Chemical Kinetics

Lecture 5

Chemical reaction rate. Chemical equilibrium.

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.

- Chemical reactions require varying lengths of time for completion.

- Some reactions
- are fast
- (photosynthesis)

Some reactions
are slow
(conversion of diamond to graphite)

We will study such questions

- How is the rate of a reaction measured?
- What conditions will affect the rate of a reaction?
- How do you express the relationship of rate to the variables affecting the rate?
- What happens on a molecular level during a chemical reaction?

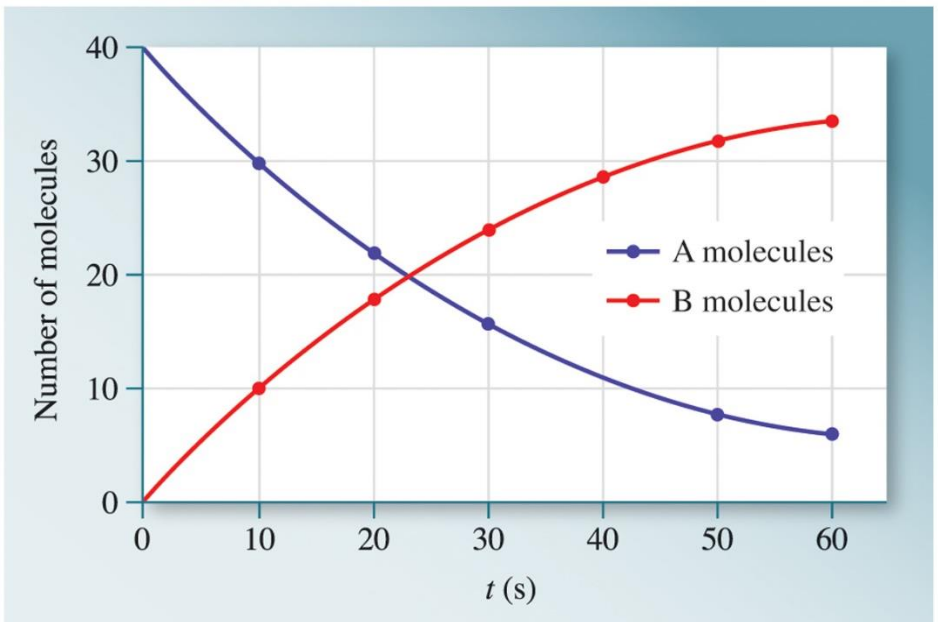
Rate of Reaction

- Expressed as either:
  - Rate of disappearance of reactants (decrease or negative)

    OR

  - Rate of appearance of products (increase or positive)

Average Reaction Rate



- **Equation A** $\rightarrow$ B

- **rate** = $-\frac{\Delta C_A}{\Delta \tau}$ or $\frac{\Delta C_B}{\Delta \tau}$

- Why the negative on [A]?

Average Reaction Rate

$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$

Note: Br_2 disappears over time

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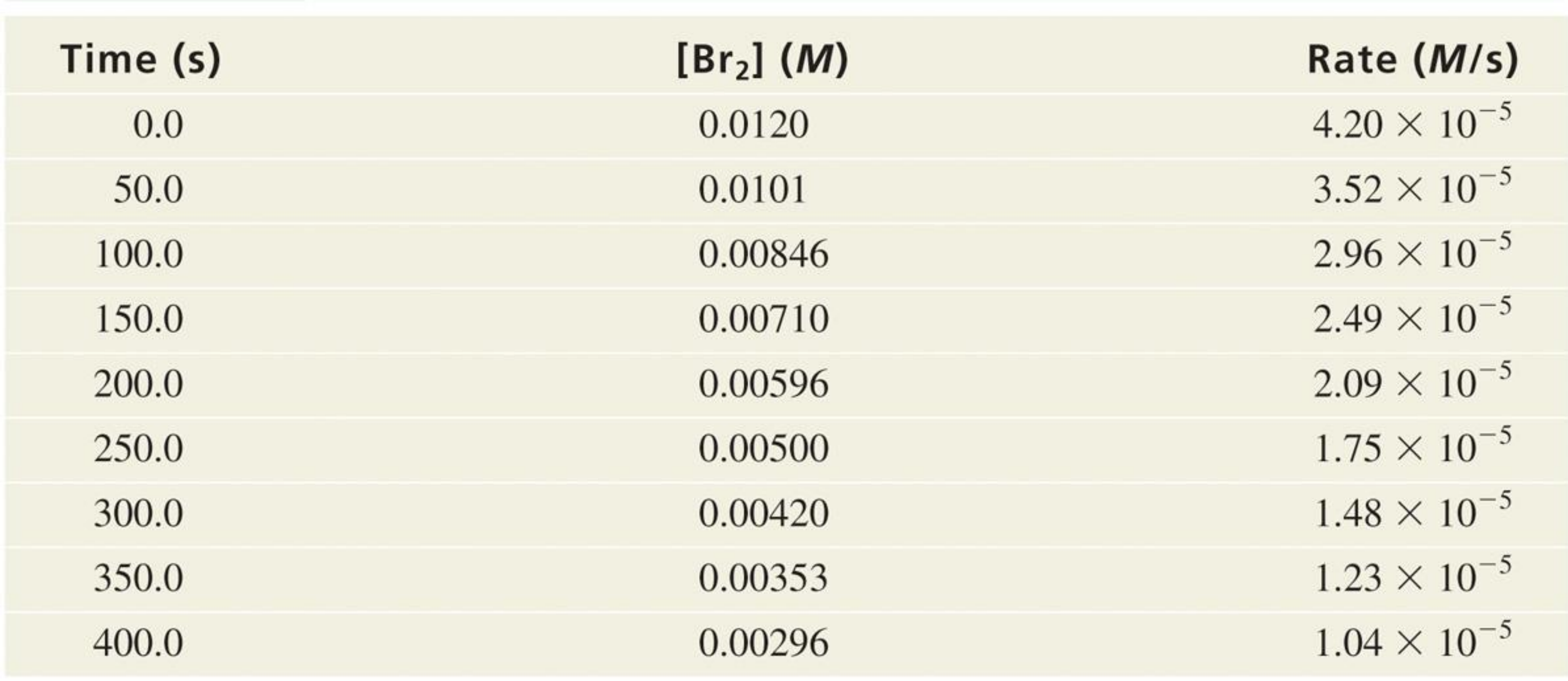
Average Reaction Rate

