Reaction Rates

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Reaction Rates

Rxn Movie

Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time **t**.

[A] = concentration of reactant A

Reaction Rate

- For the reaction A $\rightarrow$ B there are two ways of measuring **rate**:

  (1) the speed at which the reactants disappear

  (2) the speed at which the products appear

- Reactions are reversible, so as products accumulate they can begin to turn back into reactants.
- Early on the rate will depend on only the amount of reactants present. We want to measure the reactants as soon as they are mixed.
- The most useful (and general) way of measuring the rate of the reaction is in terms of change in concentration per unit time…

$$\text{Rate} = \Delta[A]/\Delta t \text{ limits to } D[A]/Dt$$

Most Common Units… Rate = M/s

Where Molarity (M) = moles/Liter

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).

$$A \longrightarrow B$$

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

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

Factors Affecting Reaction Rate Constants

Factors that Affect the Reaction Rate Constant

1. **Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy
    - **Collision Theory:** When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
    - **Kinetic Theory:** Increasing temperature means the molecules move faster.
2. **Concentrations of reactants**
    - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide
3. **Catalysts**
    - Speed up reactions by lowering activation energy

Factors Affecting Reaction Rate Constants

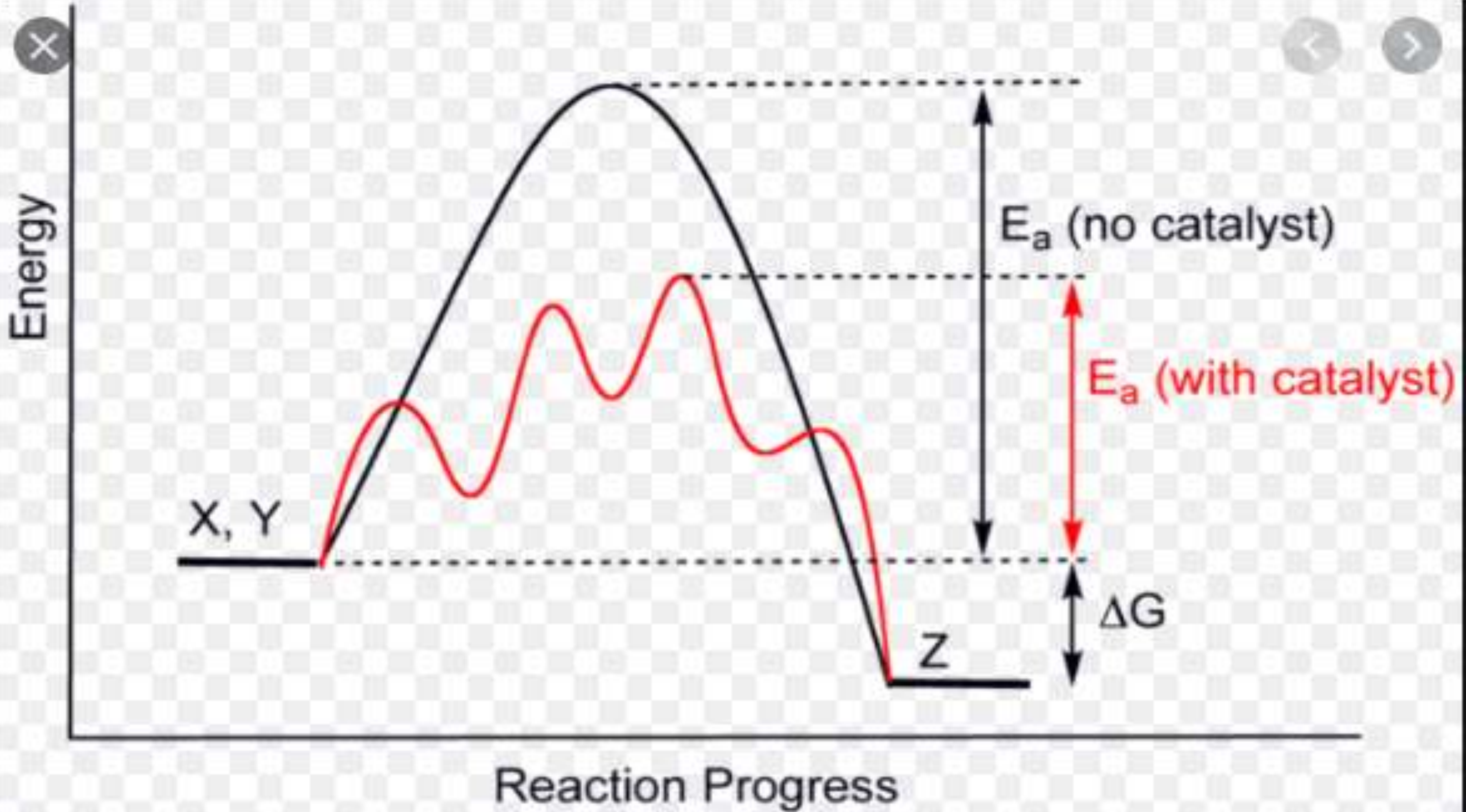
4. **Surface area of a solid reactant**
   - Bread and Butter theory: more area for reactants to be in contact
5. **Pressure of gaseous reactants or products**
   - Increased number of collisions

How do catalysts work?

