KINETICS: the study of the rates of chemical reactions

https://www.youtube.com/watch?v=OttRV5ykP7A

Kinetics = dating

(A) Factors that Affect Rates:

1) Concentration of the reactants
   - i) most: increase conc., increase rate

2) Temperature
   - i) increase temp., increase rate
   - ii) rule of thumb: 10^{o} increase doubles the rate

3) Presence of a catalyst
   - i) increases rate
   - ii) can be recovered
   - iii) ex. enzymes

4) Surface area
   - i) increase surface area, increase rate

(B) Explanations of Change in Rate

1) frequency of collisions

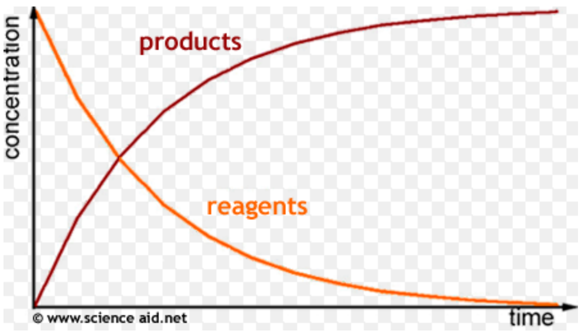
2) sufficient energy

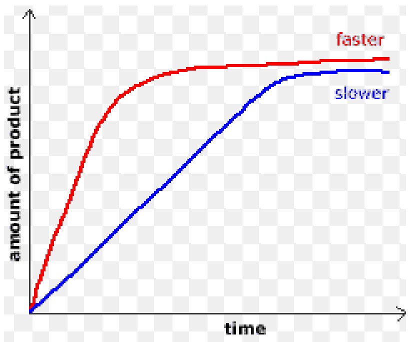
3) proper orientation

Reactions have:

A) Different Mechanisms - steps in which they take place

B) Reaction Rate - Change in concentration of reactants or product per unit of time





B) Rate:

i) The change that occurs in a given interval of time

ii) units: $Ms^{-1} = mol*L^{-1}*s^{-1}$ (M = molarity, s = sec)

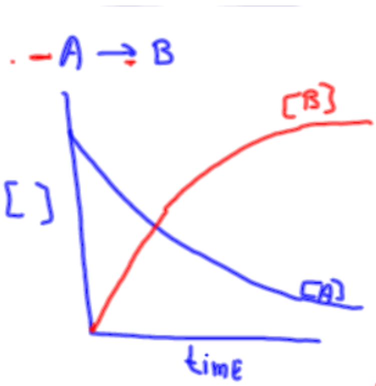
example: $2H_2O_2$ --> $2H_2O$ + O_2

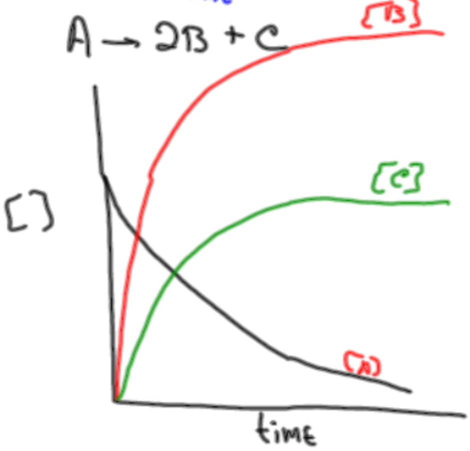
Rate =

or

Rate =

In general: aA + bB --> cC + dD





(C) Expressing Rate:

ex.1) A --> B

- Average Rate = $\frac{(mol_B - mol_B)}{t_t - t_i} = \frac{\Delta B}{\Delta t} = -\frac{\Delta A}{\Delta t}$

