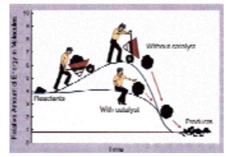


Chapter 14

CHEMICAL KINETICS

(Part II)

14.5

Reaction Mechanism

- Most reactions occur in a series of steps. The balanced equation gives information about the initial reactants and the final products. *it does not tell us how the reaction occurs*.
- There are often a series of steps which add together to give the overall reaction. The series of steps is called the ***reaction mechanism***.

Elementary reactions

$$A + B \rightarrow C$$
$$C + B \rightarrow D$$

The overall equation

$$A + 2B \rightarrow D$$

Intermediate: a species that is produced in an earlier step and is consumed in a later step, but it is not shown in the overall equation.

Elementary Reactions

- An ***Elementary reaction*** is the reaction that occurs in a single collision of the reactant molecules, and it is a part of the reaction mechanism.
  - ***Unimolecular***: one reactant molecule.
  - ***Bimolecular***: two reactant molecules.
  - ***Termolecular***: three reactant molecules. (fairly rare)

Elementary Step	Molecularity	Rate Law
$A \rightarrow$ products	*Uni*molecular	Rate $= k[A]$
$A + A \rightarrow$ products ($2A \rightarrow$ products)	*Bi*molecular	Rate $= k[A]^2$
$A + B \rightarrow$ products	*Bi*molecular	Rate $= k[A][B]$
$A + A + B \rightarrow$ products ($2A + B \rightarrow$ products)	*Ter*molecular	Rate $= k[A]^2[B]$
$A + B + C \rightarrow$ products	*Ter*molecular	Rate $= k[A][B][C]$

Elementary Reactions

- The *reaction order* of each reactant in an *elementary reaction* is equal to its *stoichiometric coefficient*. This is because the rate of an elementary reaction depends on how frequently the reactants collide with each other; which depends on the reactant concentrations.

Elementary Step	Molecularity	Rate Law
$A \rightarrow$ products	*Uni*molecular	Rate $= k[A]$
$A + A \rightarrow$ products ($2A \rightarrow$ products)	*Bi*molecular	Rate $= k[A]^2$
$A + B \rightarrow$ products	*Bi*molecular	Rate $= k[A][B]$
$A + A + B \rightarrow$ products ($2A + B \rightarrow$ products)	*Ter*molecular	Rate $= k[A]^2[B]$
$A + B + C \rightarrow$ products	*Ter*molecular	Rate $= k[A][B][C]$

14.5

Rate-Determining Step

- If the elementary reactions are known, ***the order of the overall reaction*** can be written from the stoichiometric coefficients of the ***slowest elementary reaction***.

  Rate-determining step is the *slowest* elementary step in the mechanism.
- The reaction mechanism, rate-determining step, and the rate law of a chemical reaction are proposed from experimental work in terms of logical elementary steps.

Dr. Al-Saadi 5

14.5

Rate-Determining Step

- Elementary steps of any reaction mechanism must satisfy two requirements:
  - Sum of elementary steps must equal the overall balanced equation.
  - The rate law of the rate-determining step must have the same rate law which was determined from experimental data.

Dr. Al-Saadi 6

14.5

Rate-Determining Step

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Decomposition of H_2O_2 can be facilitated by iodide ions (I^-). It takes place in two elementary steps:

From experiment, the rate law was found to be:

rate = $k[H_2O_2][I^-]$ The reaction can't be a single-step reaction

step 1: $H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$ rate-determining step

step 2: $H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^-$

- The rate law of the reaction can be determined from the rate-determining step.

Dr. Al-Saadi 7

14.5

Rate-Determining Step

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

step 1: $H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$ rate-determining step

step 2: $H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^-$

- I^- does not appear in the overall balanced equation, but it does in the rate law.
- I^- serves as a ***catalyst*** in the reaction. It is present at the start of the reaction and is present at the end (gets regenerated). It *speeds up* the reaction.
- IO^- is an ***intermediate***. It is produced in step 1 and is consumed in step 2.