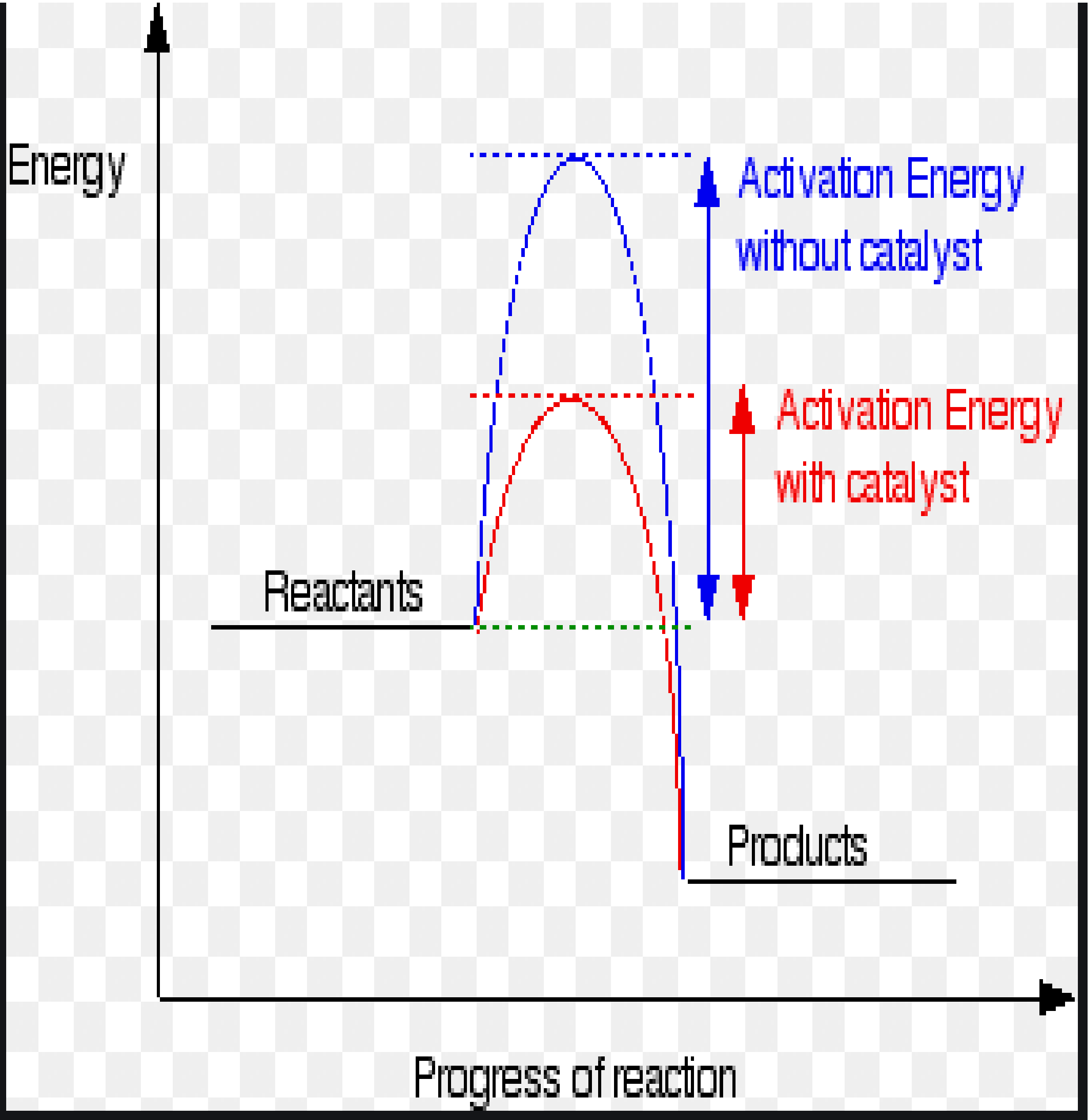
A **catalyst** increases reaction rates in a slightly different way from other methods of increasing reaction rate. The function of a catalyst is to lower the activation energy so that a greater proportion of the particles have enough energy to react. A catalyst can lower the activation energy for a reaction by:

- orienting the reacting particles in such a way that successful collisions are more likely
- reacting with the reactants to form an intermediate that requires lower energy to form the product