By convention, we express rates of reactions as positive quantities, so if finding a (-) slope for consumption of a reactant, use a (-) before the rate formula, so rate = (+)

ex. 1: $2N_2O_5$ --> $4NO_2$ + O_2

Rate of reaction =

Example 2: Compare the reaction rates for the disappearance of reactants and formation of products for the following reaction:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

$$\text{Rate} = \frac{\Delta[P_4]}{\Delta t} =$$

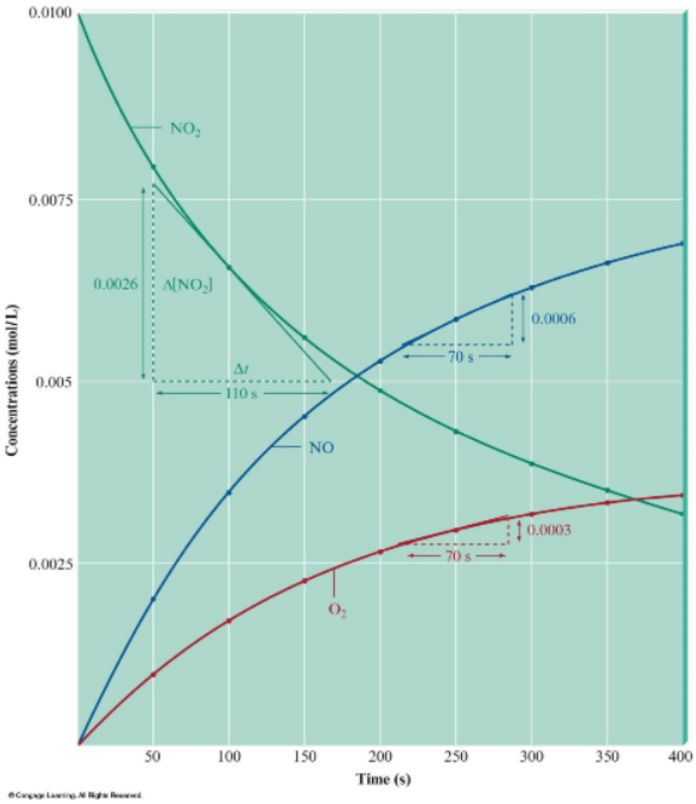
or

$$\text{Rate} = -\frac{\Delta[PH_3]}{\Delta t} =$$

Two types of rates can be found:

D) 1) The *Average Rate* of reaction during the experiment from t = 0 to t = ? is the negative of the slope

2) The *Instantaneous rate* of reaction is the negative slope of the tangent at time *t*.



Calculate:

A) The rate of NO_2 consumption between t = 0 and t = 50 sec.

B) The Instantaneous rate of NO_2 consumption at t = 100. sec

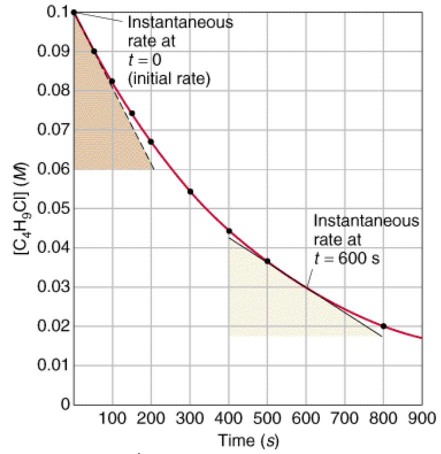
Things to Know about rates of others in the reaction:

A) Look at the balanced equation, rates are related to coefficients

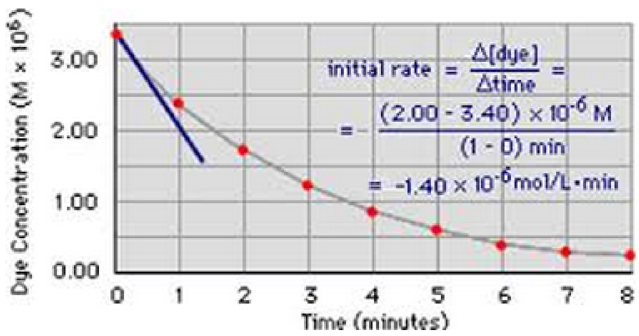
- same coefficients = same rates
- different coefficients = rates are * and / like in stoichiometry

Ex: For the above reaction, balance the equation. Then find the rate of NO production at t = 250 sec. Predict the rate of O2 at that same time, then calculate it and compare to your calculations.

Instantaneous rate



Initial rate



Using this graph, how would you find the rate for the t = 100 to t = 400 sec?

