CHEMICAL KINETICS

Chemical Kinetics:

I. The study of the Rates of Chemical Reactions:
  - how fast do chemical reactions proceed to form products

II. The study of Reaction Mechanisms:
  - the steps involved in the change from reactants to products.

I. Rates of Reactions

- Factors affecting Reaction Rates:

1. Concentration of Reactants:	Rate α Concentration of Reactants
2. Presence of a Catalyst:	A catalyst is a substance that increases the Reaction Rate without being consumed
3. Temperature:	Rate α Temperature
4. Surface Area of Reactants:	Rate α Surface Area of Reactants

Definition of Reaction Reaction Rate

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

Reaction Rate:

- increase in the molar concentration of a product per unit time

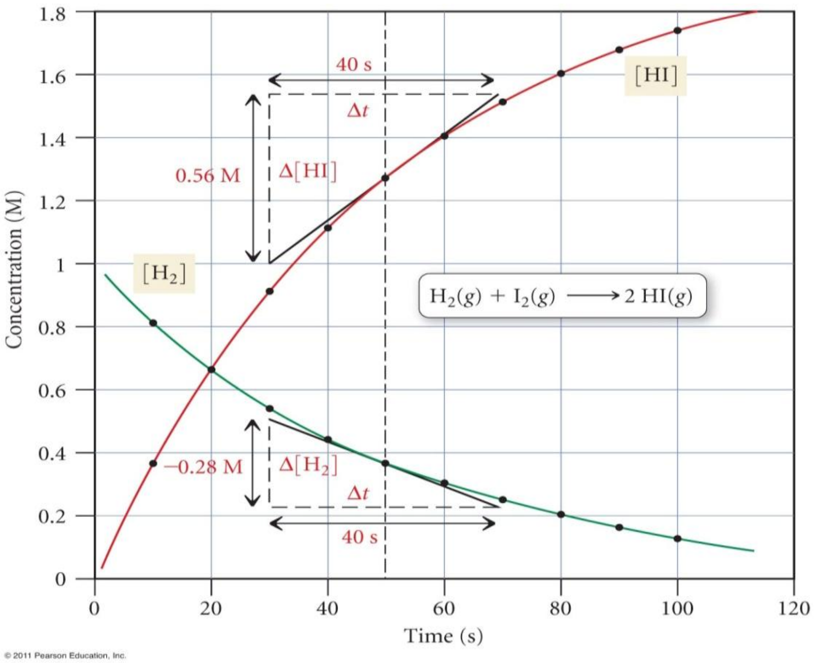
OR

- decrease in the molar concentration of reactant per unit time

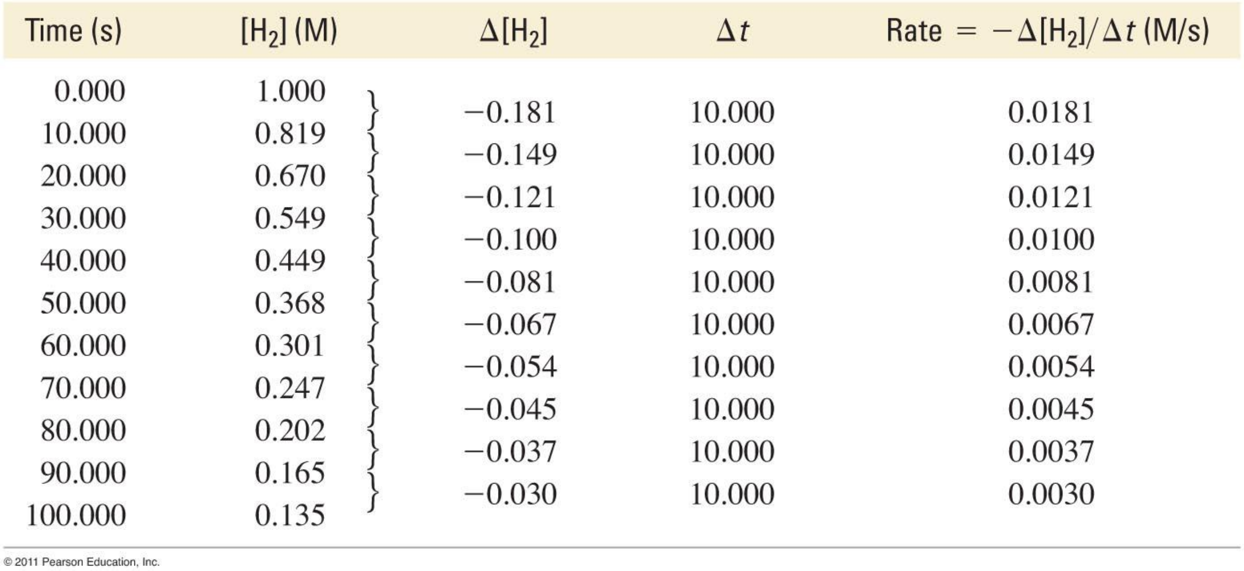
$$\text{Rate of disappearance of } H_2 = \frac{\Delta[\,H_2]}{\Delta\, t} = \frac{\text{decrease in the molar conc. of } H_2}{\text{time interval}}$$

- The expression above is referred to as: Average Rate over the time interval Δt

REACTION RATES



- Reactant concentration decreases with time, while product concentration increases with time.



Time (s)	$[H_2]$ (M)	$\Delta[H_2]$	Δt	Rate $= -\Delta[H_2]/\Delta t$ (M/s)
0.000	1.000			
		−0.181	10.000	0.0181
10.000	0.819			
		−0.149	10.000	0.0149
20.000	0.670			
		−0.121	10.000	0.0121
30.000	0.549			
		−0.100	10.000	0.0100
40.000	0.449			
		−0.081	10.000	0.0081
50.000	0.368			
		−0.067	10.000	0.0067
60.000	0.301			
		−0.054	10.000	0.0054
70.000	0.247			
		−0.045	10.000	0.0045
80.000	0.202			
		−0.037	10.000	0.0037
90.000	0.165			
		−0.030	10.000	0.0030
100.000	0.135			

REACTION RATES

- The Reaction Rate decreases as the reaction proceeds.
  Reason: the concentration of reactants decreases

- Any substance in the reaction can be used to express the Rxn. Rate

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

$$\text{Rate of disappearance of } H_2 = \frac{\Delta[H_2]}{\Delta t} = \frac{\text{decrease in the molar conc. of } H_2}{\text{time interval}}$$

$$\text{Rate of disappearance of } I_2 = \frac{\Delta[I_2]}{\Delta t} = \frac{\text{decrease in the molar conc. of } I_2}{\text{time interval}}$$

$$\text{Rate of formation of HI} = \frac{\Delta[HI]}{\Delta t} = \frac{\text{increase in the molar conc. of HI}}{\text{time interval}}$$

- Reaction Rate is always positive

$$\text{(a) Rate of formation of a product} = \frac{\Delta[\text{increase in concentration of product}]}{\Delta t}$$

$$\text{(b) Rate of decomposition of a reactant} = -\,\frac{\Delta[\text{decrease in concentration of reactant}]}{\Delta t}$$

Since: Δ[decrease in concentration of reactant] has a negative value the Reaction Rate will be positive

4. <u>Reaction Rate in terms of stoichiometry</u>

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

Rate of increase of HI = 2 x Rate of decrease of H_2

OR

$$\frac{\text{Rate of increase of HI}}{2} = \text{Rate of decrease of } H_2$$

Reason: 2 moles of HI are formed from reaction of 1 mole of H_2

REACTION RATES

Examples:

1. For the hypothetical reaction shown below, write a rate expression based on each reactant and product:

$$3\text{ A} + \text{B} \rightarrow 2\text{ C} + 4\text{ D}$$

Rate based on A =

Rate based on B =

Rate based on C =

Rate based on D =

2. Consider the following reaction:

$$H_2O_2\text{ (aq)} + 3\text{ I}^-\text{ (aq)} + 2\text{ H}^+\text{ (aq)} \rightarrow I_3^-\text{ (aq)} + 2\text{ H}_2O\text{ (l)}$$

In the first 10.0 seconds of the reaction, the concentration of I^- dropped from 1.000 M to 0.868 M.

a) Calculate the average rate of this reaction in this time interval.

b) Predict the rate of change in concentration of H^+ during this time interval.

RATE DETERMINATION

- Rate determination is done by monitoring the change in concentration of reactant or product over time.

Method:

- Withdraw samples from the reaction vessel at various times and analyze some of their physical or chemical properties that give information on the concentrations present.

Properties appropriate and easy to monitor

1. Color
   (if product or reactant absorbs light)

3. Oxidation State
   (using an electrochemical cell)

5. Volume, at constant p and T
   (useful, if:
   - gaseous reactants and/or products are present, and
   - number of moles of reactants ≠ number of moles of products)

6. Pressure, at constant V and T
   (useful, if:
   - gaseous reactants and/or products are present, and
   - number of moles of reactants ≠ number of moles of products)

7. Density
   (useful if : d(reactants) ≠ d(products))

Properties not appropriate to monitor

2. Flammability
   (difficult to measure quantitatively)

4. Mass
   (mass is conserved in a chemical reaction)

RATE LAW

Dependence of Reaction Rate on Concentration

$$2\ NO_2(g) + F_2(g) \longrightarrow 2\ NO_2F(g)$$

nitryl fluoride

Experimental observation:

Rate of Reaction = k $[NO_2]$ $[F_2]$

Meaning: - Doubling $[NO_2]$ —> Doubles the Reaction Rate
- Doubling $[F_2]$ —> Doubles the Reaction Rate

RATE LAW :

- Equation that relates the Rate of Reaction to the Concentration of Reactants and Catalyst raised to various powers.

