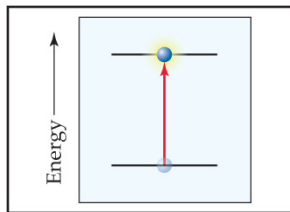


Chemical Kinetics

(Chapter 14)



10^{-15} s



1 s



10^9 s
(30 years)



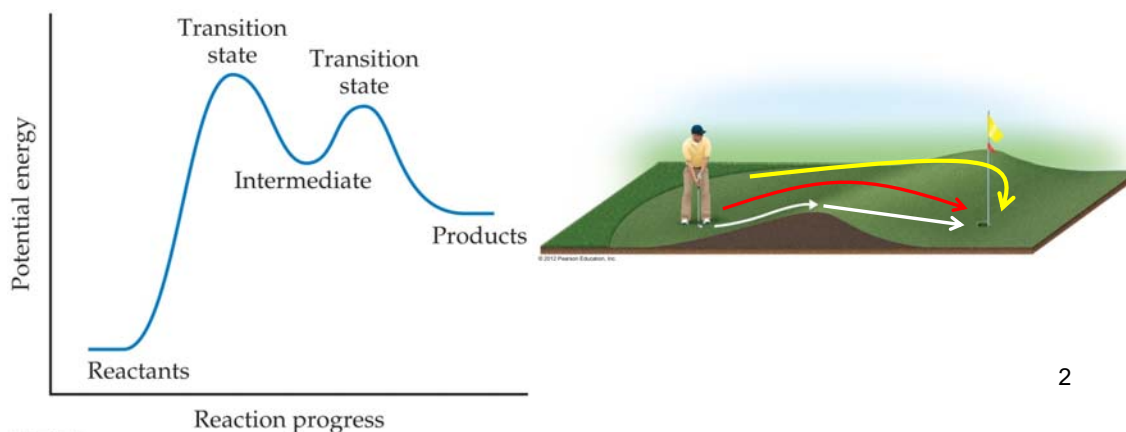
10^{15} s
(30 million years)

1. Factors affecting reaction rates.
2. Reaction rate law and order.
3. First-order and second-order reactions.
4. Half life of a reaction.
5. Arrhenius equation.
6. Effects of catalyst.

1

Why do we study kinetics?

- Provides the **rate** at which a chemical process occurs.
- Gives information on **reaction mechanism** — the detailed steps occur at molecular level when the reactants are turned into products.



2

Factors That Affect Reaction Rates

- Reaction occurs when the reactant molecules have **sufficient** energy and come in contact (or **collide**).

1. Physical State of the Reactants

- The more homogeneous the mixture of reactants, the faster the molecules can react.
- When the reactants are in different phases, the reaction rate is limited by the **contact area**.

e.g., Mixing, stirring and making the sugar in a powder help to dissolve sugar in beverage.



3

2. Concentration of Reactants

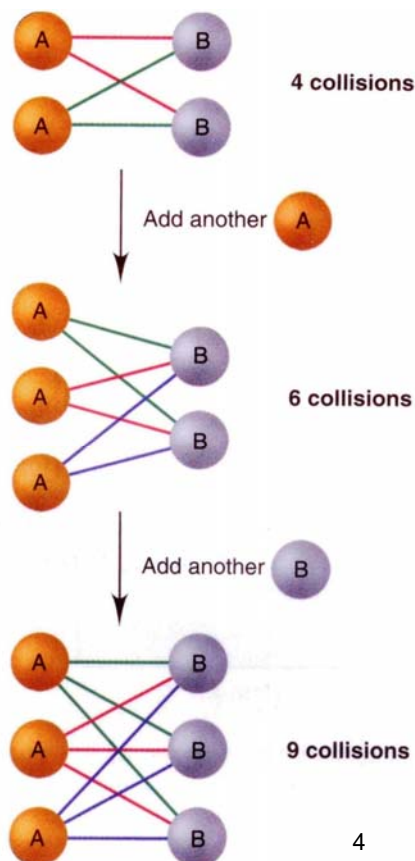
- As the concentration / pressure of reactants increases, the **number of collisions among** reactant molecules increases.



Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly



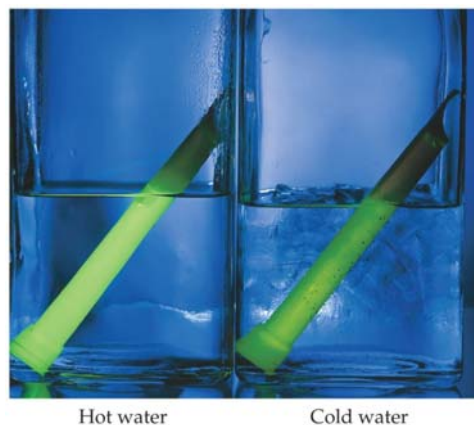
Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly



4

3. Temperature

- At a higher temperature, reactant molecules have more kinetic energy, move faster, and **collide more often** and with a greater energy.



Higher temperature increase the rate of chemiluminescence in light sticks.

4. Presence of a Catalyst

- Catalysts speed up reactions by providing alternative reaction pathway with lower **activation energy**.
- Catalysts are not consumed during the course of the reaction.

5

Reaction Rates

It is the **change** in concentration of either reactants or products as a function of **time**.

Consider a reaction: $A \rightarrow B$

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

$$\text{Rate of appearance of B} = + \frac{\Delta[B]}{\Delta t}$$

$$[\text{M} / \text{s}] \quad \text{Rate} = - \frac{\Delta[A]}{\Delta t} = + \frac{\Delta[B]}{\Delta t} \quad [\text{M}]$$

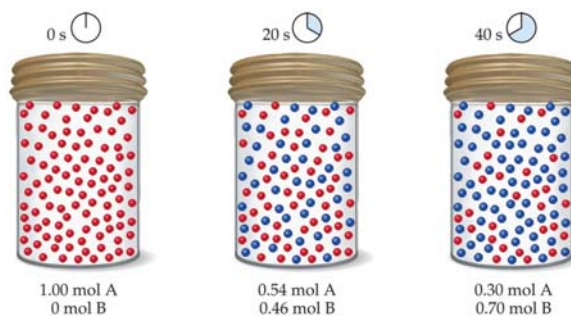
[s]

6

Reaction: $A \rightarrow B$

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

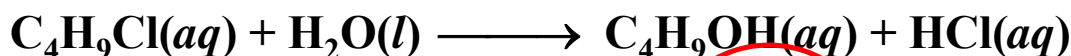
| t | [A] | [B] | Rate |
|----|------|------|-------|
| 0 | 1.00 | 0.00 | 0.023 |
| 20 | 0.54 | 0.46 | |
| 40 | 0.30 | 0.70 | 0.012 |



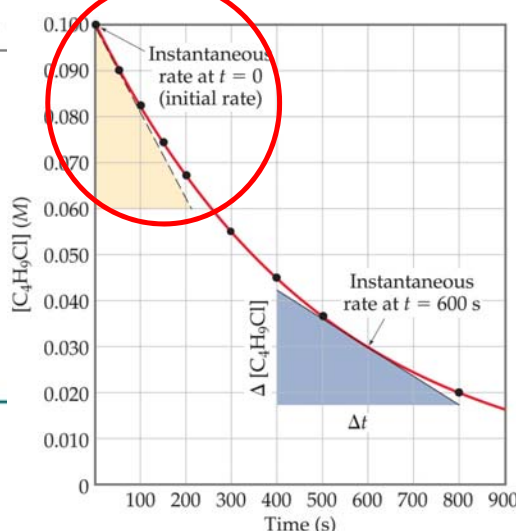
By convention, rates are always expressed as **positive** quantities.

- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules A. ⁷

Instantaneous Reaction Rate



| Time, t(s) | $[C_4H_9Cl]$ (M) | Average Rate (M/s) |
|------------|------------------|------------------------|
| 0.0 | 0.1000 | 1.9×10^{-4} |
| 50.0 | 0.0905 | |
| 100.0 | 0.0820 | 1.7×10^{-4} |
| 150.0 | 0.0741 | 1.6×10^{-4} |
| 200.0 | 0.0671 | 1.4×10^{-4} |
| 300.0 | 0.0549 | 1.22×10^{-4} |
| 400.0 | 0.0448 | 1.01×10^{-4} |
| 500.0 | 0.0368 | 0.80×10^{-4} |
| 800.0 | 0.0200 | 0.560×10^{-4} |
| 10,000 | 0 | |



- Rate is the **slope** to the tangent to the curve.
- All reactions slow down over time.
- Therefore, the best indicator of reaction rate is the **instantaneous** rate at time ≈ 0 (initial). ⁸

Reaction Rates and Stoichiometry

For a reaction: $A \rightarrow B$ $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

For a reaction: $2A \rightarrow B$ $\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$
(**2 moles** of A react to form **1 mole** of B.)

To generalize, for the reaction $aA + bB \rightarrow cC + dD$

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

Reaction Rate and Rate Law

- The rate law shows the relationship between the reaction rate and the concentrations of reactants.
- The **rate law** for the reaction $aA + bB \rightarrow cC + dD$ has a general form of :

$$(\text{Initial}) \quad \text{Rate} = k[A]^m[B]^n$$

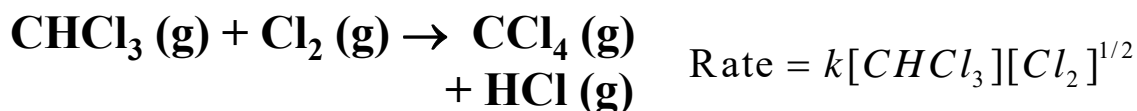
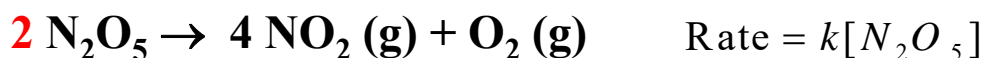
where k is the rate constant (**temperature dependent**).

m and n are the respective reaction orders with respect to A and B.

Reaction Rate Order

- The reaction orders *m* and *n* depend on reaction mechanism, they must be experimentally determined and are not related to *a* and *b*.

For example:



In most rate laws, reaction order are 0, 1 and 2. We occasionally encounter rate law in which the reaction order is **fractional** or **negative**.

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Reaction Rate Order

Given a reaction $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$:

| Rate law | The reaction is | Overall reaction order |
|-----------------------------|---|------------------------------|
| $k[\text{A}]^1[\text{B}]^1$ | first-order in A and first-order in B | 2 (bimolecular) |
| $k[\text{A}]^1$ | first-order in A and zero-order in B | 1 (unimolecular) |
| $k[\text{A}]^2[\text{B}]^3$ | second-order in A and third-order in B | 5 |

Unimolecular: [A] is doubled \Rightarrow rate is doubled.

Bimolecular: [A] & [B] are doubled \Rightarrow rate is increased by 4 times.

First-order Reaction

- The reaction rate has first-order dependence on the concentration of the reactant:

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

$$-\frac{d[A]}{dt} = k[A]$$

$$\frac{d[A]}{[A]} = -k dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

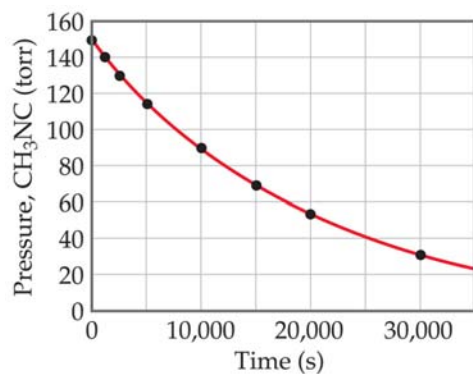
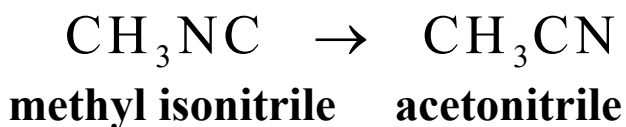
$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\text{or } \ln \frac{[A]_t}{[A]_0} = -kt$$