$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$

Rates of Reactions Bromine and Formic acid at 25 C



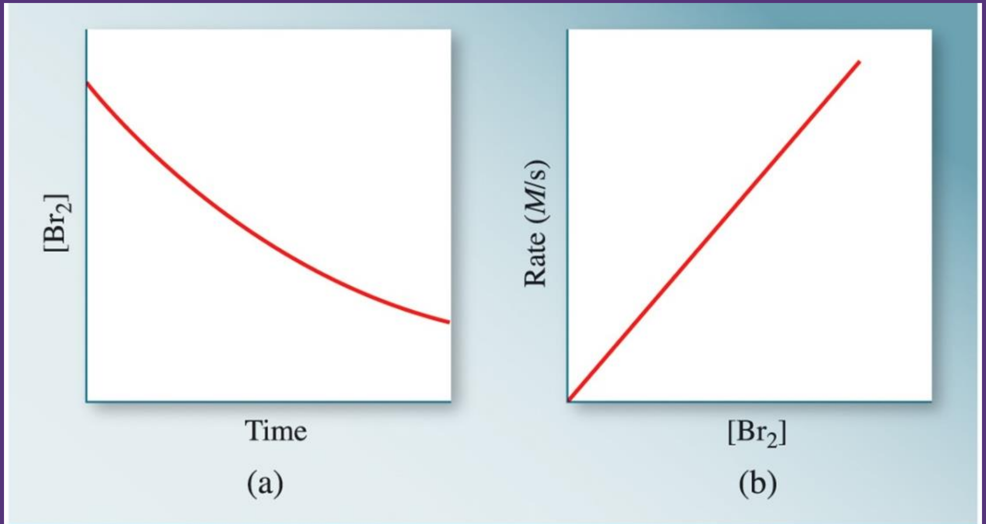
Time (s)	$[Br_2]$ (M)	Rate (M/s)
0.0	0.0120	4.20×10^{-5}
50.0	0.0101	3.52×10^{-5}
100.0	0.00846	2.96×10^{-5}
150.0	0.00710	2.49×10^{-5}
200.0	0.00596	2.09×10^{-5}
250.0	0.00500	1.75×10^{-5}
300.0	0.00420	1.48×10^{-5}
350.0	0.00353	1.23×10^{-5}
400.0	0.00296	1.04×10^{-5}

Calculate Average Rate

- Avg. rate = $$\frac{[\mathrm{Br_2}]_{final} - [\mathrm{Br_2}]_{initial}}{t_{final} - t_{initial}}$$
- Avg. rate = $$\frac{0.0101\,M - 0.0120\,M}{50\,s - 0\,s} = 3.80 \times 10^{-5}\ M/s$$

