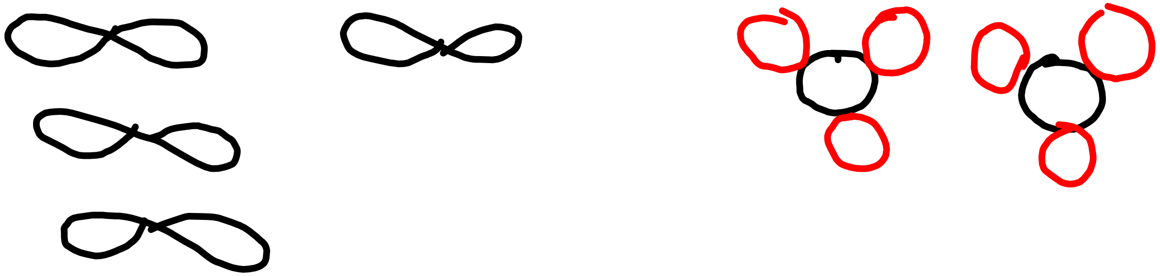
Chemical Kinetics - the study of rxn rates.

A collision happens and the collision has to be strong enough to break bonds

$$3H_2 + N_2 \rightarrow 2NH_3$$

You cannot look at a reaction and determine its rate law

$3H_2 + N_2 \rightarrow 2NH_3$ + heat



The rate law is determined by a series of mechanisms.

The rate law is determined experimently by products forming and reactants disappering.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

$$rate = k[NO]^{2}[O_2]^{1}$$

↖ proportional rate constant

NO is second order

O_2 is first order

added this is a third order rxn.

1.a)

$$2C_2H_{6(g)} + 7O_{2(g)} \longrightarrow 4CO_{2(g)} + 6H_2O_{(g)}$$

$$\frac{1}{4}\frac{\Delta[CO_2]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t} =$$

$$-\frac{1}{2}\frac{\Delta[C_2H_6]}{\Delta t} = -\frac{1}{7}\frac{\Delta[O_2]}{\Delta t}$$

1c.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}$$

$$\text{rate} = k[N_2][H_2]^2$$

1b.

$$CaCO_{3(s)} + 2HCl_{(g)} \rightarrow CaCl_{2(s)} + H_2O_{(g)} + CO_{2(g)}$$

Cannot use change in concentration for l or s but use moles.

$$\frac{\Delta mol\, CO_2}{\Delta t} = \frac{\Delta mol\, H_2O}{\Delta t} = \frac{\Delta mol\, CaCl_2}{\Delta t} = -\frac{1}{2}\frac{\Delta mol\, HCl}{\Delta t} = -\frac{\Delta mol\, CaCO_3}{\Delta t}$$

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

$$rate = k[NO]^2[O_2]$$

	Rate $M s^{-1}$	Initial Conc. [M] $[NO]$	$[O_2]$
1	1.2×10^{-8}	.10	.10
2	2.4×10^{-8}	.10	.20
3	1.08×10^{-7}	.30	.10

Exp 1 and 3 $[NO]$

Exp 1 and 2 $[O_2]$

Choose 2 trials to compare one where the conc. is doubled or tripled and the other reactant stays the same.

rate = k

zero order the rate is not dependent on the reactants

6. $2H_2O_2 \rightarrow 2H_2O + O_2$

	$[H_2O_2]$ M	Rate M/s
1	0.010	.00254
2	0.020	.00253
3	0.040	.00252

$$\frac{.02\,M}{.01\,M} = 2 \qquad \frac{.04\,M}{.01\,M} = 4$$

$$\frac{0.00253\,M/s}{0.00254\,M/s} = .9961$$

$$\frac{0.00252\,M/s}{0.00254\,M/s} = .9921$$

6. cont.

partial order

$2^x = .9961$

rate due to the change in conc.

doubling of the conc.

$\ln(.9961) = \ln(2^x) = x\ln(2)$

$x = \dfrac{\ln(.9961)}{\ln(2)} = \dfrac{-.00391}{.69315} = -.00569$

zero order

6. cont

$$4^x = .9921$$

$$\ln(.9921) = \ln(4)^x = x\ln(4)$$

$$\frac{\ln(.9921)}{\ln(4)} = -.0057$$

6 cont.

Thus the rate law is

rate = k

k = rate

rate = .00253 M/s

7. $2NO + H_2 \rightarrow N_2O + H_2O$

	[NO] atm	[H_2] atm
1	0.025	0.010
2	0.010	0.025
3	0.025	0.030
4	0.030	0.010

$$\frac{5.20 \times 10^{-7}\ atm/s}{3.61 \times 10^{-7}\ atm/s} = 1.4404$$

$$\frac{.03\ atm}{.025\ atm} = 1.2$$

7 cont.

$$1.2^x = 1.4404$$

$$\ln(1.4404) = x \ln(1.2)$$

$$x = \frac{\ln(1.4404)}{\ln(1.2)} = 2$$

$$[NO]^2$$

7 cont.

$$\frac{1.08 \times 10^{-6} \text{ atm/s}}{3.61 \times 10^{-7} \text{ atm/s}} = 2.9917$$

$$\frac{0.03 \text{ atm}}{0.01 \text{ atm}} = 3$$

$$\ln(2.9917) = x \ln(3)$$

$$x = \frac{\ln(2.9917)}{\ln(3)} = .99747$$

$[H_2]$

7.

$$3.61 \times 10^{-7}\ atm/s = k(.025\,atm)^2(.010\,atm)$$

Do 8 and solve for k for 7.

① $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl$

$rate = k[NO]^2[Cl_2]^2$

② $rate = [Hb][CO]k$

zero order

→ rate = k

→ $[A]_t = -kt + [A]_0$

1^{st} order

→ rate = $k[A]$

→ $\ln[A]_t = -kt + \ln[A]_0$

2^{nd} order

→ rate = $k[A]^2$

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2$$

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

$[A]_t$ .356 .268

$[B]_t$ 0

11.

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

$$rate = k[A]^2$$

$[A]_0 = 13.62\,M$

33.0 ms $[A]_t = 12.99\,M$

$$\frac{33.0\,ms \times 1\,s}{1000\,ms} = .0330\,s$$

$$K = \frac{\frac{1}{A_t} - \frac{1}{A_0}}{t}$$

$$\frac{\frac{1}{12.99M} - \frac{1}{13.62M}}{.0330s} = \underline{0.1079 M^{-1} s^{-1}}$$

$$rate = k[A]_0^2$$

$$rate = (0.1079 M^{-1} s^{-1})[13.62M]^2$$

$$rate = 20.0159\ M/s$$

time (s)	0.00	0.250
$[A]_t$ M	13.62	9.96
rate M/s	20.0	10.7

c. $t = .250\,s$

$$\frac{1}{A_t} = (.1079\,M^{-1}s^{-1})(.250\,s) + \frac{1}{13.62\,M}$$

$$\frac{1}{A_t} = .10039\,\frac{1}{M} ; \; 9.9605\,M$$

rate will decrease over time b/c reactants will decrease.