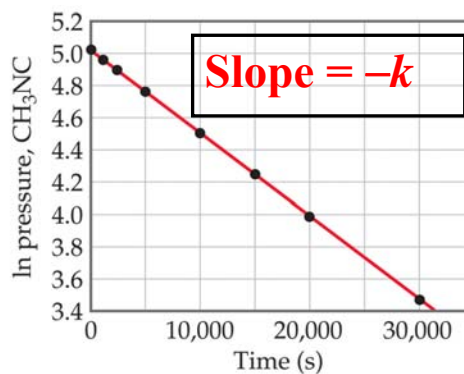
where $[A]_0$ is the initial conc. of A.

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Example: First-order reaction



Plot of P vs. t



Plot of $\ln(P)$ vs. t

1st-order reaction gives a **straight** line in $\ln(P)$ vs. t plot:

$$\ln P = \ln P_0 - kt$$

Exercise: The initial rate of a reaction $A + B \rightarrow C$ was measured for several different starting concentrations of A and B, and the results are as follows:

| Experiment Number | [A] (M) | [B] (M) | Initial Rate (M/s) |
|-------------------|---------|---------|-----------------------|
| 1 | 0.100 | 0.100 | 4.0×10^{-5} |
| 2 | 0.100 | 0.200 | 4.0×10^{-5} |
| 3 | 0.200 | 0.100 | 16.0×10^{-5} |

Determine the rate law for this reaction.

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| Experiment Number | [A] (M) | [B] (M) | Initial Rate (M/s) |
|-------------------|---------|---------|-----------------------|
| 1 | 0.100 | 0.100 | 4.0×10^{-5} |
| 2 | 0.100 | 0.200 | 4.0×10^{-5} |
| 3 | 0.200 | 0.100 | 16.0×10^{-5} |

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Second-order Reaction

- The reaction rate has second-order dependence on the concentration of the reactant:

$$\begin{aligned} \text{Rate} &= -\frac{\Delta[A]}{\Delta t} = k[A]^2 \\ -\frac{d[A]}{dt} &= k[A]^2 \\ \frac{d[A]}{[A]^2} &= -kdt \\ \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} &= -k \int_0^t dt \end{aligned} \quad \left| \quad \begin{aligned} -\frac{1}{[A]_t} + \frac{1}{[A]_0} &= -kt \\ \frac{1}{[A]_t} &= \frac{1}{[A]_0} + kt \end{aligned} \right.$$

where $[A]_0$ is the initial conc. of A.

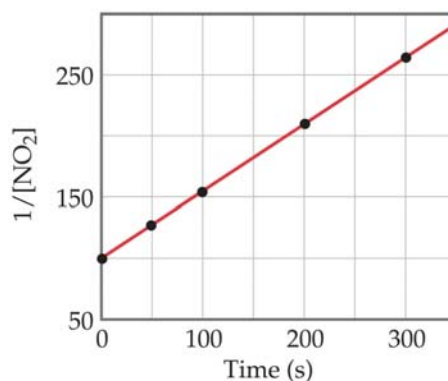
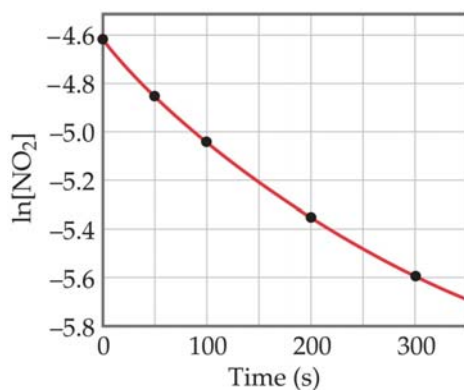
17

Example: Second-order reaction

Decomposition reaction: $\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

| Time (s) | $[\text{NO}_2]$ (M) | $\ln[\text{NO}_2]$ | $1/[\text{NO}_2]$ |
|----------|---------------------|--------------------|-------------------|
| 0.0 | 0.01000 | -4.610 | 100 |
| 50.0 | 0.00787 | -4.845 | 127 |
| 100.0 | 0.00649 | -5.038 | 154 |
| 200.0 | 0.00481 | -5.337 | 208 |
| 300.0 | 0.00380 | -5.573 | 263 |

A plot of $1/[A]$ vs. t yield a **straight** line and the slope is k .