General Form of an Equation: $aA + bB \xrightarrow{C} dD + eE$

General form for Rate Law: Rate = $k\,[A]^m[B]^n[C]^p$

m, n, and p

- are frequently, but not always integers
- must be determined experimentally
- are **not** the coefficients in the balanced chemical equation

k

- Rate Constant
- its units depend upon the form of Rate Law
- depends on temperature

REACTION ORDER

I. Reaction Order with respect to a given reactant species:

- Reaction Order is the exponent of the concentration of that species in the Rate Law, as determined experimentally

$$2\ NO_2(g) + F_2(g) \longrightarrow 2\ NO_2F(g)$$

nitryl fluoride

Experimental observation:

- Doubling $[NO_2]$ —> Doubles the Reaction Rate
- Doubling $[F_2]$ —> Doubles the Reaction Rate

Rate of Reaction = $k\ [NO_2]^m\ [F_2]^n$

Reaction is:

- First order with respect to NO_2 (m=1)
- First order with respect to F_2 (n=1)

II. Overall Reaction Order

- The overall reaction order is the sum of the orders of the reactant species

Overall Reaction Order = $m + n = 1 + 1 = 2$

Reaction is of the Second Order Overall.

Examples:

1. $2\ NO\ (g) + 2\ H_2\ (g) \longrightarrow N_2\ (g) + 2\ H_2O\ (g)$

Experimentally determined Rate Law = $k[NO]^2[H_2]$

Reaction is:

- 2nd order in NO
- 1st order in H_2
- **3rd order overall**

2. $CH_3COCH_3\ (aq) + I_2\ (aq) \xrightarrow{H^+} CH_3COCH_2I\ (aq) + HI\ (aq)$

Experimentally determined Rate Law = $k[CH_3COCH_3][H^+]$

Reaction is:

- 1st order in CH_3COCH_3
- 0 order in I_2 (does not depend on the concentration of I_2 as long as some I_2 is present)
- 1st order in the catalyst (H^+)
- **2nd order overall**

NOTE: Reaction Orders:

- are frequently whole numbers (1 or 2)
- may be fractional
- may be 0
- may be negative

- Effect of concentration change on reaction rates and orders can be summarized as:

Order	**Concentration**	**Rate**
Zero	**x 2**	**No Effect**
First	**x 2**	**x 2**
Second	**x 2**	**x 4**
Negative	**x 2**	**x ½**
Half	**x 2**	$\sqrt{2}$

EXPERIMENTAL DETERMINATION OF RATE LAW

- In determining the rate law for a reaction, first the order of reaction with respect to each reactant and catalyst must be found.
- Commonly a series of experiments are done in which the initial concentrations of reactants are varied (usually doubled).
- The results of these experiments will yield the respective orders of reaction.

Example: $2\ N_2O_5\,(g) \longrightarrow 4\ NO_2\,(g) + O_2\,(g)$

	Initial N_2O_5 Conc. (M)	**Initial Rate of Disappearance of N_2O_5 (M/s)**
Experiment 1	$1.0\text{x}10^{-2}$	$4.8\text{x}10^{-6}$
Experiment 2	$2.0\text{x}10^{-2}$	$9.6\text{x}10^{-6}$

Rate = k $[N_2O_5]^m$ m = ? (must be determined from experimental data)

$$\frac{\text{Rate Exp. 2}}{\text{Rate Exp. 1}} = \frac{k\,(2)^m}{k(1)^m} = \frac{9.6\text{x}10^{-6}}{4.8\text{x}10^{-6}} = 2$$

Experimental: ➢ Doubling $[N_2O_5]$ doubled the rate of reaction

It follows: ➢ $m = 1\ \ (2^1 = 2)$

The Reaction is: ➢ First order in N_2O_5
➢ First order overall

$$\boxed{\text{Rate} = k\,[N_2O_5]^1} \qquad \boxed{\text{Rate} = k\,[N_2O_5]}$$

Effect of Doubling the Initial Concentration of Reactant on Reaction Rate

Change in Reaction Rate	**Rate is multiplied by**	**Reaction Order**
Rate is halved	$½ = 2^{-1}$	–1
Rate is the same	$1 = 2^0$	0
Rate is doubled	$2 = 2^1$	1
Rate is quadrupled	$4 = 2^2$	2

Examples:

1. Use the rate data below to
   A) determine the reaction orders with respect to $[H_2O_2]$, $[I^-]$ and $[H^+]$ and
   B) find the rate constant k for the reaction shown below:

$$H_2O_2\,(aq) + 3\,I^-\,(aq) + 2\,H^+\,(aq) \longrightarrow I_3^-\,(aq) + 2\,H_2O\,(l)$$

	Initial Concentrations (M)			**Initial Rate (M/s)**
	$[H_2O_2]$	**$[I^-]$**	**$[H^+]$**	
Experiment 1	0.010	0.010	0.00050	$1.15\text{x}10^{-6}$
Experiment 2	0.020	0.010	0.00050	$2.3\text{x}10^{-6}$
Experiment 3	0.010	0.020	0.00050	$2.30\text{x}10^{-6}$
Experiment 4	0.010	0.010	0.00100	$1.15\text{x}10^{-6}$

Solution

A) Compare two rate experiments in which all concentrations of reactants but one are held constant:

$[H_2O_2]$: Compare **Experiment 1** and **Experiment 2**
When $[H_2O_2]$ is doubled, the **Rate is doubled**
It follows: $2^m = 2$ $m = 1$ **1st order in $[H_2O_2]$**

$[I^-]$: Compare **Experiment** 1 and **Experiment 3**
When $[I^-]$ is doubled, the **Rate is doubled**
It follows: $2^n = 2$ $n = 1$ **1st order in $[I^-]$**

$[H^+]$: Compare Experiment 1 and Experiment 4
When **$[H^+]$ is doubled, the Rate does not change**
It follows: $2^p = 1$ $p = 0$ **0 order in $[H^+]$**

$$H_2O_2\,(aq) + 3\,I^-\,(aq) + 2\,H^+(aq) \longrightarrow I_3^-(aq) + 2\,H_2O(l)$$

Summary: 1st order in $[H_2O_2]$
1st order in $[I^-]$
0 order in $[H^+]$

$$\text{RATE} = k\,[H_2O_2]^{1}\,[I^-]^{1}\,[H^+]^{0}$$

commonly written : $\boxed{\textbf{RATE} = \textbf{k}\,[H_2O_2]\,[I^-]}$

NOTE: Reaction Orders are **not** related to the coefficients of the overall equation

B) Find the Rate Constant, k

From Experiment 1: (any other experiment could be used)

$[H_2O_2] = 0.010$ M
$[I^-] = 0.010$ M
Rate = 1.15×10^{-6} M/s
k = ?

RATE = k $[H_2O_2]\,[I^-]$

$$k = \frac{\text{Rate}}{[H_2O_2][I^-]} = \frac{1.15\text{x}10^{-6}\ \text{M/s}}{(0.010\ \text{M})(0.010\ \text{M})} = 1.2\text{x}10^{-2}\ \text{M}^{-1}\text{s}^{-1}$$

2. Use the rate data below to

A) determine the rate law for the reaction A + B → C, and
B) calculate the rate constant k, and
C) calculate the rate of reaction for experiment 4

Experiment Number	**[A] (M)**	**[B] (M)**	**Initial Rate (M/s)**
1	0.100	0.100	$4.0\text{x}10^{-5}$
2	0.100	0.200	$4.0\text{x}10^{-5}$
3	0.200	0.100	$16.0\text{x}10^{-5}$
4	0.050	0.100	????

INTEGRATED RATE LAW (1^{ST} ORDER REACTION)

Concentration – Time Equations for First Order Reactions

- are derived from experimental data
- predict concentrations at all times

$$2\,N_2O_5\,(g) \longrightarrow 4\,NO_2\,(g) + O_2\,(g)$$

$$\text{Rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k\,[N_2O_5]$$

Using calculus:

$$\boxed{\ln \frac{[N_2O_5]_t}{[N_2O_5]_0} = -kt} \quad \text{OR} \quad \boxed{\log \frac{[N_2O_5]_t}{[N_2O_5]_0} = \frac{-kt}{2.303}}$$

more commonly used!

$[N_2O_5]_t$: concentration at time t
$[N_2O_5]_0$: concentration at time 0

These equations can be used to calculate:

- concentration of $[N_2O_5]$ at any time,
- the time it takes for $[N_2O_5]$ to decrease to a particular value

In General:

$$a\,A \longrightarrow \text{Products}$$

Assuming First Order Rate Law: Rate = k[A]

Differential Rate Law: $\boxed{-\frac{\Delta[A]}{\Delta t} = k[A]}$

Integrated Rate Law: $\boxed{\ln \frac{[A]_t}{[A]_0} = -kt}$ OR $\boxed{\log \frac{[A]_t}{[A]_0} = \frac{-kt}{2.303}}$

Example 1:

Sulfuryl chloride, SO_2Cl_2, decomposes when heated:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

- In an experiment, the initial concentration of SO_2Cl_2 was 0.0248 M
- The Rate Constant is $2.2 \times 10^{-5}\ s^{-1}$. The Reaction is first order.
- What is the concentration of SO_2Cl_2 after 2.5 hours?

