

# Lecture 3.

‘Theoretical basis of  
bioenergetics.

Chemical kinetics and  
biological processes.

Electrochemistry.’

***ass. Falfushynska Halina***



**Biological thermodynamics** is sometimes used to refer to **bioenergetics**, the study of energy transformation in the biological sciences.

Biological thermodynamics may be defined as the quantitative study of the energy transductions that occur in and between living organisms, structures, and cells and of the nature and function of the chemical processes underlying these transductions.

The field of biological thermodynamics is focused on principles of chemical thermodynamics in biology and biochemistry. Principles covered include the first law of thermodynamics, the second law of thermodynamics, Gibbs free energy, statistical thermodynamics, reaction kinetics, and on hypotheses of the origin of life.

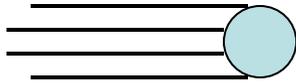
Presently, biological thermodynamics concerns itself with the study of internal biochemical dynamics as: ATP hydrolysis, protein stability, DNA binding, membrane diffusion, enzyme kinetics, and other such essential energy controlled pathways.



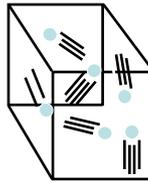
# Energy

- Many Different Forms

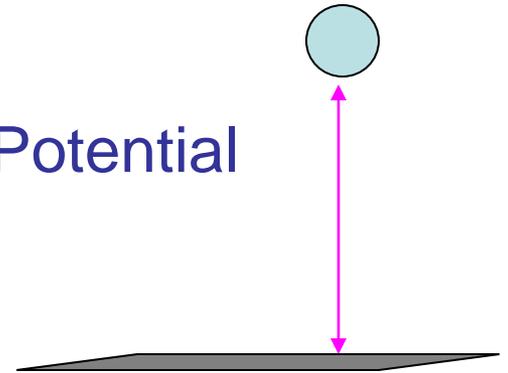
Kinetic



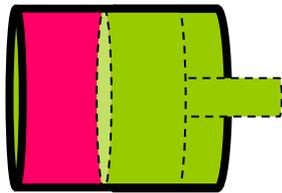
Internal



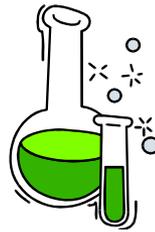
Potential



Mechanical



Chemical



Electrical



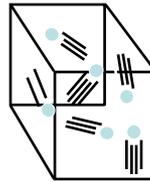
Chemical  
Thermodynamics



You know that energy cannot be created nor destroyed.

# Energy

## Internal



Internal energy = kinetic + potential energy  
of the molecules or atoms  
of a body (e.g. parcel)

Kinetic energy = translation, rotation, vibration  
of the molecules or atoms

$$E_k = \frac{1}{2} \cdot m \cdot v^2$$

## Units of Energy

- SI Unit for energy is the joule, J:

$$E_k = \frac{1}{2} \cdot m \cdot v^2 = \frac{1}{2} \cdot (2 \text{ kg}) \cdot (1 \text{ m/s})^2$$
$$= 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ J} \quad \text{establish the equation}$$

sometimes the calorie is **used** instead of the joule:

$$1 \text{ cal} = 4.184 \text{ J (exactly)}$$

A nutritional Calorie:

$$1 \text{ Cal} = 1000 \text{ cal} = 1 \text{ kcal}$$

# First Law of Thermodynamics

The **first law of thermodynamics** is an expression of the principle of conservation of energy. The law states that energy can be transformed, i.e. changed from one form to another, but cannot be created nor destroyed. It is usually formulated by stating that the change in the internal energy of a system is equal to the amount of heat supplied to the system, minus the amount of work performed by the system on its surroundings.

- Energy is Conserved

$$E = \text{constant}$$

$$(E_{\text{Kinetic}} + E_{\text{Potential}} + E_{\text{Internal}} + E_{\text{Chemical}} + E_{\text{Mechanical}} + E_{\text{Electrical}}) = \text{constant}$$

$$\Delta E = q + w$$

# First Law of Thermodynamics

## supervenience

- Total energy of the universe is a constant.
- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.