E) In the reaction: A + 2B --> C + 3D, the rate of disappearance of B is 6.2×10^{-4} Ms^{-1}

a) What is the rate of disappearance of A?

b) What is the rate of the formation of D?

c) What is the rate of formation of C?

<u>Things to know about rate laws:</u>

A) Rate laws are found through experiment and analysis of its data

B) Rate laws can be found for reactants or products (our book does reactants)

C) Rate law = expression that shows how the rate depends on the concentration of reactants

$2NO_2$ ---> $2NO$ + O_2

Rate = k $[NO_2]^n$

D) Why do we want to know a rate law?

i) helps us work backward to infer rxn intermediate steps

ii) determine the "fast" step of reaction

iii) helps us determine how to speed the "slow step"

$2I^- + S_2O_8^{-2} \rightarrow I_2 + 2SO_4^{-2}$

[I-]	[$S_2O_8^{-2}$]	Initial rate(mol/L*s (I_2))
0.080	0.040	12.5×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.00×10^{-6}
0.060	0.030	7.00×10^{-6}

Determine the rate law, value of the rate constant (k), and the order of the reaction per each reactant.

For the reaction $2NO + O_2 \rightarrow 2NO_2$

Determine the rate law, the rate constant and its proper units

[NO]	[O_2]	Initial Rate (NO_2) :M/s
1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

In the study of the kinetics of the reaction represented above, the following data were obtained at 298K.

AP QUESTION:

EXPT	Initial $[Br^-]$ mol/L	Initial $[BrO_3^-]$ mol/L	Initial $[H^+]$ mol/L	Rate of Disappearance of BrO_3^- mol/L s
1	0.100	0.100	0.100	8.0×10^{-4}
2	0.100	0.200	0.100	1.6×10^{-3}
3	0.200	0.200	0.100	3.2×10^{-3}
4	0.100	0.100	0.200	3.2×10^{-3}

a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

i) Br^- ii) BrO_3^- iii) H^+

b) Write the rate law for the overall reaction

c) Determine the overall reaction order

d) Determine the value of the specific rate constant for the reaction at 298K. Include the correct units.

e) Calculate the value of the standard cell potential, E^o, for the reaction using the information in the table below.

HALF-REACTION	E^o (V)
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.065
$BrO_3^-(aq) + 6H^+(aq) + 5e^- \rightarrow 1/2Br_2(l) + 3H_2O(l)$	+ 1.52

f) Determine the total number of electrons transferred in the overall reaction.

Using the integrated rate law to determine reaction order

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

$\text{Rate} = k\,[A]^x$

then: $$k[A]^x = \frac{-\Delta[A]}{\Delta t}$$

Zero Order Rxn

a) if $x = 0$

b) $[A] = -kt + [A]_0$ initial conc. $t = 0$

c) if I plot [A] vs t .... and get a straight line, it is order = 0

d) slope = $-k$

1st Order Rxn

a) if $x = 1$

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

$(\ln[A] - \ln[A^{-}]_0) = -kt$

c) If I plot ln [A] vs t and get a straight line... it is order = 1

d) slope = $-k$

2nd Order Rxn

a) if $x = 2$

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

c) If I plot $\frac{1}{[A]}$ vs t and get a (+) straight line.... it is order = 2

d) slope = k

The gas phase decomposition of NO_2,

$NO_2(g)$ --> $NO(g)$ + $O_2(g)$,

is studied at 383°C, giving the following data:

Time(s)	$[NO_2]$ (M)
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

(A) Determine whether the reaction is first or second order with respect to the concentration of NO_2

(B) Determine the value of the rate constant.

Order	Equation	Plot	Slope	Units (k)
0	$[A] = -kt + [A]_0$	[A] vs t	-k	mol/L*s; $M{*}s^{-1}$
1	$\ln[A] = -kt + \ln[A]_0$	ln[A] vs t	-k	s^{-1}
2	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs t	k	L/mol*s; $M^{-1}{*}s^{-1}$

EX 1:

We carry out the reaction A --> B + C at a particular temperature. What is the order of the reaction, the rate law expression , and the value of k at this temperature.