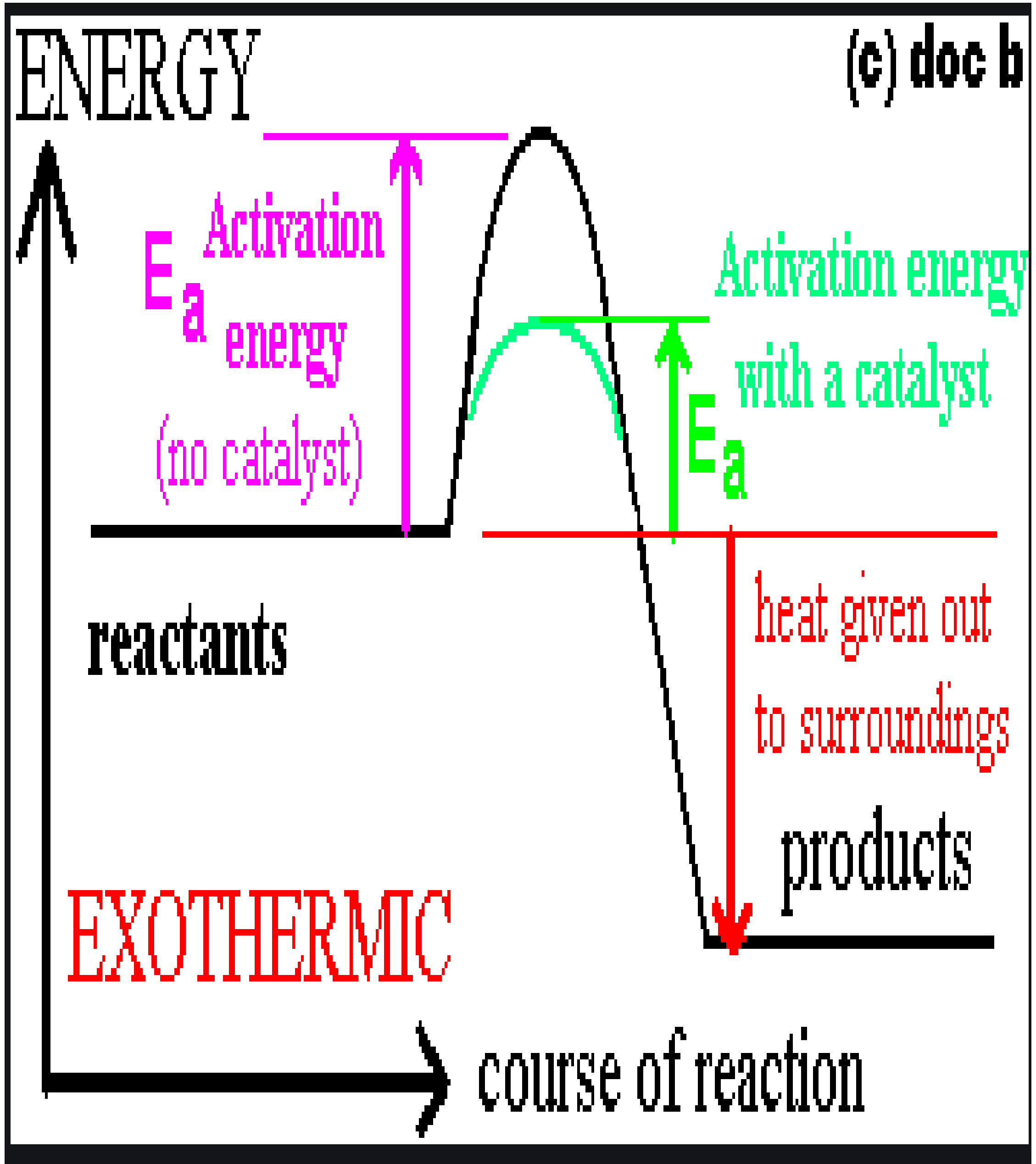
Some *metals* e.g. platinum, copper and iron can act as catalysts in certain reactions. In our own bodies, we have *enzymes* that are catalysts, which help to speed up biological reactions. Catalysts generally react with one or more of the reactants to form a chemical intermediate,