## Isochoric Process

$$V = \text{const}, A=0$$

$$Q_v = U_2 - U_1 = \Delta U$$

- Changes in
  - Heat Added or Removed
  - Temperature
  - Pressure

## Isobaric Process

$$p = \text{const}$$

$$Q_p = \Delta U + p \Delta V = \Delta H$$

- Changes in
  - Heat Added or Removed
  - Temperature
  - Volume

## Isothermal Process

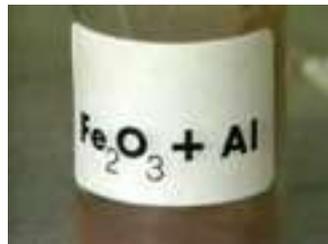
$$T = \text{const}$$

- Changes in: Heat Added or Removed
  - Pressure; Volume

# The First Law of Thermodynamics

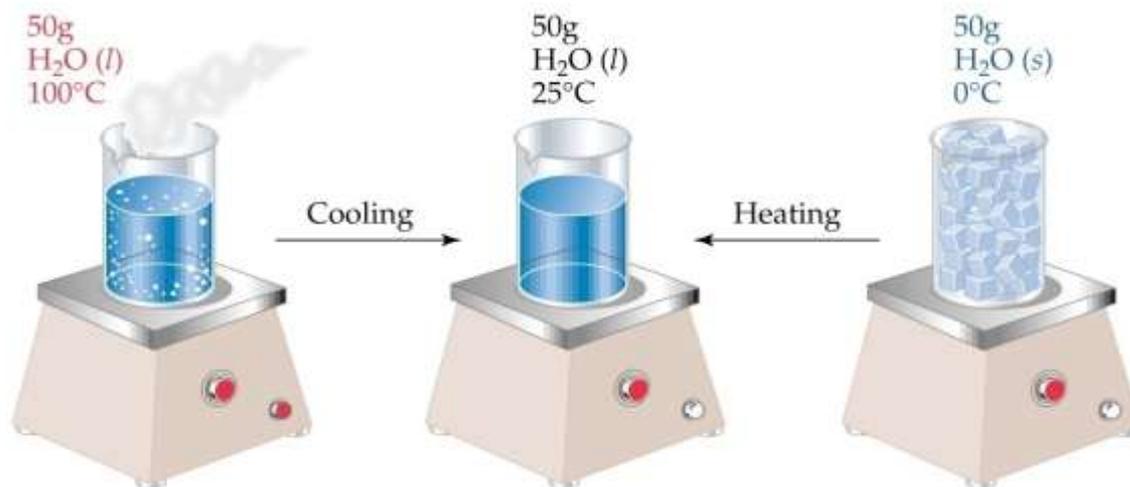
## Exothermic and Endothermic Processes

- **Endothermic**: absorbs heat from the surroundings.
- An endothermic reaction feels cold,  $\Delta H > 0$
  
- **Exothermic**: transfers heat to the surroundings.
- An exothermic reaction feels hot,  $\Delta H < 0$  (combustion).



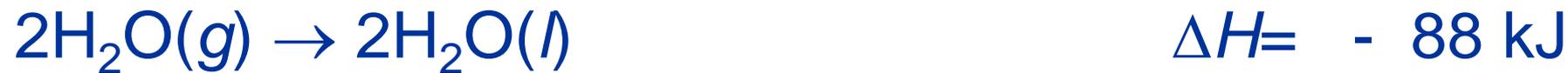
# The First Law of Thermodynamics

- Heat effect of reaction is a state function: depends only on the initial and final states of system, not on how the internal energy is used.



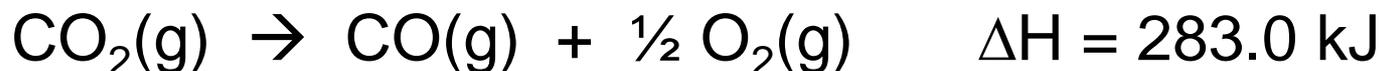
# Hess's Law

- **Hess's law:** if a reaction is carried out in a number of steps,  $\Delta H$  for the overall reaction is the sum of  $\Delta H$  for each individual step.
- For example:



# Another Example of Hess's Law

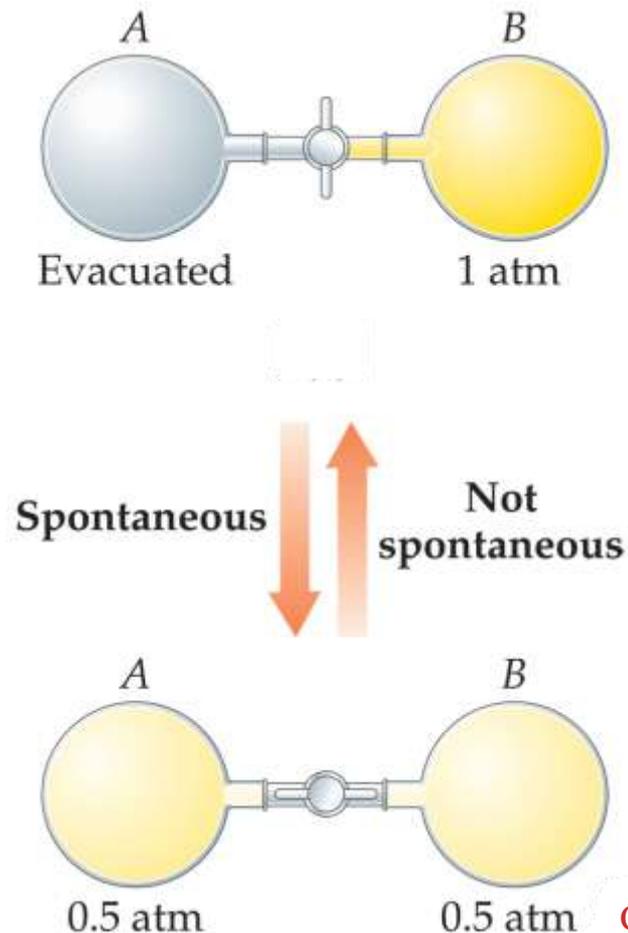
Given:



Calculate  $\Delta\text{H}$  for:  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