$[A]_0 = 0.0248$ M $\qquad k = 2.2 \times 10^{-5}\ s^{-1}$ $\qquad t = 2.5$ h ($9\underline{0}00$ s)

$$\log \frac{[A]_t}{[A]_0} = \frac{-kt}{2.303} \qquad \log \frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0} = \frac{-kt}{2.303}$$

$$\log \frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0} = \frac{-(2.2 \times 10^{-5}\ s^{-1})(9000\ s)}{2.303} = -0.086$$

Take antilogarithms of both sides;

$$\frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_0} = 0.82 \qquad [SO_2Cl_2]_t = (0.82) \times [SO_2Cl_2]_0$$

$$[SO_2Cl_2]_t = (0.82)(0.0248\ M) = \mathbf{2.0 \times 10^{-2}\ M}$$

Significant Figures, Logs and Antilogs

Find log of (3.6×10^{-12})

$$\log(\underbrace{3.6}_{\text{2 Sig Figs}} \times 10^{-12}) = -11.\underbrace{44}_{\text{2 decimals}}$$

Given: -11.44, find antilog:

$$\text{Antilog} = 10^{-11.\underbrace{44}_{\text{2 decimals}}} = \underbrace{3.6}_{\text{2 Sig Figs}} \times 10^{-12}$$

Example 2:

Cyclobutane, C_4H_8 decomposes, when heated to give ethylene:

$$C_4H_8\,(g) \longrightarrow 2\,C_2H_4\,(g)$$

- The reaction is first order.
- In an experiment, the initial concentration of C_4H_8 was 0.00150 M.
- After heating at 450°C for 455 seconds, this was reduced to 0.00119 M.
- What was the concentration of C_4H_8 after a total of 827 seconds?

$[C_4H_8]_0 = 0.00150$ M $[C_4H_8]_{455} = 0.00119$ M $[C_4H_8]_{827} = ?$

a) Calculate rate constant (k) for the reaction:

$$\log\frac{[C_4H_8]_{455}}{[C_4H_8]_0} = \log\frac{0.00119\text{ M}}{0.00150\text{ M}} = -\frac{k\,(455\text{ s})}{2.303} = -19\underline{7}.57\,k$$

$$\log 0.79\underline{3}3 = -19\underline{7}.57\,\mathbf{k}$$

$$-0.10\underline{0}54 = -19\underline{7}.57\,\mathbf{k}$$

$$\mathbf{k} = 5.0\underline{8}9 \text{ x } 10^{-4}\text{ s}^{-1}$$

b) Calculate concentration of C_4H_8 at 827 s:

$$\log\frac{[C_4H_8]_{827}}{[C_4H_8]_0} = = -\frac{k\,(t)}{2.303} = -\frac{(5.0\underline{8}9 \text{ x } 10^{-4}\text{ s}^{-1})(827\text{ s})}{2.303} = -0.18\underline{2}7$$

Taking the antilog of both sides:

$$\frac{[C_4H_8]_{827}}{[C_4H_8]_0} = 0.65\underline{6}6$$

Substituting $[C_4H_8]_0$

$$\frac{[C_4H_8]_{827}}{0.00150\text{ M}} = 0.65\underline{6}6$$

$$\mathbf{[C_4H_8]_{827}} = 9.85 \text{ x } 10^{-4}\text{ M}$$

HALF-LIFE ($t_{1/2}$) OF A FIRST ORDER REACTION

- Half-life is the time it takes for the reactant concentration to decrease to one-half of its initial value.

$$\log \frac{[A]_t}{[A]_0} = \frac{-k\,t}{2.303}$$

In one half-life ($t_{1/2}$): $[A]_t = \frac{1}{2}[A]_0 \Longrightarrow \log \frac{\frac{1}{2}[A]_0}{[A]_0} = \frac{-k\,(t_{1/2})}{2.303}$

$$-0.301 = \frac{-k\,(t_{1/2})}{2.303} \Longrightarrow t_{1/2} = \frac{0.301 \times 2.303}{k}$$

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

NOTES:

- Half-Life does not depend on the initial concentration, $[A]_0$
- The half-life is the same at any time during the reaction

Example:
Dinitrogen pentoxide, decomposes when heated in carbon tetrachloride solvent:

$$N_2O_5\,(g) \longrightarrow 2\,NO_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

The rate law is first order in N_2O_5 with a rate constant of $6.2\text{x}10^{-4}\ \text{min}^{-1}$.

(a) What is the half-life for this reaction?

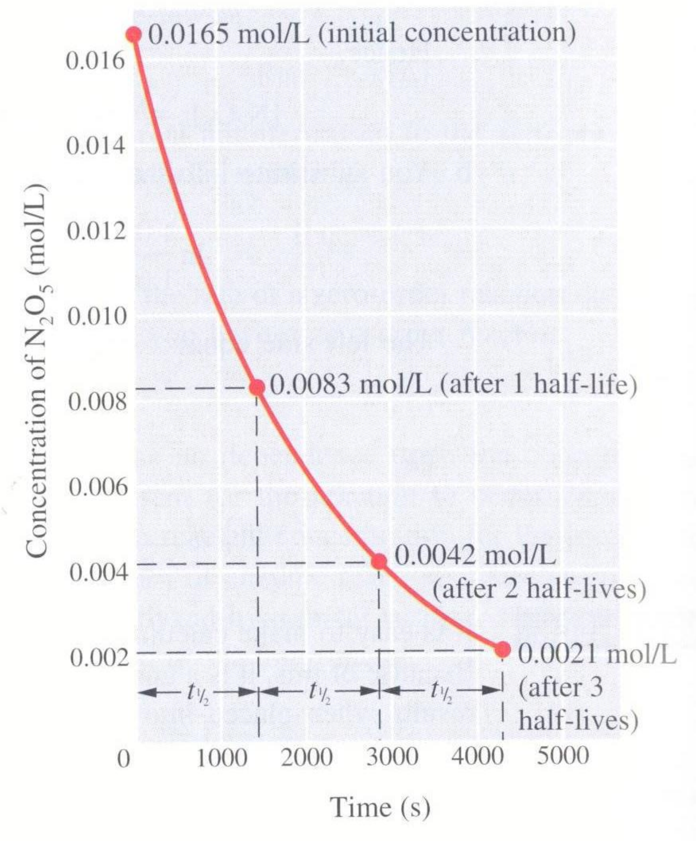
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2\text{x}10^{-4}\ \text{min}^{-1}} = 1118\ \text{min} = 1.1\text{x}10^{3}\ \text{min}$$

(b) How long would it take for the concentration of N_2O_5 to decrease to 25 % of its initial value?

$$t_{25\,\%\ \text{left}} = t_{1/4\ \text{left}} = 2 \text{ x } t_{1/2} = 2\,(1.1 \text{ x } 10^3\ \text{min}) = 2.2 \text{ x } 10^3\ \text{min}$$

(c) How long would it take for the concentration of N_2O_5 to decrease to 12.5 % of its initial value?

$$t_{12.5\,\%\ \text{left}} = t_{1/8\ \text{left}} = 3 \text{ x } t_{1/2} = 3\,(1.1 \text{ x } 10^3\ \text{min}) = 3.3 \text{ x } 10^3\ \text{min}$$



- In each half-life the concentration of the reactant is halved.
- First half-life: concentration changes from 0.016 M to 0.008 M (1440 s)
- Second half-life: concentration changes from 0.008 M to 0.004 M (2880 s)
- Third half-life: concentration changes from 0.004 M to 0.002 M (4320 s)
- **Half-life of first order reactions is independent of concentration**

Concentration (M)	Decrease in Concentration	Time Elapsed (s)	Number of Half-lives Elapsed
0.0120	0	0	0
0.0060	50%	1300	1
0.0030	25%	2600	2
0.0015	12.5%	3900	3
0.00075	6.25%	5200	4

In General:

Concentration	Time	Number of Half-lives
A_0	0	0
½ A_0 = 50% A_0	$t_{½}$	1
¼ A_0 = 25%	$t_{¼}$	2
1/8 A_0 = 12.5%	$t_{1/8}$	3
1/16 A_0 = 6.25%	$t_{1/16}$	4

GRAPHING FIRST ORDER REACTIONS

- The order of a reaction can be determined by graphing the experimental data.

- The experimental data are plotted by
  1. First assuming a first-order reaction,
  2. Second, assuming a second-order reaction,
  3. Third, assuming a third-order reaction, and so on.

- The graph which best fits the experimental data gives the order of a reaction.

