Topic 7E - Catalysis

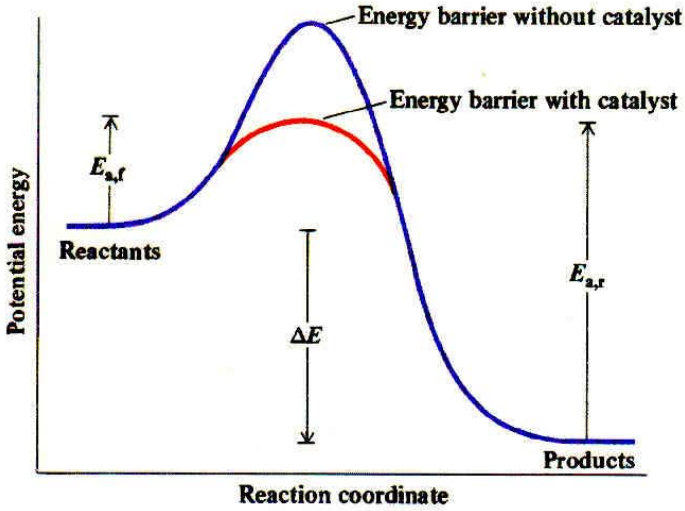


Figure 11-17
The most important way in which catalysts speed reactions is by reducing the activation energy.