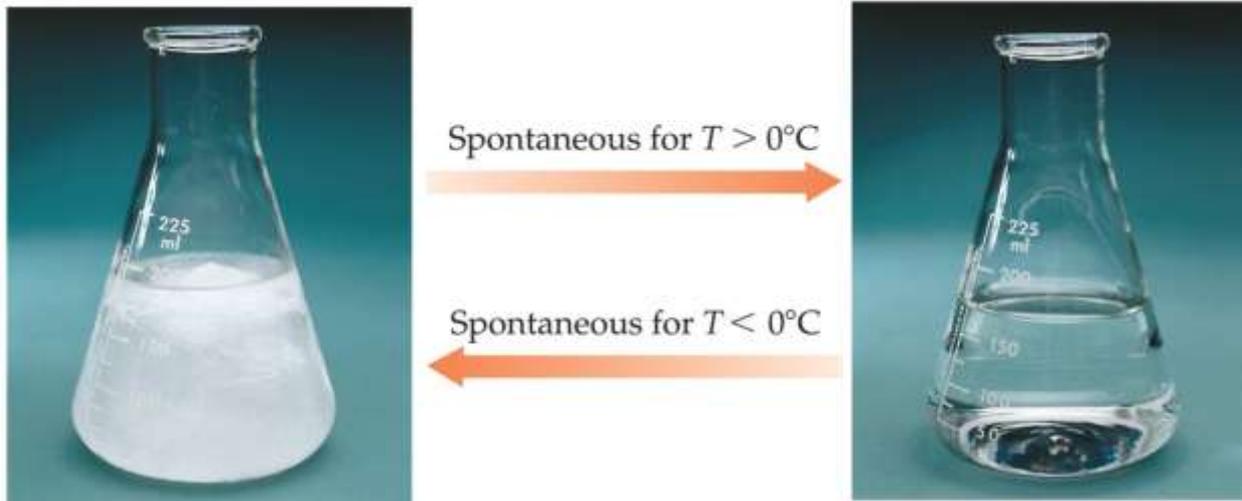
# Spontaneous Processes

- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously

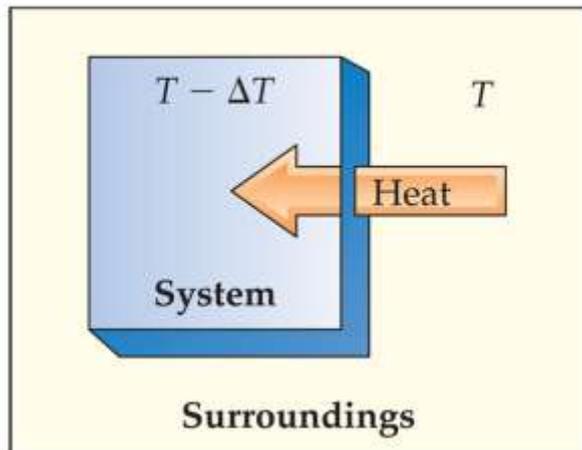
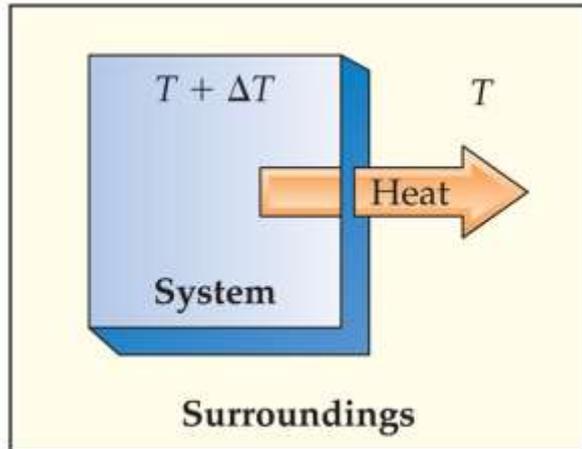


# Spontaneous Processes

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above  $0^{\circ}\text{C}$  it is spontaneous for ice to melt.
- Below  $0^{\circ}\text{C}$  the reverse process is spontaneous.



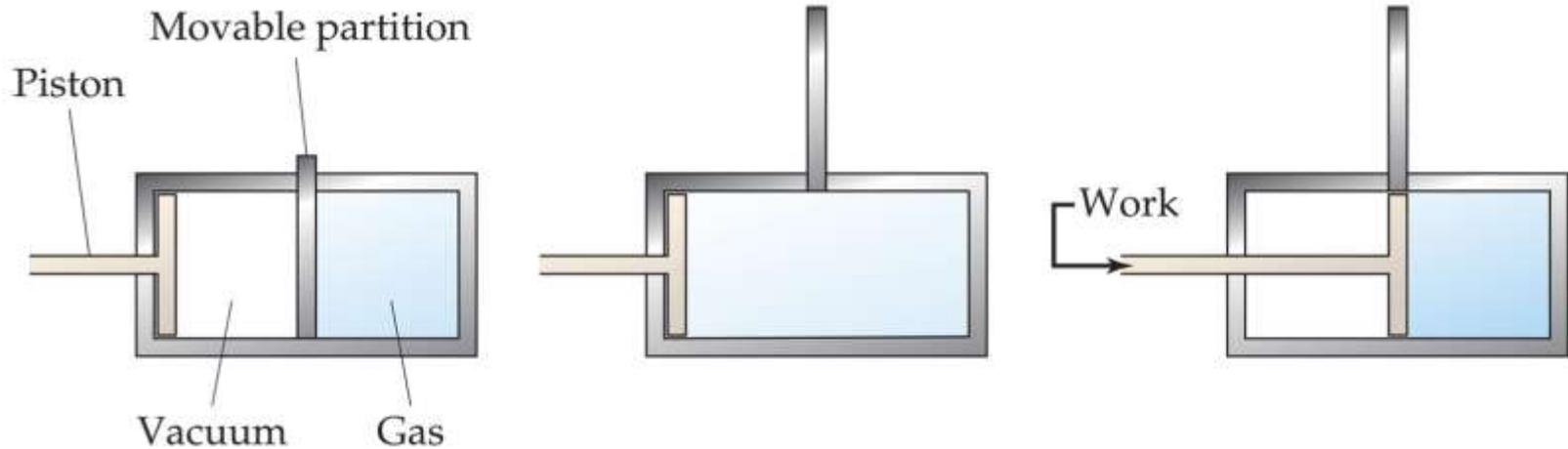
# Reversible Processes



In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

Changes are infinitesimally **small** in a reversible process.

# Irreversible Processes



- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.

# Entropy

- *Entropy* ( $S$ ) is a term coined by Rudolph Clausius in the 19th century. Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered,  $\frac{q}{T}$
- Entropy can be thought of as a measure of the randomness of a system. It is related to the various modes of motion in molecules

# Entropy

- Like total energy,  $E$ , and enthalpy,  $H$ , entropy is a state function.
- Therefore,  $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- For a process occurring at constant temperature (an isothermal process):

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$q_{\text{rev}}$  = the heat that is transferred when the process is carried out **reversibly** at a constant temperature.

$T$  = temperature in Kelvin.

# Second Law of Thermodynamics

*The second law of thermodynamics:*

The entropy of the universe does not change for reversible processes

and

increases for spontaneous processes.

Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

# Second Law of Thermodynamics

The entropy of the universe increases (real, spontaneous processes).

But, entropy can decrease for individual systems.

