CATALYSIS

Catalysis

- **Catalysis is** a term describing a process in which the rate and/or the outcome of the reaction is influenced by the presence of a substance (the **catalyst**) that is not consumed during the reaction and that is subsequently removed if it is not to constitute as an impurity in the final product.
- **Catalysis is** the process of speeding up a reaction
- **Catalysis** is the process of changing the rate of reaction by catalysts.
- **Catalysis is** divided into Positive and negative **catalysis**: In positive **catalysis**, the reaction rate is increased by the presence of a **catalyst**, but in negative **catalysts**, the rate of reaction is decreased by the presence of a **catalyst**.

Positive catalysis

- **Positive catalysis** is the term given to the phenomenon in which certain substances, called catalysts, increase the rate of a reaction while they themselves, although participating in the reaction, in the end remain chemically unchanged. This effect may be very strong, catalysts be able to change the rate of a reaction in million times or even more.
- Catalysts display *high specificity*

Negative catalysis

- There are also inhibitors (or negative catalysts), which decreases the rate of a reaction. The retarding effect of negative catalysts is frequently due to their poisoning, i.e., lowering of the activity of the positive catalysts.
- Examples of the use of negative catalysts are provided by antioxidants in rubber and plastics to retard atmospheric oxidation which causes perishing, stabilizers in rocket fuels, and rust inhibitors in antifreeze mixtures for use in internal combustion engines

Catalysis

- **The mechanism of catalytic effect** is the following: the catalyst forms an intermediate substance the catalyst with the reactants, facilitating the formation of the products by lowering the activation energy.
- **Catalysts do not affect the equilibrium** of a given reaction, but only facilitate its establishment. Although a catalyst cannot change the equilibrium constant, a homogeneous catalyst can change the equilibrium composition of a system.
- Depending on a reagent and catalyst aggregate states catalysis are divided into ***homogeneous***, ***heterogeneous*** and ***enzyme (or microheterogeneous)***.

Autocatalysis

- One of the products of a reaction may act as a catalyst for the reaction. The phenomenon is known as autocatalysis, and the initial reaction rate rises, as the catalytic product is formed, instead of decreasing steadily. The plot of reaction rate against time shows a maximum.
- Example of autocatalytic reaction, with the product acting as the catalyst underlined, is represented by the following equation:

$$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow 2\ \underline{\mathbf{MnSO_4}} + K_2SO_4 + 8\ H_2O + 10\ CO_2$$

Homogeneous catalysts

- **In homogeneous catalysis** a catalyst is in the same phase as the reaction mixture. A well-known example of homogeneous catalysis is the oxidation of sulfur dioxide with the aid of nitrogen oxides as catalyst. The mechanism of homogeneous catalysis is explained by activated complex theory.
- **Homogeneous catalysts** are catalysts that form a uniform distribution between themselves and the reactant molecules. These catalysts are in a solution along with the reactant molecules. Because they are dispersed within a solution, the surface area of the catalyst is maximized, and usually, these types of catalysts tend to be more efficient in increasing product formation at a lower temperature.

Homogeneous catalysts

Let us consider reaction A + B → C + D. Without a catalyst, this reaction, according of transition state, occurs by the following scheme:

$$\mathbf{A + B \rightarrow AB^{\#} \rightarrow C + D}$$

where $\mathbf{AB^{\#}}$ is the activated complex.

In presence of a catalyst process proceeds as following

$$\mathrm{A+K} \overset{k_1}{\underset{k_2}{\leftrightarrows}} \mathrm{AK}$$

$$\mathrm{AK + B} \xrightarrow{k_3} \mathrm{ABK^{\#}}$$

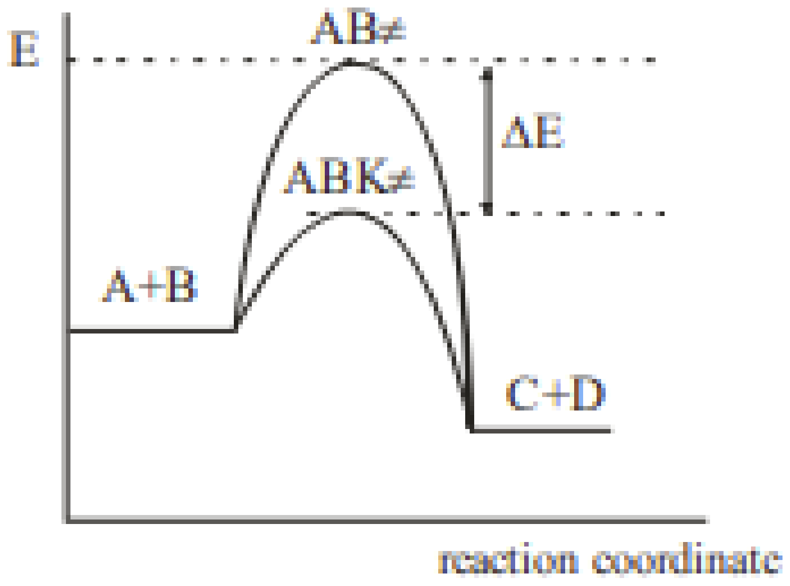
$$\mathrm{ABK^{\#}} \xrightarrow{k_4} \mathrm{C + D + K}$$

Homogeneous catalysts

$$\mathbf{A + B \rightarrow AB^{\#} \rightarrow C + D}$$

In the first stage the reactant A interacts with the catalyst (this stage is reversible), then the intermediate product AK with another reactant B is formed an activated complex, which is destroyed by product formation and catalyst regeneration. Activated complex **$ABK^{\#}$** has a lower activation energy then **$AB^{\#}$** .