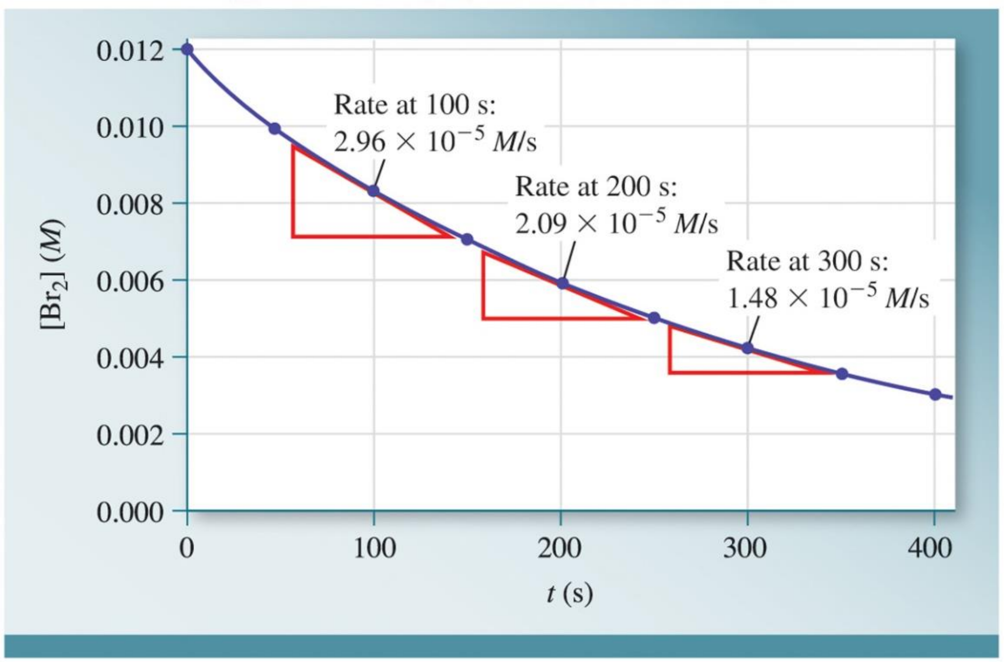
Average Rate

- Average rate depends on time interval
- Plot of $[Br_2]$ vs time = curve
- Plot of Rate vs $[Br_2]$ = straight line



Instantaneous Rate

- **Instantaneous**: rate at a specific instance in time (slope of a tangent to the curve)



Rate Constant

- Using data from PreviousTable
- - what can you conclude?

Time (s)	$[Br_2]$	Rate (*M*/*s*)
50	0.0101	3.52×10^{-5}
250	0.00596	1.75×10^{-5}

When the $[Br_2]$ is halved; the rate is halved
Rate is directly proportional to $[Br_2]$
rate = $k\,[Br_2]$
k = proportionality constant and is constant as long as temp remains constant

Rate Constant

- If we will calculate the value of the rate constant for any set of data we get basically the same answer!
- k = rate / $[Br_2]$

$$k = \frac{3.52 \text{ x } 10^{-5}\ M/\text{s}}{0.0101\ M} = 3.5 \text{ x } 10^{-3}\ /\text{s}$$

Dependence of Reaction Rate on Reactant Concentration

- **Rate law expression**

For the general equation:

$$aA + bB \rightarrow cC + dD$$

$$\text{rate law} = k[A]^x[B]^y$$

k = proportionality constant

x and y = the order of the reaction with respect to each reactant

Order

- Exponents represent order
- Only determined via experimental data
  - **1st order** - rate directly proportional to concentration
  - **2nd order** - exponential relationship
  - **0 order** - no relationship
- Sum of exponents (order) indicates overall reaction order

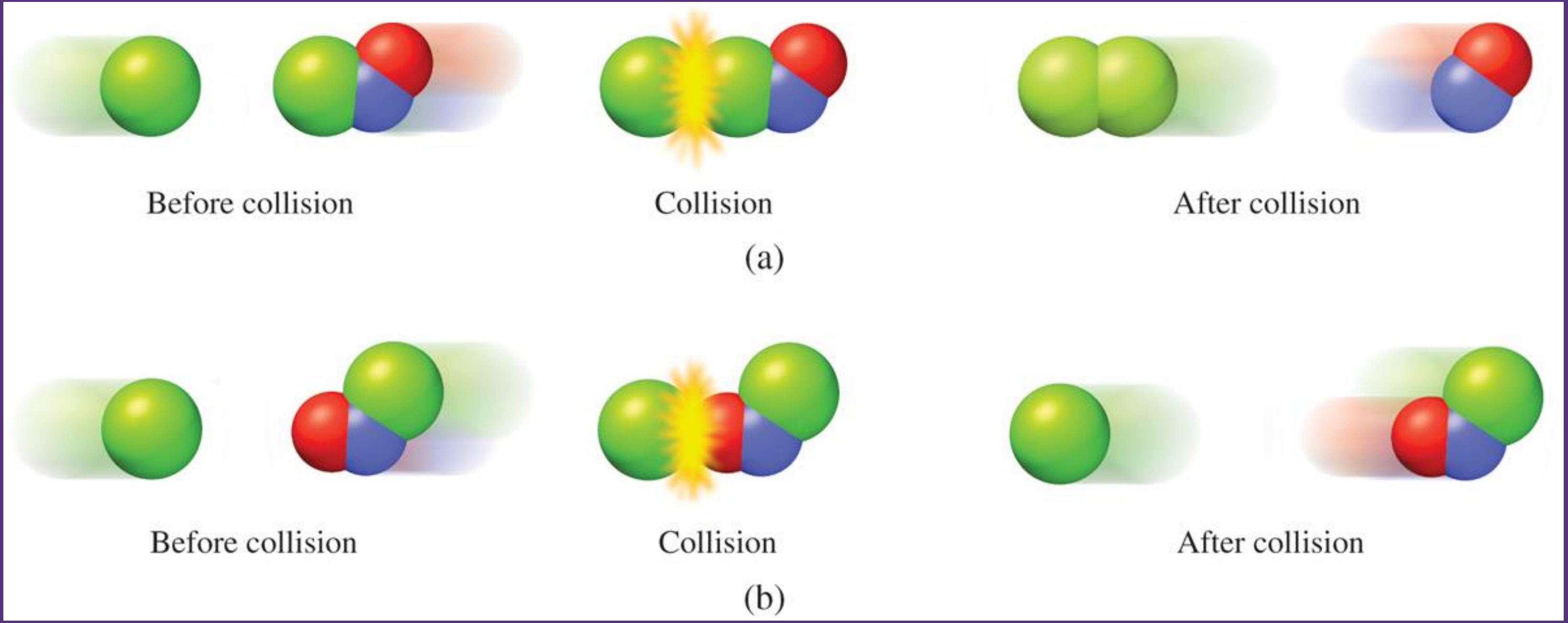
Dependence of Reaction Rate on Temperature