Reversible (ideal):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

# Practical uses: surroundings & system ...Gibbs Free Energy

$-T\Delta S_{\text{universe}}$  is defined as the Gibbs free energy,  $\Delta G$ .

For spontaneous processes:  $\Delta S_{\text{universe}} > 0$

And therefore:  $\Delta G < 0$

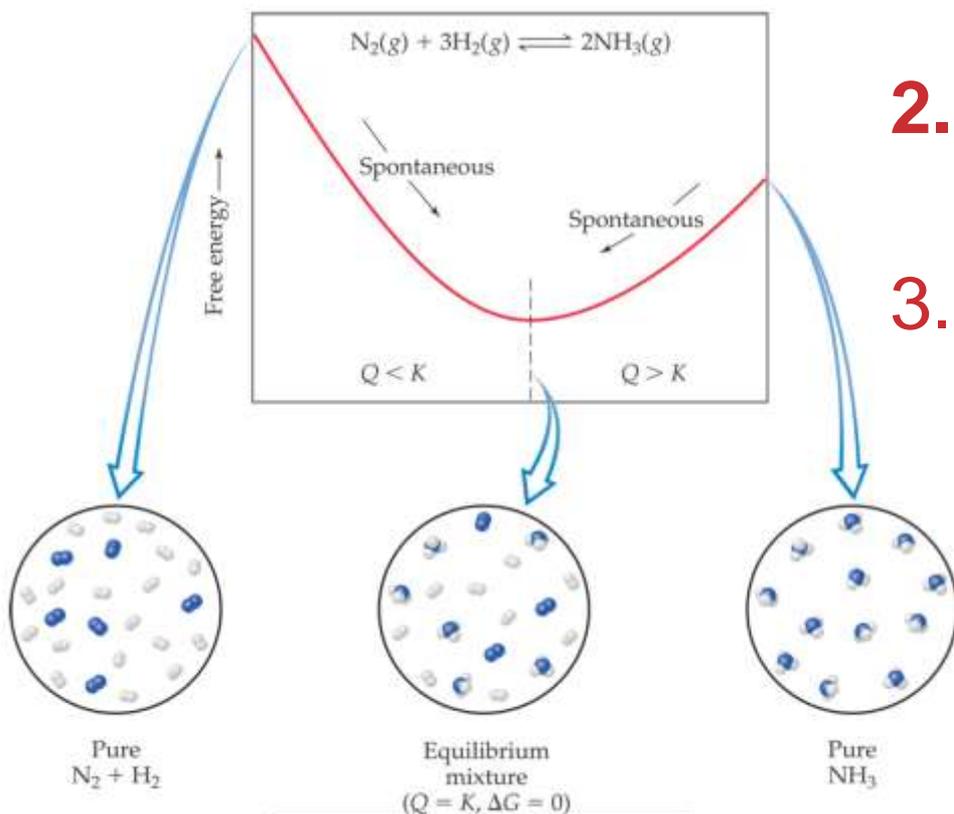
*$\Delta G$  is easier to determine than  $\Delta S_{\text{universe}}$ .*

*So:*

*Use  $\Delta G$  to decide if a process is spontaneous.*

# Gibbs Free Energy

1. If  $\Delta G$  is negative, the forward reaction is spontaneous.
2. If  $\Delta G$  is 0, the system is at equilibrium.
3. If  $\Delta G$  is positive, the reaction is spontaneous in the reverse direction.



# Standard Free Energy Changes

Standard free energies of formation,  $\Delta G_f^\circ$  are analogous to standard enthalpies of formation,  $\Delta H_f^\circ$ .

$$\Delta G_f^\circ = \sum \Delta G_{\text{reactants}}^\circ - \sum \Delta G_{\text{products}}^\circ$$

$\Delta G^\circ$  can be looked up in tables,  
*or*  
calculated from  $S^\circ$  and  $\Delta H^\circ$ .

# Free Energy Changes

Very key equation:

$$\Delta G = \Delta H_{sys}^{\circ} - T\Delta S_{system}$$

This equation shows how  $\Delta G^{\circ}$  changes with temperature.

(We assume  $S^{\circ}$  &  $\Delta H^{\circ}$  are independent of T.)

# Free Energy and Equilibrium

Under non-standard conditions, we need to use  $\Delta G$  instead of  $\Delta G^\circ$ .

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Note: at equilibrium:  $\Delta G = 0$ .

away from equil, sign of  $\Delta G$  tells which way rxn goes spontaneously.

# Part 2.

- Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

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



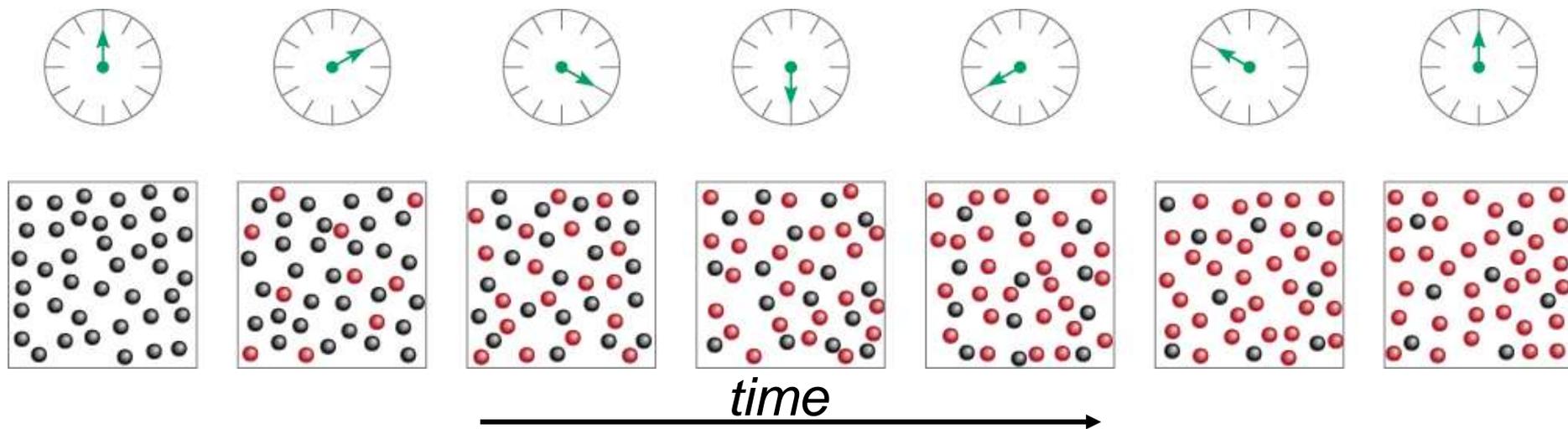
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