- First order Rate Law:

$$\log \frac{[A]_t}{[A]_0} = \frac{-k\,t}{2.303}$$

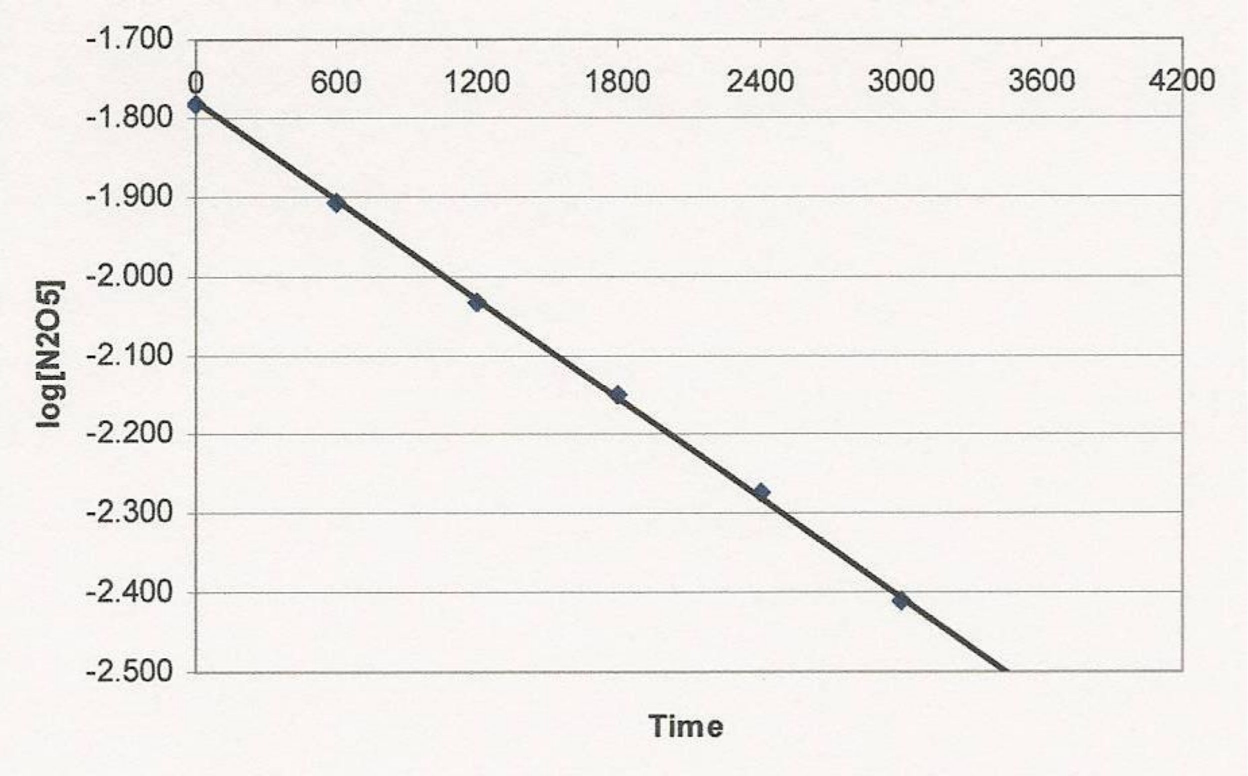
- This equation may be rewritten:

$$\log [A]_t = \left(\frac{-k\,t}{2.303}\right) + \log [A]_0$$ (This is the equation of a straight line)

$$\log [A]_t = \left(\frac{-k}{2.303}\right) t + \log [A]_0 \qquad y = mx + b$$

- A plot of **log [A] (y)** versus **time (x)** should give a straight line for a first order reaction.

Time	**$[N_2O_5]$**	**$\log [N_2O_5]$**
0	0.0165	–1.783
600	0.0124	–1.907
1200	0.0093	–2.032
1800	0.0071	–2.149
2400	0.0053	–2.276
3000	0.0039	–2.409
3600	0.0029	–2.538



- NOTE: The points lie on a straight line
- MEANING: The Rate Law is First Order

$$m = \text{slope of the straight line} = \frac{\Delta y}{\Delta x} = \frac{(-2.538)-(-1.783)}{(3600-0)\ \text{s}} = \frac{-0.755}{3600\ \text{s}} = -2.10 \times 10^{-4}\ \text{s}^{-1}$$

This can be used to calculate k, the Rate constant

Recall: $\log [A]_t = \left(\frac{-k\,t}{2.303}\right) + \log [A]_0$ $y = mx + b$

It follows:

$$m = \frac{-k}{2.303} \qquad k = -2.303\,(-2.10 \times 10^{-4}\ \text{s}^{-1}) = 4.84 \times 10^{-4}\ \text{s}^{-1}$$

INTEGRATED RATE LAW (2ND ORDER REACTION)

Concentration – Time Equations for First Order Reactions

$$a\,A \longrightarrow \text{Products}$$

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

Differential Rate Law

By using calculus:

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

Integrated Rate Law

Example:

1. For the reaction

$$2\,NO_2\,(g) \longrightarrow 2\,NO\,(g) + O_2\,(g)$$

At 330 K:

$k = 0.775\ M^{-1}s^{-1}$ $[A]_0 = 0.0030\ M$ $\mathbf{[A]_{645}} = ?$

$$\frac{1}{[A]_t} = (0.775\ M^{-1}s^{-1})(645\ s) + \frac{1}{0.0030\ M}$$

$$\frac{1}{[A]_t} = (49\underline{9}.9\ M^{-1}) + (3\underline{3}3.3\ M^{-1}) = 8.3\text{x}10^{2}\ M^{-1}$$

$$\mathbf{[A]_t = 0.0012\ M}$$

HALF-LIFE ($t_{1/2}$) OF A SECOND ORDER REACTION

- Half-life is the time it takes for the reactant concentration to decrease to one-half of its initial value.

For a second order reaction: Rate = $k\,[A]^2$ and $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

In one half-life ($t_{1/2}$): $[A]_t = \dfrac{1}{2}[A]_0 \Longrightarrow \dfrac{1}{0.5[A]_0} = kt + \dfrac{1}{[A]_0}$

$$kt_{1/2} = \frac{1}{0.5[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} \Longrightarrow \boxed{t_{1/2} = \frac{1}{k\,[A]_0}}$$

NOTES:

- Half-Life depends on the initial concentration, $[A]_0$
- Half-Life increases as reaction progresses

Example:

1. For a particular 2nd order reaction $k = 0.775\ M^{-1}s^{-1}$.

a) How long does it take to the concentration to decrease from 0.0030 M to 0.0015?

For concentration to drop to half of its original value, t = half-life

$$t_{1/2} = \frac{1}{k\,[A]_0} = \frac{1}{(0.775\ M^{-1}s^{-1})(0.0030\ M)} = 430\ s$$

b) How long does it take for the concentration to be halved again?

$$t_{1/2} = \frac{1}{k\,[A]_0} = \frac{1}{(0.775\ M^{-1}s^{-1})(0.0015\ M)} = 860\ s \longleftarrow$$

Twice as long

GRAPHING SECOND ORDER REACTIONS

$$\begin{array}{ccccc}
\boxed{\frac{1}{[A]_t}} & = & k\ \ t & + & \boxed{\frac{1}{[A]_0}} \\
\uparrow & & \uparrow\ \ \uparrow & & \uparrow \\
y & = & m\ \ x & + & b \\
 & & \uparrow & & \uparrow \\
 & & \text{slope} & & \text{intercept}
\end{array}$$

Meaning:

- **A plot of $\frac{1}{[A]_t}$ (y) versus time (s) should give a straight line for a second order reaction**

<u>Summary</u>:

To determine the order of a reaction,

1. Collect time vs. concentration data for the reaction.
2. Assuming 1st order, plot log [A] vs. time.
3. If a linear graph is obtained, then it is 1st order.
4. If no linear graph, then plot 1/[A] vs. time.
5. If a linear graph is obtained, then it is 2nd order.

Example:

1. Given the experimental data listed below, determine if the reaction is 1st or 2nd order, and determine the rate constant (k) for the reaction shown below:

$$2\ NO_2(g) \longrightarrow 2\ NO(g) + O_2(g)$$

Time (s)	**$[NO_2]_0$ (M)**
0	1.00×10^{-2}
60	0.683×10^{-2}
120	0.518×10^{-2}
180	0.418×10^{-2}
240	0.350×10^{-2}
300	0.301×10^{-2}
360	0.264×10^{-2}

Strategy:

- We must first see if the data fits the Rate Law for 1st Order Reactions. If it does, the reaction is of the 1st order
- If it does not, we must see if the data fits the Rate Law for 2nd Order If it does, the reaction is of the 2nd order

First Order Rate Law:

$$\log [A]_t = \left(\frac{-k\,t}{2.303}\right) + \log [A]_0$$

Plot log $[A]_t$ as a function of t

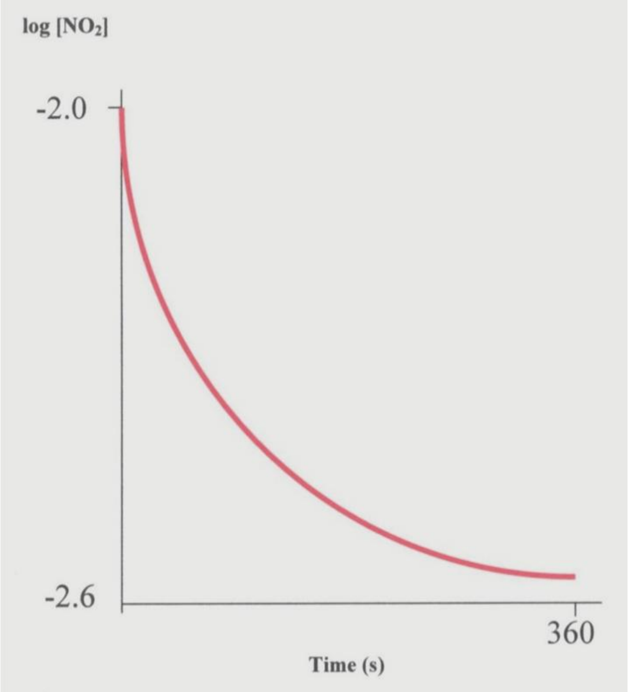
$$\boxed{y \;=\; m\,x \;+\; b}$$

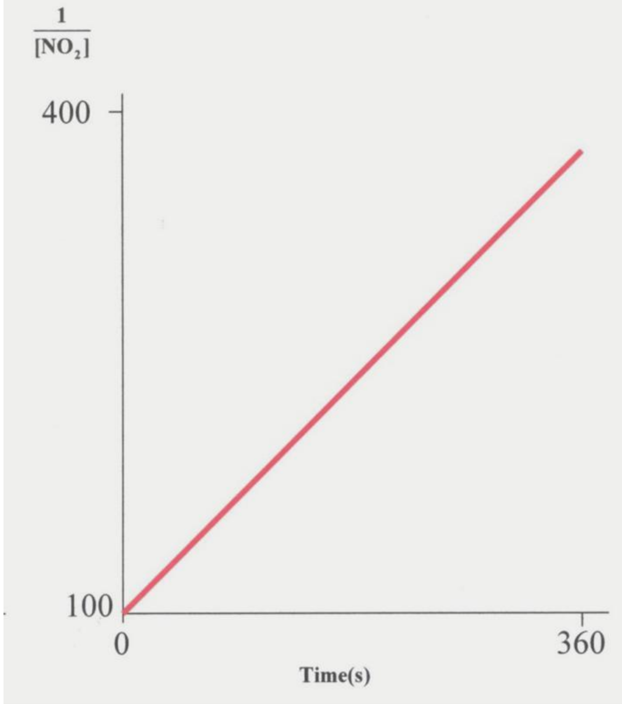
Second order Rate Law

$$\frac{1}{[A]_t} = k\,t + \frac{1}{[A]_0}$$

Plot $1/[A]_t$ as a function of t

Time (s)	**$[NO_2]_0$ (M)**	**log $[A]_t$**	**$1/[A]_t$ (M^{-1})**
0	1.00×10^{-2}	–2.000	100
60	0.683×10^{-2}	–2.166	146
120	0.518×10^{-2}	–2.286	193
180	0.418×10^{-2}	–2.379	239
240	0.350×10^{-2}	–2.456	286
300	0.301×10^{-2}	–2.521	332
360	0.264×10^{-2}	–2.2578	379





- Not a straight line
- Reaction is not of 1st Order

- A straight line is obtained
- **Reaction is of 2nd Order**

$$k = \text{slope} = \frac{\Delta y}{\Delta t} = \frac{(379 - 100)\ M^{-1}}{(360 - 0)} = 0.775\ M^{-1}s^{-1}$$

SUMMARY OF KINETICS EQUATIONS

Order	Rate Law	Differential Rate Law	Integrated Rate Law	Half-Life	Graphical Plot for a Straight Line
0	k	$-\frac{\Delta[A]_t}{\Delta t} = k$	$[A] = -k\,t + [A]_0$	$\frac{[A]_0}{2\,k}$	[A] vs. t
1	Rate = k [A]	$-\frac{\Delta[A]_t}{\Delta t} = k\,[A]$	$\log \frac{[A]_t}{[A]_0} = -\frac{kt}{2.303}$ or $\log [A]_t = (\frac{-k\,t}{2.303}) + \log [A]_0$	$\frac{0.693}{k}$	log [A] vs. t
2	Rate = k $[A]^2$	$-\frac{\Delta[A]_t}{\Delta t} = k\,[A]^2$	$\frac{1}{[A]_t} = k\,t + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$	$\frac{1}{[A]_0}$ vs. t

Examples:

1. Ethylene oxide, $C_2H_4O(g)$, decomposes when heated to give methane and carbon monoxide:

$$C_2H_4O\,(g) \longrightarrow CH_4\,(g) + CO\,(g)$$

The following kinetic data were observed for the reaction at 688K

	$[C_2H_4O]_0$ (M)	Initial Rate (M/s)
Experiment 1	0.00272	5.57×10^{-7}
Experiment 2	0.00544	1.11×10^{-6}

Find the Rate Law and the value of the Rate Constant.

Rate =

k =

Examples:

3. In a kinetic study of the reaction shown below, the following data were obtained for the initial rates of disappearance of NO and O_2 :

$$2\ NO\ (g)\ +\ O_2\ (g) \longrightarrow 2\ NO_2\ (g)$$

	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
Experiment 1	0.0125	0.0253	0.0281
Experiment 2	0.0250	0.0253	0.112
Experiment 3	0.0125	0.0506	0.0561

Obtain the Rate Law and the Rate Constant.

Rate =

k =

4. In the presence of excess thiocyanate ion (SCN^-) the following reaction is 1st order with respect to Fe^{3+} with a rate constant of 1.27 s^{-1}.

$$Fe^{3+}(aq)\ +\ SCN^-(aq) \longrightarrow Fe(SCN)^{2+}(aq)$$

a) What is the Half-Life in seconds?

$t_{1/2}$ =

b) How many seconds would be required for the initial concentration of Fe^{3+} to decrease to each of the following values? (25.0 % and 12.5 %)

c) How many seconds are required for 90.0% of reaction to be completed?

5. Methyl acetate (CH_3COOCH_3) reacts in basic solution to give acetate ion (CH_3COO^-) and methanol (CH_3OH).

$$CH_3COOCH_3\,(aq) \quad + \quad OH^-\,(aq) \longrightarrow CH_3COO^-\,(aq) \quad + CH_3OH\,(aq)$$

The overall order of reaction was determined by starting with methyl acetate, CH_3COOCH_3 and hydroxide ion, OH^- , at the same concentrations, so $[CH_3COOCH_3] = [OH^-] = x$.

Then $\text{Rate} = k\,[CH_3COOCH_3]^m\,[OH^-]^{n\,=}\,k\,x^{m+n}$

Determine the overall order and the value of the rate constant by plotting data assuming first- and then second-order kinetics.

Time (min)	$[CH_3COOCH_3]$ (M)		
0.00	0.01000		
3.00	0.00740		
4.00	0.00683		
5.00	0.00634		

TEMPERATURE AND RATE

- The Rate of Reaction depends on Temperature.

Recall:

- k (rate constant) is temperature dependent.
- In most cases k increases with temperature

Example: $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$

Temperature	**k**
25^0 C	$4.9 \times 10^{-6}\ M^{-1}s^{-1}$
35^0 C	$15 \times 10^{-6}\ M^{-1}s^{-1}$

NOTE:

- In this case, **"k"** (the Rate Constant) is more than tripled for a 10^0 C increase in temperature.
- Consequently, for this reaction, the Reaction Rate is also more than tripled for a 10^0 C increase in temperature.

Why?

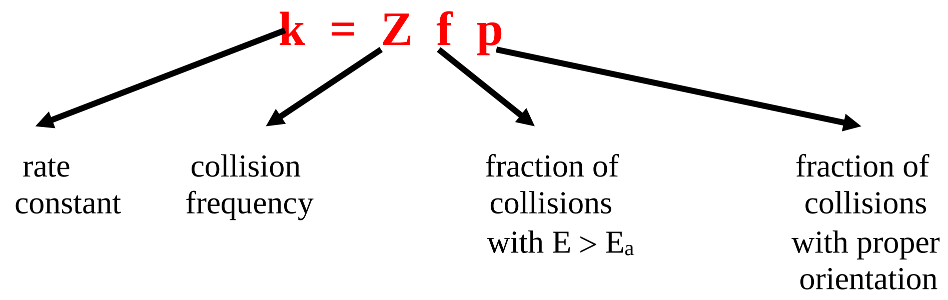
COLLISION THEORY

- Collision theory states that for a reaction to occur, the reactant molecules must collide:
    - with an **energy** greater that some minimum value, called Activation Energy (E_a)

and

- with the **proper orientation**
- **“k”** is shown to depend on 3 factors:

$$k = Z\ f\ p$$



For the previous example:

$$NO\ (g) + Cl_2\ (g) \longrightarrow NOCl\ (g) + Cl\ (g)$$

Z = collision frequency – (depends on temperature)

- (As **“t”** increases —> molecules move faster —> molecules collide more often)
- Root-mean-square (r m s) ≈ average molecular speed = u

$$\mathbf{u = \sqrt{\frac{3RT}{M_m}}}$$

- This relationship shows that :
    - At 25^0C, a 10^0C increase in temperature, increases Z by 2 %
    - This does not explain the large increase in rate with temperature

f = fraction of molecules with $E > E_a$

$$f = e^{-\frac{E_a}{RT}}$$

$e = 2.718$
$R = 8.31$ J/molK
$E_a = 8.5 \times 10^4$ J/mol

For: $NO(g) + Cl_2(g) \longrightarrow NOCl(g) + Cl(g)$

At : 25^0 C (298K) $f = 1.2 \times 10^{-15}$

35^oC (308) $f = 3.8 \times 10^{-15}$

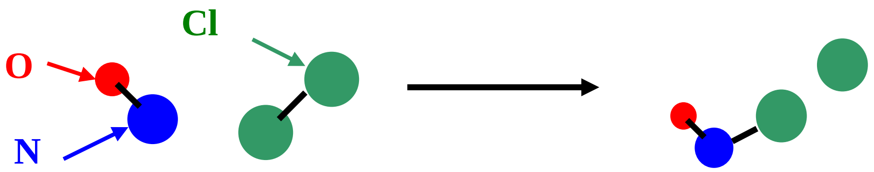
NOTE: 1. "f " triples with a 10^0C increase in temperature