The difference between value of activation energy in reaction with and without catalyst



$$\frac{k_{cat}}{k_{uncat}} = e^{\Delta E / RT}$$

Homogeneous catalysts

Activated complex [ABK]$^{\#}$ is the intermediate species, the concentration of which is very small and unknown, so we need in another approximation to express it by initial reactants. In general multistep reaction mechanism usually involves one or more intermediate species that do not appear in the overall equation. These intermediates are very reactive and therefore do not accumulate to any significant extent during the reaction. Therefore it is frequently a good approximation to take their rate equal to zero for each reactive intermediate. This is the steady-state (or stationary state) approximation. The steady-state approximation assumes that (after the induction period) the rate of the formation of an intermediate essentially equals to its rate of destruction, so as to keep it at a near constant steady-state concentration. According this approximation the rate of the third stage (where complex **[ABK]$^{\#}$** appears) is equal to the rate of the forth stage

Kinetic equation for homogeneous catalysis

The rate of the product C accumulation is equal to

$$\frac{d[C]}{dt} = k_4[ABK^{\#}]$$

$$k_3[AK][B] = k_4[ABK^{\#}]$$

$$[ABK^{\#}] = \frac{k_3[AK][B]}{k_4}$$

$$k_1[A][K] = k_2[AK] + k_3[AK][B]$$

from which

$$[AK] = \frac{k_1[A][K]}{k_2 + k_3[B]}$$

Kinetic equation for homogeneous catalysis

The kinetic equation of the homogeneous catalysis

$$\frac{d[C]}{dt}=\frac{k_1k_3[A][B][K]}{k_2+k_3[B]}$$

If **$k_2>>k_3$** the intermediate AK almost entirely transformed into the initial species in this case it is called the ***Arhenius's intermediate*** and the equation comes to the following form:

$$\frac{d[C]}{dt}=\frac{k_1k_3}{k_2}[K][A][B]$$

If **$k_2<<k_3$** the intermediate AK is completely transformed to the products and called ***Van't Hoff's intermediate*** and the equation has the following form:

$$\frac{d[C]}{dt}=k_1[K][A]$$

Heterogeneous catalysts

- **Heterogeneous catalysts** are sometimes called surface catalysts because they position the reactant molecules on their very surface. Many metals serve as heterogeneous catalysts in which the reactant molecules have an interface between themselves and the catalyst surface. In the reaction known as Hydrogenation, double bonds between carbons accept two hydrogen atoms and use the Pi electrons between the two carbons in order to attach these hydrogen atoms to the carbon atom.
- **Heterogeneous catalytic reactions** are the reactions in which the catalyst is in a separate phase, and the reaction takes place on its surface. This means that the nature of the surface and its size, the chemical composition of the surface layer, its state and structure should have a direct bearing on the activity of the catalyst.

Heterogeneous catalysts

The surface of a solid is not smooth and uniform and only some areas on the surface possess catalytic activity. They called active centers of a catalyst. The activity of a catalyst may increase and its lifetime extended by the addition of substances called promotors. Small amounts of certain substances that bound strongly to the catalyst can inactivate (or poison) it.

Heterogeneous catalysts

Steps of fluid-phase reactions:

- Diffusion of the reactant molecules to the solid surface.
- Sorption of at least one reactant species on the surface.
- Chemical reaction between molecules adsorbed on adjacent sites of the surface.
- Desorption of the products from the surface.
- Diffusion of products into the bulk fluid.

Heterogeneous catalysts

In many cases, one of these steps is much slower than all the others, and only the rate of the slowest step needs to be considered (limiting-stage rate). By this reason overall rate of heterogeneous reaction could be calculated by equation of diffusion rate (if the slowest is the first step) or by the rate of adsorption (if the slowest is the second step) or by kinetic equation (if the slowest is the third step). Found by this way (by experimental methods) the rate of the reaction is called seeming rate. The rate suitable to the kinetic equation of the certain reaction (step 3) is called ***true rate of a reaction***. In case when the slowest is the third step the seeming and the true rates coincides to each other. In other cases they are different.

Heterogeneous catalysts

Step 3 may consist of more than one elementary chemical reaction. Since the detailed mechanisms of the surface reaction are usually unknown, we adopt the simplifying assumption of taking step 3 to consist of a single gaseous unimolecular reaction. Then the reaction rate per unit surface area will be proportional to the number of adsorbed molecules of a gas per unit surface area, and this in turn will be proportional to θ – the fraction of adsorption sites occupied by reactant molecule

$$V = k\theta \qquad \theta = \frac{KP}{1+KP} \qquad V = k\frac{KP}{1+KP}$$

Heterogeneous catalysts

The theories of heterogeneous catalysis:

- The multiplet theory
- The electron-chemical theory

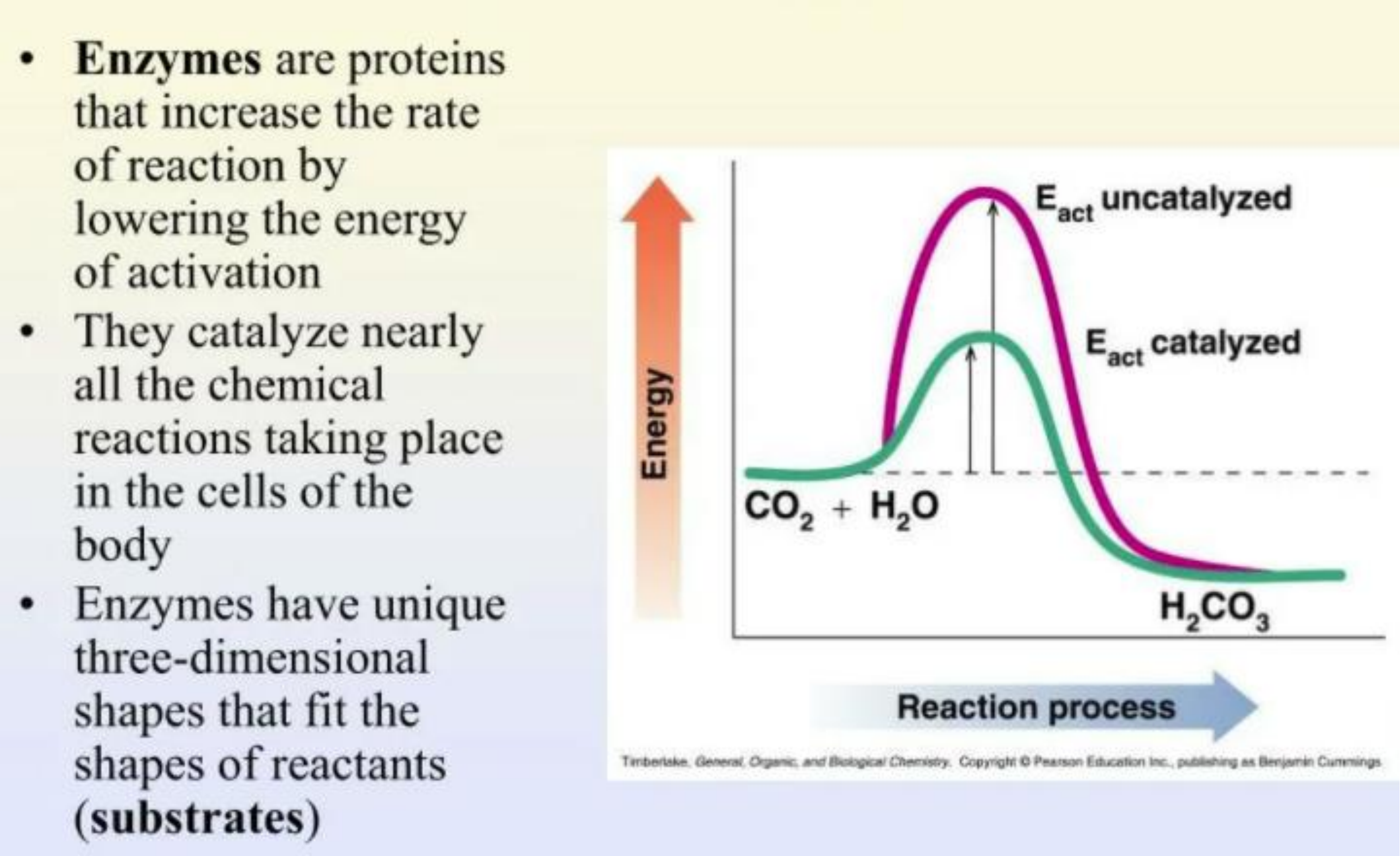
The theories of heterogeneous catalysis

- ***The multiplet theory of heterogeneous catalysis*** is based on the principle of geometrical correspondence between the arrangement of the atoms on the catalyst surface and the atoms of the reactant molecules, and of correspondence in bond energies.
- ***Multiplets*** are the names given to associations on the catalyst surface of several atoms or ions regularly arranged in correspondence with the structure of the crystal lattice of the catalyst (active centers).
- ***Catalytic activity appears*** when the arrangement of the atoms or ions is in geometric conformity with the arrangement of the atoms in the molecules of the reactants. Besides, there must be the energetic correspondence of the bonds between the atoms in the reactant molecules and the bonds formed by these atoms with the catalyst

The theories of heterogeneous catalysis

- ***The electron-chemical theory***. In recent studies the mechanism underlying the action of certain semiconductor and metal catalysts is approached from the standpoint of possible electron transitions between various energy levels on the catalyst surface corresponding to different states of the catalyst.

Enzyme catalysis



- **Enzymes** are proteins that increase the rate of reaction by lowering the energy of activation
- They catalyze nearly all the chemical reactions taking place in the cells of the body
- Enzymes have unique three-dimensional shapes that fit the shapes of reactants (**substrates**)

Timberlake, *General, Organic, and Biological Chemistry*. Copyright © Pearson Education Inc., publishing as Benjamin Cummings

Enzyme catalysis

- Most of the reactions that occur in living organisms are catalyzed by molecules called enzymes (or ferments).
- They are biological catalysts consisting of protein molecules with molar mass from thousands to millions of grams.
- An enzyme is highly specific in its action; many enzymes catalyze only the conversation of a particular reactant to a particular product; other enzymes catalyze only a certain class of reactions (for example, ester hydrolysis).
- Enzymes speed up reaction rates very substantially, and in their absence most biochemical reactions occur at negligible rates.