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

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

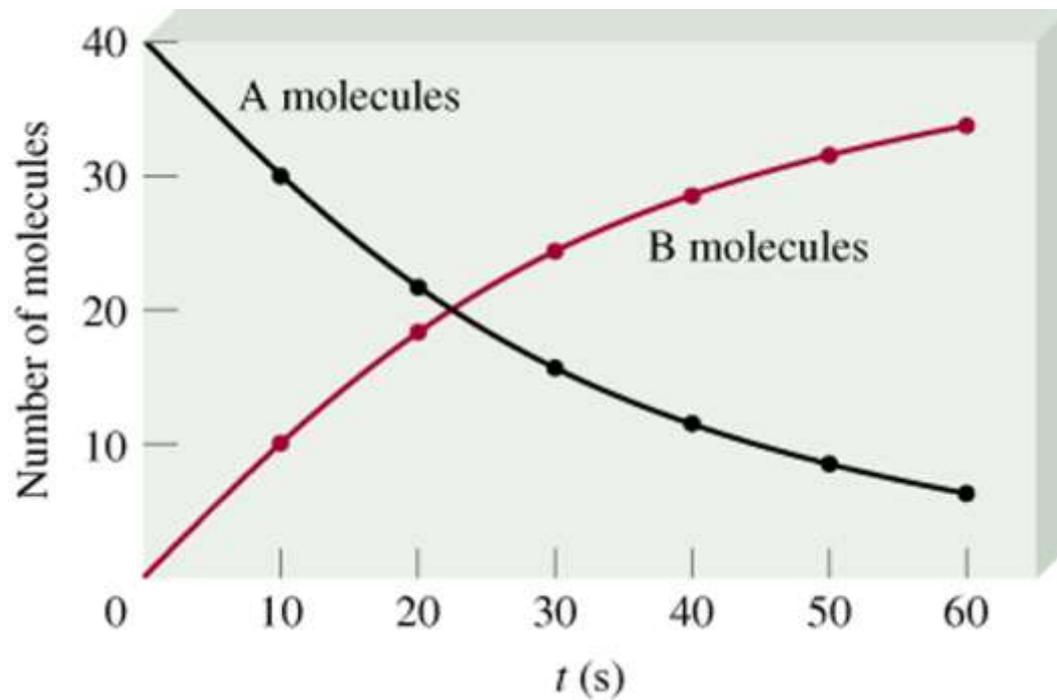
$\Delta[B]$  = change in concentration of B over time period  $\Delta t$

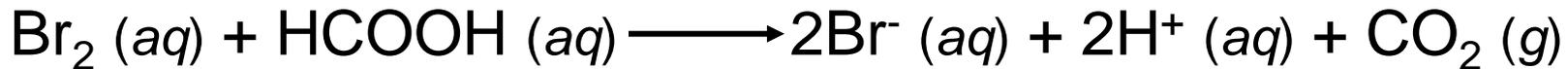
Because [A] decreases with time,  $\Delta[A]$  is negative.



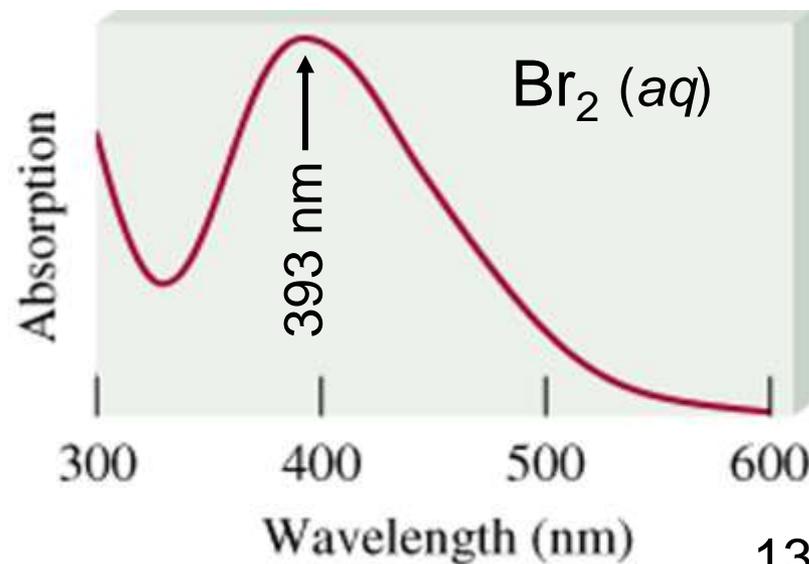
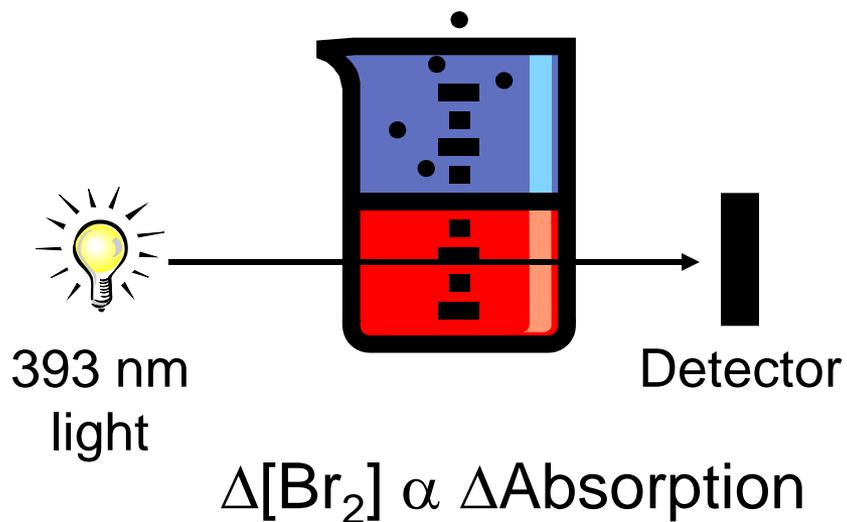
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