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Zero-order vs. First-order

- The reaction rate has no dependence on the concentration of the reactant.

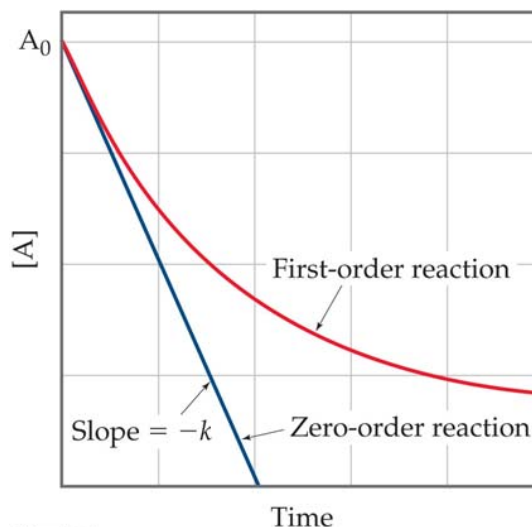
$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$$

$$d[A] = -k dt$$

$$[A]_t = [A]_o - kt$$

- Exponential decay for a 1st-order reaction:

$$[A]_t = [A]_o e^{-kt}$$



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Half-life of a reaction

- Defined as the time ($t_{1/2}$) required for the concentration of reactant to decrease by half.

1st-order: $\ln \frac{[A]_t}{[A]_o} = -kt$

$$[A]_t = \frac{1}{2}[A]_o$$

$$\Rightarrow \ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

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

$t_{1/2}$ is a **constant** and **independent** of initial concentration.

2nd-order: $\frac{1}{[A]_t} = \frac{1}{[A]_o} + kt$

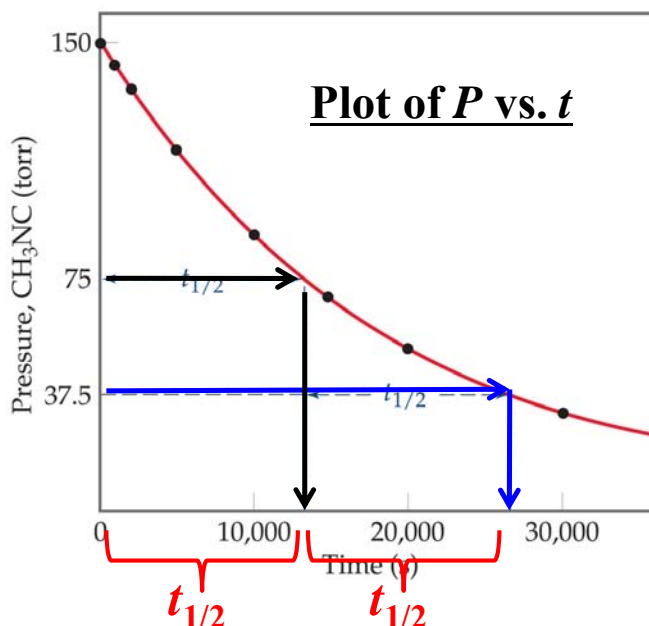
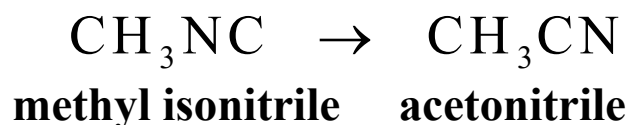
$$[A]_t = \frac{1}{2}[A]_o$$

