

Chemical Kinetics

- Studies rate at which a reaction occurs (how fast)

- Also sheds light on reaction mechanism (steps in how the reaction occurs)



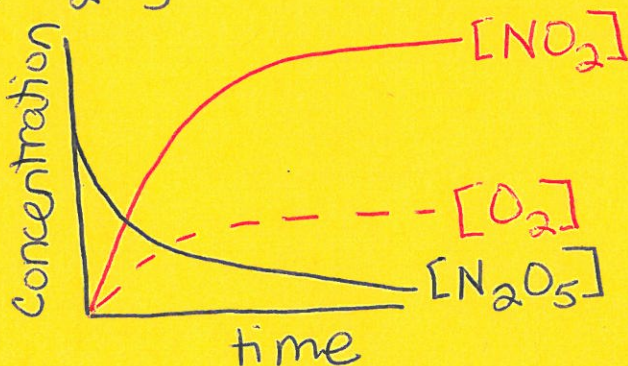
$$\text{rate} = \frac{-\Delta[A]}{a \Delta t} = \frac{-\Delta[B]}{b \Delta t} = \frac{\Delta[C]}{c \Delta t} = \frac{\Delta[D]}{d \Delta t}$$

brackets = molarity

⊖ because reactants are disappearing

⊕ because products are appearing

- expresses how concentration of a reactant/product changes over time



- As the reaction proceeds the rate will decrease as the N_2O_5 concentration decreases

$$\text{rate} = -\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Factors Affecting Reaction Rates: (2)

- Concentration of reactants
- Physical state of reactants (solid, liquid, gas, particle size, etc.)
- Temperature
- Presence of a catalyst

Rate law - an expression showing dependence of the reaction rate on concentration of each reactant



Forward rxn: $\text{rate} = k[A]^m[B]^n$

k = rate constant (for given rxn. at given temp)

m, n, \dots = reaction order

(determined experimentally, not ~~from~~ the coefficient from balanced equation)

ex.

$$\text{rate} = k[\text{Br}_2]^1[\text{HCOOH}]^0 = k[\text{Br}_2]$$

first order in $[\text{Br}_2]$

zeroeth order in $[\text{HCOOH}]$

- sum of exponents equals overall rxn. order, so first order overall

\therefore rate is independent of the concentration of $[\text{HCOOH}]$

ex. Decolorization of a Dye

$$\text{rate} = k[\text{dye}]^n$$

Order of a rxn. for a single reactant (3)

<u>[dye]</u>	<u>n=0 rates</u>	<u>n=1 rates</u>	<u>n=2 rates</u>
0.100M	$3.4 \times 10^3 \frac{\text{M}}{\text{s}}$	$\left[\begin{array}{l} 340 \frac{\text{M}}{\text{s}} \\ 680 \frac{\text{M}}{\text{s}} \\ 1020 \frac{\text{M}}{\text{s}} \end{array} \right] \times 3$	$\left[\begin{array}{l} 34 \frac{\text{M}}{\text{s}} \\ 136 \frac{\text{M}}{\text{s}} \\ 306 \frac{\text{M}}{\text{s}} \end{array} \right] \times 9$
0.200M	$3.4 \times 10^3 \frac{\text{M}}{\text{s}}$		
0.300M	$3.4 \times 10^3 \frac{\text{M}}{\text{s}}$		

For $n=0$, the rate does not change as concentration increases.

For $n=1$, doubling the concentration doubles the rate and tripling the concentration triples the rate.

For $n=2$, ~~rate~~ doubling concentration quadruples rate (2^2) and tripling concentration increases rate by a factor of 9 (3^2)

ex. $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$

<u>[CH₃CHO]</u>	<u>rate (mol/L·s)</u>
0.20M	.34
0.30M	.76

Determine order:

$$\frac{\text{rate 2}}{\text{rate 1}} = \left(\frac{[\text{A}_2]}{[\text{A}_1]} \right)^m$$

$$\frac{.76}{.34} = \left(\frac{.3}{.2} \right)^m$$

$$2.2 = 1.5^m$$

$$\frac{\log 2.2}{\log 1.5} = m$$

$m = 2$

ex.



Find rxn. order:

(4)

choose 2 data sets

[A]	rate $\frac{M}{min}$
.10	.20
.20	.56
.30	1.04
.40	1.60

$$\frac{rate_2}{rate_1} = \left(\frac{[A_2]}{[A_1]} \right)^m$$

$$\frac{0.56}{0.20} = \frac{0.20^m}{0.10^m}$$

$$m = 1.5$$

Calculate the rate constant:

rate expression: $rate = k[A]^{1.5}$

$$1.60 = k[0.40]^{1.5}$$

$$k = \frac{1.60 \frac{mol}{L \cdot min}}{(0.40 \frac{mol}{L})^{1.5}} = \frac{6.3}{min}$$

Find the rate of the rxn. if $[A] = 0.50M$.

$$rate = k[A]^{1.5}$$

$$= \left(\frac{6.3}{min} \right) (0.50M)^{1.5} = \frac{2.2M}{min}$$

ex. Decomposition of ozone:

rate = $kP_{O_3}^n$	P_{O_3}	Initial rate
	0.44 atm	0.01848 atm/min
	0.88 atm	0.03696 atm/min

Determine order of rxn:

1st order (P_{O_3} doubles, rate doubles)

Calculate k: $\frac{0.01848 \text{ atm}}{min} = k(0.44 \text{ atm})$

$$k = \frac{0.042}{min}$$

$$rate = \frac{0.042}{min} P_{O_3}^1$$

ex. rate = k[KI]ⁿ

[KI]

initial rate

x3 [0.10M
0.30M]

[8.4 x 10⁻⁶ M/s
7.6 x 10⁻⁵ M/s] x 9

Determine order:

2nd order, concentration tripled and rate changed by a factor of 9

rate 2 / rate 1 = ([A₂] / [A₁])^m

7.6 x 10⁻⁵ / 8.4 x 10⁻⁶ = 3 / 0.1^m

9 = 3^m

m = 2

Calculate k:

rate = k[KI]^m

8.4 x 10⁻⁶ M/s = k(0.10M)²

k = 8.4 x 10⁻⁴ / M²s

Units = same change flip
M/s x 1/M² = 1/Ms

ex. rate = k[H₂O₂]ⁿ

[H₂O₂]

initial rate

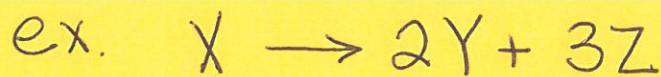
0.20M
0.56M

382 M/s
382 M/s

Changing [H₂O₂] did not change the rate, so rxn. order = 0

rate = k[H₂O₂]⁰

k = 382M / s



$[X]$	rate M/s
0.10	0.30
0.20	0.42
0.30	0.52
0.40	0.60

Find order of rxn:

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{[A_2]^m}{[A_1]^m}$$

$$\frac{0.42}{0.3} = \frac{0.2}{0.1}$$

$$1.4 = 2^m$$

$$m = 0.5$$

Write the rate expression:

$$\text{rate} = k[X]^{0.5}$$

Calculate k:

$$0.3 = k[0.1]^{0.5}$$

$$k = \frac{0.95}{0.316}$$

~~$$k = \frac{0.95}{0.316} \frac{M}{M}$$~~

What is the initial concentration if the rate is $0.90 \frac{\text{mol}}{\text{L}\cdot\text{s}}$?

$$\frac{0.90}{0.95} = \frac{0.95}{0.95} [X]^{0.5}$$

$$0.95 = X^{0.5}$$

$$(0.95)^{1.5} = (X^{0.5})^{1.5}$$

$$0.90M = X$$

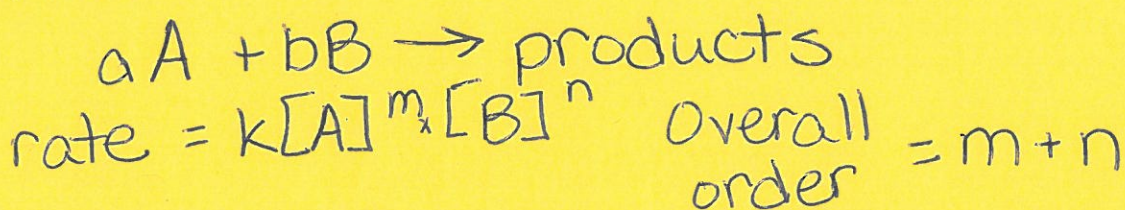
$$[X^{1/2}]^2 = (2)^2$$

$$X = 2$$

Order of Reaction w/ 2 or More Reactants

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- Order of rxn. must be determined with respect to each reactant
- Choose data where only the concentration of the reactant in question is changing and the other reactant has the concentration held constant



ex.

Expt.	[A] M	[B] M	Rate (mol/L·s)
1	0.200	0.200	2.5×10^{-3}
2	0.400	0.200	1.0×10^{-2}
3	0.400	0.400	1.0×10^{-2}

Find order with respect to A and B.

For A: $\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[A_2]}{[A_1]}\right)^m$

$$\frac{1.0 \times 10^{-2}}{2.5 \times 10^{-3}} = \left(\frac{0.400}{0.200}\right)^m$$
$$4 = 2^m \quad m=2 \quad \text{2nd order in A}$$

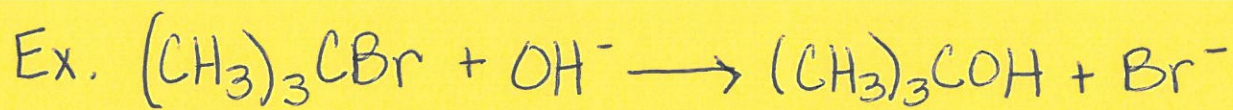
For B: doubling concentration has no effect on rate rate, so zero order in B

$$\frac{1.0 \times 10^{-2}}{1.0 \times 10^{-2}} = \left(\frac{0.400}{0.200}\right)^n$$

$$1 = 2^n$$
$$n=0$$

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

2nd order overall



Expt.	$[(\text{CH}_3)_3\text{CBr}]$	$[\text{OH}^-]$	Rate
1	0.5	0.05	0.005
2	1	0.05	0.01
3	1.5	0.05	0.015
4	1	0.1	0.01
5	1	0.2	0.01

forgot rate unit

Order $(\text{CH}_3)_3\text{CBr}$: expt. 1 & 3 b/c OH^- constant

$$\frac{0.015}{0.005} = \left(\frac{1.5}{0.5}\right)^m$$

$$3 = 3^m$$

$$m = 1$$

Order OH^- : expt. 2 & 5 where $(\text{CH}_3)_3\text{CBr}$ constant

$$\frac{0.01}{0.01} = \left(\frac{0.2}{0.05}\right)^n$$

$$1 = 4^n$$

$$n = 0$$

rate = $k[(\text{CH}_3)_3\text{CBr}]^1$
first order overall



Expt.	$[\text{A}] \text{ M}$	$[\text{B}] \text{ M}$	Rate $\left(\frac{\text{mol}}{\text{L}\cdot\text{s}}\right)$
1	0.100	0.100	0.040
2	0.100	0.200	0.160
3	0.200	0.200	0.320