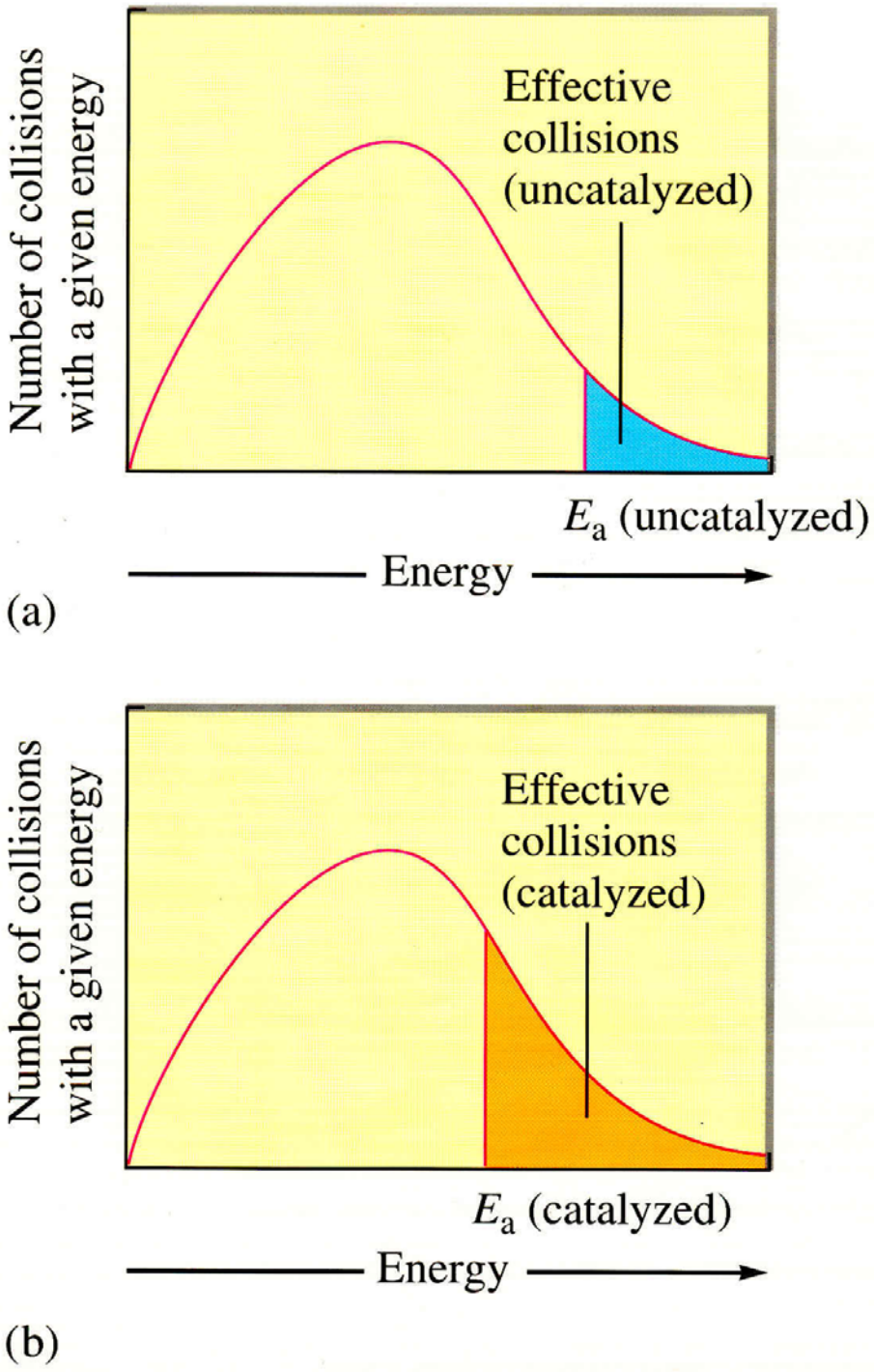
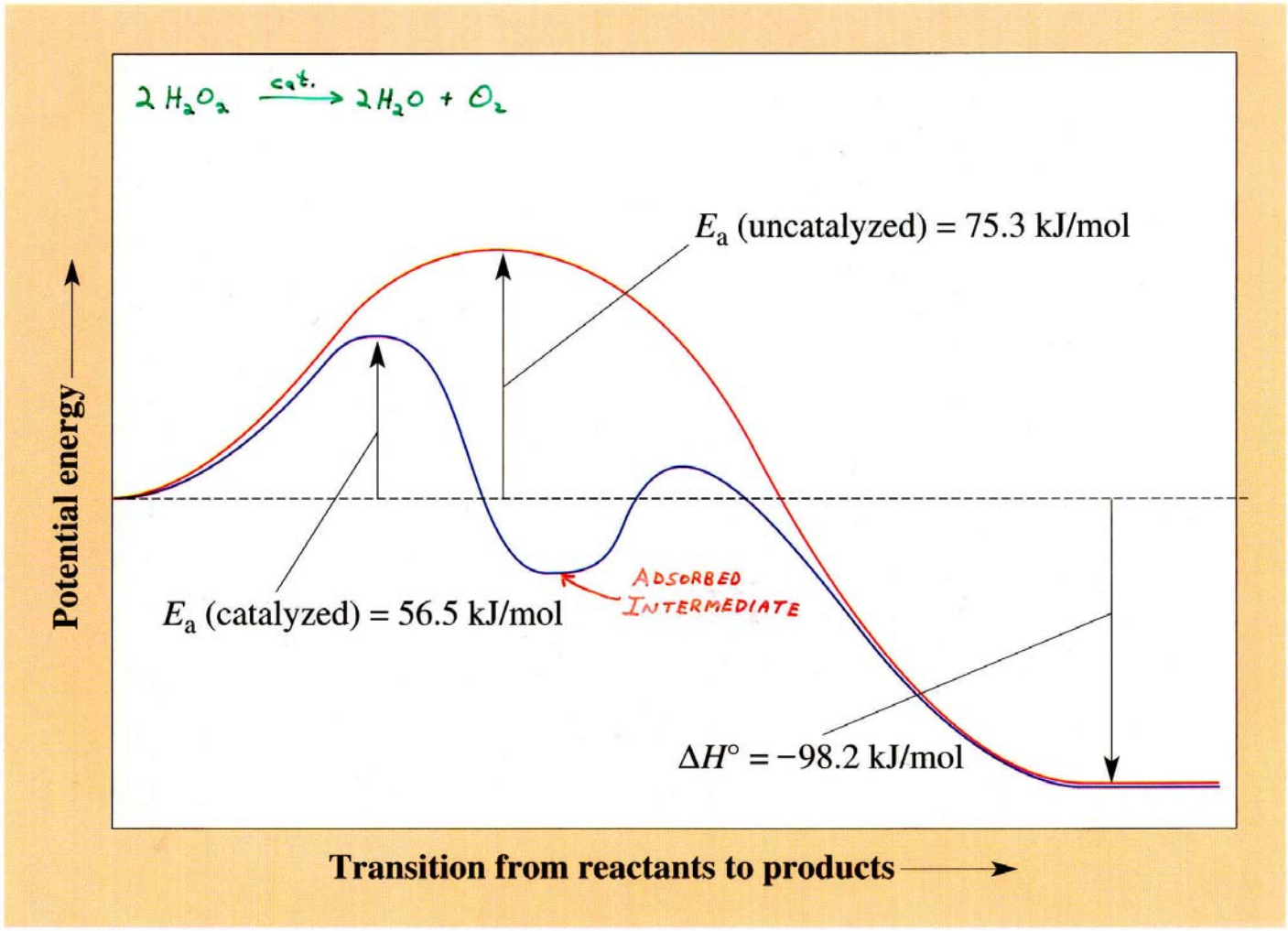