- Most reactions occur faster at a higher temperature.

Collision Theory

- Particles must collide in order to react
- The greater frequency of collisions, the higher the reaction rate
- Only two particles may react at one time
- Many factors must be met:
  - Orientation
  - Energy needed to break bonds (activation energy)

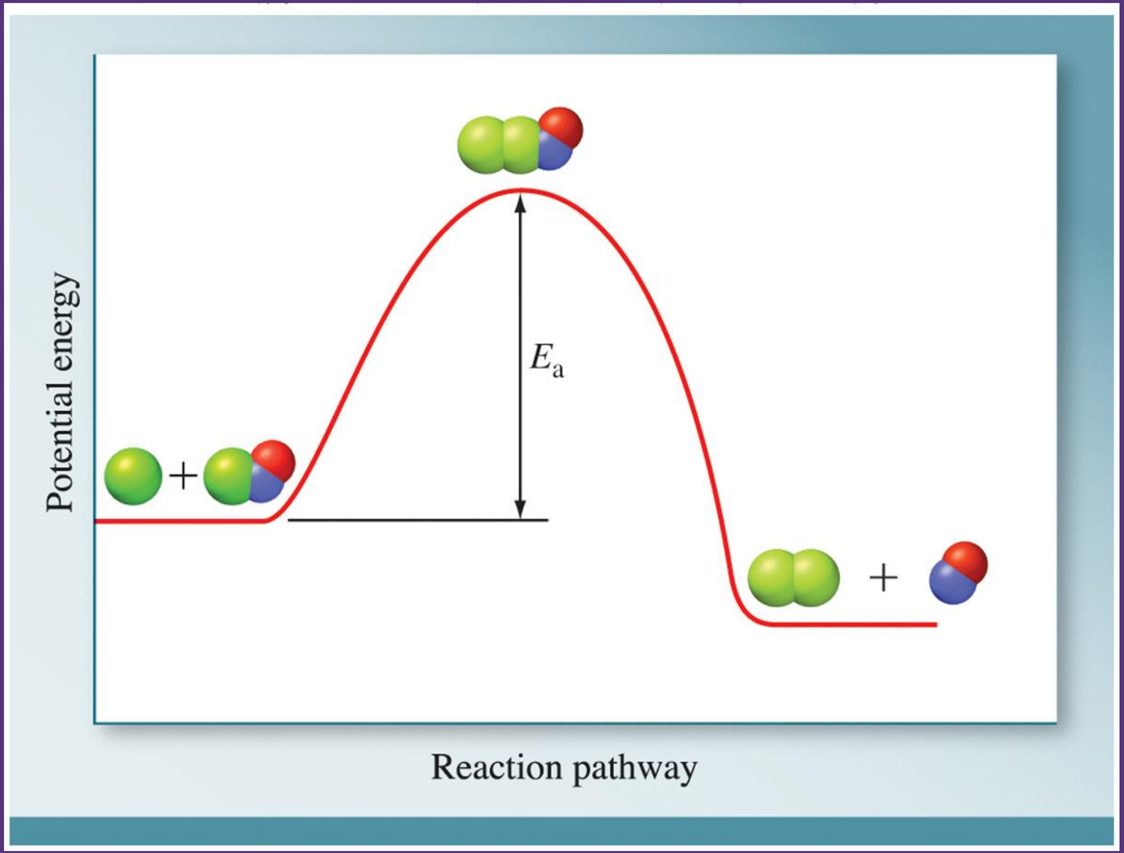
Collision Theory



Collision Theory

- Though it seems simple, not all collisions are effective collisions
- **Effective collisions:** a collision that does result in a reaction
- An activated complex (transition state) forms in an effective collision

Activation Energy



The Arrhenius Equation

- The dependence of the rate constant of a reaction on temperature can be expressed

$$\boxed{k = Ae^{-E_a/RT}}$$

E_a = activation energy

R = universal gas constant

A = frequency factor T = Kelvin temp

We will use empirical rule of Van't Hoff.