Order A: $\frac{0.32}{0.16} = \left(\frac{0.2}{0.1}\right)^m$

$$2 = 2^m$$

$$m = 1$$

Order B: $\frac{0.16}{0.04} = \left(\frac{0.2}{0.1}\right)^n$

$$4 = 2^n$$

$$n = 2$$

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

3rd order overall

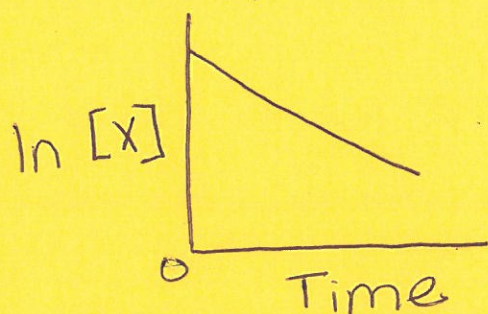
Reaction Concentration and Time

• Concentration of reactant decreases as rxn. proceeds; the concentration is a function of time

• First order Rxn: $X \rightarrow \text{Products}$

$$\text{Rate} = -\frac{\Delta[X]}{\Delta t} = k[X]^1$$

Rearrange and integrate to show a linear relationship:



$$k = \text{slope}$$
$$b = \ln[X_0]$$

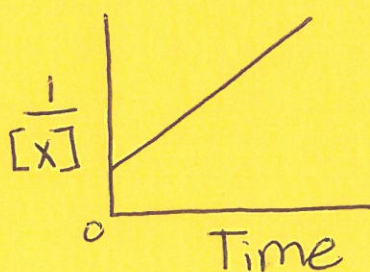
$$\ln[X] = -kt + \ln[X_0]$$

• Second order rxn:

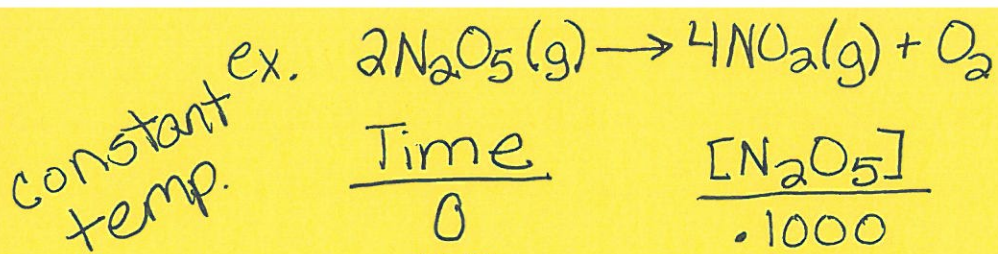
$$\text{Rate} = -\frac{\Delta[X]}{\Delta t} = k[X]^2$$

Rearrange and integrate to show a linear relationship:

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



$$k = \text{slope}$$
$$b = \frac{1}{[X]_0}$$



Time	$[\text{N}_2\text{O}_5]$
0	.1000
50	.0707
100	.0500
200	.0250
400	.00625

First order -
a plot of
 $\ln[\text{N}_2\text{O}_5]$ vs. time
is linear

a) Calculate rate constant

$$\ln[R] = -kt + \ln[R_0]$$

$$k = -\frac{1}{t} \ln\left(\frac{[R]}{[R_0]}\right)$$

$$k = \frac{1}{400.5} \ln\left(\frac{.00625\text{M}}{.1000\text{M}}\right) = \underline{.00693}$$

b) What is the concentration of N_2O_5 at $t = 10.0\text{s}$?

$$\ln[R] = -\left(\frac{0.0693}{\text{s}}\right)(10.0\text{s}) + \ln(.1000)$$

$$\ln[R] = -2.37$$

$$[R] = e^{-2.37} = 0.0933\text{M}$$

ex. $\text{CH}_3\text{NC}(\text{g}) \rightleftharpoons \text{CH}_3\text{CN}(\text{g})$ isomerization =
The concentration of CH_3NC is 85.0% of
its original value after 247s. new molecular arrangement

a) What is the rate constant? \star first order

$$k = -\frac{1}{t} \ln\left(\frac{[R]}{[R_0]}\right) = -\frac{1}{247\text{s}} \ln\left(\frac{85.0}{100}\right)$$

$$k = 6.58 \times 10^{-4} \text{s}^{-1}$$

b) At what time (in min.) will the concentration of CH_3NC be 25.0% of its original value?

$$t = -\frac{1}{k} \ln\left(\frac{[R]}{[R_0]}\right) = -\left(\frac{1}{6.58 \times 10^{-4}\text{s}}\right) \ln\left(\frac{25.0}{100}\right) = 2106.9\text{s}$$

$$2106.9\text{s} \times \frac{1\text{min}}{60\text{s}} = 35.1\text{min}$$

ex.

	$[N_2]$	$[H_2]$	Rate M/s
Trial 1	$4.3 \times 10^{-3} M$	$2.2 \times 10^{-4} M$	$9.6 \times 10^{-6} M/s$
Trial 2	$4.3 \times 10^{-3} M$	$4.4 \times 10^{-4} M$	$9.6 \times 10^{-6} M/s$
Trial 3	$8.6 \times 10^{-3} M$	$4.4 \times 10^{-4} M$	$1.92 \times 10^{-5} M/s$

Order of rxn. with respect to N_2 :
first order

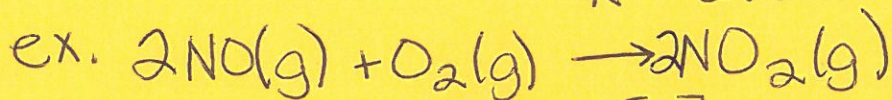
Order of rxn. with respect to H_2 :
zero order

$$\text{rate} = k [N_2] [H_2]^0 \text{ or } \text{rate} = k [N_2]$$

Rate constant:

$$9.60 \times 10^{-6} \frac{M}{s} = k (4.3 \times 10^{-3} M) \quad (1)$$

$$k = 2.2 \times 10^{-3} s^{-1}$$



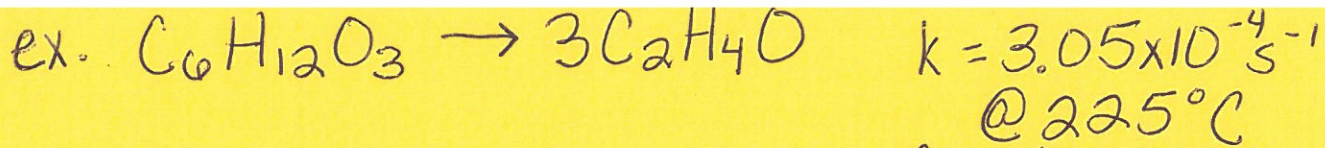
Expt.	$[NO]$	$[O_2]$	Initial rate (M/s)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