Enzyme catalysis

substrate

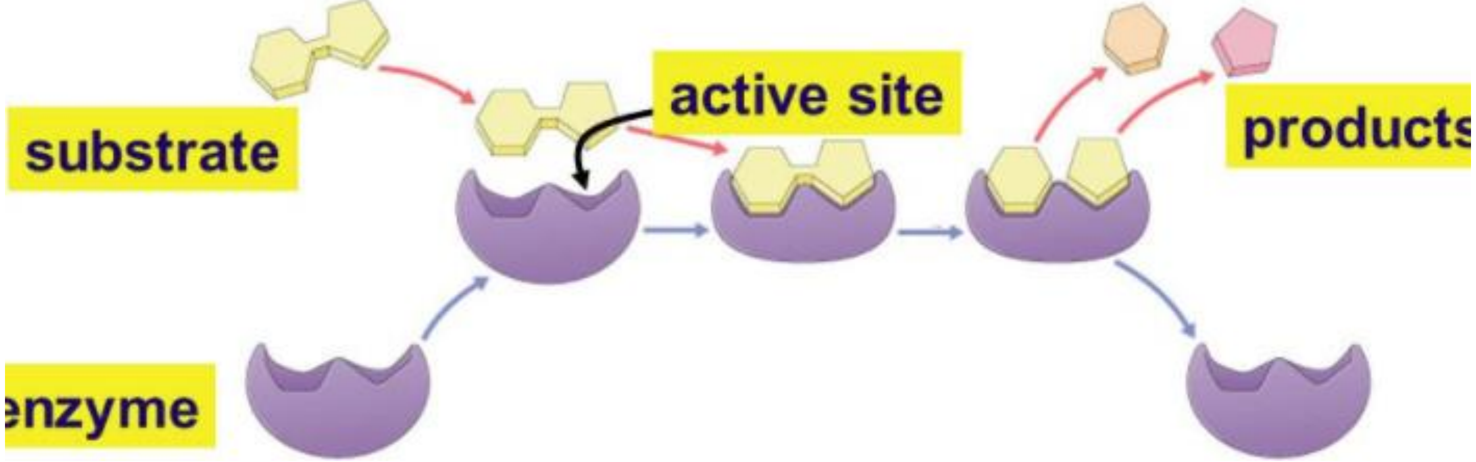
- reactant which binds to enzyme
- enzyme-substrate complex: temporary association

product

- end result of reaction

active site

- enzyme's catalytic site; substrate fits into active site



Enzyme catalysis. The simplest mechanism of an enzyme catalysis

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \longrightarrow E + P$$

$$V_0 = \frac{d[P]}{dt} = k_2[ES]$$

$$[ES] = \frac{k_1[E_0][S]}{k_1[S] + k_{-1} + k_2}$$

$$V_0 = \frac{k_2[E_0][S]}{[S] + \frac{k_{-1} + k_2}{k_1}}$$

Replacing one constant **Km (Michaelis constant)** instead of $\frac{k_{-1} + k_2}{k_1}$

$$V_0 = \frac{k_2[E_0][S]}{[S] + K_m}$$

which is called the **Michaelis-Menten equation** for enzyme catalysis.