Figure 12.14
Collision energy distribution versus activation energy for catalyzed and uncatalyzed reactions

Potential Energy Profiles for the Catalyz and Uncatalyzed Decomposition of H_2O_2



$$CH_2{=}CH_2 + H_2 \xrightarrow{\text{Pt cat.}} CH_3CH_3$$

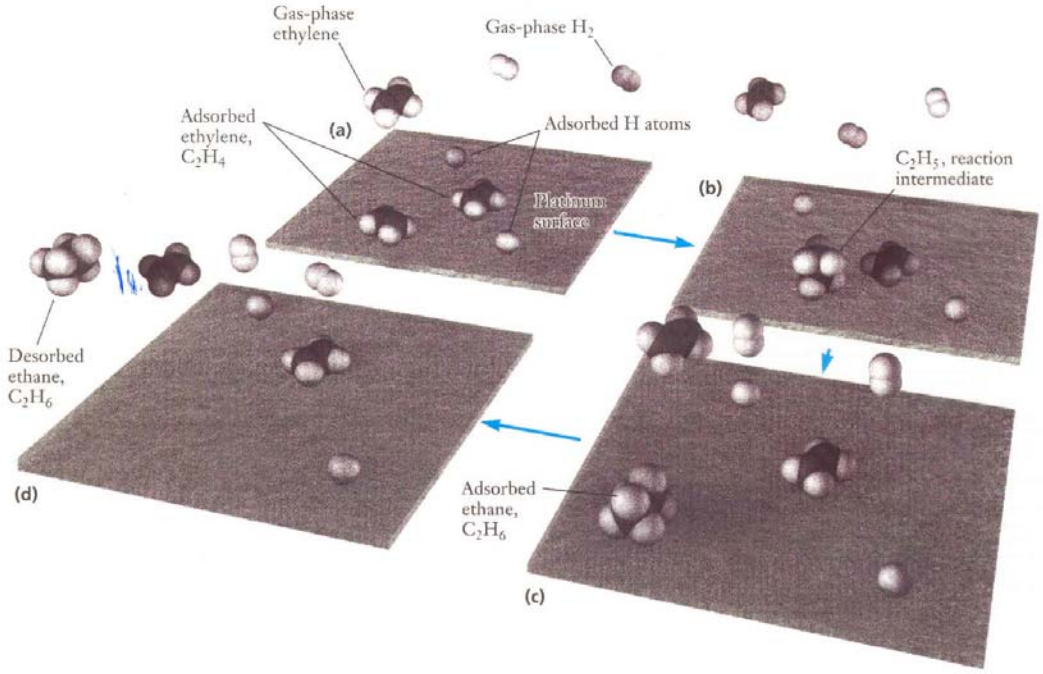


FIGURE 13.15 Platinum catalyzes the reaction $H_2 + C_2H_4$ by providing a surface that promotes the dissociation of H_2 to H atoms, which can then add to the C_2H_4 stepwise to give ethane, C_2H_6.

Catalysis

Homogeneous

Heterogeneous

In enzyme catalysis, reactant molecules (substrate) bind to "active sites" of the enzyme. After reaction, the enzyme is released unchanged for subsequent reaction with another substrate molecule. The process is represented kinetically as:

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

$$ES \xrightarrow{k_2} E + P$$

where E = enzyme, S = substrate, and P = product.