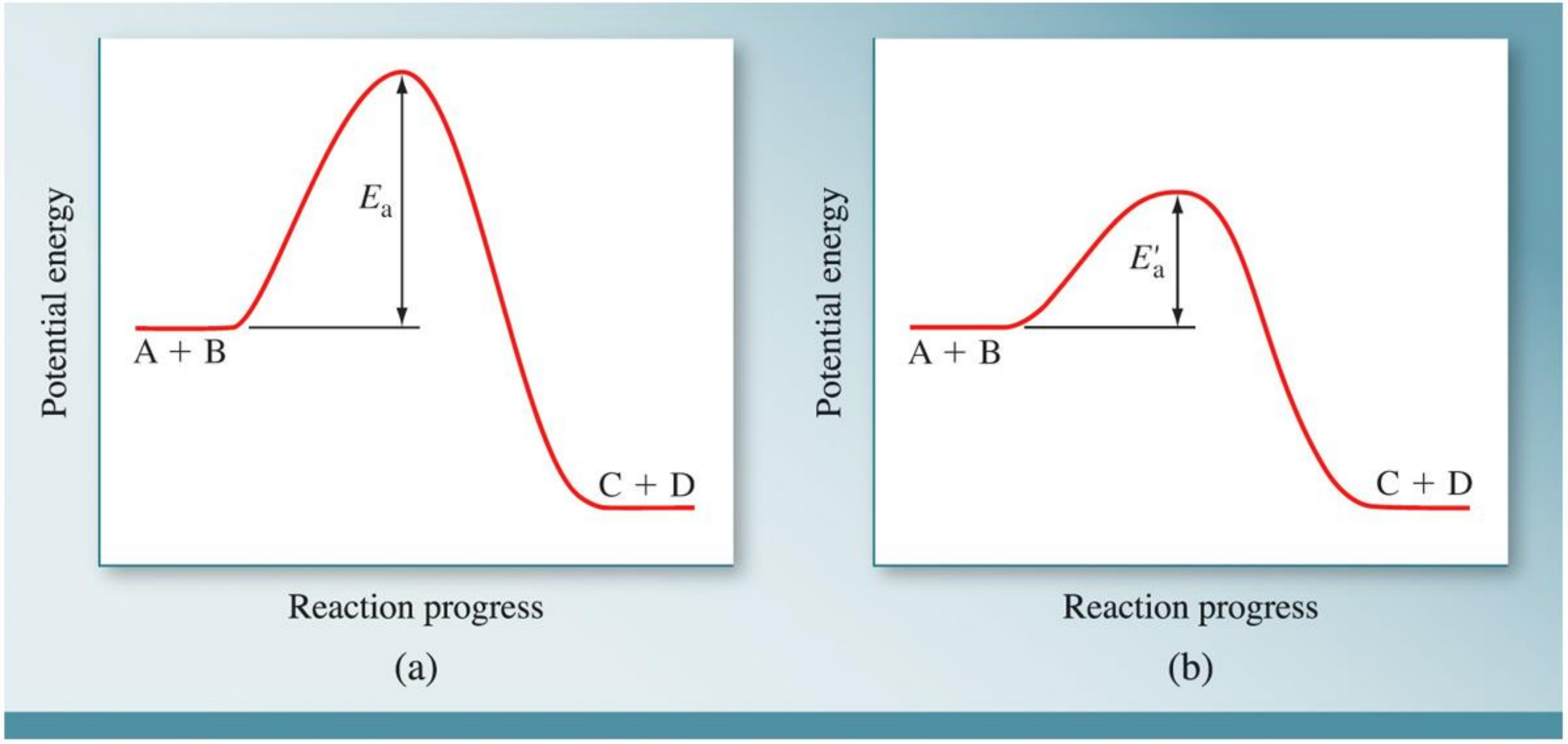
Such rule states that when the temperature rises for every 10, the rate of chemical reaction increases by a factor of 2-4.

$$\frac{\mathrm{Rate}T2}{\mathrm{Rate}T1} = \gamma^{\frac{T2 - T1}{10}}$$

Dependence of Reaction Rate on Catalysis

- **Catalyst** - a substance that increases the rate of a chemical reaction without being used up itself
- Provides a set of elementary steps with more favorable kinetics than those that exist in its absence
- Many times a catalyst lowers the activation energy