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





$\xrightarrow{\text{time}}$   
bleaching of solution



# Factors that Affect Reaction Rate

## 1. Temperature

- **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

- More reactants mean more collisions if enough energy is present

## 3. Catalysts

- Speed up reactions by lowering activation energy

## 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

# 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.



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

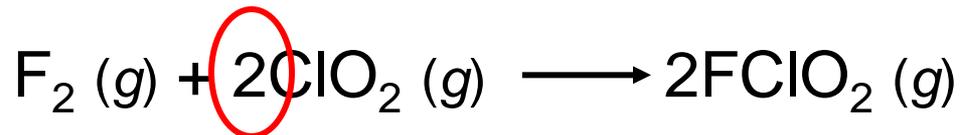
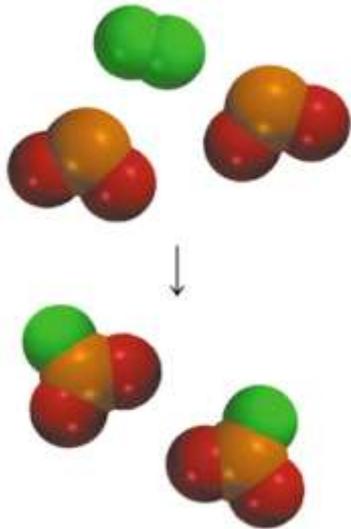
reaction is **xth order** in A

reaction is **yth order** in B

reaction is **(x + y)th order overall**

# 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.



$$\text{rate} = k [\text{F}_2][\text{ClO}_2]^1$$



Determine the rate law and calculate the rate constant for the following reaction from the following data:



Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial Rate (M/s)
1	0.08	0.034	$2.2 \times 10^{-4}$
2	0.08	0.017	$1.1 \times 10^{-4}$
3	0.16	0.017	$2.2 \times 10^{-4}$

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^x [\text{I}^-]^y$$

$$y = 1$$

$$x = 1$$

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

Double  $[\text{I}^-]$ , rate doubles (experiment 1 & 2)

Double  $[\text{S}_2\text{O}_8^{2-}]$ , rate doubles (experiment 2 & 3)

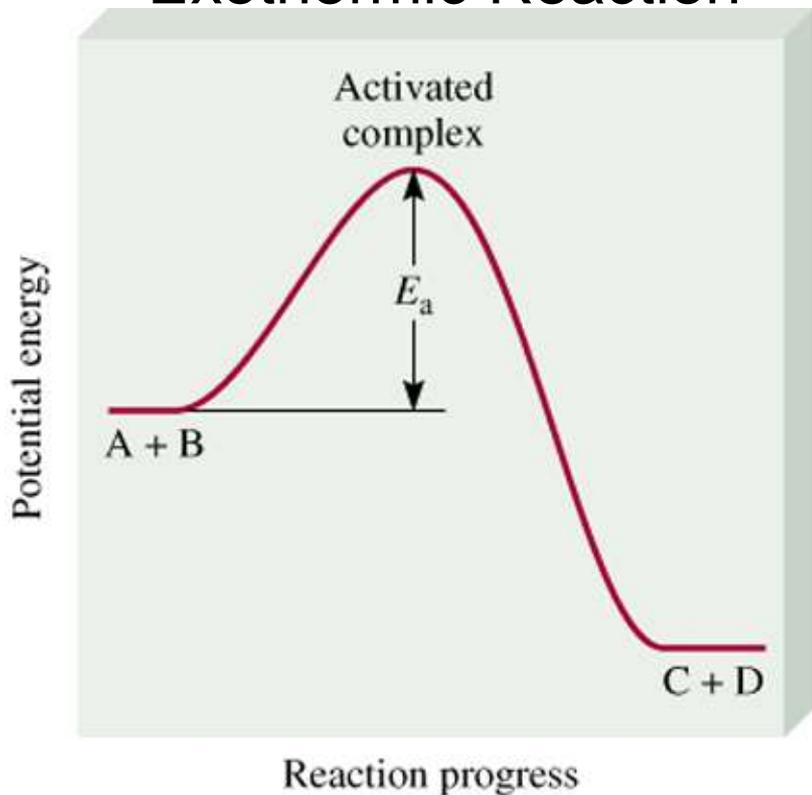
$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}] [\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08/\text{M}\cdot\text{s}$$

# Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

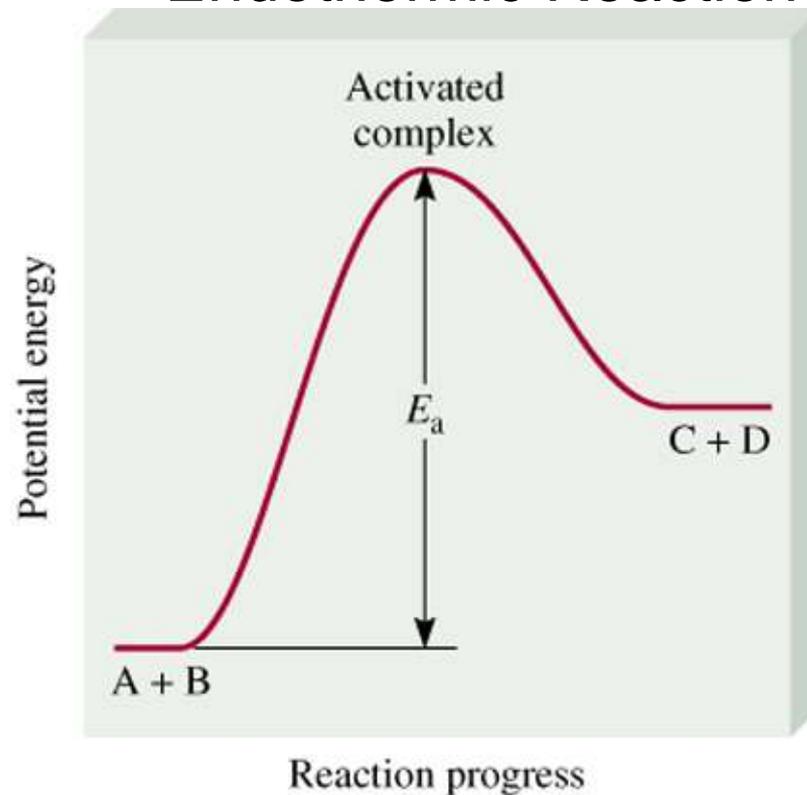
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = $k$	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$



### Exothermic Reaction



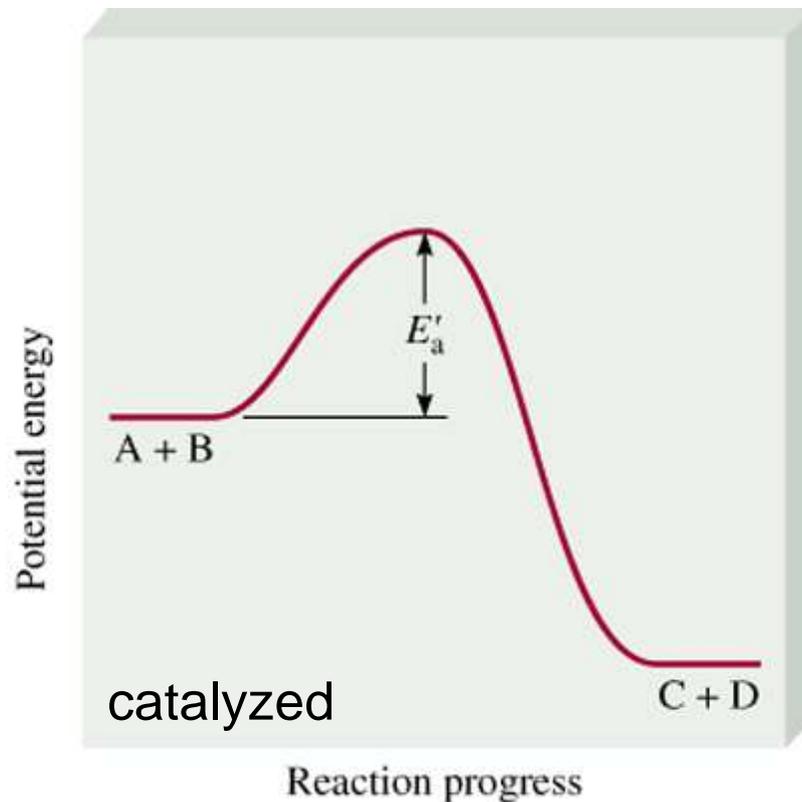
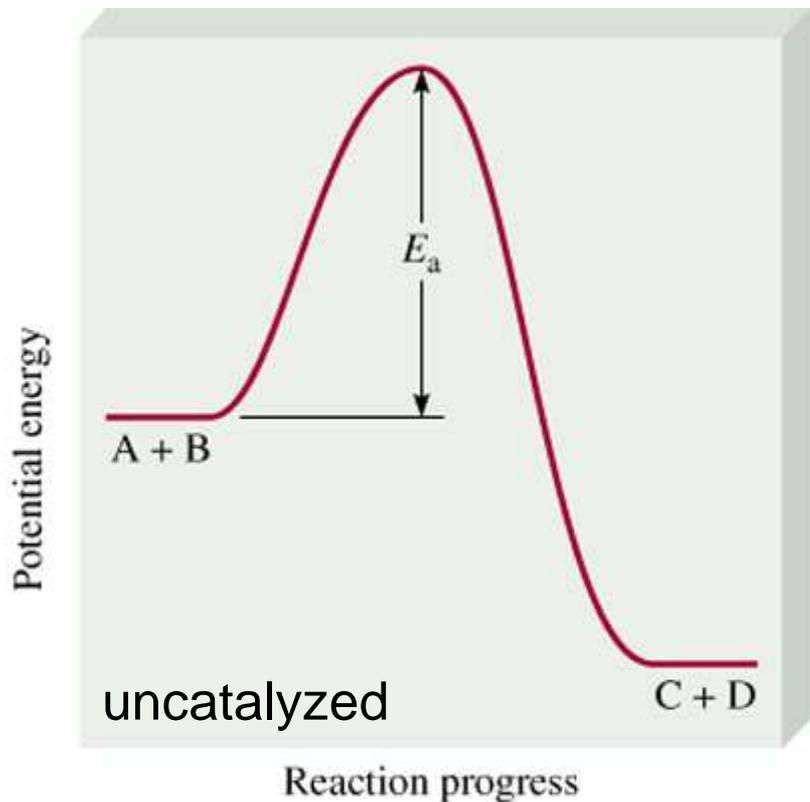
### Endothermic Reaction



The **activation energy** ( $E_a$ ) is the minimum amount of energy required to initiate a chemical reaction.