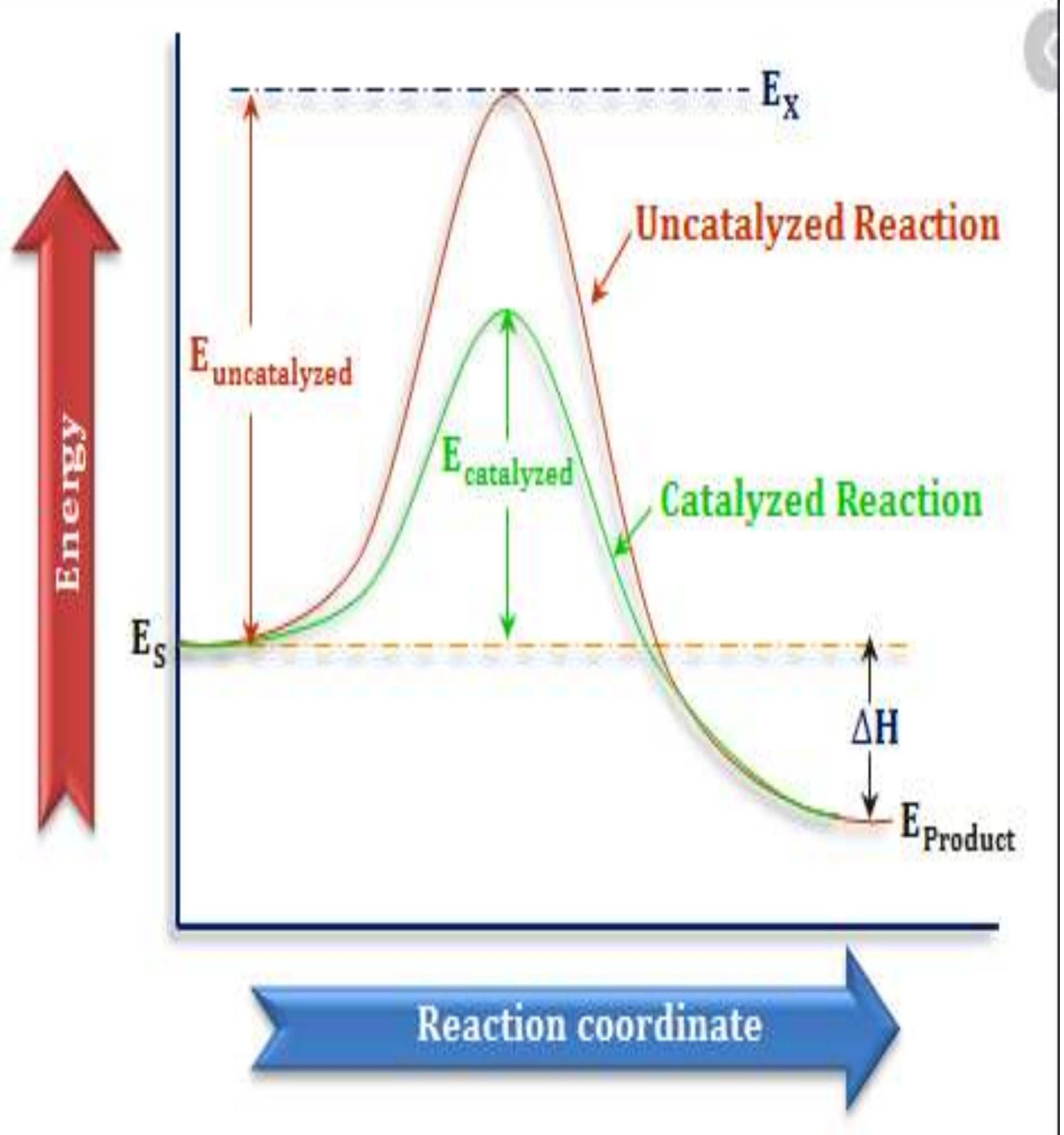
Energy
X, Y
E_a (no catalyst)
E_a (with catalyst)
ΔG
Z
Reaction Progress



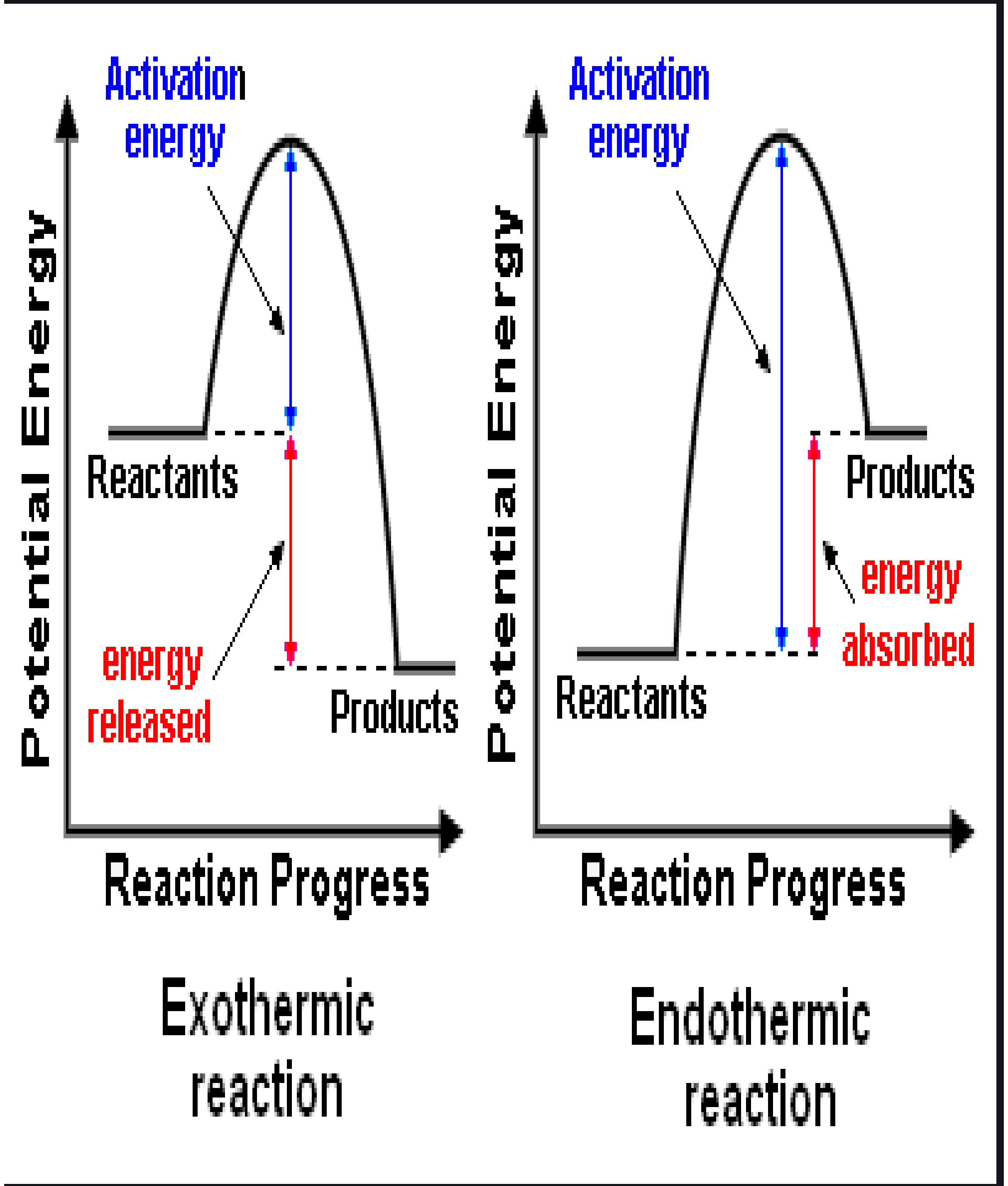
Energy
Activation Energy without catalyst
Activation Energy with catalyst
Reactants
Products
Progress of reaction