TIME(min)	[A] (mol/L)
0.00	2.000
2.00	1.107
4.00	0.612
6.00	0.338
8.00	0.187
10.00	0.103

TIME(min)	[A]	ln[A]	1/[A]
0.00	2.000	0.693	0.5000
2.00	1.107	0.102	0.9033
4.00	0.612	-0.491	1.63
6.00	0.338	-1.085	2.95
8.00	0.187	-1.677	5.35
10.00	0.103	-2.273	9.71

ex. 2: It is found that 54 min. is required for the concentration of substance A to decrease from 0.75M to 0.20M. What is the rate constant for this first order decomposition? A --> B + C ex. 3: The rate constant for the decomposition of nitrogen dioxide

$2NO_2$ --> $2NO$ + O_2

is 1.70 M^{-1}* min^{-1}. Find the time, in seconds, needed to decrease 2.00-mol/L of NO_2 to 1.25-mol/L. What is the concentration of NO and O_2 after that time?

When doing percentage problems:

ex. Calculate the value of the rate constant if after 40 min, 35% of the reaction is complete. The $[A]_o$ = 0.50M

A) **If 1st Order: either way will give the correct answer (use % or actual conc.)**

1) ln(65) = -k(40) + ln(100) or 2) ln(0.325) = -k(40) + ln(0.50)

because ln65 - ln100 = ln.325 - ln .5

B) **If 2nd Order: ONLY way is to use the actual concentrations**

1) 1/.325 = k(40) + 1/.50

because 1/65 - 1/100 and 1/.325 - 1/.5 are not equal ex.3: How long will it take for 75% of the concentration of A to decompose if k is 50 s^{-1}?

3) Answer the following questions related to the kinetics of chemical reactions:

$I^-(aq) + ClO^-(aq) \xrightarrow{OH^-} IO^-(aq) + Cl^-(aq)$

Iodide ion, I^-, is oxidized to hypoiodite ion, IO^-, by hypochlorite, ClO^-, in basic solution according to the equation above. Three initial-rate experiments were conducted; the results are shown in the following table.

EXPT FORM. IO	[I⁻]	[ClO⁻]	INIT RATE of Form. [IO⁻]
1	0.017M	0.015M	0.156M/s
2	0.052M	0.015M	0.476M/s
3	0.016M	0.061M	0.596M/s

A) Determine the order of the reaction with respect to each reactant listed below.
   i) $I^-(aq)$ Show your work
   ii) $ClO^-(aq)$

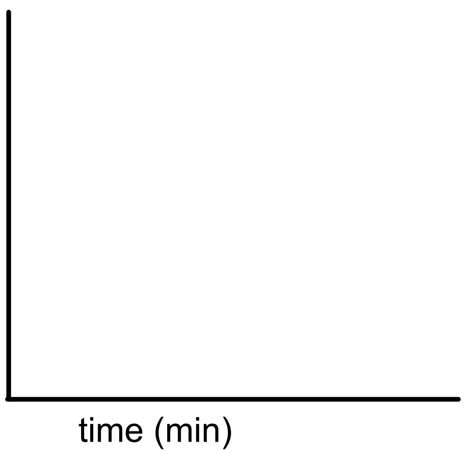
B) For the reaction,
   i) Write the rate law that is consistent with the calculations in part (A).
   ii) Calculate the value of the specific rate constant, k, and specify units.

The catalyzed decomposition of hydrogen peroxide,
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

The kinetics of the decomposition reaction were studied and the results analyzed. Some of the experimental data are shown in the table below. Determine the order of the reaction.

$[H_2O_2]$	Time (min)
1.00M	0.0
0.78M	5.0
0.61	10.0

C) During the analysis of the data, the graph was produced:
   i) Label the vertical axis of the graph that would give a straight line and draw line
   ii) What is the rate constant, K, and its proper units for the decomposition of $H_2O_2(aq)$?