The rate of formation of P, obtained by applying the steady-state approximation to the intermediate [ES], is:

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

The total amount of enzyme present in the system, $[E]_0$, is the sum of the bound amount, [ES], plus the unbound smount, [E]:

$$[E]_0 = [E] + [ES]$$

or

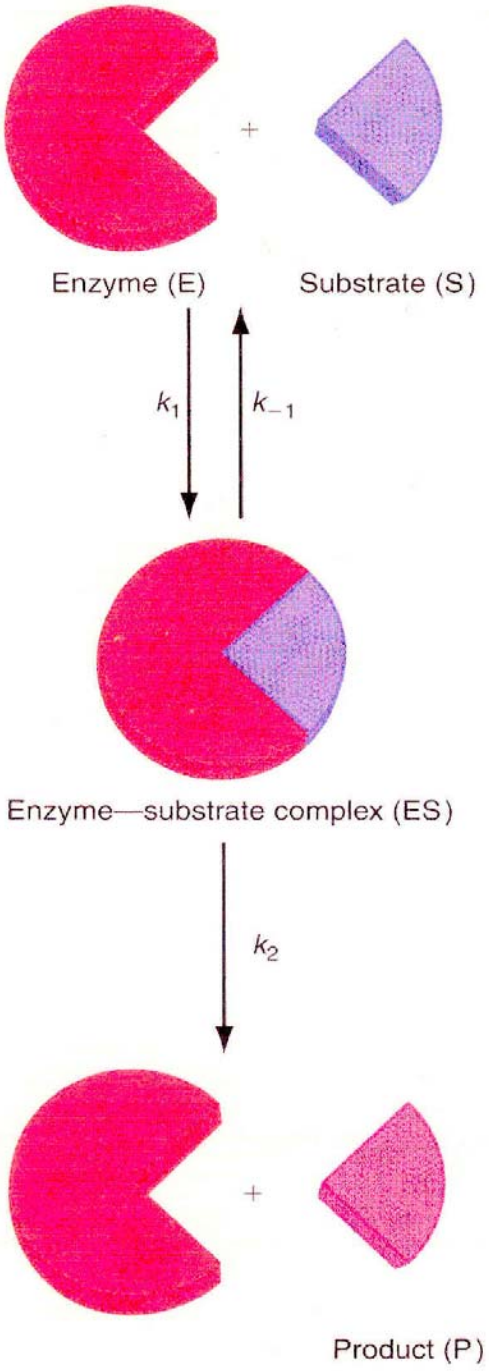


FIGURE 19.6
Schematic of enzyme catalysis.

$$[E] = [E]_0 - [ES]$$

Thus,

$$\frac{d[ES]}{dt} = 0 = k_1[E]_0[S] - k_1[ES][S] - k_{-1}[ES] - k_2[ES]$$

Solving for [ES] gives:

$$[ES] = \frac{k_1[E]_0[S]}{k_1[S] + (k_{-1} + k_2)}$$

Letting $K_M = \frac{k_{-1} + k_2}{k_1}$, then $[ES] = \frac{[E]_0[S]}{[S] + K_M}$

The rate of formation of product P is then

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E]_0[S]}{[S] + K_M}$$

This is the **Michaelis-Menten** equation, which is applicable to many enzyme-catalyzed reactions.

Taking the inverse of both sides of this equation gives:

$$\frac{1}{\frac{d[P]}{dt}} = \frac{1}{k_2[E]_0} + \frac{K_M}{k_2[E]_0[S]}$$

Hence, a plot of $(Rate)^{-1}$ vs. $[S]^{-1}$ for an enzyme-catalyzed reaction that obeys Michaelis-Menten kinetics should give a straight line, with

$$Slope = \frac{K_M}{k_2[E]_0} \text{ and}$$

$$Intercept = \frac{1}{k_2[E]_0}$$

thus allowing both K_M and k_2 to be separately determined (since $[E]_0$ is known).

Examining the limiting forms of the Michaelis-Menten equation, it is apparent that when [S] is very low ($[S] << K_M$), then

$$\frac{d[P]}{dt} \approx \frac{k_2[E]_0[S]}{K_M} = k'[E]_0[S]$$

and the reaction appears to be first-order in [S].