ENERGY
(c) doc b
Ea Activation energy (no catalyst)
Activation energy with a catalyst
Ea
reactants
heat given out to surroundings
products
EXOTHERMIC
course of reaction

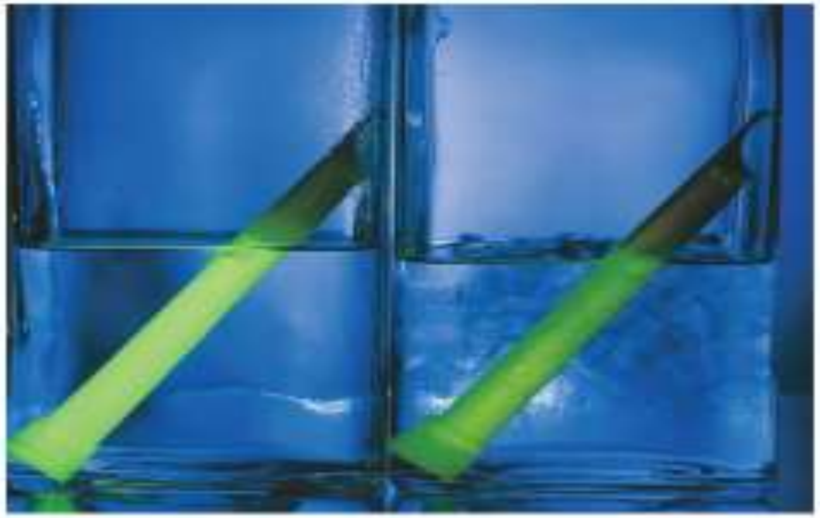


Energy
E_X
Uncatalyzed Reaction
$E_{uncatalyzed}$
$E_{catalyzed}$
Catalyzed Reaction
E_S
ΔH
$E_{Product}$
Reaction coordinate

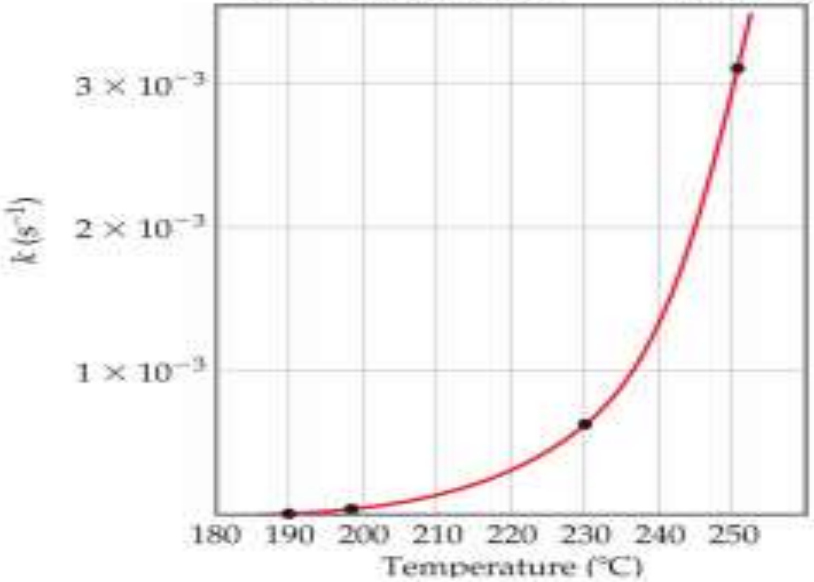


Activation energy
Potential Energy
Reactants
energy released
Products
Reaction Progress
Exothermic reaction
Activation energy
Potential Energy
Products
energy absorbed
Reactants
Reaction Progress
Endothermic reaction

Temperature



Higher temperature Lower temperature



- Generally, as temperature increases, so does the reaction rate.
- This is because *k* is temperature dependent.