2. The Effect of E_a is impressive:

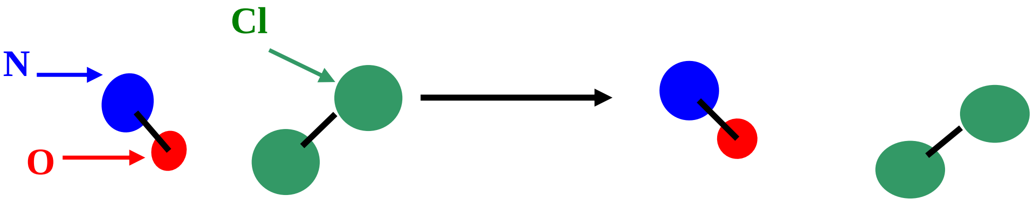
- If E_a is large —>"f" is small" —> "k" is small—>reaction is slow
- If E_a is small —>"f" is large" —> "k" is large—>reaction is fast

p = fraction of collisions with proper orientation

- The only effective orientation is the one in which:
  - The NO molecules approaches with N atom toward Cl_2
  - The angle of approach is about that expected for the formation of bonds in NOCl (slightly less than 120^0)
  - See below an effective orientation:



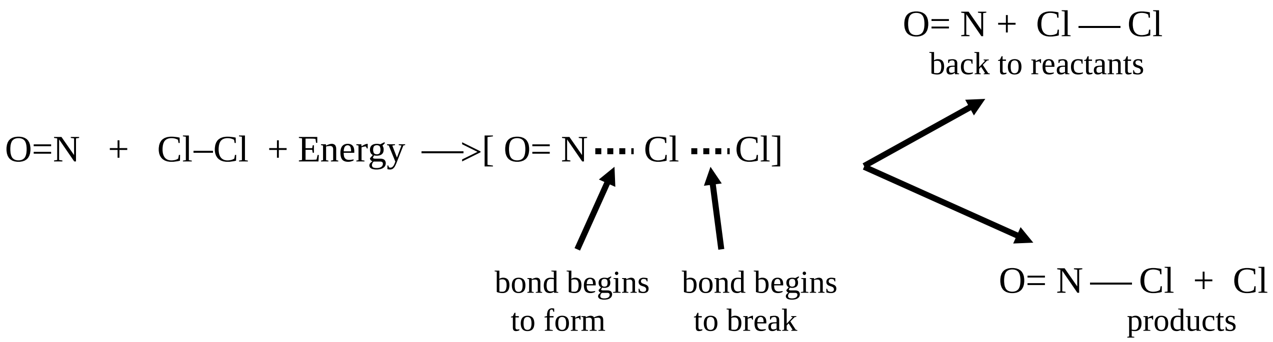
  - All other orientations will result in ineffective collisions:



TRANSITION STATE THEORY

- This theory explains the reaction resulting from the collision of 2 molecules, in terms of an ***activated complex***.

- An Activated Complex (***Transition State***) is an unstable grouping of atoms that can break up to form products:



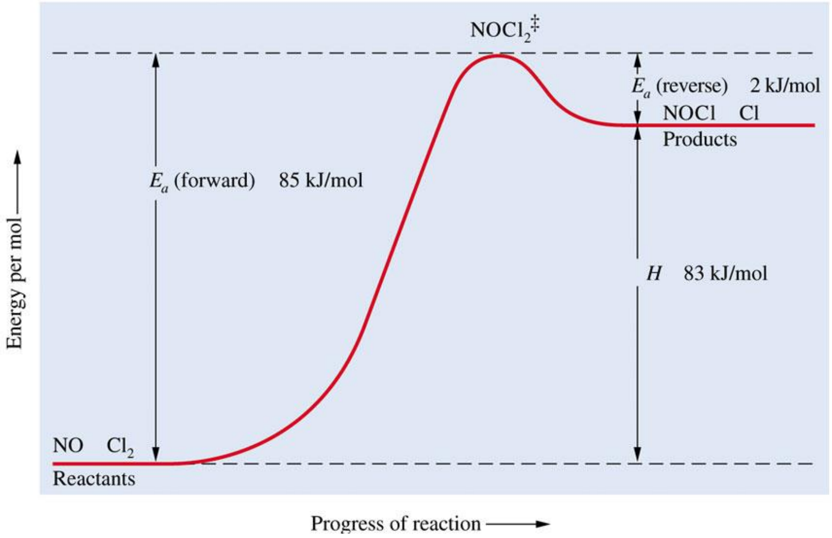
- Which bond breaks depends on where the absorbed energy is concentrated.

POTENTIAL – ENERGY DIAGRAMS FOR REACTIONS

I. Endothermic Reactions

Reactants + 83 kJ/mol ——> Products $\Delta H = + 83$ kJ/mol
Energy of Reactants < Energy of Products

Example: NO + Cl_2 ——> $NOCl_2^*$ ——> NOCl + Cl
activated complex



NOTEs:

1. Sum of (Kinetic Energy + Potential Energy) is constant throughout the reaction. (Law of Conservation of Energy)
2. From: Reactants ———> Activated Complex
   (NO + Cl_2) ($NOCl_2^*$)
   - Potential Energy increases (outer electrons of molecules repel, as molecules get closer)
   - Kinetic Energy decreases (molecules slow down)
   - Kinetic Energy changes into Potential Energy
3. The reaction will yield product only if : PE(max) ≥ Activation Energy (Ea). This will only occur if reactant molecules possess sufficient KE to start with.

   KE (reactants) ———> PE max (of activated complex) ≥ Activation Energy (E_a)
4. Comparing the forward and the reverse reactions.

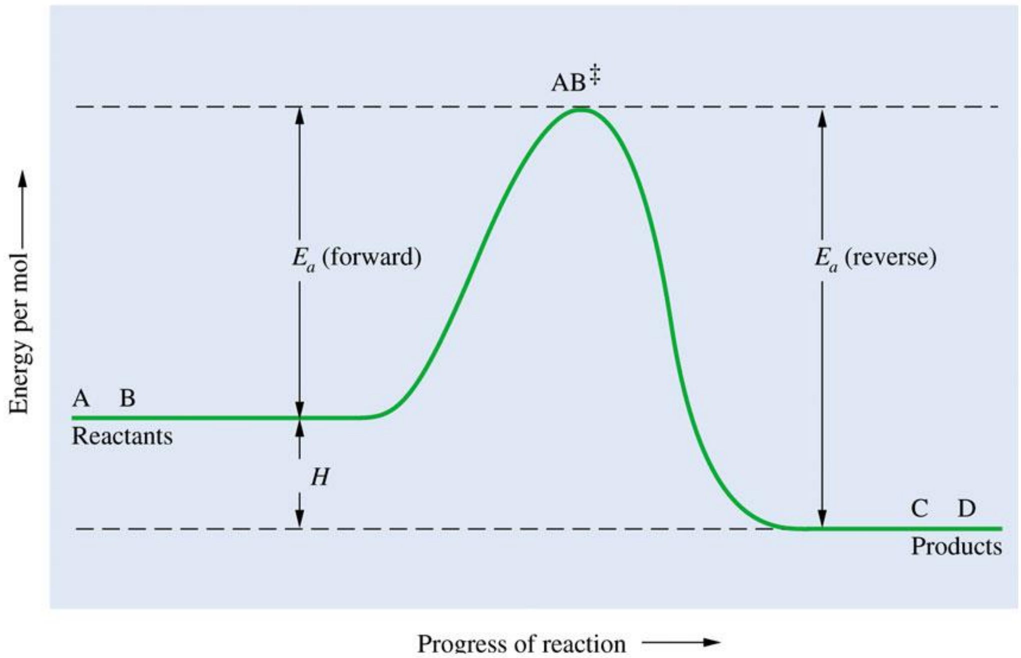
Forward Rxn		Reverse Reaction
NO + Cl_2 —> NOCl + Cl		NOCl + Cl —> NO + Cl_2
Ea = 85 kJ/mol	>>>>>>>>>>>>>	Ea = 2 kJ/mol
k is much smaller		k is much larger
Reaction is much slower		Reaction is much faster

II. **Exothermic Reactions**

Reactants – ΔH ——> Products ΔH is negative

Energy of Reactants > Energy of Products

Example: A + B ——> C + D+ Energy



ARRHENIUS EQUATION

$$\boxed{k = A\,e^{-\frac{Ea}{RT}}}$$

e = 2.718
Ea = Activation Energy
R = gas constant = 8.31 J/K x mol
T = absolute temperature
A = frequency factor

- The equation expresses the dependence of k on temperature.