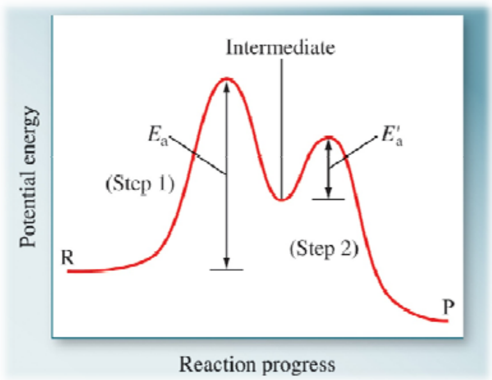
Dr. Al-Saadi 8

Potential Energy Profile

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

step 1: $H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$ rate-determining step

step 2: $H_2O_2 + IO^- \xrightarrow{k_2} H_2O + O_2 + I^-$



The rate-determining step has a larger activation energy than the faster step

Reaction Mechanism

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

The experimental rate law was found from experiment to be

$$\text{rate} = k[H_2][I_2]$$

However, the reaction involves two steps and not just one.

Step 1 : $I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2I$ (fast)

Step 2 : $H_2 + 2I \xrightarrow{k2} 2HI$ (slow)

14.5

Reaction Mechanism

Since step 2 is the rate-determining step, the rate law should have the form:

$$\text{rate} = k_2[H_2][I]^2$$

This rate expression does not meet the requirements. Why?

Because I is an intermediate and must not appear in the rate expression.

- So, consider the first equilibrium step:

the forward rate is equal to the reverse rate.

$$k_1[I_2] = k_{-1}[I]^2$$

$$k_1/k_{-1}[I_2] = [I]^2$$

Dr. Al-Saadi 11

14.5

Reaction Mechanism

The rate law of step 2 can be now rewritten in terms of I_2 rather than atomic iodine; I.

$$\text{rate} = k_2[H_2]\,k_1/k_{-1}[I_2]$$

$$\text{rate} = (k_2k_1/k_{-1})[H_2][I_2]$$

Thus, the reaction rate law is:

$$\text{rate} = k[H_2][I_2]$$

$$\text{where } k = k_2k_1/k_{-1}$$

Indecently, it happened that the rate law is the same if the reaction were to take place in a single step.

Dr. Al-Saadi 12

14.5

Reaction Mechanism

- Exercise:

$$NO_2 + NO_2 \xrightarrow{k_1} NO + NO_3$$
$$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$$

The experimental rate law is: rate = $k[NO_2]^2$

(a) Write the equation for the overall reaction.

(b) Identify the intermediate(s).

(c) Identify the rate-determining step.

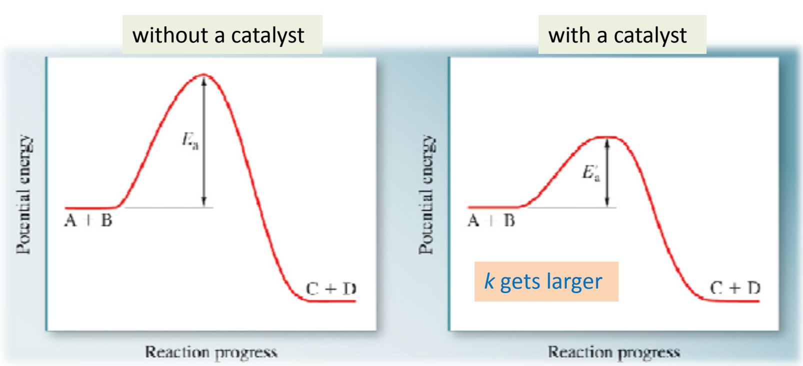
Dr. Al-Saadi 13

14.6

Catalysis

- ***Catalyst*** - a substance that increases the rate of a chemical reaction without itself being consumed.

$$A + B \xrightarrow{k} C + D$$



Dr. Al-Saadi 14

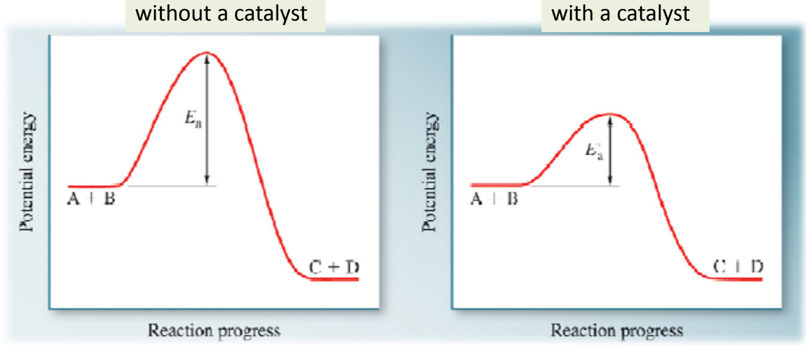
14.6

Catalysis

- Using a catalyst results in:
  - o Speeding up the reaction (higher rate).
  - o Increasing the value of the rate constant.
  - o Lowering the activation energy.

without a catalyst

with a catalyst



Dr. Al-Saadi 15

14.6

Types of Catalysts

- **Heterogeneous catalysts** - reactants and catalyst are in different phases (Usually, catalyst is solid, and reactants are gas or liquid).
- **Homogeneous catalysts** - reactants and catalysts are dispersed in single phase.
- **Enzyme catalysts** - biological catalysts, found mostly in the human body.