Concentration Affects Reaction Rate Constant

- Here's another way of looking at reaction rates…

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

- Notice that for every 1 mole of O_2 that appears, 4 x as many moles of NO_2 will also appear. In the meantime, twice as many moles of N_2O_5 will be disappearing as moles of O_2 forming.
- Changes in concentrations of the reactants and/or products is ***inversely proportional*** to their stoichiometric proportions.
- This means that the rate of the reaction could be written like this…

$$\text{Rate} = -\tfrac{1}{2}\,\Delta[N_2O_5]/\Delta t \;=\; \tfrac{1}{4}\,\Delta[NO_2]/\Delta t \;=\; \Delta[O_2]/\Delta t$$

* (Notice the negative sign on the rate of $[N_2O_5]$ reminds us that it is disappearing.)

- In general, for a reaction that looks like this… $aA + bB \rightarrow cC + dD$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Reaction Rate Laws

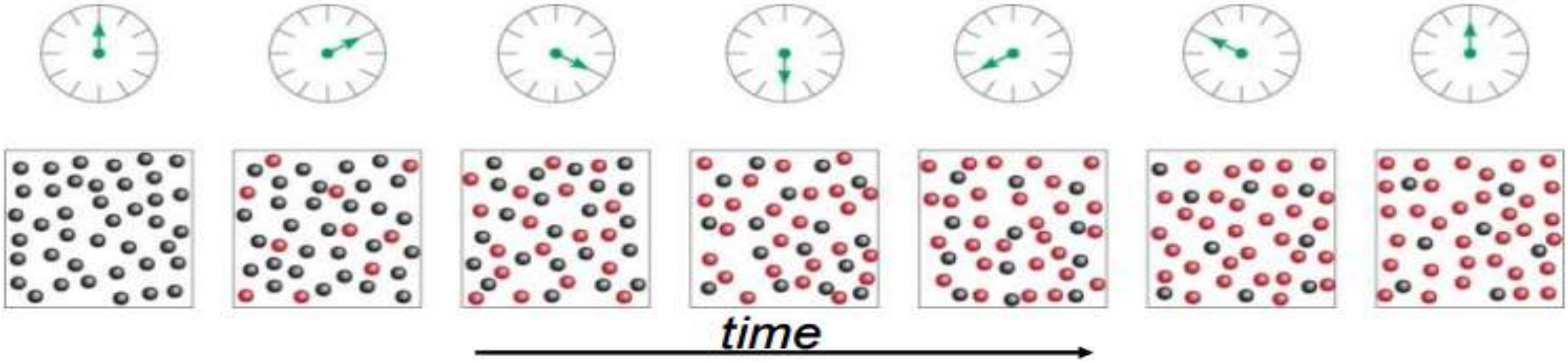
Concentration and Rate

Each reaction has its own equation that gives its rate as a function of reactant concentrations.

This is called its **Rate Law**

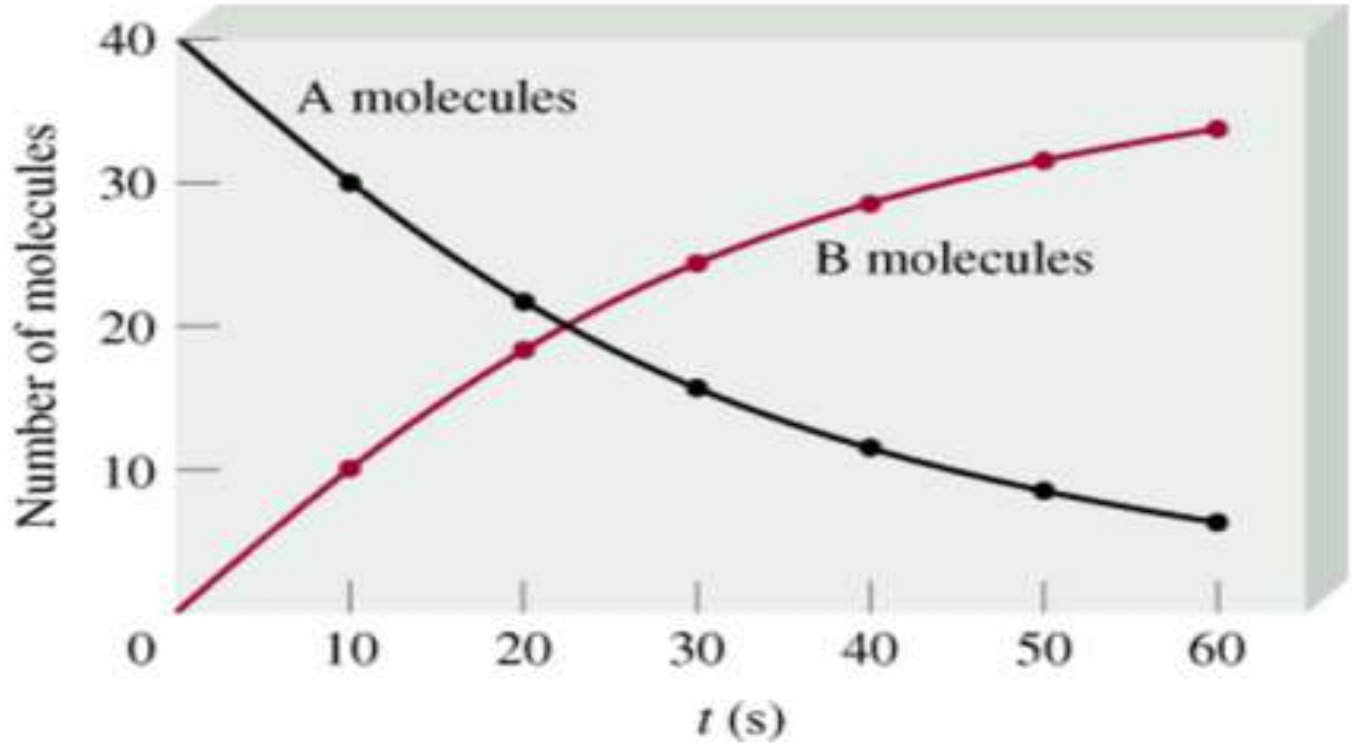
To determine the rate law we measure the rate at different starting concentrations.