Enzyme catalysis. The simplest mechanism of an enzyme catalysis

There are two case of interaction of enzyme and substrate

1) in the low concentration of substrate $k_m >> [S]$

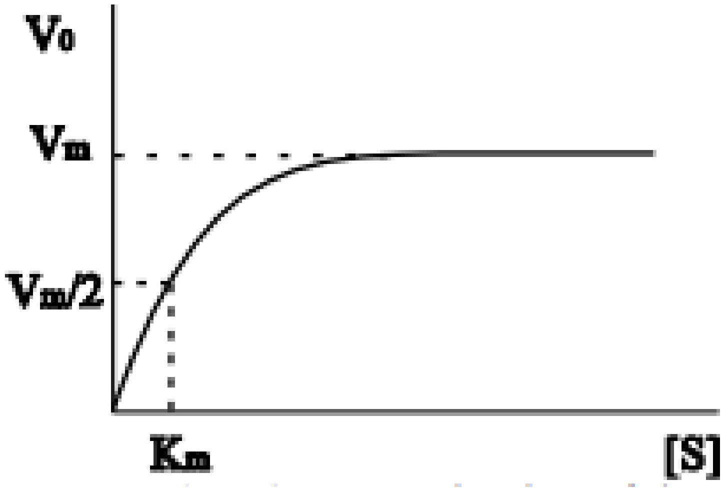
$$V = \frac{k_2\ [E_0][S]}{k_M}$$

2) in the high concentration of substrate $k_m << [S]$

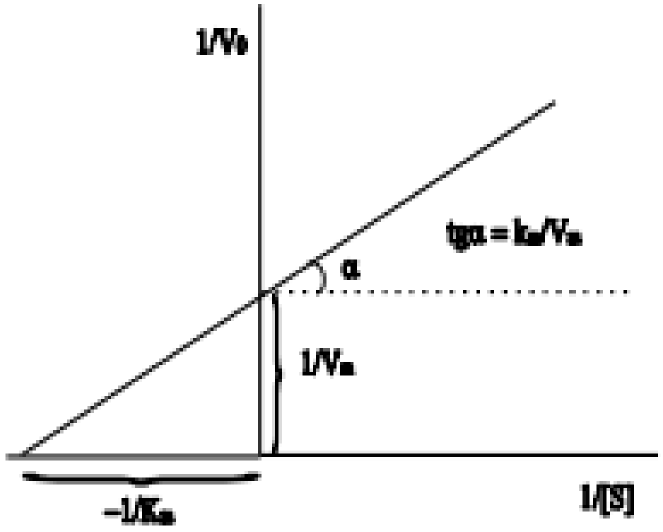
$$V = k_2[E_0] = V_{max}$$

Enzyme catalysis

Determination of the value of Km and Vm

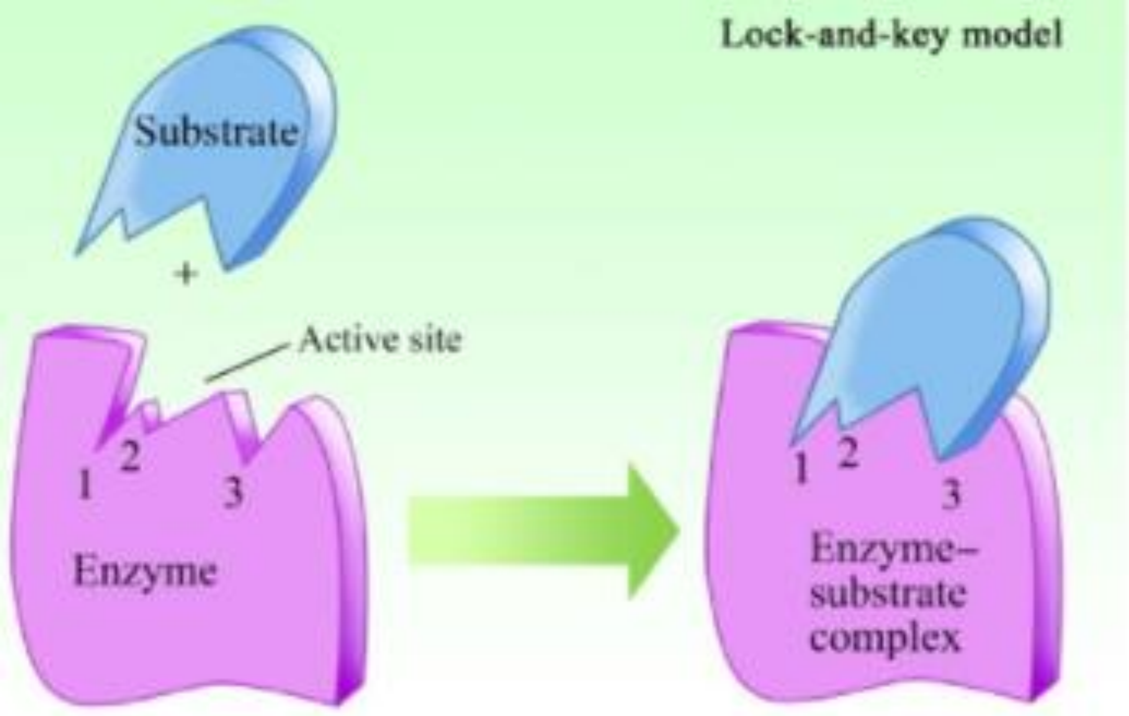


Determination of the value of Km and Vm



The earliest model was called the **"lock and key"** model of enzyme activity. According to this model, once the substrate molecule has been positioned with the help of the prostetic group and perhaps a Co-factor metal ion, then the bond breaking and bond formation can begin. Once the product has been formed, the product disengages from the ***active site*** in order for the process to be repeated. According to this model, the shape of the substrate molecule must be compatible to the active site like a key is compatible with a specific lock. This would explain the unusual high specificity of enzymes capable of only catalyzing one reaction. If the wrong substrate tries to fit into the active site, it does not fit (wrong key) and so the enzyme does not catalyze its conversion to some other product. If the active site of the enzyme is stretched or compressed then even the real substrate molecule will not fit the distorted active site.

Theories of enzyme catalysis

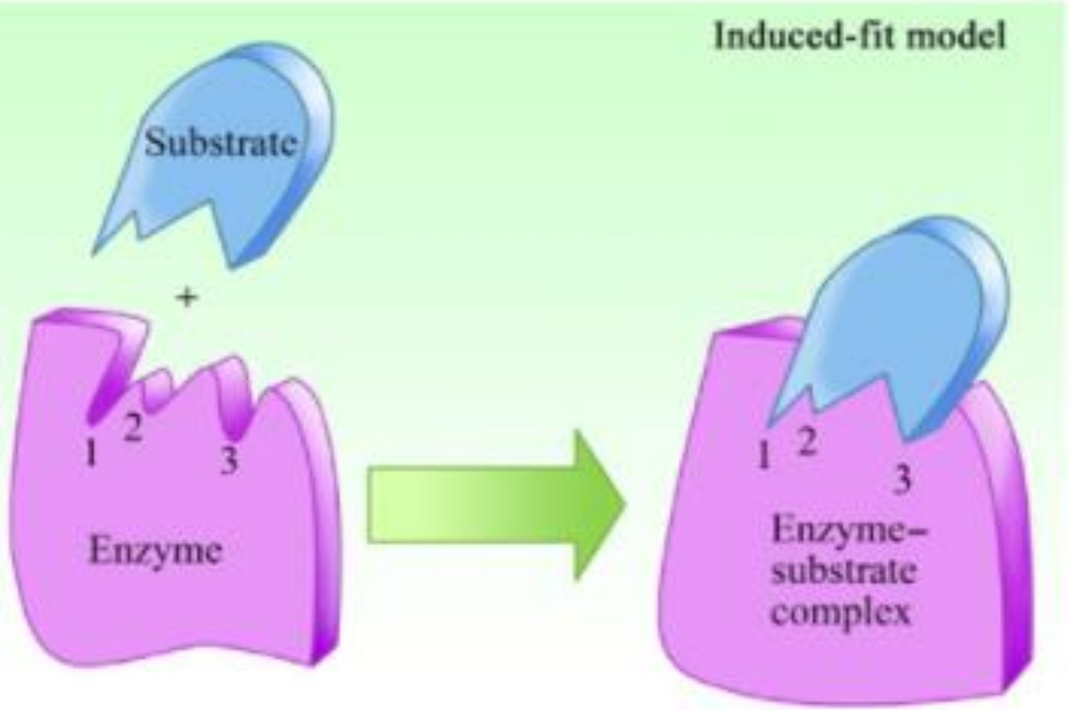


In the lock-and key model, the shape of the substrate and the confirmation of the active site are complementary to one another.