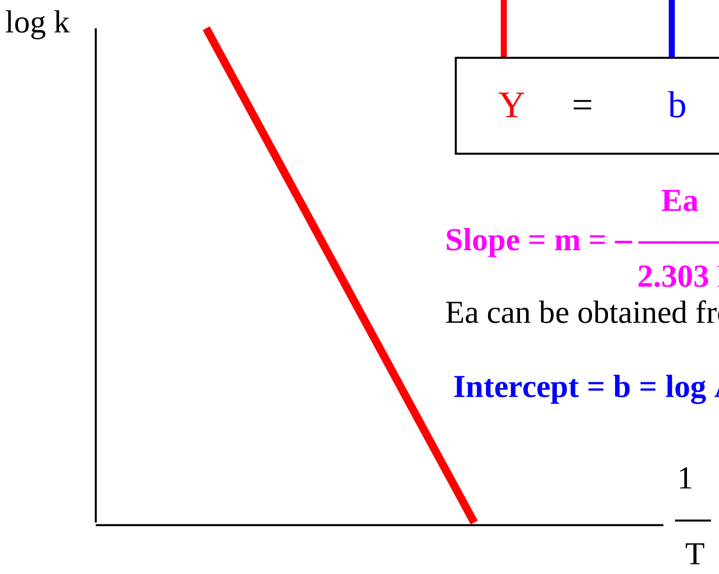
  A = frequency factor

  - A is related to the frequency of collisions (Z) with proper orientation (p)
  - A depends slightly on temperature (but can be ignored)

$$\ln k = \ln A - \frac{Ea}{RT} \qquad\qquad \log k = \log A - \frac{Ea}{2.303\,RT}$$

$$\underset{\underset{Y}{\uparrow}}{\log k} = \underset{\underset{b}{\uparrow}}{\log A} - \underset{\underset{m}{\uparrow}}{\left(\frac{Ea}{2.303\,R}\right)}\underset{\underset{x}{\uparrow}}{\left(\frac{1}{T}\right)}$$

$$\boxed{Y \;=\; b \;+\; m \qquad x}$$



$$\text{Slope} = m = -\frac{Ea}{2.303\,R}$$

Ea can be obtained from the slope

Intercept = b = log A

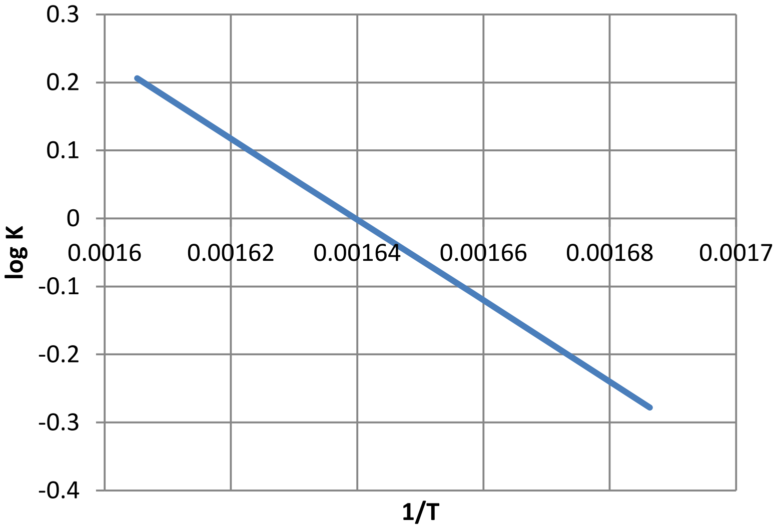
Examples:

1. Sketch a potential energy diagram for the decomposition of nitrous oxide:

$$2\ N_2O\ (g) \rightarrow 2\ N_2\ (g) + O_2\ (g)$$

The activation energy for the forward reaction is 251 kJ; the ΔH° is +167 kJ. What is the activation energy for the reverse reaction? Label the diagram appropriately.

2. The rate constant for a particular reaction was studies at various temperatures and a plot of log k vs. 1/T was obtained as shown below. Determine the activation energy of this reaction based on the graph below.



REACTION MECHANISMS

- Reaction Mechanisms show the steps involved in the change from Reactants to Products

- Mechanisms consist of a set of "**Elementary Reactions**" whose overall effect is the Net Chemical Equation.

Elementary Reactions:

- **Elementary reactions** are single molecular events that result in a reaction and are caused by molecular collisions

$NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g)$ Net Chemical Equation

Below 500K, this reaction takes place in 2 steps:

Elementary Reaction 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$

Reaction
intermediate
(short-lived)

Elementary Reaction 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$

- Adding the steps (Elementary Reactions) yields the Overall Equation:

$$\begin{array}{l} \cancel{NO_2} + NO_2 \longrightarrow \cancel{NO_3} + NO \\ \cancel{NO_3} + CO \longrightarrow \cancel{NO_2} + CO_2 \\ \hline NO_2 + CO \longrightarrow NO + CO_2 \end{array}$$

Overall Equation

Example 1:

The decomposition of Ozone (O_3) is believed to occur in 2 steps:

Elementary Reaction 1: $O_3 \rightleftharpoons O_2 + O$

Elementary Reaction 2: $O_3 + O \longrightarrow 2O_2$

Identify any Reaction Intermediate:
What is the Overall equation?

Example 2:

Sodium hydrogen carbonate (**$NaHCO_3$**), also called sodium bicarbonate can been synthesized through a sequence of 3 elementary steps:

$$CO_2\ g) \quad + \quad H_2O \rightleftharpoons H_2CO_3\ (aq)$$

$$H_2CO_3\ (aq) \quad + \quad NH_4OH \longrightarrow NH_4HCO_3\ (aq) + H_2O\ (l)$$

$$NH_4HCO_3\ (aq) + NaCl\ (aq) \longrightarrow \mathbf{NaHCO_3\ (s)} + NH_4Cl\ (aq)$$

Identify the Reaction Intermediates:

Write the Overall Equation:

$$CO_2\ g) \quad + \quad H_2O\ (l) \rightleftharpoons H_2CO_3\ (aq)$$

$$H_2CO_3\ (aq) \quad + \quad NH_4OH \longrightarrow NH_4HCO_3\ (aq) + H_2O\ (l)$$

$$NH_4HCO_3\ (aq) + NaCl\ (aq) \longrightarrow \mathbf{NaHCO_3\ (s)} + NH_4Cl\ (aq)$$

MOLECULARITY

- **Molecularity** is the number of molecules on the reactant side of an Elementary Reaction.

Unimolecular Reactions:

- **Unimolecular** reactions are Elementary Reactions that involve **ONE** reactant molecule.
- These are commonly the decomposition reactions of unstable species.

Example: $O_3^* \longrightarrow O_2 + O$

excited
molecule

Bimolecular Reactions:

- Bimolecular reactions are Elementary Reactions that involve **TWO** reactant molecules.
- These are very common reactions.

  Example: $O{=}N + Cl{-}Cl \longrightarrow O{=}N{-}Cl + Cl$

Termolecular Reactions:

- **Termolecular** reactions are Elementary Reactions that involve **THREE** reactant molecules.
- These are less common because the chance of three molecules coming together with the right orientation is unlikely.

Example 1:

What is the molecularity of each of the following elementary reactions?

$O + O_2 + N_2 \longrightarrow O_3 + N_2^*$

$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$

$Cl + H_2 \longrightarrow HCl + H$

$CS_2 \longrightarrow CS + S$

Rate Equation for an Elementary Reaction

I. For an Overall Reaction, the Rate Law cannot be predicted by the Overall Equation

Reasons:

- The majority of reactions consist of several elementary steps.
- The Rate Law is the combined result of the elementary steps
- The rate of all the elementary reactions must be known in order to predict the rate law for the overall equation.

II. For an Elementary Reaction, the Rate Law can be written directly from the Elementary Equations

- The rate of an elementary reaction is proportional to the product of the concentrations of each reactant molecule.

1. Unimolecular Elementary Reactions

$A \longrightarrow B + C$ Rate = k [A]

2. Bimolecular Elementary Reactions

$A + B \longrightarrow C + D$ Rate = k [A] [B]

Reason:

- The frequency of collisions is proportional to the number of A molecules (n_A) and the number of B molecules (n_B)

3. Termolecular Elementary Reactions

$A + B + C \longrightarrow D + E$ Rate = k [A] [B] [C]

Examples:

Write Rate Equations for each of the elementary reactions shown below
:

1) $O_3 + NO \longrightarrow O_2 + NO_2$

Rate =

2) $CS_2 \longrightarrow CS + S$

Rate =

3) $2NO_2 \longrightarrow N_2O_4$ or $NO_2 + NO_2 \longrightarrow N_2O_4$

Rate =

NOTE:

- For Elementary Reactions **ONLY,** the coefficients of the balanced chemical elementary reaction are the exponents to which the concentrations of the reactants are raised.

THE RATE LAW AND THE MECHANISM

- The Suggested Mechanism for a particular reaction:
  - cannot be observed directly,
  - is a rationalized explanation based on experimental data,
  - is accepted provisionally, and may be replaced by another suggested mechanism based on further experimentation.

- A Suggested Mechanism
  - Is considered **correct** if it **agrees** with the experimentally determined Rate Law
  - Is considered **incorrect** if it **does not agree** with the experimentally determined Rate Law

Example 1:

Overall Equation: $2\ NO_2\ (g) + F_2\ (g) \longrightarrow 2\ NO_2F\ (g)$

Experimental Rate Law: Rate = k $[NO_2]\ [F_2]$

NOTE: 1st order with respect to NO_2

1st order with respect to F_2

2nd order Overall

Predicted Possible Mechanisms:

1. One Single Elementary Reaction

$NO_2 + NO_2 + F_2 \longrightarrow 2\ NO_2F$ (Termolecular)

Predicted Rate Law: Rate: k $[NO_2]^2\ [F_2]$

NOTE: 2nd order with respect to NO_2

1st order with respect to F_2

3rd order overall

- The predicted Rate Law does not agree with the experimental Rate Law
- This mechanism must be incorrect.

2. Two Single Elementary Reactions

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \qquad \text{(slow step)}$$

$$NO_2 + F \xrightarrow{k_2} NO_2F \qquad \text{(fast step)}$$

Overall: $2\,NO_2 + F_2 \longrightarrow 2\,NO_2F$

Reaction Intermediate: F

NOTE:

- The Rate Law is determined by the slow step
- **THE SLOWEST STEP ——> THE RATE DETERMINING STEP**
- Predicted Rate Law = RATE (rate-determining-step) = $k_1[NO_2]\,[F_2]$

NOTE:
1^{st} order with respect to NO_2
1^{st} order with respect to F_2
2^{nd} order overall

- The predicted Rate Law agrees with the experimental Rate Law
- This mechanism must be correct.

