction RATES.

For a chemical reaction:



The reaction rate = $\frac{\Delta \text{concentration}}{\Delta \text{time}} = \frac{\Delta [\text{N}_2\text{O}_4]}{\Delta t} = -\frac{1}{2} \frac{\Delta [\text{NO}_2]}{\Delta t}$



Experimental data:

time	$[\text{N}_2\text{O}_5]$	$[\text{NO}_2]$	$[\text{O}_2]$ (all in 10^{-2} M)
0	1.24	0	0
10	0.92	0.64	0.16
20	0.68	1.12	0.28
30	0.5	1.48	0.37
40	0.37	1.74	0.44
50	0.28	1.92	0.48
100	0.06	2.36	0.59

Calculate the average reaction rate
 I choose to do this with O_2 because there is not a fraction or (-) to consider

$$\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{0.59 \text{ M} - 0 \text{ M}}{100 \text{ min} - 0 \text{ min}} = 5.9 \times 10^{-3} \frac{\text{M}}{\text{min}}$$

Calculate the reaction rate @ its fastest point.
 this would be when $[\text{N}_2\text{O}_5]$ is maximal!

$$\text{rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{0.16 \text{ M} - 0 \text{ M}}{10 \text{ min} - 0 \text{ min}} = 1.6 \times 10^{-2} \frac{\text{M}}{\text{min}}$$

The rate law predicts the slope @ ALL times

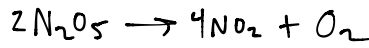
$$\text{rate} = k [\text{NO}_2]^x$$

rate constant order

(order)

We can figure out the coefficient using the Method of Initial Rates. Basically, we simply measure the rate @ $t=0$ for a variety of reactant concentrations

$[N_2O_5]_0$ (M)	V_0 (M hr^{-1}) <small>initial rate</small>
0.01	0.018
0.02	0.036
0.04	0.072



$$\text{rate} = k[N_2O_5]^x$$

$$\frac{\text{rate}_2 = k[N_2O_5]_2^x}{\text{rate}_1 = k[N_2O_5]_1^x} = \frac{0.02 = k(0.036)^x}{0.01 = k(0.018)^x}$$

We can now calculate k for the reaction!

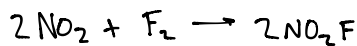
$$0.018 \frac{M}{hr} = k(0.01M)^1$$

$$k = 1.8 \text{ hr}^{-1}$$

$$2 = 2^x$$

$$x = 1$$

1st order with respect to N_2O_5



$$\text{rate} = k[NO_2]^x [F_2]^y$$

	$[NO_2]_0$ (M)	$[F_2]_0$ (M)	V_0 (M s^{-1})
①	1.00	1.00	1.00×10^{-4}
②	2.00	1.00	2.00×10^{-4}
③	1.00	2.00	2.00×10^{-4}
④	2.00	2.00	4.00×10^{-4}

The experiment is set up so that

① vs. ② } allows us to determine x
 ③ vs. ④ }
 ① vs. ③ } allows determination of y
 ② vs. ④ } or

$$\frac{\text{①}}{\text{②}} \quad \frac{1.00 \times 10^{-4}}{2.00 \times 10^{-4}} = \frac{k}{k} \cdot \frac{(1.00)^x}{(2.00)^x} \cdot \frac{(1.00)^y}{(1.00)^y} \quad \frac{1}{2} = \left(\frac{1}{2}\right)^x \quad x=1$$

$$\frac{\text{①}}{\text{③}} \quad \frac{1.00 \times 10^{-4}}{2.00 \times 10^{-4}} = \frac{k}{k} \cdot \frac{(1.00)^x}{(1.00)^x} \cdot \frac{(1.00)^y}{(2.00)^y} \quad \frac{1}{2} = \left(\frac{1}{2}\right)^y \quad y=1$$

$$k \Rightarrow 1.00 \times 10^{-4} \text{ M s}^{-1} = k (1.00 \text{ M}) (1.00 \text{ M}) \quad k = 1.00 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

Rate Law: $\text{rate} = k [NO_2][F_2]$

Overall order = sum of individual
overall = $1+1 = 2$

So k must have the units of a 2nd order reaction ($M^{-1}s^{-1}$)

Let's look at 1 more:

	$[NO]_0$	$[Br_2]_0$	rate $M \text{ min}^{-1}$
①	1.00	1.00	1.30×10^{-3}
②	1.50	1.00	2.93×10^{-3}
③	1.50	3.00	8.78×10^{-3}

$$\frac{1.3 \times 10^{-3}}{2.93 \times 10^{-3}} = \frac{k}{k} \cdot \frac{(1)^x}{(1.5)^x} \cdot \frac{(1)^y}{(1)^y}$$

$$0.444 = (0.667)^x$$

Rules of log functions let us do this! $\rightarrow \log 0.444 = x \log 0.667$

$$x = 2.00$$

$$\text{rate} = k [NO]^2 [Br_2]^1$$

3rd order

units of k : $M \text{ min}^{-1} = k (M)^2 (M)$

$$k = M^{-2} \text{ min}^{-1}$$

$$1.3 \times 10^{-3} M \text{ min}^{-1} = k (1M)^2 (1M)$$

$$k = 1.3 \times 10^{-3} M^{-2} \text{ min}^{-1}$$

$$\frac{2.93}{8.78} = \frac{k}{k} \cdot \frac{(1.5)^x}{1.5^x} \cdot \frac{(1.00)^y}{(3.00)^y}$$

$$0.333 = \left(\frac{1}{3}\right)^y \quad y = 1.00$$

This approach ALWAYS works! However, sometimes it is not particularly convenient. An alternate approach is to use integrated rate laws. These are incredibly useful because they let you quickly calculate concentrations as time passes.

0th order $[A] = -kt + [A]_0$

plotting $[A]$ vs $t \rightarrow$ y-int = $[A]_0$
slope = $-k$

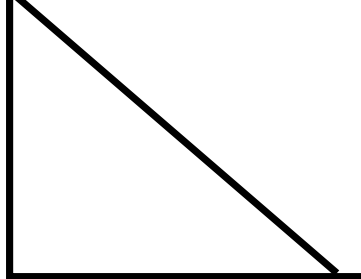
1st order $\ln[A] = -kt + \ln[A]_0$

$\ln[A]$ vs $t \rightarrow$ y-int = $\ln[A]_0$
slope = $-k$

2nd order $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

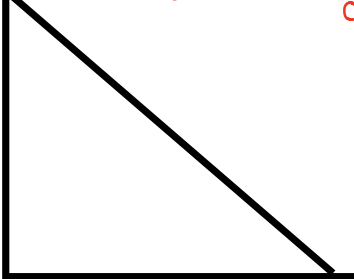
$\frac{1}{[A]}$ vs. $t \rightarrow$ y-int = $\frac{1}{[A]_0}$
slope = k

0th order
 $[A]$



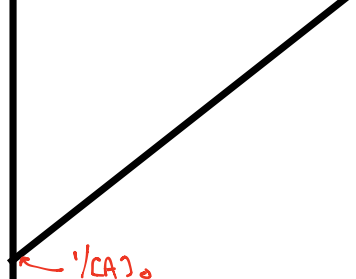
time

1st order
 $\ln[A]$



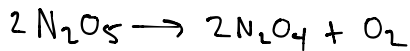
time

2nd order
 $\frac{1}{[A]}$



time

Using the rate laws:



$$\text{rate} = 11.0 \text{ s}^{-1} [\text{N}_2\text{O}_5]$$

If a reaction vessel starts with 0.200 M N_2O_5 , what is the concentration of all reactants and products after 1 seconds?

1st order

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

$$\ln[\text{N}_2\text{O}_5] = -11 \text{ s}^{-1} (1 \text{ s}) + \ln 0.2 \text{ M}$$

$$\ln[\text{N}_2\text{O}_5] = -12.61$$

$$[\text{N}_2\text{O}_5] = 3.34 \times 10^{-6} \text{ M}$$

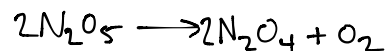
Determine: $\text{rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$ to figure out how much $\text{N}_2\text{O}_4 + \text{O}_2$ were produced!

$$-\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = -\frac{1}{2} \frac{[\text{N}_2\text{O}_5]_{\text{final}} - [\text{N}_2\text{O}_5]_{\text{initial}}}{11 \text{ seconds}} = -\frac{1}{2} \left(\frac{3.34 \times 10^{-6} \text{ M} - 0.2 \text{ M}}{11} \right) = \frac{9.09 \times 10^{-3} \text{ M}}{\text{s}}$$

$$\frac{9.09 \times 10^{-3} \text{ M}}{\text{s}} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_4]}{\Delta t} = \frac{1}{2} \left(\frac{[\text{N}_2\text{O}_4] - 0}{11 \text{ sec}} \right) \quad [\text{N}_2\text{O}_4] = 0.1999 \text{ M}$$

$$\frac{9.09 \times 10^{-3} \text{ M}}{\text{s}} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2] - 0}{11 \text{ sec}} \quad [\text{O}_2] = 0.0999 \text{ M}$$

Using the information below, determine the order of the decomposition reaction AND calculate the rate constant.