Theories of enzyme catalysis

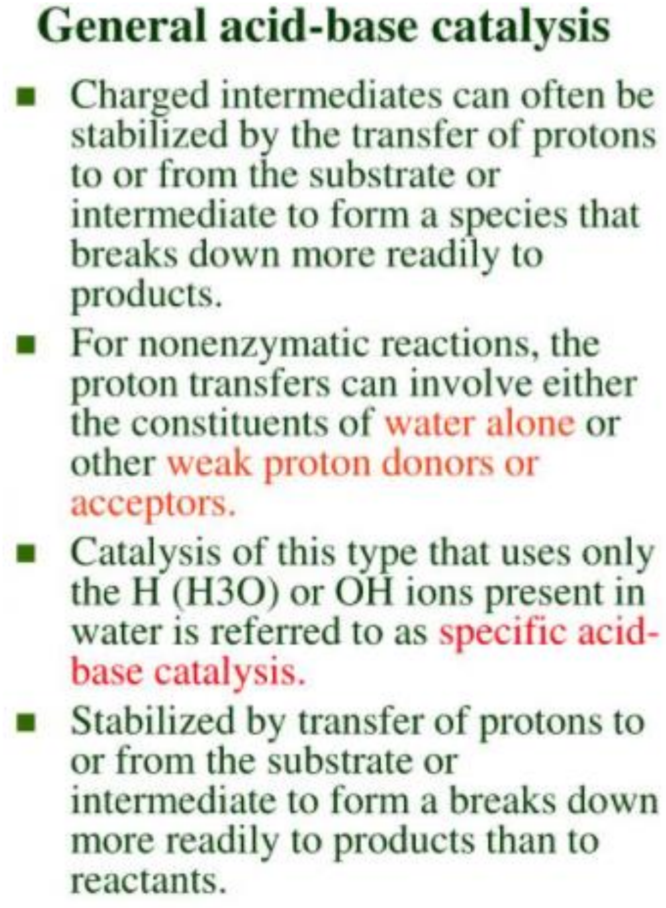
Induced Fit Model (or Hand and Glove) of Enzyme Activity. The Induced Fit model is a modification of the lock and key model. Instead of having a ridged substrate molecule that will only fit into a specific active site, we have an active site that can stretch to accept a range of molecular shapes for the substrate analogous to how gloves stretch to fit more than one size hand. This model explains more adequately how active site blockers can block the active site and inhibit the enzyme molecule.

Theories of enzyme catalysis



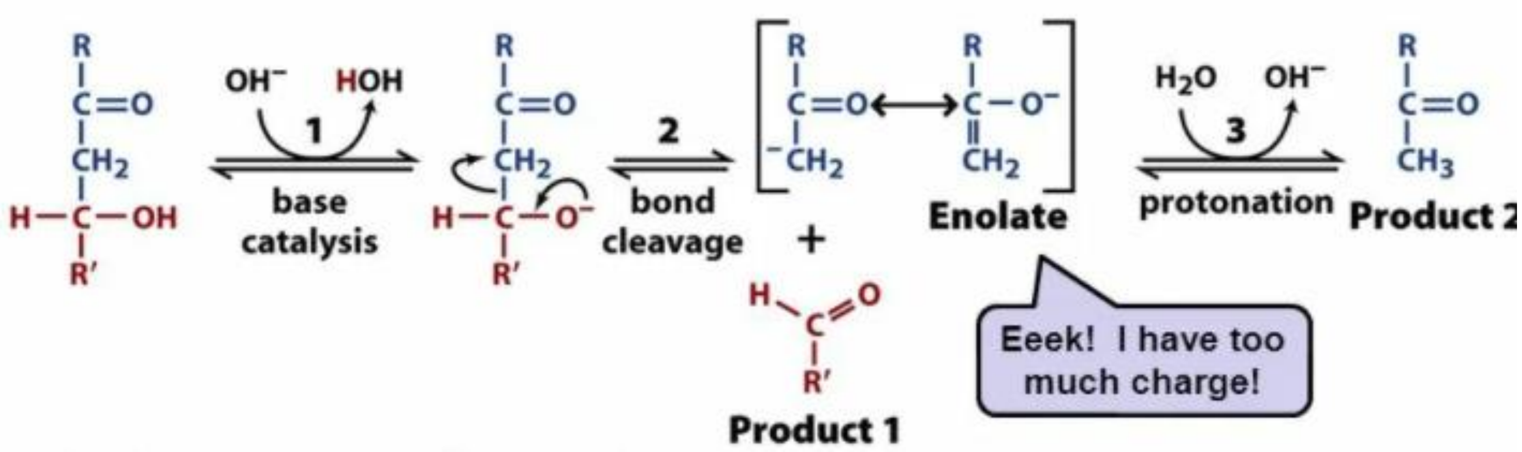
In the linduced-fit model, the enzyme undergoes a confirmational change upon binding to substrate. The shape of the active site becomes complementary to the shape of the substrate only after the substrate binds to the enzyme.