Predicted Rate Law	Experimental Rate Law
RATE = $k_1[NO_2]\,[F_2]$	RATE = $k\,[NO_2]\,[F_2]$

The two Rate Laws are identical if: $k_1 = k$

Example 2:

The following mechanism has been proposed for decomposition of ozone to oxygen gas:

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O \qquad \text{(fast equilibrium)}$$

$$O_3 + O \xrightarrow{k_2} 2\,O_2 \qquad \text{(slow)}$$

Determine the Rate Law based on this mechanism.

CATALYSIS

- A **Catalyst** is a substance that speeds up a reaction without being consumed.
- In theory the catalyst may be used over and over again.
- In practice, however, there is some loss of catalyst through other reactions that occur at the same time (side-reactions).

Importance of Catalysts:

- Catalysts allow reactions to occur much faster.
- Catalysts allow reactions to occur at lower temperatures (energy savings).

Characteristics of Catalysts:

- Catalysts are often quite specific. They increase the rate of some reactions but not others.
- Enzymes (catalysts used in biological organisms) are extremely selective.

How Catalysts Work:

- A catalyst is an active participant in the reaction.
- A catalyst must participate in one step of a reaction and be regenerated in a later step.
- The catalyzed reaction mechanism makes available a reaction path having an **increased overall rate of reaction** by:
    - ➢ increasing the frequency factor A, or
    - ➢ decreasing the **Activation Energy, Ea** (most dramatic effect)

$$k = A\,e^{-\frac{Ea}{RT}}$$

Examples:

1. The commercial preparation of sulfuric acid, H_2SO_4 from SO_2 (the early process)

First step: $2\,SO_2(g) + O_2(g) \xrightarrow{\textbf{NO} \longleftarrow \textbf{catalyst}} 2\,SO_3(g)$

Proposed Mechanism:

$$2NO + O_2 \longrightarrow 2\,NO_2$$
$$NO_2 + SO_2 \longrightarrow NO + SO_3$$

(must occur **twice** each time the first step occurs once)

$$\cancel{2NO} + O_2 \longrightarrow \cancel{2NO_2}$$
$$\cancel{2NO_2} + 2SO_2 \longrightarrow \cancel{2NO} + 2SO_3$$

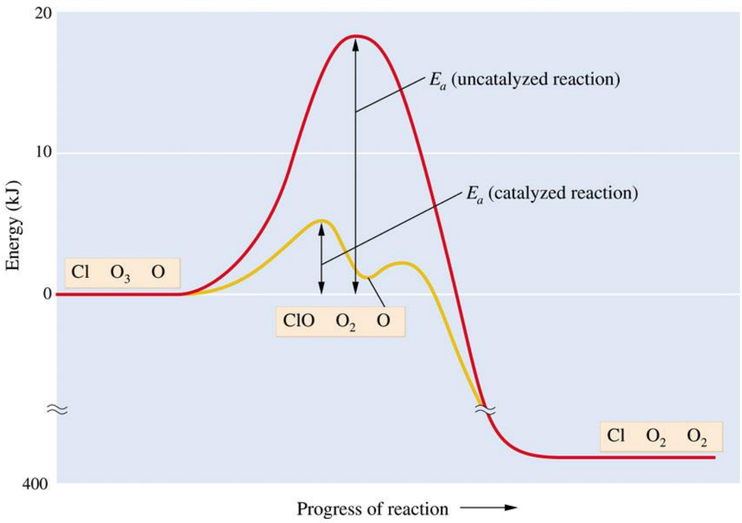
Overall: $2\,SO_2 + O_2 \longrightarrow 2SO_3$

2. The Cl-catalyzed decomposition of ozone (O_3) in the stratosphere
(Cl atoms originate from the decomposition of chloro-fluorocarbons, compounds used as refrigerants and aerosol propellants)

Mechanism of catalyzed reaction:

$$\cancel{Cl\,(g)} + O_3(g) \longrightarrow \cancel{ClO\,(g)} + O_2(g)$$
$$\cancel{ClO\,(g)} + O\,(g) \longrightarrow \cancel{Cl\,(g)} + O_2(g)$$

$$O_3(g) + O\,(g) \longrightarrow 2\,O_2(g)$$



HOMOGENEOUS & HETEROGENEOUS CATALYSIS

- **Homogeneous catalysis** is a catalyzed process in which the catalyst is in the same physical phase as the reacting species.

Example:
The commercial preparation of sulfuric acid, H_2SO_4 from SO_2 (the early process)
Catalyst (NO) and reactants (SO_2 and O_2) are all in gaseous phase.

- **Heterogeneous catalysis** is a catalyzed process in which the catalyst exists in a different phase from the reactants.
- In these types the catalyst is usually a solid in contact with a gaseous or liquid solution of reactants.
- Heterogeneous catalysis occurs by the **adsorption** of the reactant molecules to the surface of the solid catalyst.
- **Adsorption** is the attraction of molecules to a surface and it can be of two types:

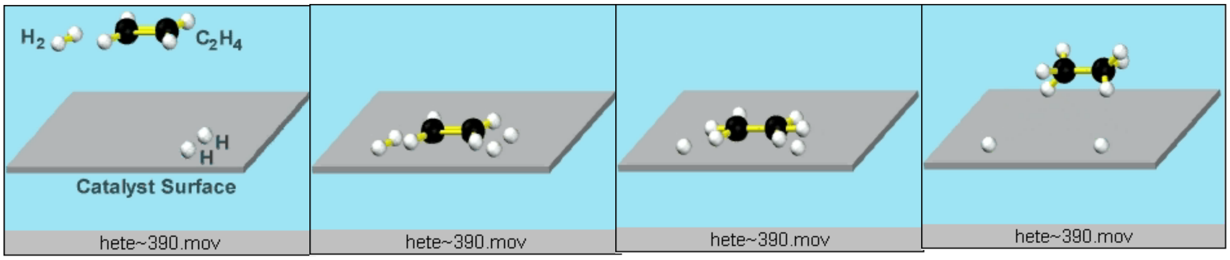
  - Physical Adsorption
    The molecules are attracted to the catalyst surface by weak intermolecular forces.
  - Chemisorption
    The molecules are attached to the catalyst surface by chemical bonds.

Examples:

3. Surface catalysts are used in the catalytic converters of cars to convert potential atmospheric pollutants (such as CO and NO) into CO_2 and N_2.

2. The catalytic hydrogenation of ethylene:

$$\underset{\text{ethylene}}{C_2H_4\,(g)} \quad + \quad H_2\,(g) \xrightarrow{\text{Pt or Ni}} \underset{\text{ethane}}{C_2H_6\,(g)}$$



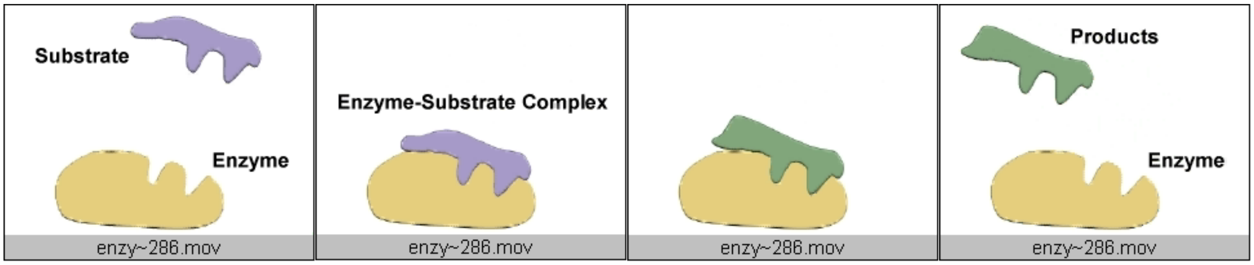
Ethylene and Hydrogen chemisorb to the catalyst surface

Ethane then diffuses of the catalyst surface

ENZYME CATALYSIS

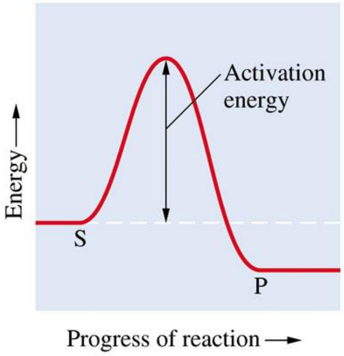
- **Enzymes** are the catalysts of biological organisms.
- Enzymes are huge protein molecules (Molecular Weights over a million amu) that are **highly specific**:
    - Each enzyme acts only on a **specific substance** or a **specific type of substance.**
    - Each enzyme catalyzes a **specific substance** to undergo a **specific reaction.**
- Substrate (S) is the substance whose reaction the enzyme catalyzes.

How an enzyme (E) works



The enzyme molecule folds into a roughly spherical shape with an **active site**	Substrate molecule and enzyme molecule fit into each other like a lock and key	Substrate changes into products, and they diffuse away and the enzyme is regenerated

$$E + S \underbrace{\longrightarrow ES}_{\text{enzyme-substrate complex}} \qquad ES \longrightarrow E + P$$



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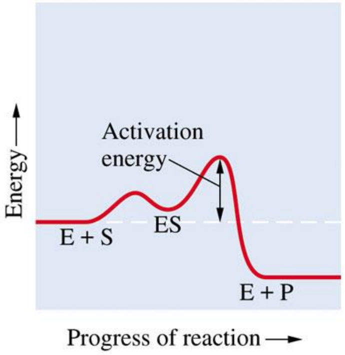

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