Dr. Al-Saadi 16

14.6

Heterogeneous Catalysts

- They are most important in industrial chemistry. Petrochemical and oil industries mostly used heterogeneous catalysts.
- Also used also in catalytic converters in automobiles. Efficient catalytic converter serves two purposes;
  - o oxidizes CO and unburned hydrocarbons into CO_2 and H_2O.
  - o converts NO and NO_2 into N_2 and O_2 .

Without catalysts:

Hydrocarbons —Incomplete combustion→ $CO(g)$

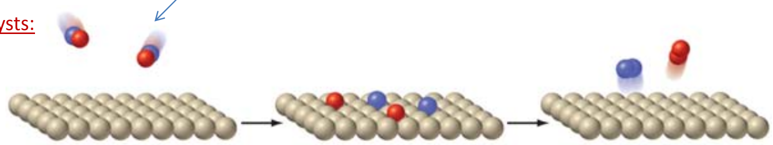
$N_2(g) + O_2(g) \rightarrow 2NO(g)$ —O_2 in atmosphere→ $NO_2(g)$

Car engine with high temp.

Exhaust

Major pollutants to the atmosphere

With catalysts:



Dr. Al-Saadi

14.6

Homogeneous Catalysts

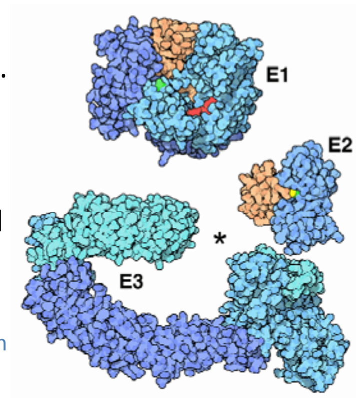
- Usually they are dispersed in the liquid phase.
- Acid and base catalyses are the most important types of homogeneous catalysis in liquid solutions.
- Advantages of homogeneous catalysts:
  - o Reactions performed at normal conditions.
  - o Less expensive.
  - o Can be designed to function selectively.

Dr. Al-Saadi

14.6

Enzymes: Biological Catalysts

- Enzymes are large protein molecules that contain active sites where interactions with substrates occur.
- Enzymes:
  - o are complicated in their structure.
  - o speed up many chemical reactions essential to our bodies. (factors ranging from 10^6 to 10^{18}).
  - o are highly specific. (like a lock and a key)



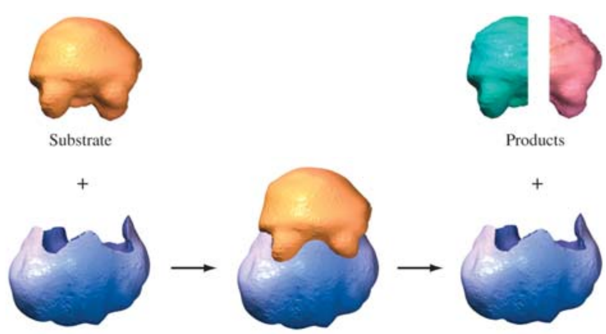
There are more than 3000 enzymes in a healthy body. Each enzyme catalyses a specific reaction with a specific substrate (*lock and key*) and converts it into an appropriate product that the body needs.

Dr. Al-Saadi 19

14.6

The Action of Enzymes

- The lock-and-key theory was first proposed in 1894 by E. Fischer who was awarded Nobel Prize in Chemistry in 1902.

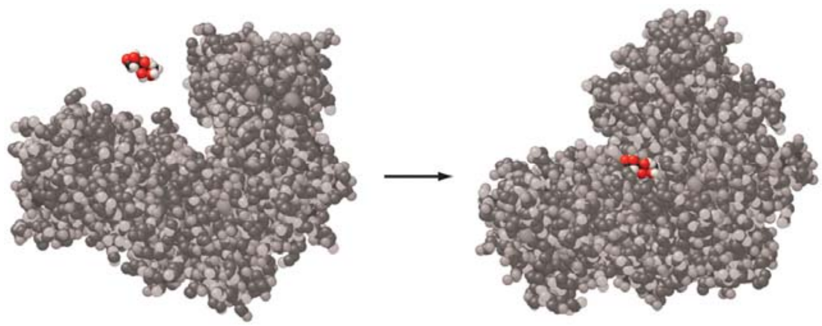


Dr. Al-Saadi 20

14.6

The Action of Enzymes

- Binding of glucose to hexokinase (an enzyme in the metabolic pathway) is an example of the enzyme activities inside our bodies.