Order of rxn. w/ respect to NO : first order
Order of rxn. w/ respect to O_2 : 2nd order

$$\text{rate} = k [NO] [O_2]^2$$

$$2.5 \times 10^{-4} \frac{M}{s} = k (0.10 M) (0.10 M)^2$$

$$k = \frac{0.25}{M^2 s}$$



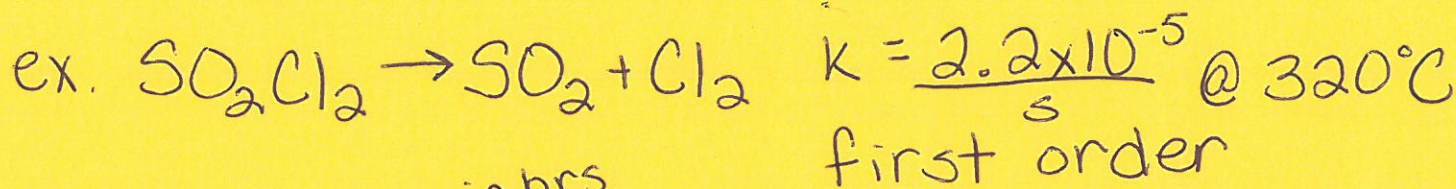
first order
 If we start with a 0.250M $C_6H_{12}O_3$ solution what will its concentration be after 2 min

$$\ln[X] = -kt + \ln[X_0]$$

$$\ln[X] = \left(\frac{3.05 \times 10^{-4}}{s} \right) 120s + \ln[0.250]$$

$$\ln[X] = -1.423$$

$$[X] = e^{-1.423} = \boxed{0.241 M}$$



How long ^{in hrs.} will it take to decompose 20.0% of the SO_2Cl_2 ?

~~$t = \frac{1}{k} \ln \frac{[R]}{[R_0]}$~~

$$t = \frac{1}{k} \ln \frac{[R]}{[R_0]}$$

$$t = \frac{1}{2.2 \times 10^{-5} / s} \ln \frac{[100] \cdot 80}{[80] \cdot 100}$$

$$t = \frac{1}{2.2 \times 10^{-5} / s} \times 0.223$$

$$t = 10136s \times \frac{1 \text{ min}}{60s} \times \frac{1 \text{ hr}}{60 \text{ min}} = \boxed{2.8 \text{ hrs}}$$

$$6 \text{ hrs} = 21,600s$$

After 6 hrs, 0.100M SO_2Cl_2 is left. What was the initial concentration?

$$\ln[X] = -kt + \ln[X_0]$$

$$\ln[0.1M] = \left(-\frac{2.2 \times 10^{-5}}{s} \right) (21,600s) + \ln[X_0]$$

$$\ln[X_0] = -1.8248$$

$$[X_0] = \boxed{0.16M}$$

derive the value of the rate constant k from the slope (m) of the straight-line plot follows:

$$m = (y_2 - y_1)/(x_2 - x_1) = -1.50/410 \text{ s} = -3.66 \times 10^{-3} \text{ s}^{-1}$$

$$k = -(\text{slope}) = -(-3.66 \times 10^{-3} \text{ s}^{-1}) = 3.66 \times 10^{-3} \text{ s}^{-1}$$

Example 13.4 and Exercise 13.4A illustrate two types of calculations that are possible with the integrated rate law for a first-order reaction. Exercise 13.4B applies the integrated rate law in a broader context.

Example 13.4

For the first-order decomposition of $\text{H}_2\text{O}_2(\text{aq})$, given $k = 3.66 \times 10^{-3} \text{ s}^{-1}$ and $[\text{H}_2\text{O}_2]_0 = 0.882 \text{ M}$, determine (a) the time at which $[\text{H}_2\text{O}_2] = 0.600 \text{ M}$ and (b) $[\text{H}_2\text{O}_2]$ after 225 s.

STRATEGY

We must use the *integrated* rate law for this first-order reaction, that is, Equation (13.7). In each part, we know three of the four quantities in the equation and can solve for the fourth. In part (a), two concentrations and the rate constant are known and we solve for the time, t . In part (b), the rate constant and time are known and we solve for the ratio $\ln [A]_t/[A]_0$. We know $[A]_0$, and $[A]_t$ is the final result we seek.

SOLUTION

- (a) Let's evaluate the left side of Equation (13.7), using the two known concentrations and then solve for t .

$$\begin{aligned} \ln \frac{0.600 \text{ M}}{0.882 \text{ M}} &= -3.66 \times 10^{-3} \text{ s}^{-1} \times t \\ \ln 0.680 &= -0.386 = -3.66 \times 10^{-3} \text{ s}^{-1} \times t \\ t &= \frac{-0.386}{-3.66 \times 10^{-3} \text{ s}^{-1}} = 105 \text{ s} \end{aligned}$$

- (b) We now know the quantities k and t on the right side of the integrated rate law and so can solve for the left side.

$$\begin{aligned} \ln \frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} &= -kt \\ &= -\{3.66 \times 10^{-3} \text{ s}^{-1} \times 225 \text{ s}\} \\ &= -0.824 \end{aligned}$$

Next we seek the number whose natural logarithm is -0.824 . This number is equal to the ratio of concentration terms.