Reaction Pathway with Catalyst



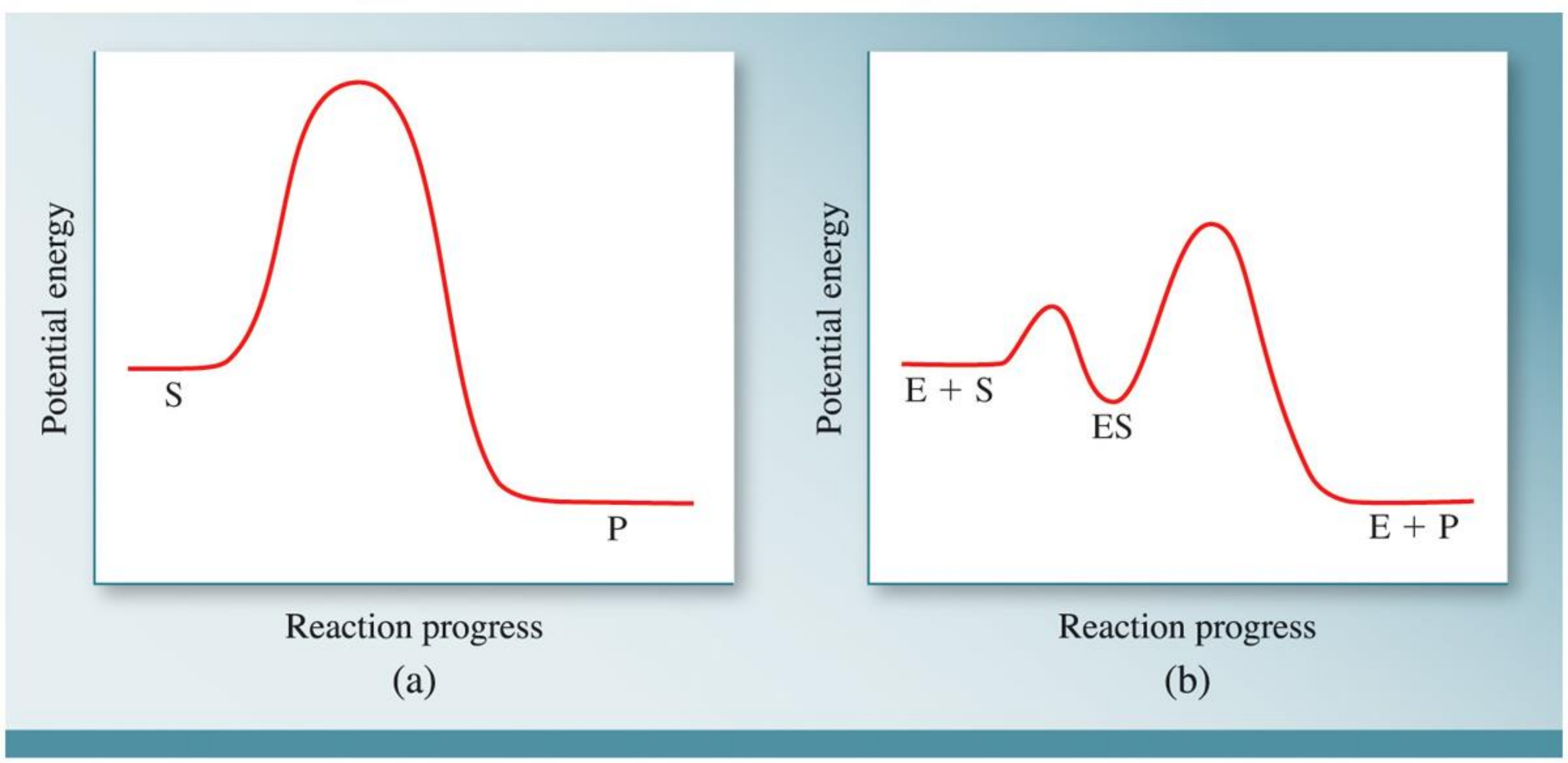
Types of Catalysts

- **Heterogeneous catalysts** - reactants and catalyst are in different phases
- **Homogeneous catalysts** - reactants and catalysts are dispersed in single phase
- **Enzyme catalysts** - biological catalysts