$$\Rightarrow \frac{2}{[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$$

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

$t_{1/2}$ is dependent on initial concentration. ²⁰

Determination of k by measuring $t_{1/2}$



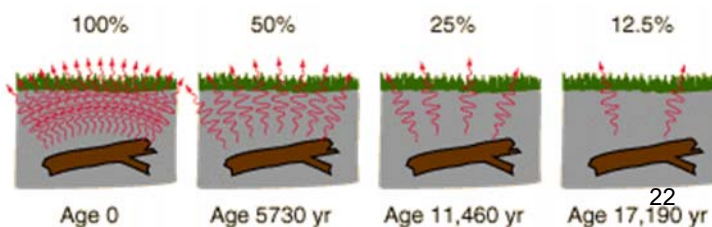
By plotting P vs. t , the half life for this reaction is determined to be $\approx 13,000$ seconds.

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Carbon dating and half-life

- Carbon dating is used to estimate the age of dead animal or plant.
- Radioactive decay: ${}^{14}_6\text{C} \rightarrow {}^{14}_7\text{N} + \text{electron}$
- The $t_{1/2}$ for this radioactive decay of carbon-14 is ≈ 5730 years.
- A living matter has a **constant** level of ${}^{14}\text{C}$, but its ${}^{14}\text{C}$ amount keeps **decreasing** for a dead matter.

By measuring the ${}^{14}\text{C}$ level, the age of a dead tree trunk can be estimated.



22

Arrhenius equation

Svante Arrhenius proposed a mathematical relationship between k , E_a and T :

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

$$E_a \uparrow \quad k \downarrow$$

where A is the frequency factor

and E_a is the activation energy of the reaction.

Alternative form: $\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$

$y = mx + c$

Gas constant.

Measuring k at several T 's allow us to determine E_a from the **slope** of a plot of **$\ln k$** vs. **$1/T$** .

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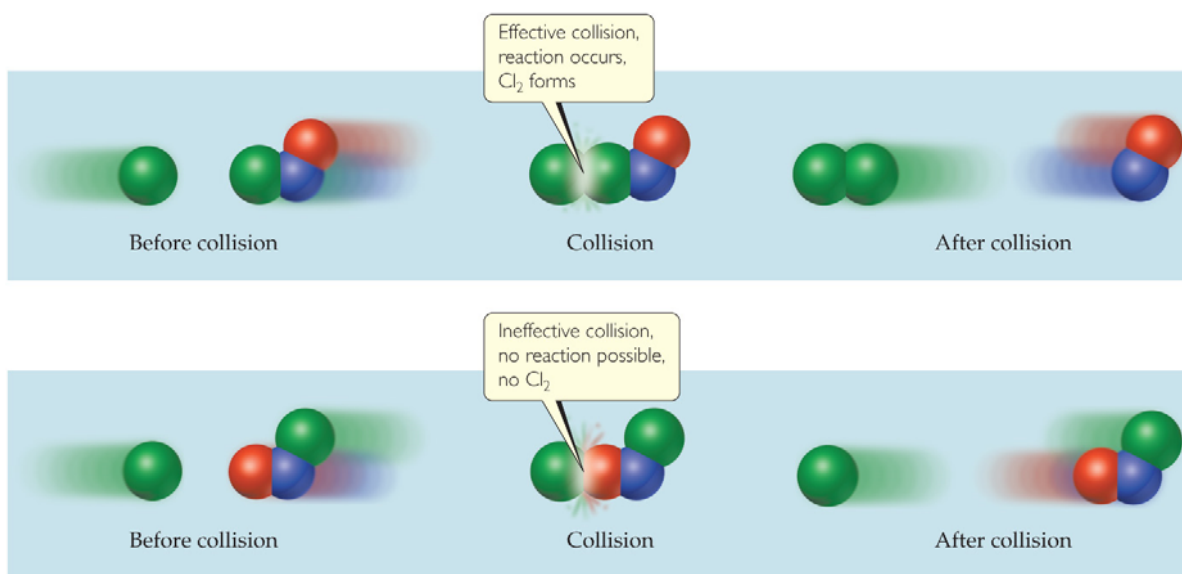
Frequency factor (A)

- The frequency factor is related to
 - the frequency of the collisions;
 - the probability of the **effective collisions** that cause reactions.
- Reaction happens only if the reactants collide with each other.
- Molecules must collide with the **proper orientation** and with **enough energy** to make reactions happen.