HALF-LIFE

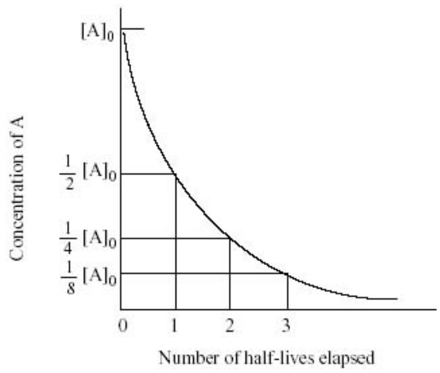
A) Half-life ($t_{1/2}$) is time for reactant to reach 1/2 its original conc.

1st order:

$$t_{1/2} = \frac{0.693}{k}$$

* for a 1st order reaction $t_{1/2}$ does not depend on concentration

2nd order: $t_{1/2} = \frac{1}{k[A]_0}$



Comparison of $t_{1/2}$ for 1st order and 2nd order rxns

1st order	**2nd order**
- $t_{1/2}$ depends on k	- $t_{1/2}$ depends on k and [A]
- constant time required to reduce the reactant rxn by 1/2	- each successive 1/2 life is approximate double thhe $t_{1/2}$ of the preceeding

EX. 1: A certain first order reaction has a half-life of 20.0-min.

A) Calculate the rate constant for this reaction.
B) How much time is required for this reaction to be 75% complete?

2) A certain reaction has the following general form:

aA --> bB

At a particular temperature and $[A]_o = 2.00 \times 10^{-2}$M, concentration time data were collected for this reaction and a plot of ln[A] versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2}\ min^{-1}$.

A) Determine the rate law
B) Calculate the half-life
C) How much time is required for the concentration of A to decrease to 2.50×10^{-3}M?

3) A certain reaction has the following general form:

aA --> bB

At a particular temperature and [A]o = 2.80×10^{-2} M, concentration time data were collected for this reaction and a plot of 1/[A] versus time resulted in a straight line with a slope value of 3.60×10^{-2} L * mol^{-1} * min^{-1}.

A) Determine the rate law
B) Calculate the half-life
C) How much time is required for the concentration of A to decrease to 7.00×10^{-4} M?

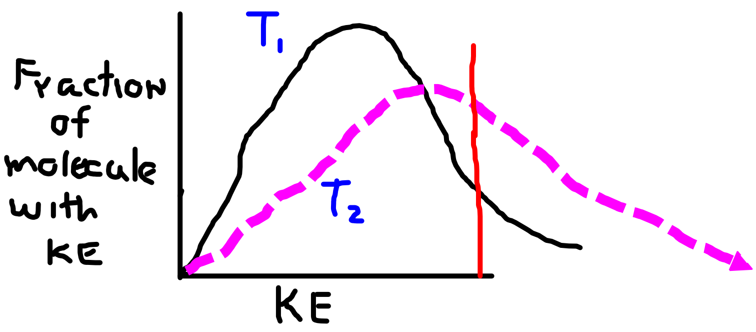
Collision Theory:

In order for a reaction to occur, reactant molecules must collide with an energy greater than some minimum value (activation energy,E_a) and with proper orientation.

k = pfz where k = rate constant
p = fraction of collisions with proper orientation
f = fraction of collisions having energy greater than the minimum
z = collision frequency - proportional to speed
- proportional to temperature

Increase in temperature

1) inc. collision frequency
2) inc. number of molecules with minimum energy



Things to remember with collision theory:

A) Collision has too little energy = no rxn

B) Collision not correct orientation = no rxn

C) How can we increase the chances of having enough collisions with proper orientation and enough energy?

D) Formula:

# of collisions with needed E_a = (Total # collisions) $e^{-Ea/RT}$

Fraction of collisions with enough energy

E) E_a = activation energy - minimum energy required to break reactant bonds

F) At the point E_a is hit, transition state of molecules occurs

Arrhenius Equation:

$k = Ae^{-E_a/RT}$ where A = frequency factor (A= pz)

$\ln(k) = -E_a/R(1/T) + \ln(A)$

$\ln(k_2/k_1) = -E_a/R(1/T_{K2} - 1/T_{K1})$

E_a = usually in kJ/mol

R = 8.314 J/mol-K

Ex 1: The reaction:

$2N_2O_{5(g)}$ ---> $4NO_{2(g)}$ + $O_{2(g)}$

Was studied at several temperatures and the following k values found:

k (s^{-1})	T (C)
2.0×10^{-5}	20
7.3×10^{-5}	30
2.7×10^{-4}	40
9.1×10^{-4}	50
2.9×10^{-3}	60

Calculate the E_a value for this reaction.