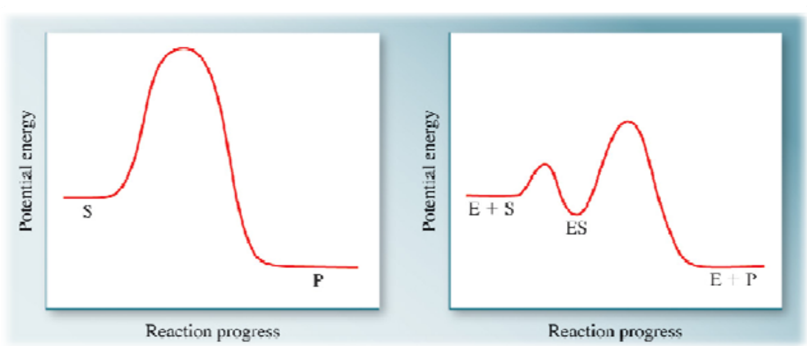


Dr. Al-Saadi 21

14.6

Enzymes: Biological Catalysts

- Reaction Pathway without and with Enzyme-Substrate.



Dr. Al-Saadi 22

Review Questions

- Chlorine dioxide (ClO_2) is a disinfectant used in municipal water-treatment plants. It dissolves in basic solution producing ClO_3^- and ClO_2^-:

  $2ClO_2\,(aq) + 2OH^-\,(aq) \rightarrow ClO_3^-\,(aq) + ClO_2^-\,(aq) + H_2O\,(l)$

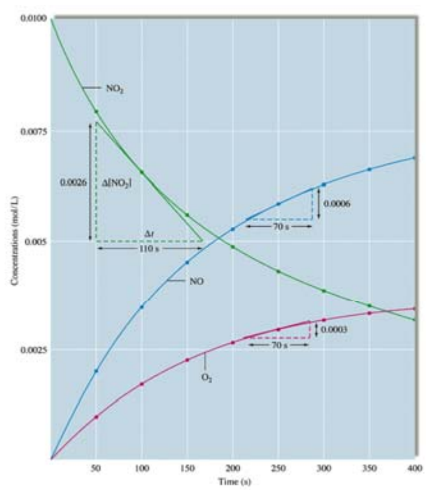
  Of the following, which would not be a proper expression to relate information about the rate of the reaction?

  a) $-\Delta ClO_2/\Delta t = 2\Delta ClO_3^-/\Delta t$
  b) $-\Delta ClO_2/\Delta t = \Delta OH^-/\Delta t$
  c) $-\Delta ClO_2/\Delta t = \Delta ClO_2^-/\Delta t$
  d) $-\Delta OH^-/\Delta t = 2\Delta ClO_2^-/\Delta t$

Review Questions

- Of the following, which is the approximate rate of O_2 appearance at 50 sec?

a) 0.0080 mol/L · s
b) 0.000016 mol/L · s
c) 0.00020 mol/L · s
d) 0.000030 mol/L · s



Review Questions

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

- Using the rate law rate = $k[BrO_3^-][Br^-][H^+]^2$ for the reaction shown here, and k value of 8.0 L/mol · s, what would be the rate in a yet untested experiment #5 when the initial concentrations of all components could be 0.20 *M*?

a) 0.064 mol/L · s
b) 0.00020 mol/L · s
c) 0.013 mol/L · s
d) 0.0064 mol/L · s

Review Questions

- While studying the shelf life of a particular antibiotic, a chemist found that when the initial concentration was 0.0036 *M* the rate of decay was 1.5×10^{-4} mol/L · s. In another experiment under the same conditions a concentration of 0.0013 *M* decayed at a rate of 1.9×10^{-5} mol/L · s. What is the order of this decay reaction?

a) More information is needed. This cannot be determined from only two experiments.
b) Zero order
c) First order
d) Second order

Review Questions

- Which of the following represents a correct conclusion:

a) The forward reaction is endothermic.
b) The activation energy for the forward reaction is less than the activation energy of the reverse reaction.
c) The transition state is at a lower energy than the products.
d) The energy of the reactants represents a lower energy level than both the transition state and the products.