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Effective collision

For example: $\text{Cl} + \text{NOCl} \rightarrow \text{NO} + \text{Cl}_2$



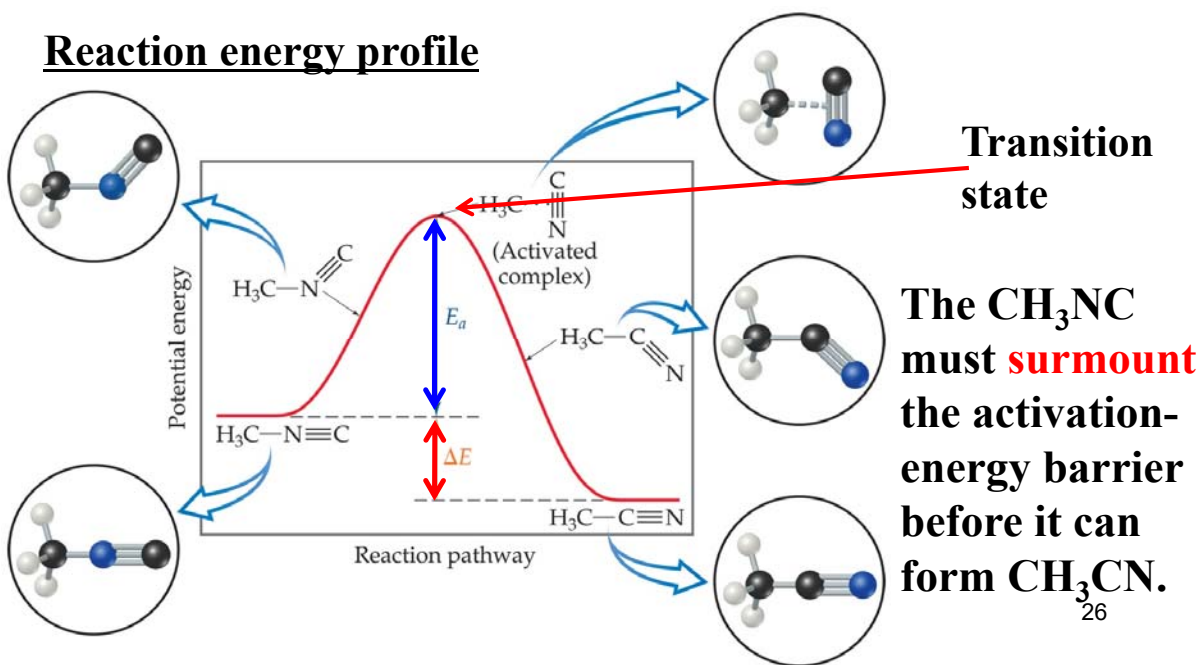
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Activation energy

- The **minimum** amount of energy required for reaction is the activation energy (E_a).

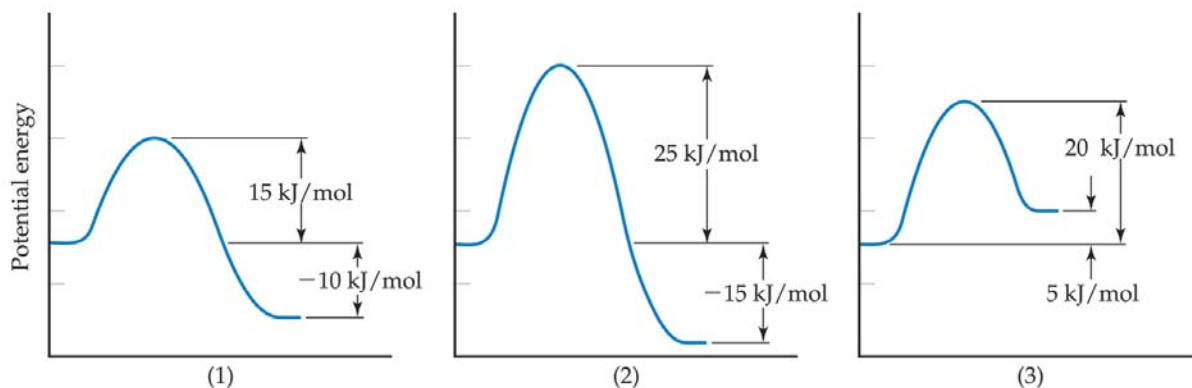
Reaction energy profile



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Activation energy

Consider the following three energy profiles:



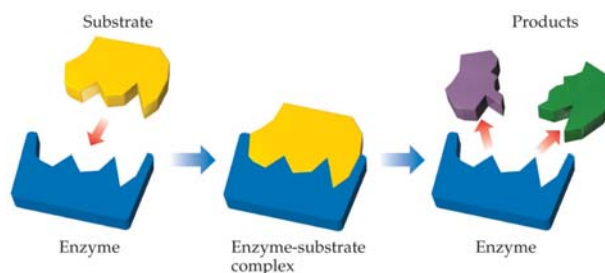
Assume all three reactions have similar frequency factors, the reaction rates rank from slowest to fastest:

$$k(2) < k(3) < k(1).$$

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Effect of catalysts

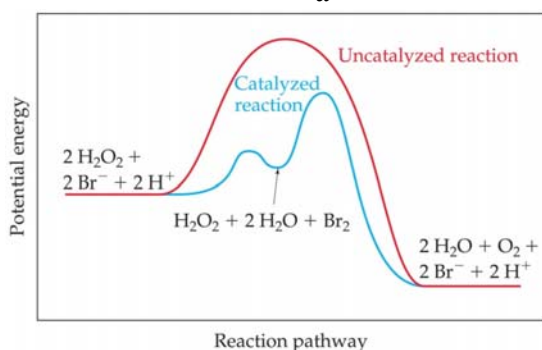
- A catalyst is a substance that changes the **speed** of a chemical reaction without a **permanent** chemical/physical change itself.
- Catalysts **increase** the rate of a reaction by decreasing the activation energy of the reaction.
- Catalysts change the mechanism by which the process occurs.
- Catalysts (or enzyme) works for specific substrate.



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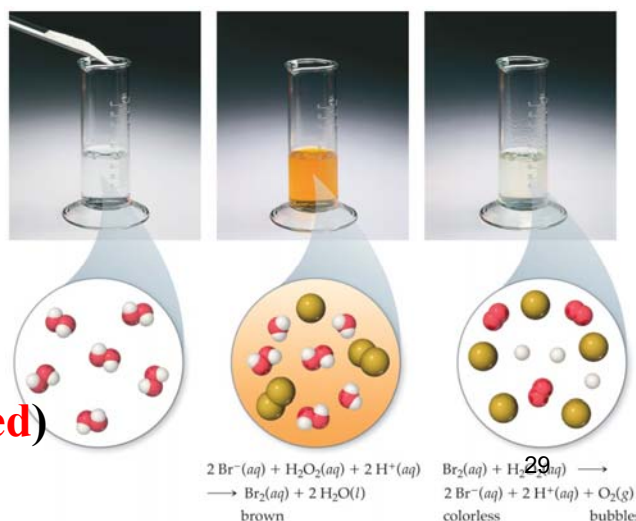
Catalysts and activation energy

- Catalyst speed up a reaction by providing an **alternative** reaction pathway (**blue**) of **lower** E_a .
- Lowering the E_a means more molecules having energy above the E_a .



Br^- – catalyst (**regenerated**)

Br_2 – intermediate



Heterogeneous catalyst: catalytic converter

- The exhaust gases of automobiles always contain some unburned CO , NO and C_xH_y , which are the air-pollutants.
- A catalytic converter is used to **speed up** the oxidations of these pollutants into harmless gases before exhausting into the environment.

Catalysts: $\text{CuO} + \text{Cr}_2\text{O}_3$

Reactants and catalyst are in different phases, the design is to **maximize** the surface area.