$$\frac{[\text{H}_2\text{O}_2]_t}{[\text{H}_2\text{O}_2]_0} = e^{-0.824} = 0.439$$

Finally, we can use the known value of $[\text{H}_2\text{O}_2]_0$ to calculate $[\text{H}_2\text{O}_2]_t$.

$$\begin{aligned} [\text{H}_2\text{O}_2]_t &= 0.439 \times [\text{H}_2\text{O}_2]_0 \\ &= 0.439 \times 0.882 \text{ M} \\ &= 0.387 \text{ M} \end{aligned}$$

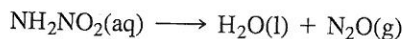
ASSESSMENT

Here is a way to check the answer to part (b): In part (a), we found that it took 105 s for $[\text{H}_2\text{O}_2]$ to fall from 0.882 M to 0.600 M. Suppose we follow the reaction for another 120 s from this point (that is, $105 \text{ s} + 120 \text{ s} = 225 \text{ s}$). When we redo the calculation in part (b) to determine $[\text{H}_2\text{O}_2]_t$ at 120 s with $[\text{H}_2\text{O}_2]_0 = 0.600 \text{ M}$, we get the same answer as previously: 0.387 M.

$$\begin{aligned} \ln[\text{H}_2\text{O}_2]_t/0.600 \text{ M} &= -3.66 \times 10^{-3} \text{ s}^{-1} \times 120 \text{ s} = -0.439 \\ e^{-0.439} &= 0.645 \quad \text{and} \quad [\text{H}_2\text{O}_2]_t = 0.645 \times 0.600 \text{ M} = 0.387 \text{ M} \end{aligned}$$

EXERCISE 13.4A

The decomposition of nitramide, NH_2NO_2 , is a first-order reaction:



The rate law is $\text{rate} = k[\text{NH}_2\text{NO}_2]$, with $k = 5.62 \times 10^{-3} \text{ min}^{-1}$ at 15°C . Starting with 0.105 M NH_2NO_2 , (a) at what time will $[\text{NH}_2\text{NO}_2] = 0.0250 \text{ M}$ and (b) what is $[\text{NH}_2\text{NO}_2]$ after 6.00 h?

EXERCISE 13.4B

Refer to the reaction in Exercise 13.4A. Starting with 0.0750 M NH_2NO_2 , what is the rate of the reaction after 35.0 min? (*Hint:* You will need to use both the rate law and the integrated rate law.)

Half Life ($t_{1/2}$)

• time it takes for the concentration of a single reactant to reach one half its original value

First order: $t_{1/2} = \frac{-1}{k} \ln \frac{1}{2} \frac{[R_0]}{[R_0]} = \frac{0.6931}{k}$

Second order: $t_{1/2} = \frac{1}{k[A_0]}$

ex. Calculate the rate constant:



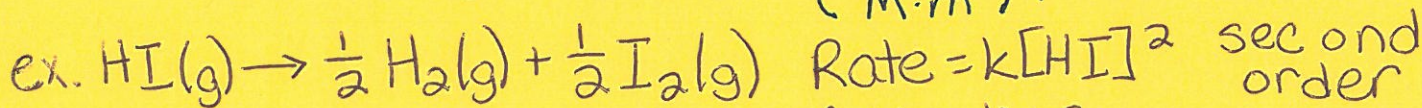
$$[A_0] = 0.100M$$

the rxn is 20.0% complete in 60.0min

$$k = \frac{\frac{1}{[A]} - \frac{1}{[A]_0}}{t} = \frac{\frac{1}{.0800M} - \frac{1}{.100M}}{60.0 \text{ min}} = \frac{.0417}{M \cdot \text{min}}$$

Find half life:

$$t_{1/2} = \frac{1}{k[A_0]} = \frac{1}{\left(\frac{.0417}{M \cdot \text{min}}\right) (.100M)} = 240. \text{ min}$$



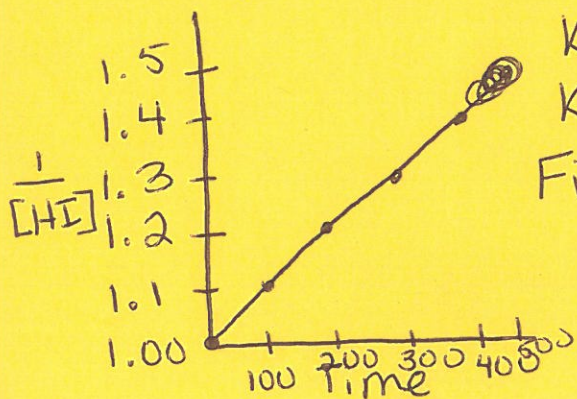
$k = \text{slope of the line}$

$$k = 1.2 \times 10^{-3} / (M \cdot s) \quad k = \frac{1.46 - 1.00}{400 - 0} = \frac{.44 M^{-1}}{400s}$$

Find half life of decomp. of 1.00M HI

$$t_{1/2} = \frac{1}{k[A_0]} = \frac{1}{(1.2 \times 10^{-3} M^{-1} s^{-1}) (1.00 M)}$$

$$t_{1/2} = 8.3 \times 10^2 s$$



ex. $2C_4H_6(g) \rightarrow C_8H_{12}(g)$ second order
rate expression: $\text{rate} = k[C_4H_6]^2$