A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

$$k = A \cdot \exp(-E_a/RT) \quad E_a \downarrow \quad k \uparrow$$



$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

$$E'_a < E_a$$

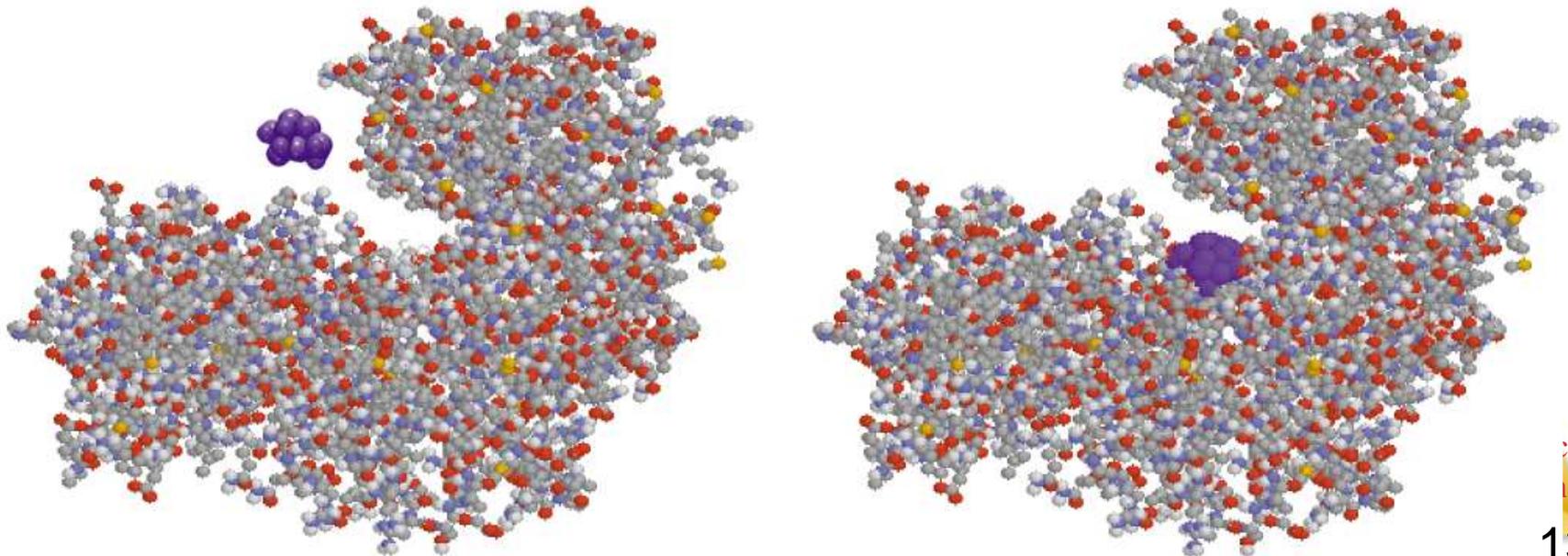
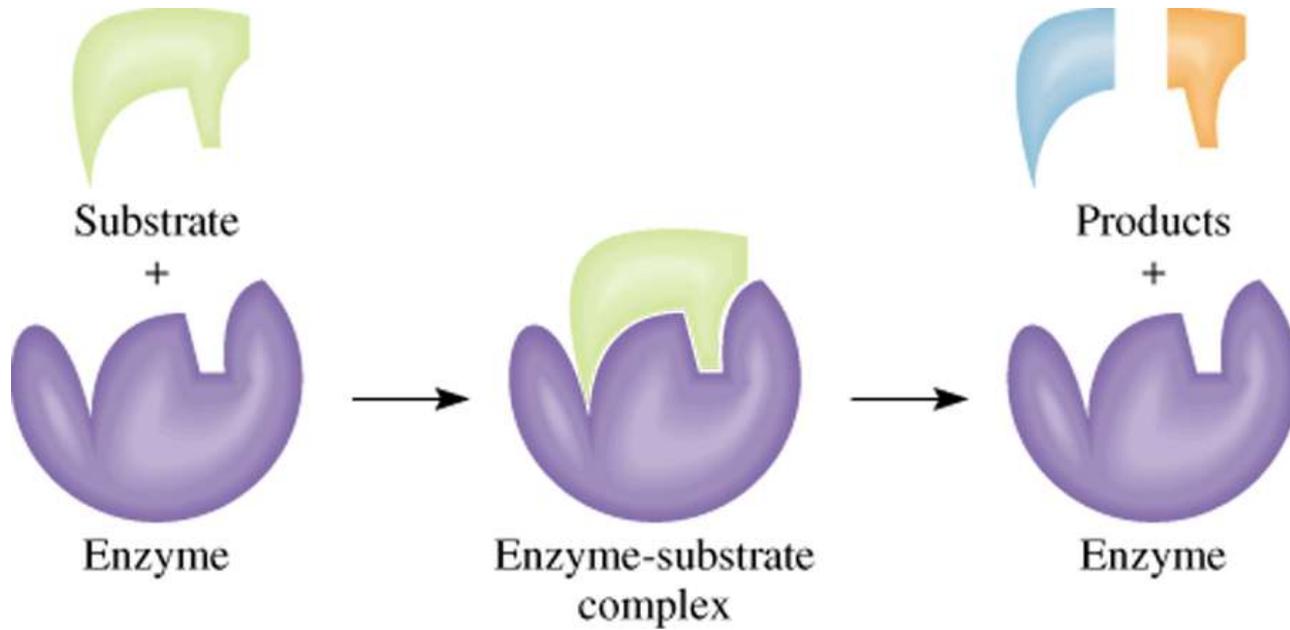
In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

# Enzyme Catalysis



# van't Hoff's rule

The velocity of chemical reactions is increased twofold or more for each rise of 10° C in temperature; generally true only when temperatures approximate those normal for the reaction.

$$V_2 = V_1 \cdot \gamma^{\frac{T_2 - T_1}{10}}$$

$$\gamma = (V_2/V_1)^{10/(T_2 - T_1)}$$