Ex 2: The gas-phase reaction between methane and diatomic sulfur is given:

$CH_{4(g)}$ + $2S_{2(g)}$ ---> $CS_{2(g)}$ + $2H_2S_{(g)}$

At 550 C the rate constant of this reaction is 1.1 L/mol*s and at 625 C the rate constant is 6.4 L/mol*s. Using these values, calculate E_a for this reaction.

REACTION MECHANISM:

The set of elementary reactions where overall effect is given by the net chemical equation.

A) Mechanisms are PROBABLE AND LIKELY, but experiments must be done to support or disprove proposed mechanism

B) Mechanism must agree with the rate law

C) Sum of the elementary steps (each individual rxn) must = the overall balanced equation

D) K_1 and K_2... refer to the rates of each elementary step

E) Reference to molecularity (rate based on reactants)

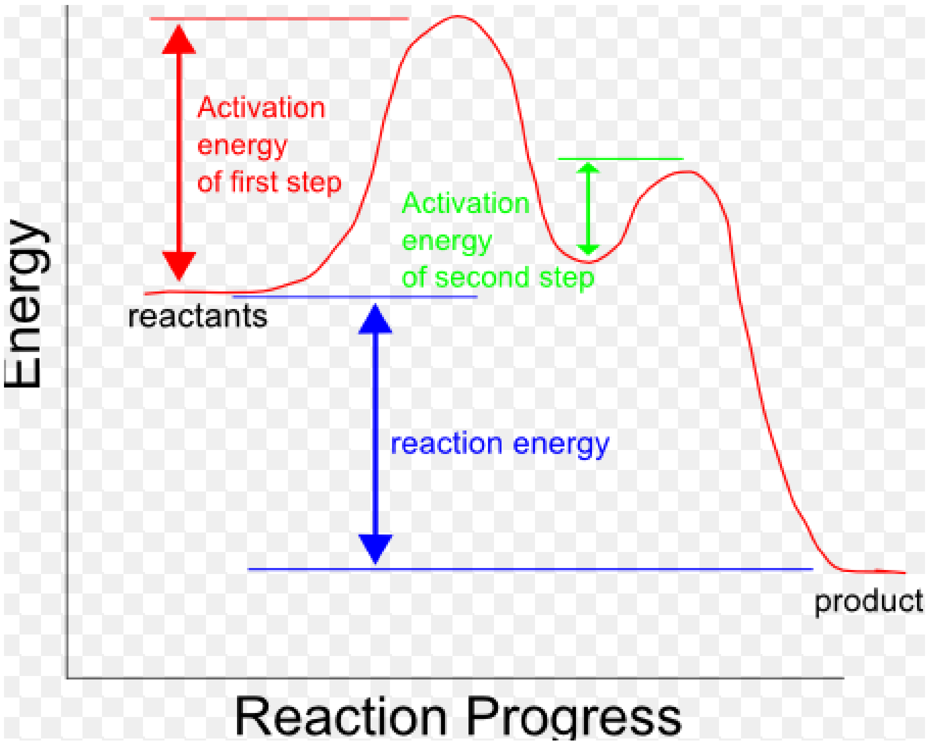
unimolecular = (1) reactant	rate = k [A]
bimolecular = (2) reactants	rate = k $[A]^2$
	rate = k [A][B]
termolecular = (3) reactants	rate = k $[A]^2[B]$
	rate = k [A][B][C]

F) Rxns will have 1 slow step and the rest = fast steps (slow step = rate determining step)

1) Cl_2 <=> 2Cl

$Cl + CHCl_3$ --> $HCl + CCl_3$

$Cl + CCl_3$ --> CCl_4


Activation
energy
of first step
Activation
energy
of second step
reactants
reaction energy
product
Energy
Reaction Progress