If $k = 0.0140 M^{-1}s^{-1}$ at $500^\circ C$, determine the concentration of C_4H_6 after 115.0 seconds if the initial concentration of C_4H_6 is $0.0500 M$

$$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$$

$$\frac{1}{[A]} = (0.0140 M^{-1}s^{-1})(115.0 s) + \frac{1}{[0.0500 M]}$$

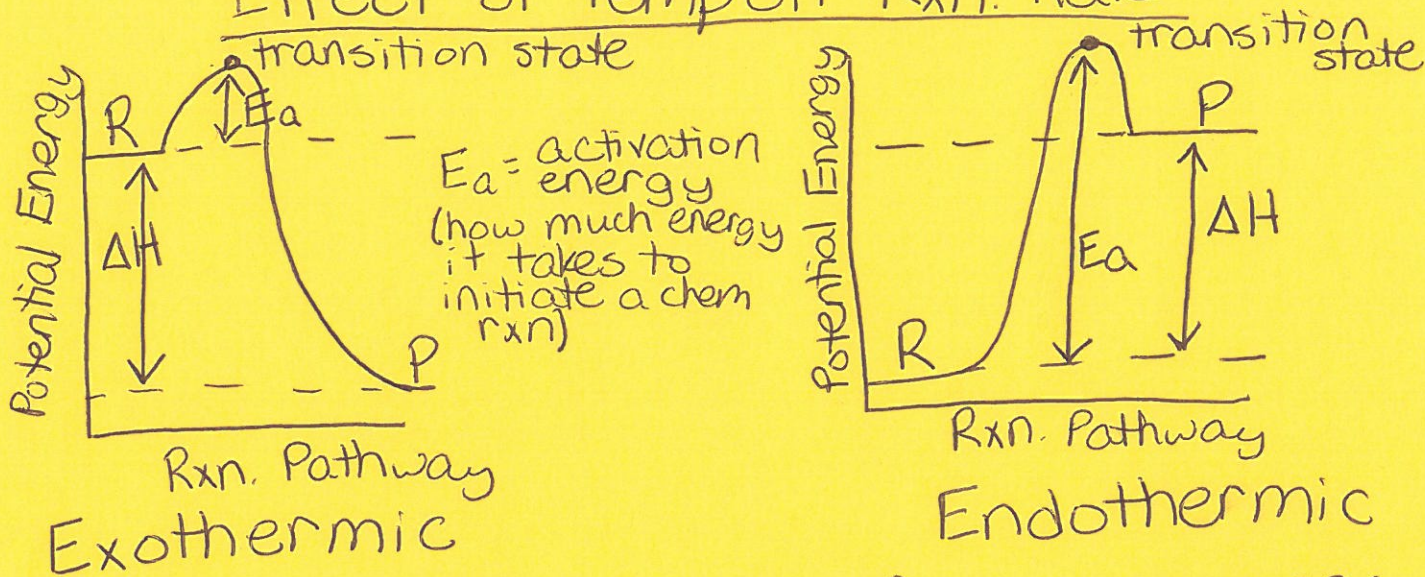
$$\frac{1}{[A]} = \cancel{32.3} \quad 21.61$$

$$[A] = \cancel{0.0310 M} \quad 0.0463 M$$

Calculate half life when the initial concentration of C_4H_6 is $0.0500 M$.

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(0.0140 M^{-1}s^{-1})(0.0500 M)} = 1430 s$$

Effect of Temp on Rxn. Rate



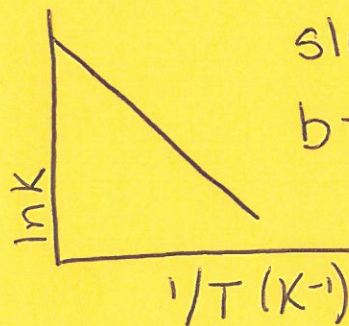
• As temp increases, rate of rxn. increases (at higher temp, more molecules have energy above activation energy, which increases reaction rate)

• Arrhenius Equation: expresses the dependence of reaction rate on temp.

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$$

A = frequency factor
collision frequency

$$R = 8.314 \text{ J/kmol}$$

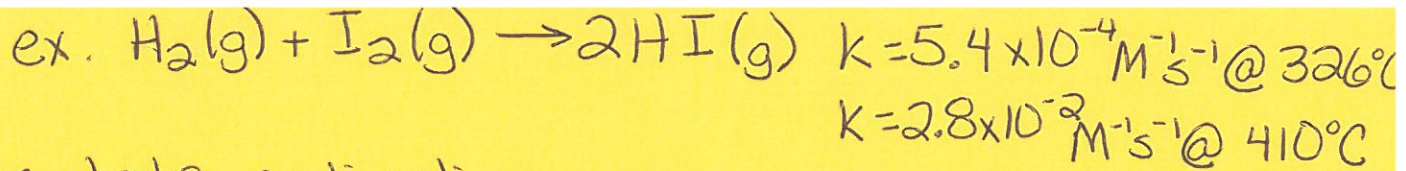


$$\text{slope} = \frac{-E_a}{R}$$

$$b = \ln A$$

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

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

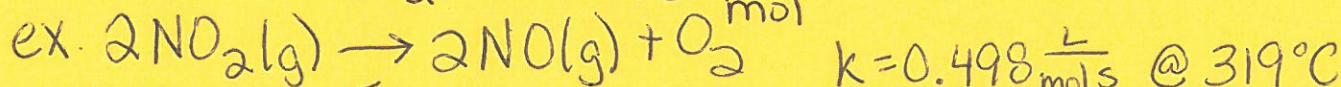


Calculate activation energy and frequency factor

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln\left(\frac{5.4 \times 10^{-4} \text{M}^{-1}\text{s}^{-1}}{2.8 \times 10^{-2} \text{M}^{-1}\text{s}^{-1}}\right) = \frac{E_a}{8.314 \frac{\text{J}}{\text{K mol}}} \left(\frac{1}{683\text{K}} - \frac{1}{599\text{K}} \right)$$

$$E_a = 1.6 \times 10^5 \frac{\text{J}}{\text{mol}}$$



Calculate E_a :

$$k = 4.74 \frac{\text{L}}{\text{mol s}}$$
 @ 383°C

$$\ln\left(\frac{0.498 \frac{\text{L}}{\text{mol s}}}{4.74 \frac{\text{L}}{\text{mol s}}}\right) = \frac{E_a}{8.314} \left[\frac{1}{656} - \frac{1}{592} \right]$$

$$E_a = 1.1 \times 10^5 \frac{\text{J}}{\text{mol}}$$

ex. Nitrogen oxide reacts with chlorine to form NOCl . The activation energy is 17.5kJ/mol . At 273K , the rate constant is $4.50 \text{L}^2/(\text{mol}^2\text{s})$. At what temp (in $^\circ\text{C}$) will the rate be $8.00 \text{L}^2/(\text{mol}^2\text{s})$?