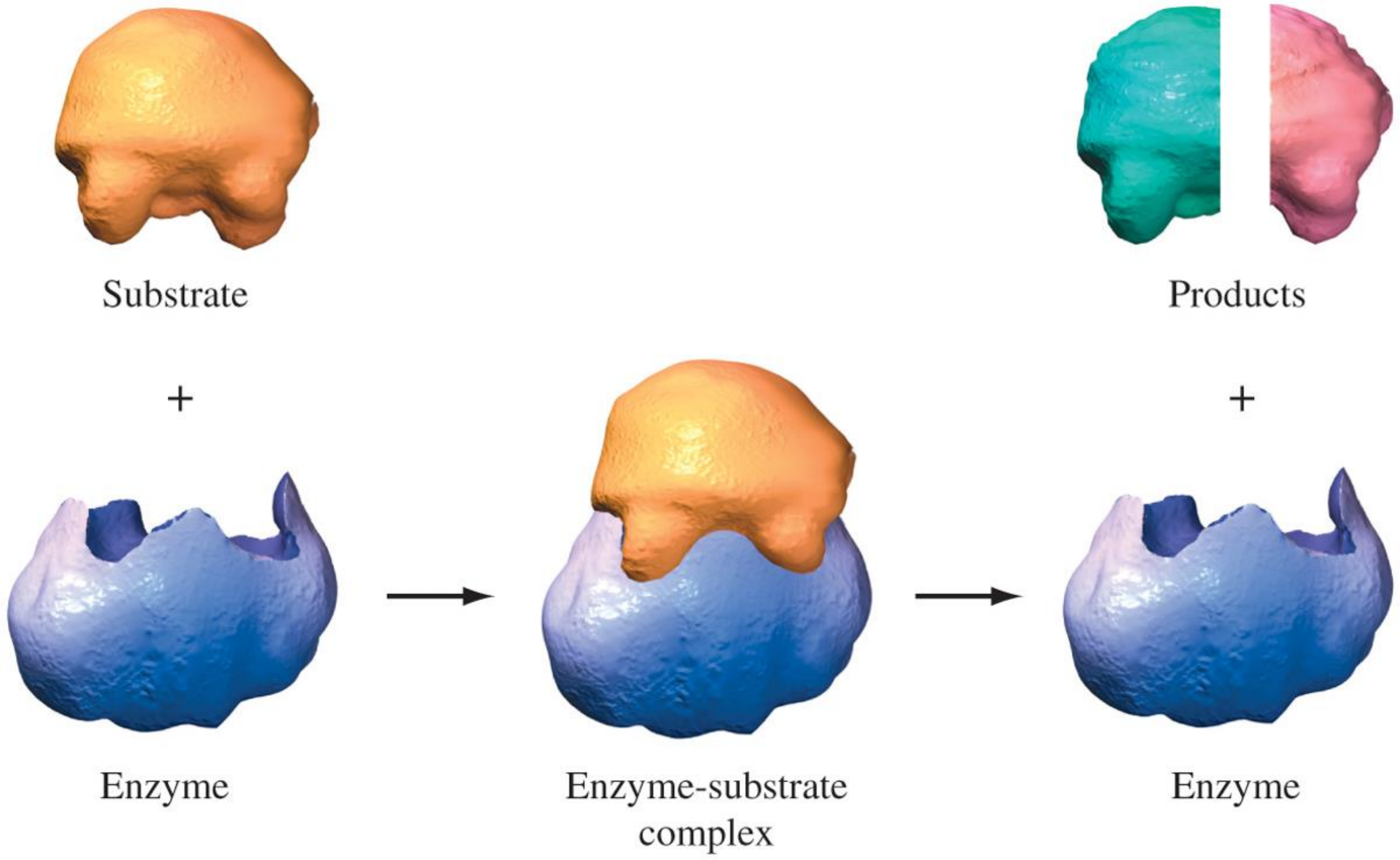
Biological Catalysts

- Enzymes: large protein molecule that contains one or more active sites where interactions with substrates occur
- Enzymes are highly specific (lock and key)

Reaction Pathway without and with Enzyme-Substrate

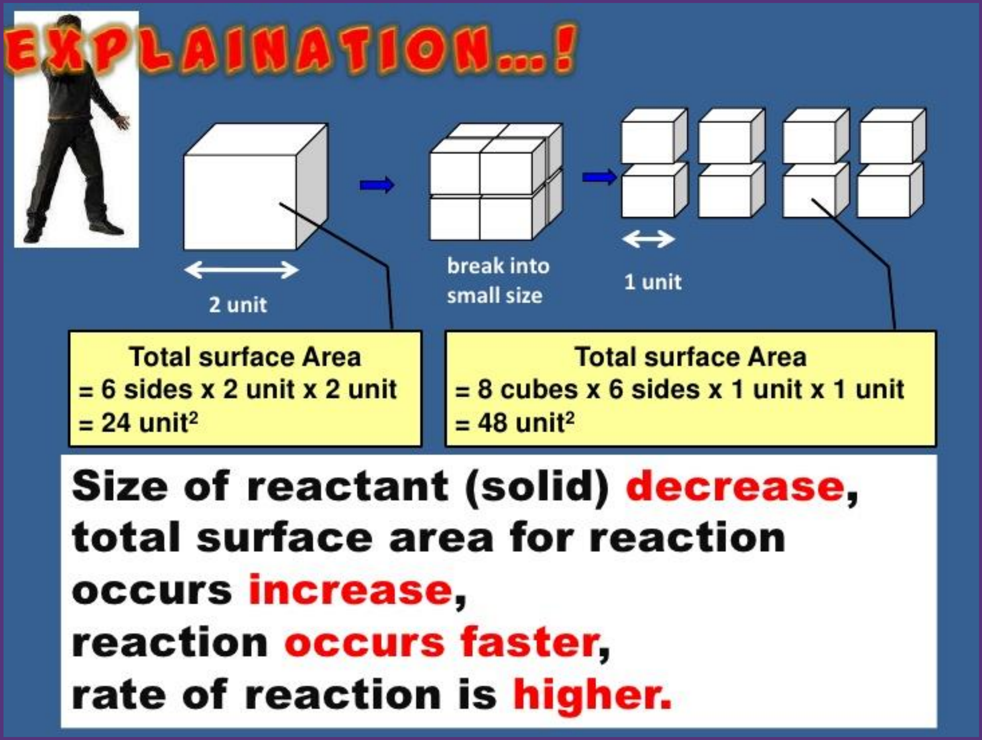


Enzyme-Substrate Complex



Dependence of Reaction Rate on Surface area of a solid reactant

- Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area.



Total surface Area
= 6 sides x 2 unit x 2 unit
= 24 unit^2

Total surface Area
= 8 cubes x 6 sides x 1 unit x 1 unit
= 48 unit^2

Size of reactant (solid) decrease,
total surface area for reaction occurs increase,
reaction occurs faster,
rate of reaction is higher.

Chemical equilibrium

The state of a reaction in which the rates of the forward and reverse reactions are the same.