Acid-base catalysis

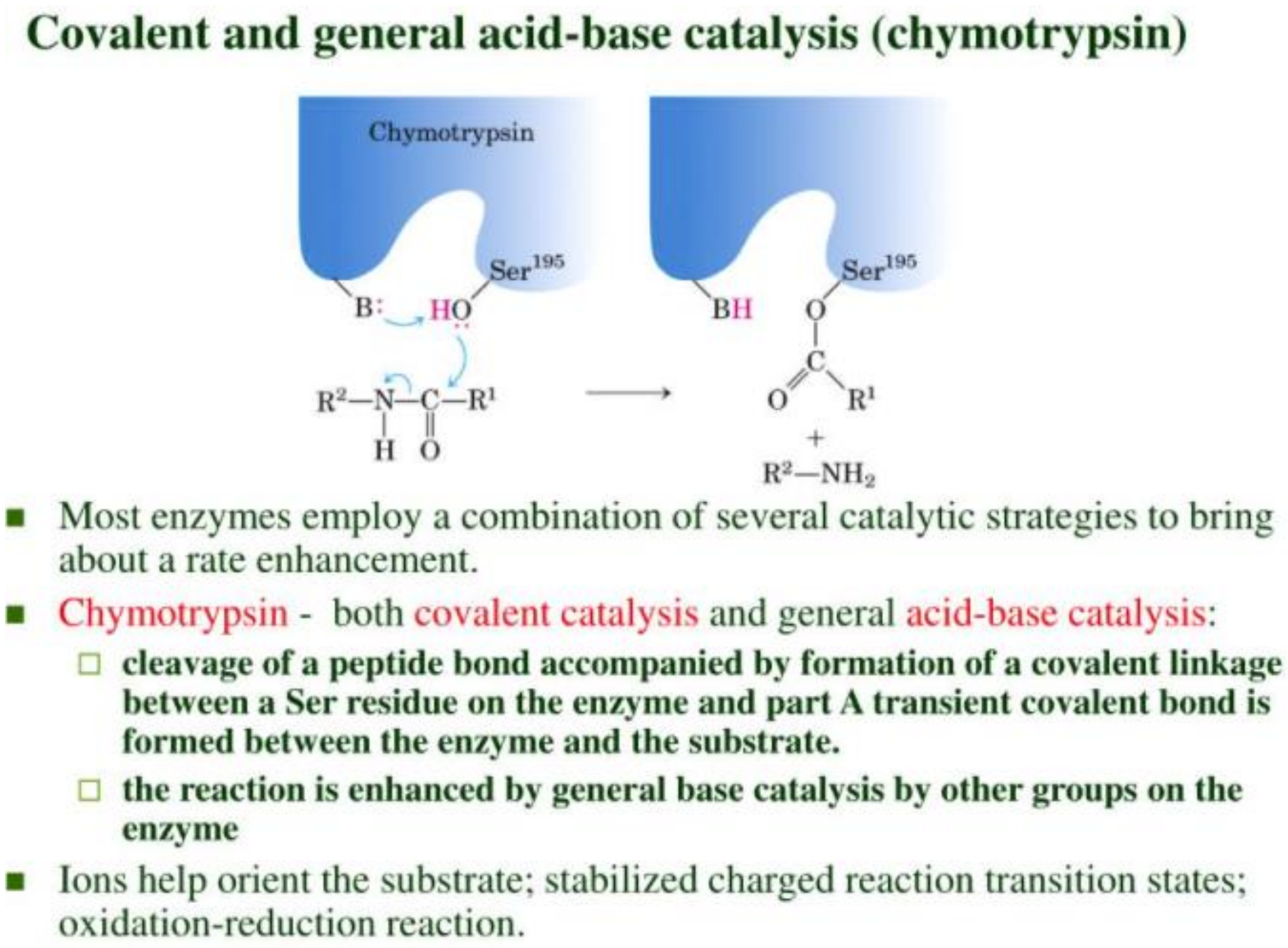


General acid-base catalysis

- Charged intermediates can often be stabilized by the transfer of protons to or from the substrate or intermediate to form a species that breaks down more readily to products.
- For nonenzymatic reactions, the proton transfers can involve either the constituents of water alone or other weak proton donors or acceptors.
- Catalysis of this type that uses only the H (H3O) or OH ions present in water is referred to as specific acid-base catalysis.
- Stabilized by transfer of protons to or from the substrate or intermediate to form a breaks down more readily to products than to reactants.



Acid-base catalysis

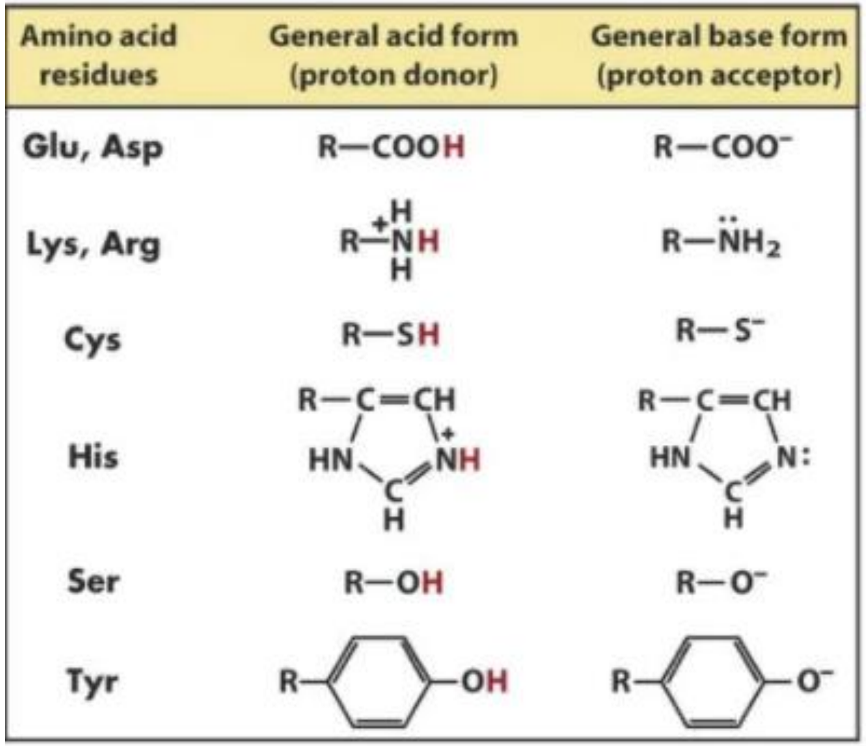


Covalent and general acid-base catalysis (chymotrypsin)

- Most enzymes employ a combination of several catalytic strategies to bring about a rate enhancement.
- Chymotrypsin - both covalent catalysis and general acid-base catalysis:
  - ☐ **cleavage of a peptide bond accompanied by formation of a covalent linkage between a Ser residue on the enzyme and part A transient covalent bond is formed between the enzyme and the substrate.**
  - ☐ **the reaction is enhanced by general base catalysis by other groups on the enzyme**
- Ions help orient the substrate; stabilized charged reaction transition states; oxidation-reduction reaction.