$$17.5 \frac{\text{kJ}}{\text{mol}} = 17,500 \frac{\text{J}}{\text{mol}}$$

$$\star \ln \frac{4.50}{8} = \frac{17500}{8.314} \left[\frac{1}{T_2} - \frac{1}{273} \right]$$

$$-0.575 = 2104.88 \left[\frac{1}{T_2} - 0.00366 \right]$$

$$-0.575 = \frac{2104.88}{T_2} - 7.71$$

$$+7.71 \quad \quad \quad +7.71$$

$$7.135 = \frac{2104.88}{T_2}$$

$$7.135 T_2 = 2104.88$$

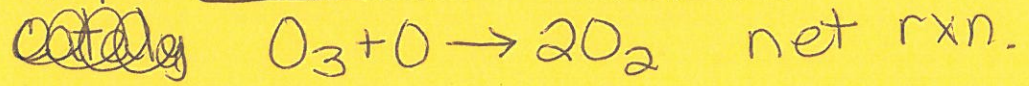
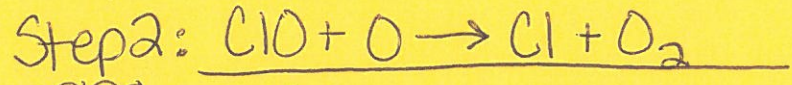
$$T_2 = 295\text{K} = 22^\circ\text{C}$$

Reaction Mechanisms:

- description of a path or sequence of steps by which a rxn occurs
- Rxn. order depends on the mechanism by which the rxn. takes place

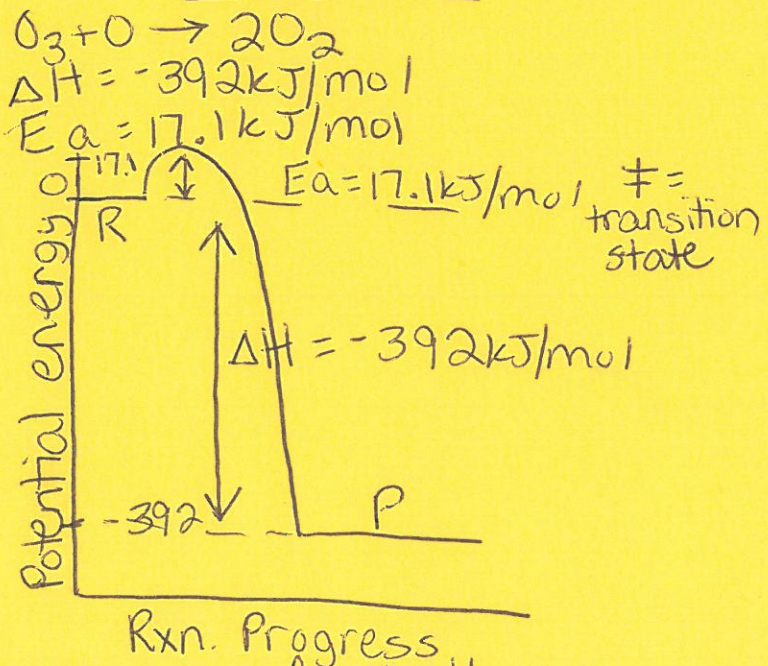
- Catalyst - species present to react in the beginning of the rxn but is regenerated by the end of the process
- Intermediates - not present at the beginning or the end of the rxn. but are generated and consumed at an intermediate step