2) O_3 + NO_2 --> O_2 + NO_3 (slow)
NO_3 + NO_2 --> N_2O_5 (fast)

3) H_2O_2 + Br^- --> BrO^- + H_2O
H_2O_2 + BrO^- --> Br^- + H_2O + O_2

4) For NO_2 + CO --> CO_2 + NO and Rate = $k[NO_2]^2$

Proposed: $2NO_2$ --> NO_3 + NO (slow)
NO_3 + CO --> NO_2 + CO_2 (fast)

5) For H_2 + I_2 --> 2HI

Proposed: $I_2 \underset{K_r}{\overset{K_f}{\Leftrightarrow}} 2I$ (fast)

$I + I + H_2 \xrightarrow{K_1} 2HI$ (slow)

6) $2\ O_3 \text{ --> } 3O_2$ and experimental rate = $k[O_3]^2/[O_2]$

Proposed: $O_3 \text{ <=> } O_2 + O$ (fast)

$O + O_3 \text{ --> } 2O_2$ (slow)

Catalysts:

1) Provides another pathway for the reaction mechanism to proceed, new pathway has a lower E_a (so more collisions have minimum energy needed)

   ***Reactants and products still have same amount of energy and enthalpy (ΔH) change is the same

2) Is not used in the reaction, is still present in same amount at end

3) Two classes of catalysts:

   A) **homogeneous -** same phases as reactants

   B) **heterogeneous -** different phase than reactants, usually solid

4) Examples:

Pt, Ni, Pd	used in hydrogentation of oils to make margarine
VO_2	used to catalyze SO_2 ----> SO_3
Catalytic converter	contains transition metals and noble metals
	such as Pt and Pd, converts bad emissions

5) Enzymes - act as an catalysts in the bodies of animals and plants

GRAPHS:

1) ENERGY PATHWAY:

2) NUMBER OF MOLECULESVS KINETIC ENERGY
(change in temperature)

3) NUMBER OF MOLECULES vs KINETIC ENERGY (ACTIVATION ENERGY)

4) CATALYST vs NO CATALYST (ACTIVATION ENERGY)

5) ORDERS OF REACTANTS:

6) RATE CONSTANT vs TEMPERATURE

The following mechanism has been proposed for the gas-phase reaction of chloroform, $CHCl_3$, and chlorine.

Step 1: Cl_2 (g) $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ 2Cl(g) fast

Step 2: Cl(g) + $CHCl_3$ (g) $\xrightarrow{k_2}$ HCl(g) + CCl_3 (g) slow

Step 3: Cl(g) + CCl_3 (g) $\xrightarrow{k_3}$ CCl_4 (g) fast

a) What is the overall reaction?

b) What is (are) the intermediate(s)?

c) What is the molecularity of each of the elementary steps?

d) What is the rate determining step?

e) What is the rate law predicted by this mechanism?

Extra Rate Law practice

Determine the rate law expression and the value of the rate constant for the reaction:

EXPT	INITIAL [A]	INITIAL [B]	INITIAL [C]	INITIAL RATE OF FORMATION OF E
1	0.20M	0.20M	0.20M	2.4×10^{-6} M * min^{-1}
2	0.40M	0.30M	0.20M	9.6×10^{-6} M * min^{-1}
3	0.20M	0.30M	0.20M	2.4×10^{-6} M * min^{-1}
4	0.20M	0.40M	0.60M	7.2×10^{-6} M * min^{-1}

Hydroxide ion is involved in the mechanism but is not consumed in this reaction in aqueous solution. Determine the rate law, the rate constant and its proper units.

$$OCl^{-1} + I^{-1} \xrightarrow{OH^{-1}} OI^{-1} + Cl^{-1}$$

$[OCl^{-1}]$	$[I^{-1}]$	$[OH^{-1}]$	Rate of Formation OI^{-1}, $M \cdot s^{-1}$
0.0040	0.0020	1.00	4.8×10^{-4}
0.0020	0.0040	1.00	4.8×10^{-4}
0.0020	0.0020	1.00	2.4×10^{-4}
0.0020	0.0020	0.50	4.8×10^{-4}
0.0020	0.0020	0.25	9.6×10^{-4}