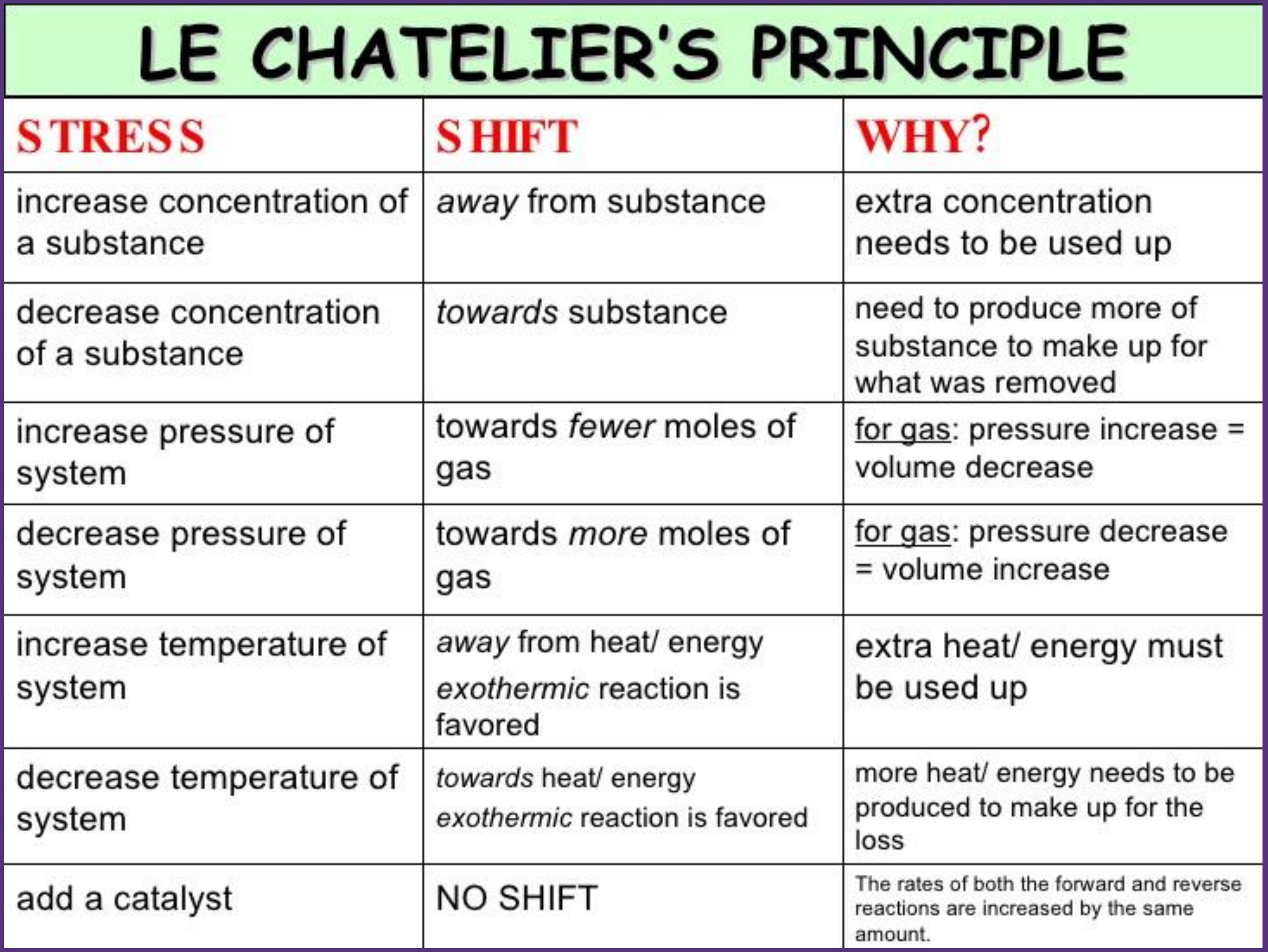
Le Chatelier's principle , also called **Chatelier's principle** or "The Equilibrium Law", can be used to predict the effect of a change in conditions on a chemical equilibrium. The principle is named after Henry Louis Le Chatelier and sometimes Karl Ferdinand Braun who discovered it independently.

Chemical equilibrium

A statement of Le Chatelier's Principle
If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

Chemical equilibrium

$$N_2 + 3H_2 \Leftrightarrow 2NH_3; \Delta H < 0$$



LE CHATELIER'S PRINCIPLE

STRESS	**SHIFT**	**WHY?**
increase concentration of a substance	*away* from substance	extra concentration needs to be used up
decrease concentration of a substance	*towards* substance	need to produce more of substance to make up for what was removed
increase pressure of system	towards *fewer* moles of gas	for gas: pressure increase = volume decrease
decrease pressure of system	towards *more* moles of gas	for gas: pressure decrease = volume increase
increase temperature of system	*away* from heat/ energy *exothermic* reaction is favored	extra heat/ energy must be used up
decrease temperature of system	*towards* heat/ energy *exothermic* reaction is favored	more heat/ energy needs to be produced to make up for the loss
add a catalyst	NO SHIFT	The rates of both the forward and reverse reactions are increased by the same amount.