Acid-base catalysis

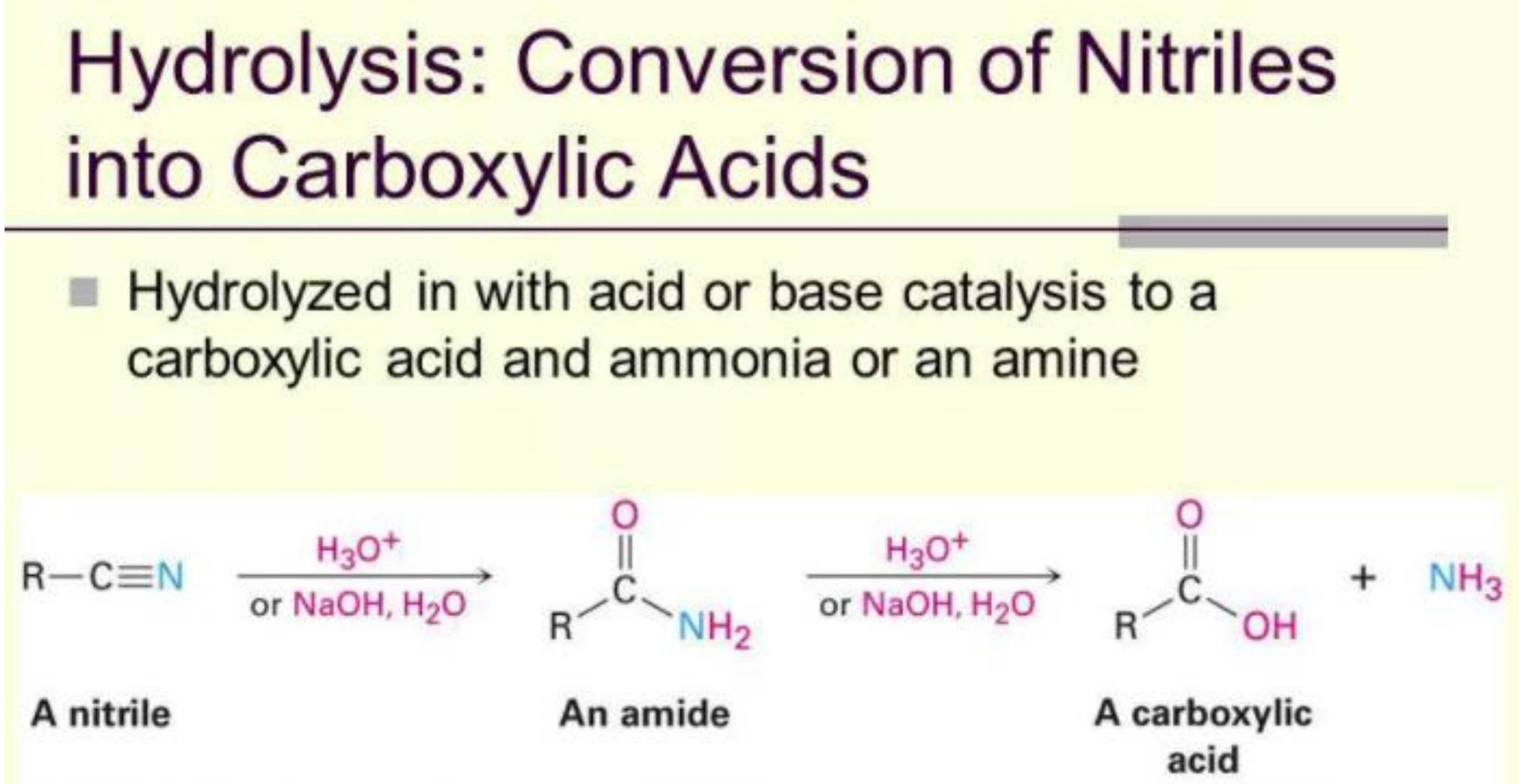
Amino acids in general acid-base catalysis



Amino acid residues	General acid form (proton donor)	General base form (proton acceptor)
Glu, Asp	$\mathrm{R-COOH}$	$\mathrm{R-COO^-}$
Lys, Arg	$\mathrm{R-\underset{H}{\overset{+H}{N}}H}$	$\mathrm{R-\ddot{N}H_2}$
Cys	$\mathrm{R-SH}$	$\mathrm{R-S^-}$
His	$\mathrm{R-C=CH}$ $\mathrm{HN}\quad\mathrm{\overset{+}{N}H}$ $\mathrm{\underset{H}{C}}$	$\mathrm{R-C=CH}$ $\mathrm{HN}\quad\mathrm{N:}$ $\mathrm{\underset{H}{C}}$
Ser	$\mathrm{R-OH}$	$\mathrm{R-O^-}$
Tyr	$\mathrm{R-}\quad\mathrm{-OH}$	$\mathrm{R-}\quad\mathrm{-O^-}$

- Many organic reactions are promoted by proton donors (general acids) or proton acceptors (general bases).
- The active sites of some enzymes contain amino acid functional groups, that can participate in the catalytic process as proton donors or proton acceptors.

Acid-base catalysis



Hydrolysis: Conversion of Nitriles into Carboxylic Acids

- Hydrolyzed in with acid or base catalysis to a carboxylic acid and ammonia or an amine

$$R{-}C{\equiv}N \xrightarrow[\text{or NaOH, } H_2O]{H_3O^+} R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow[\text{or NaOH, } H_2O]{H_3O^+} R{-}\overset{\overset{O}{\|}}{C}{-}OH + NH_3$$