$$r = k [\text{N}_2\text{O}_5]^?$$

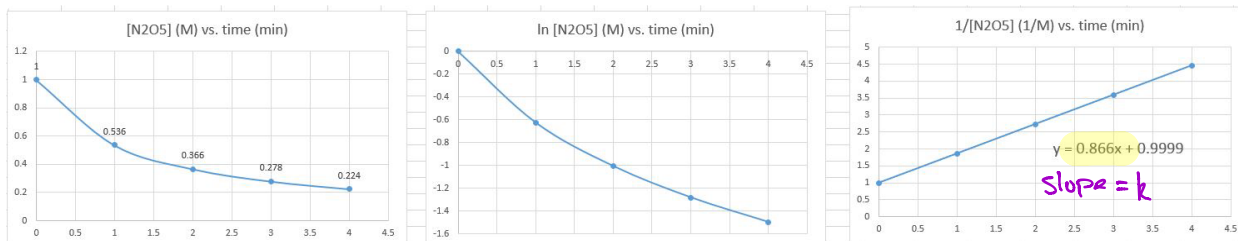
Time (minutes)	$[\text{N}_2\text{O}_5]$ (M)
0	1
1	0.536
2	0.366
3	0.278
4	0.224

This info can tell you the reaction order!

Use Excel (or another spreadsheet program). Plot each of the following:

$[\text{N}_2\text{O}_5]$ vs t $\ln[\text{N}_2\text{O}_5]$ vs t $\frac{1}{[\text{N}_2\text{O}_5]}$ vs t

The straight line = correct order!



$k = 0.866 \text{ M}^{-1} \text{ min}^{-1}$
 units of 2nd order rate constant

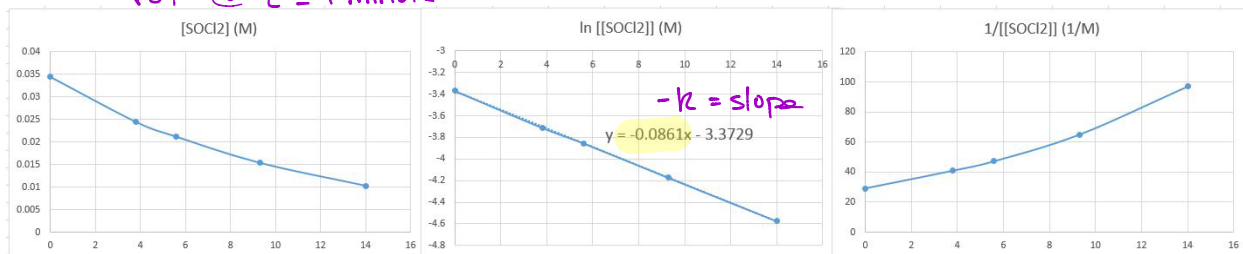
Rate = $0.866 \text{ M}^{-1} \text{ min}^{-1} [\text{N}_2\text{O}_5]^2$
 this is the rate law!



Determine:

- k
- rate law
- initial rate
- $[\text{SO}_2\text{Cl}_2]$ @ $t = 1 \text{ minute}$
- rate @ $t = 1 \text{ minute}$

time (sec)	$[\text{SO}_2\text{Cl}_2]$ (M)
0	0.0345
3.8	0.0245
5.6	0.0212
9.3	0.0154
14	0.0103



1st order Integrated rate law: $\ln[A] = -kt + \ln[A]_0$
 $-k = \text{slope}$

$k = 0.0861 \text{ s}^{-1}$

1st order, so time⁻¹ → seconds because time is in seconds!

rate law: $\text{rate} = 0.0861 \text{ s}^{-1} [\text{SO}_2\text{Cl}_2]$

Initial rate: $\text{rate} = 0.0861 \text{ s}^{-1} (0.0345 \text{ M}) = 2.97 \times 10^{-3} \frac{\text{M}}{\text{s}}$

$[\text{SO}_2\text{Cl}_2]$ @ $t = 1 \text{ min} = 60 \text{ seconds}$ → use integrated rate law!

$\ln [\text{SO}_2\text{Cl}_2] = -0.0861 \text{ s}^{-1} (60 \text{ s}) + \ln 0.0345 \text{ M}$

$\ln [\text{SO}_2\text{Cl}_2] = -8.533 \text{ M}$ $[\text{SO}_2\text{Cl}_2] = 1.969 \times 10^{-4} \text{ M}$

rate @ $t = 60 \text{ sec}$

$$\text{rate} = 0.0861 \text{ s}^{-1} [\text{SO}_2\text{Cl}_2] = 0.0861 \text{ s}^{-1} (1.969 \times 10^{-4} \text{ M})$$

$$\text{rate} = 1.695 \times 10^{-5} \frac{\text{M}}{\text{s}}$$