Chemical Kinetics:

The study of the rate at which chemical reactions occur.

reactant → product

$$\text{rate} = \frac{-\Delta[\text{reactant}]}{\Delta t} = \frac{\Delta[\text{product}]}{\Delta t}$$

Δ[reactant]: change in reactant concentration.

Δ[product]: change in product concentration.

Δt: time period(t_{FINAL} - $t_{INITIAL}$)

General Rate of a Reaction:

For

$$rR \rightarrow pP$$

$$\text{general rate} = \frac{1}{r} \times \frac{-\Delta[R]}{\Delta t} = \frac{1}{p} \times \frac{\Delta[P]}{\Delta t}$$

Ex:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

$$\text{rate} = \frac{-\Delta[C_6H_{12}O_6]}{\Delta t} = \frac{1}{2} \times \frac{\Delta[C_2H_5OH]}{\Delta t}$$

Calculating Reaction Rates:

Ex: Calculate the reaction rate in terms of A and C for the following:

$$A + 2B \rightarrow 3C + 2D$$

if at some time [A] = 0.4658 M and that 125 seconds later, [A] = 0.4282 M.

Rate Laws and Reaction Order:

Reaction rates depend on reactant concentration.

$$aA \;+\; bB \rightarrow \text{products}$$

Rate Law relates reactant concentrations to reaction rates.

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

k: rate constant

m, n: exponents

[A], [B]: concentration of reactants in molarity

Reaction Order:

Reaction order refers to the values of the exponents in a rate law. In other words the value of m and n.

Example:

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

Rate 2nd order in A, 1st order in B, and 3rd order overall.

Method of Initial Rates:

Used to determine exponents. Consider the following.

$$A + B \rightarrow C$$

Exp#	[A]	[B]	Rate(M/s)
1	0.15 M	0.15 M	0.048
2	0.30 M	0.15 M	0.192
3	0.15 M	0.30 M	0.096
4	0.30 M	0.30 M	0.384

From data: Rate = $k[A]^2[B]$

First Order Reaction:

$$A \rightarrow \text{products}$$

Rate = k[A]

Integrated Rate Law:

$$\ln \frac{[A]_t}{[A]_o} = -kt$$

$[A]_o$ = [A] at t = 0 s.

$[A]_t$ = [A] at time t.

k = rate constant.

t = time.

Integrated Rate Law Example:

Ex:

$$2H_2O_2(aq) \rightarrow 2H_2O(aq) + O_2(g)$$

If the reaction is first order and $k = 1.8 \times 10^{-5}\ s^{-1}$ at 20 °C, and the initial concentration of H_2O_2 is 0.30 M.

a) Calculate the concentration of H_2O_2 after 4.00 hours?

Integrated Rate Law Example cont…:

b) How long will it take the concentration to drop to 0.12 M?

c) How long will it take for 90% of the H_2O_2 to decompose?

Half-Life for First Order:

Time for the reactant concentration to decrease by half.

For First Order Reactions,

$$t_{1/2} = \frac{\text{In}2}{k}$$

Second Order Reactions:

For a single reactant.

$$A \rightarrow products$$

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

Integrated Rate Law

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

Half Life For Second Order:

$$t_{1/2} = \frac{1}{k[A]_o}$$

Example:

The second order decomposition of HI(g) at 700 K is as follows:

$$HI(g) \rightarrow 1/2H_2(g) + 1/2I_2(g)$$

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

Calculate the half life if the initial concentration of HI is 1.00 M and $k = 0.0012\ M^{-1} \cdot s^{-1}$.

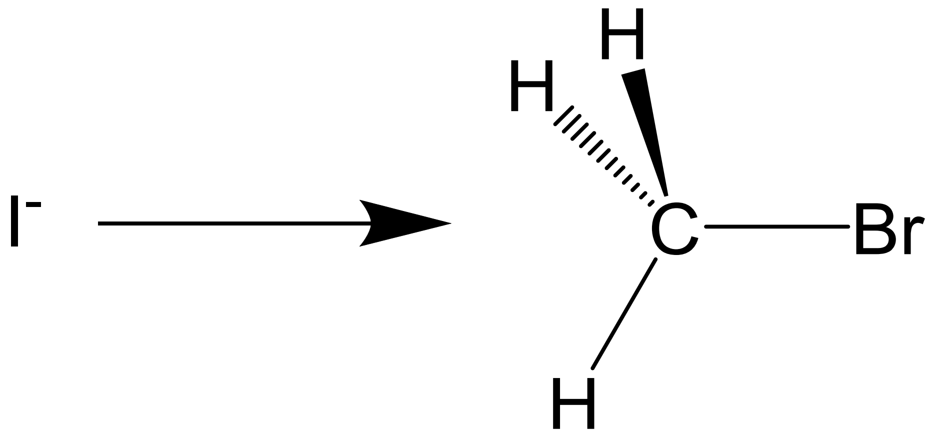
Chemical Kinetic Theories:

Collision Theory:

If molecules, atoms, or ions collide into each other with enough energy, existing bonds will be broken and products will be formed.

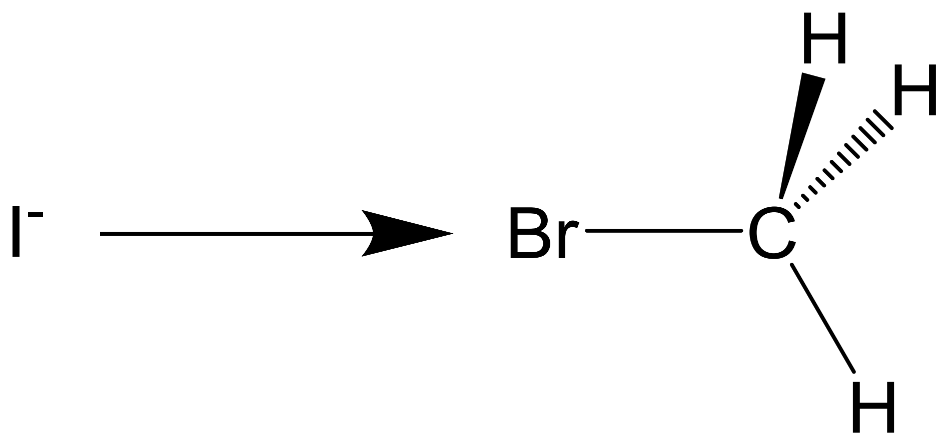
Activation Energy(E_a): The minimum energy required in a collision for a reaction to occur.

Orientation of molecules is important.



Proper
Orientation

REACTION OCCURS



Not
Proper
Orientation

NO REACTION

Transition State Theory:

Reactants come together, form an activated complex, and dissociate into products.

Consider the reaction:

$$I^- + CH_3\text{-}Br \rightarrow I\text{- -}CH_3\text{- -}Br \rightarrow I\text{-}CH_3 + Br^-$$

Activated Complex
Transition State

Arrhenius Equation:

Relates reaction rate to temperature.

$$\text{In}k = \frac{-E_A}{RT} + \text{In}A$$

E_A: activation energy(J/mole)
k: rate constant
R: 8.314 J/K·mole
T: temperature in Kelvin
A: frequency factor

Arrhenius Example:

$$N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g)$$

A plot of lnk versus 1/T for the decomposition of $N_2O_5(g)$ had a slope of -1.2×10^4 K. Calculate E_A.

Arrhenius Example2:

Activation energy can be determined by measuring the rate at two different temperatures.

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

Ex:

Estimate a value of k at 375 K for decomposition of $N_2O_5(g)$ if k = 2.5×10^{-3} s^{-1} at 332 K.

Reaction Mechanism:

Chemical reactions can occur in a single step or in a series of small steps.
Reaction mechanism is a series of simple steps that leads from initial reactants to products.
elementary reaction – Single step in an overall reaction mechanism.

Reaction Mechanism cont…:

Reaction mechanism must:

1) Account for the known rate law.

2) Agree with the stoichiometry of the overall net equation.

Ex: Consider the formation of nitrosyl fluoride.

$$2NO + F_2 \rightarrow 2ONF$$

$$\text{rate} = k[NO][F_2]$$

Catalysis:

A catalyst speeds up the rate of a chemical reaction and is not used up in the process.

Ex:

Catalysed Depletion of ozone.

Step 1: $O_3 + Cl \rightarrow ClO + O_2$

Step 2: $ClO + O \rightarrow Cl + O_2$

NET: $O_3 + O \rightarrow 2O_2$

Cl: catalyst. Required! Not consumed!