$A \longrightarrow B$



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

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



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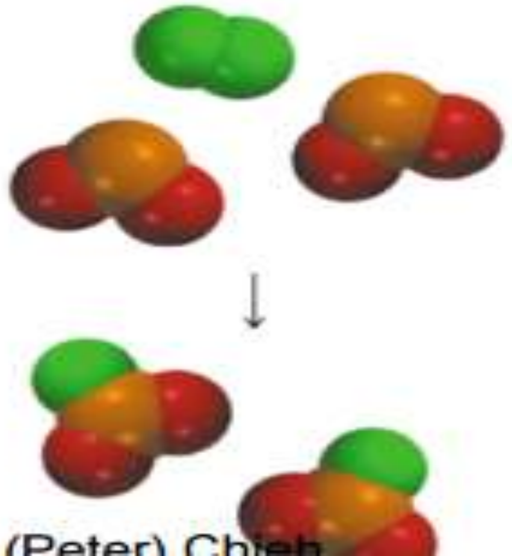
Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^1$$

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Rate Law

- In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.
- The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.
- Here's what a general rate law for a reaction will look like…

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

  - [A] & [B] represent the reactants.
  - The exponents m and n are called "**reaction orders**".
  - The proportionality constant k is called the **rate constant**.
  - The **overall reaction order** is the sum of the reaction orders:

$$m + n$$

Reaction Rates and Stoichiometry

- To generalize, for the reaction

$$aA + bB \longrightarrow cC + dD$$

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

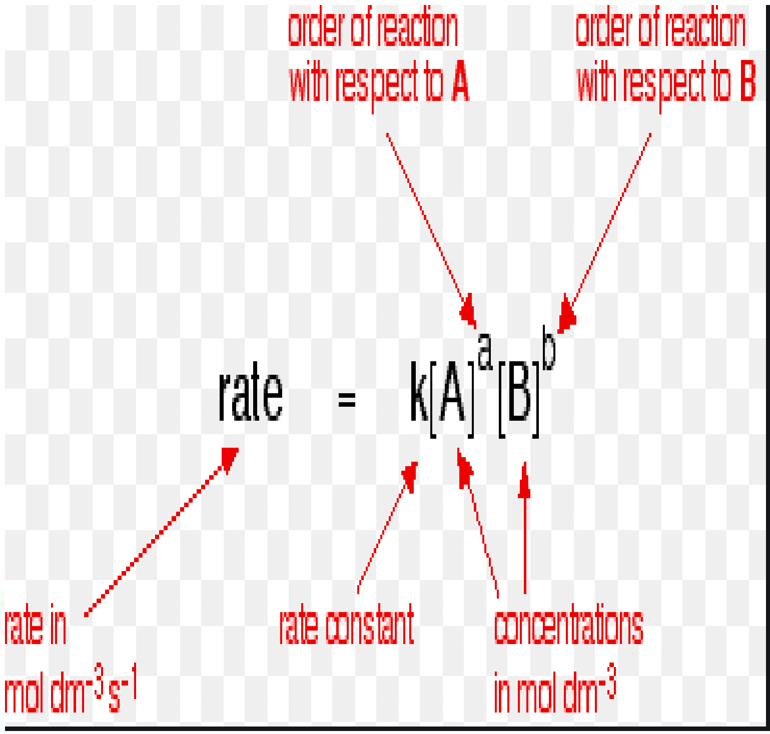
Reactants (decrease) Products (increase)

The Rate Law

The ***rate law*** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$aA + bB \longrightarrow cC + dD$$

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



reaction is ***m*th order** in A

reaction is ***n*th order** in B

reaction is **(m+n)th order overall**

Rate Law Example

- Consider the following reaction:

$$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$$

- Let's say that the following observations from several experiments were made…
  - as $[NH_4^+]$ doubles the rate doubles with $[NO_2^-]$ constant.
  - as $[NO_2^-]$ doubles the rate doubles with $[NH_4^+]$ constant.