ex. Ozone depletion

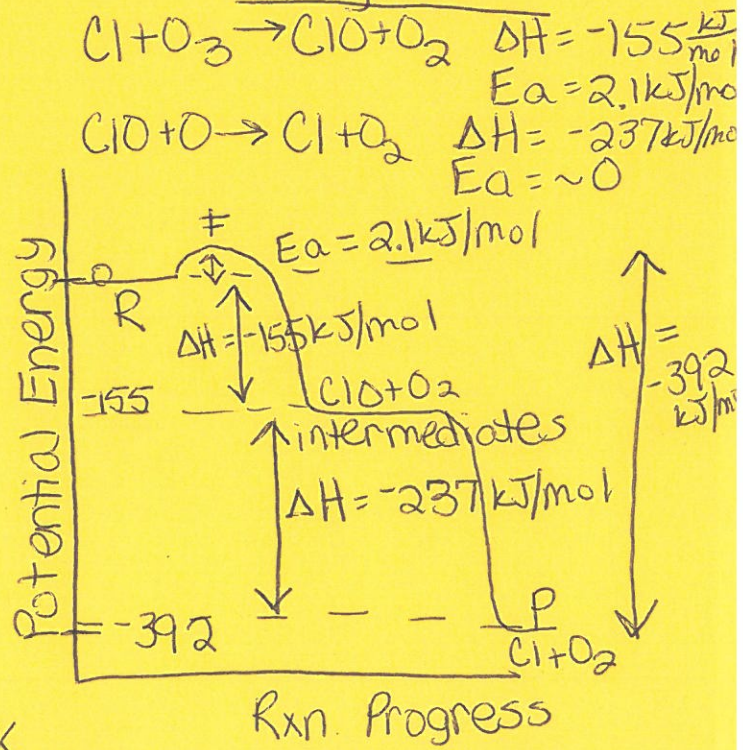


catalyst = Cl
intermediate = ClO

Uncatalyzed Rxn. Coordinate Diagram



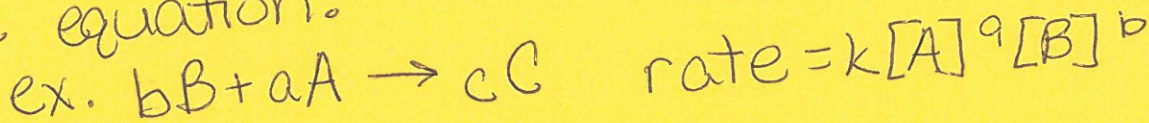
Catalyzed Rxn. Coordinate Diagram



* ΔH same for both
Catalyzed has lower E_a , higher K

Reaction Mechanisms

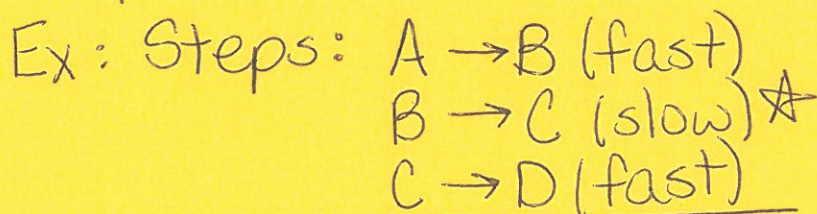
- Reaction order for the overall rxn. is only determined experimentally.
- Rxn. order for an elementary step equal to its stoichiometric coefficient from the equation:



• Types of steps:

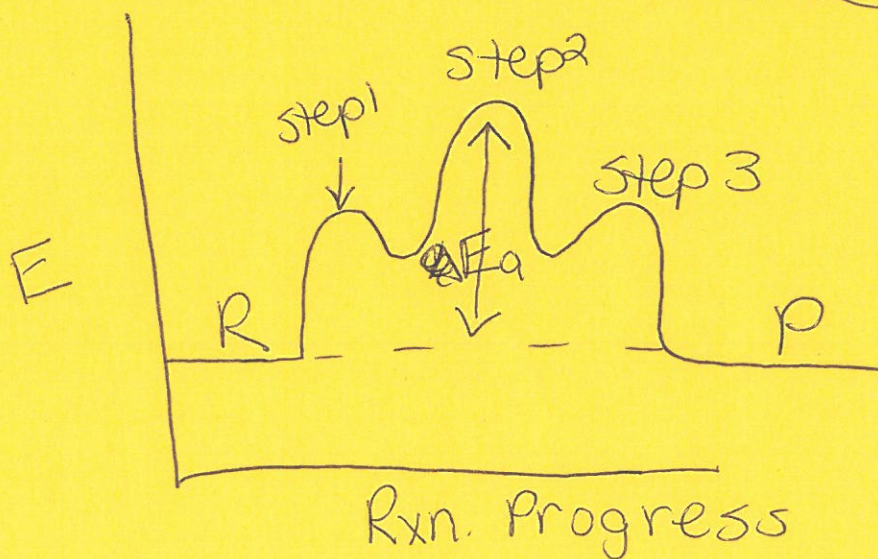
- Unimolecular: $A \rightarrow B + C$ $\text{rate} = k[A]^x$
- Bimolecular: $A + B \rightarrow C + D$ $\text{rate} = k[A]^x[B]^y$
- Termolecular: $A + B + C \rightarrow D + E$ $\text{rate} = k[A]^x[B]^y[C]^z$

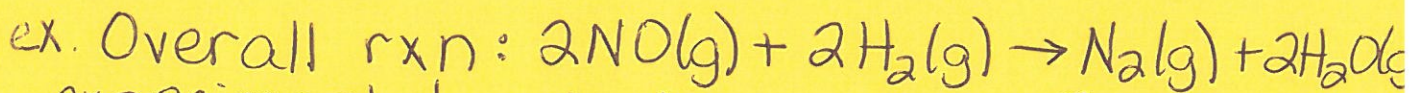
• In a series of steps of the rxn. mechanism, the slowest step is the rate determining step. (Usually has highest E_a)



$A \rightarrow D$ limited by $B \rightarrow C$

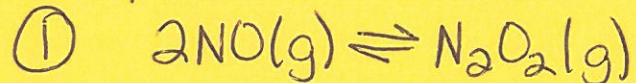
~~$\text{rate} = k[A]^x$~~



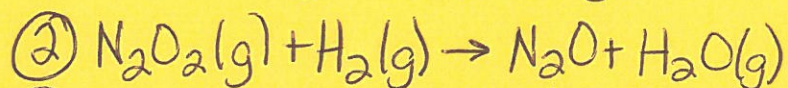


experimental rate law: $\text{rate} = k[\text{NO}]^2[\text{H}_2]$

Proposed mechanism:



Rate law of Forward step Rate
 $\text{rate} = k_1[\text{NO}]^2$ fast



$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$ slow



$\text{rate} = k_3[\text{N}_2\text{O}][\text{H}_2]$ fast

Step 2 is rate determining step, but an intermediate can't appear in our rate law

$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$

from step 1: $\text{rate}_{\text{forward}} = k_{1f}[\text{NO}]^2$

$\text{rate}_{\text{reverse}} = k_{1r}[\text{N}_2\text{O}_2]$

$k_{1f}[\text{NO}]^2 = k_{1r}[\text{N}_2\text{O}_2]$

$[\text{N}_2\text{O}_2] = \frac{k_{1f}[\text{NO}]^2}{k_{1r}}$

rate forward equals rate reverse

plug into our rate law

$\text{rate} = k_2 \left(\frac{k_{1f}[\text{NO}]^2}{k_{1r}} \right) [\text{H}_2]$

$\text{rate} = k[\text{NO}]^2[\text{H}_2]$ matches experimental rate law