- The rate of this reaction would be expressed as….

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

- The reaction is said to be "first order" with respect to $[NH_4^+]$ and "first order" with respect to $[NO_2^-]$.

- But the ***overall order*** of the reaction is said to be "second order."

- Reaction rates come from experiment data, not stoichiometry!

Examples of Reaction Rate Laws

Example Reaction: Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^- \longrightarrow N_2(g) + 2H_2O(l)$$

Compare Experiments 1 and 2:

when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Likewise, compare Experiments 5 and 6: when [NO_2^-] doubles, the initial rate doubles.

Concentration and Rate

$$rate \propto [NH_4^+]$$

$$rate \propto [NO_2^-]$$

$$rate \propto [NH_4^+]\,[NO_2^-]$$

$$rate = k\,[NH_4^+]\,[NO_2^-]$$

This equation is called the rate law, and *k* is the rate constant.

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Rate Laws

- A rate law shows the relationship between the reaction rate and the concentrations of reactants.
  - For gas-phase reactants use P_A instead of [A].

- The rate constant k is a constant that has a specific value for each reaction.
- The value of k is determined experimentally. For example

$$rate = k\left[NH_4^+\right]\left[NO_2^-\right]$$

"Constant" is relative here:

k is unique for each reaction

k changes with Temporature

Rate Laws

- Exponents tell the order of the reaction with respect to each reactant.
- This reaction is

  First-order in $[NH_4^+]$

  First-order in $[NO_2^-]$
- The overall reaction order can be found by adding the exponents on the reactants in the rate law.
- This reaction is *second-order overall*.

$$rate = k\left[NH_4^+\right]^1\left[NO_2^-\right]^1$$

$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

Table 13.2 **Rate Data for the Reaction between F_2 and ClO_2**

	$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

$$\text{rate} = k\,[F_2]^x[ClO_2]^y$$

Double $[F_2]$ with $[ClO_2]$ constant

Rate doubles

$x = 1$

Quadruple $[ClO_2]$ with $[F_2]$ constant

Rate quadruples

$y = 1$

$$\text{rate} = k\,[F_2][ClO_2]$$

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g) \quad \text{(phosgene)}$$

	CO(mol)	Cl_2(mol)	$\text{rate}_0 \left(\frac{\text{mol}}{\text{s}}\right)$
1	0.1	0.16	0.450
2	0.1	0.32	1.35
3	0.2	0.32	2.30

$$\text{Order for } Cl_2 = \frac{\dfrac{Rate_2}{Rate_1}}{\dfrac{[Cl_2]_2}{[Cl_2]_1}} = \frac{3}{2}$$

$$\text{Rate} = k\,[CO]^{\square}[Cl_2]^{\square}$$

$$\text{Order for CO} = \frac{\dfrac{Rate_3}{Rate_2}}{\dfrac{[CO]_3}{[CO]_2}} = 1$$

$$k = \frac{\text{Rate}}{[CO]^{\square}[Cl_2]^{\square}}$$

Ex#	[A] (M)	[B] (M)	initial rate of C (M/s)
1	.100	.100	4.0×10^{-5}
2	.100	.200	4.0×10^{-5}
3	.300	.100	3.6×10^{-4}

Answer: doubling [B] had no effect on the rate so B is zero order

tripling [A] caused the rate to multiply by 9 or by 3^2, so A is 2nd order.

$\text{rate} = k[A]^2[B]^0 = k[A]^2$

$4.0\times10^{-5} = k(.100)^2$ $\quad$ $k = 4.0\times10^{-3}\ M^{-1}s^{-1}$

Determine the rate law for the reaction

$$2ClO_2 + 2OH^- \longrightarrow ClO_3^- + ClO_2 + H_2O$$

Given the following data

Expt	$[ClO_2]$	$[OH^-]$	Rate (M/s)
1	0.005	0.04	0.262
2	0.005	0.08	0.523
3 M	0.01	0.04	1.04 *
4	0.01	0.02	0.522
5	0.06	0.06	??

$\text{rate} = K[ClO_2]^2[OH^-]$

* value with units?

Expt 3

$$1.04\,\frac{M}{s} = K\,[0.01\,M]^2\,[0.04\,M]$$

$$\frac{}{(0.01)^2\,(0.04)}$$

$$\frac{1.04\,\frac{\cancel{M}}{s}}{(0.01\,M)^2(0.04\,\cancel{M})} = K \qquad \frac{1.04\,\frac{1}{s}}{4\times10^{-6}\,M^2} = K = 2.6\times10^5\ M^{-2}s^{-1}$$

$M^{-}\cdot s^{-1}$