When [S] is high ($[S] >> K_M$), then

$$\frac{d[P]}{dt} \approx k_2[E]_0$$

and the reaction appears to be zero-order in [S], because all enzyme molecules are already bound to S, and addition of more S has no further effect on the rate.

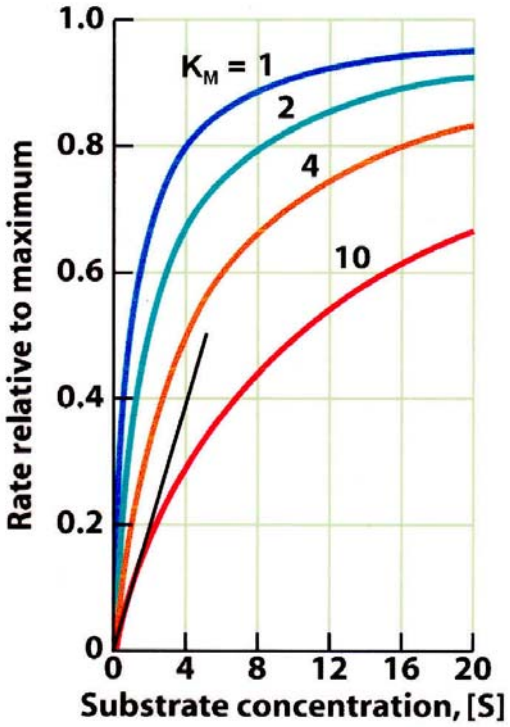
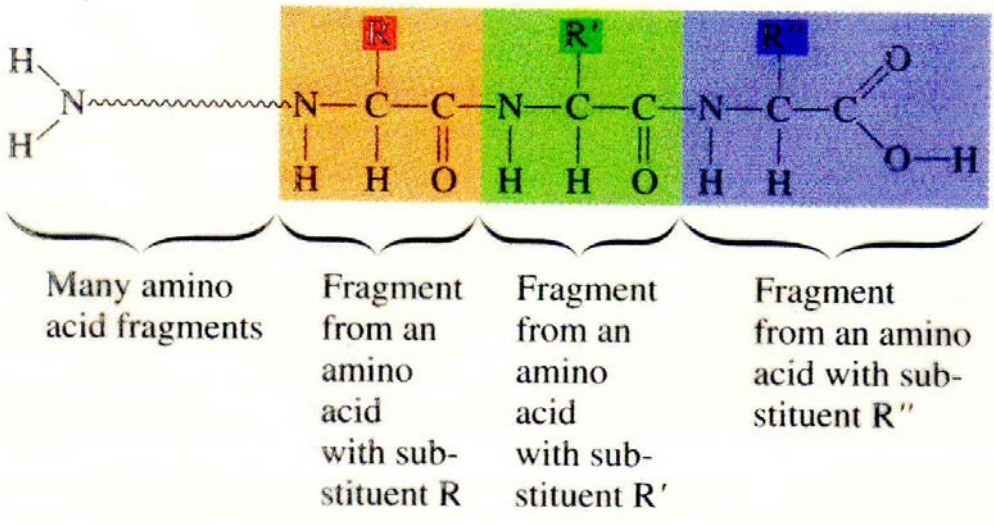


FIGURE 13.40 A plot of the rate of an enzyme-catalyzed reaction (relative to its maximum value, $k_2[E]_0$, when S is in very high concentration) as a function of concentration of substrate for various values of K_M. At low substrate concentrations, the rate of reaction is directly proportional to the substrate concentration (as indicated by the black line for $K_M = 10$). At high substrate concentrations, the rate becomes constant at $k_2[E]_0$ once the enzyme molecules are "saturated" with substrate. The units of [S] are the same as those of K_M.

Michaelis-Menten Equation:

$$\text{Rate} = \frac{d[P]}{dt} = k_2[E \cdot S] = \frac{k_2[E]_0[S]}{[S] + K_M}$$

PROTEINS ARE POLYMERS CONSISTING OF MANY LINKED AMINO ACIDS :



PROTEINS IN FOOD MUST BE BROKEN INTO THEIR CONSTITUENT AMINO ACIDS DURING DIGESTION :

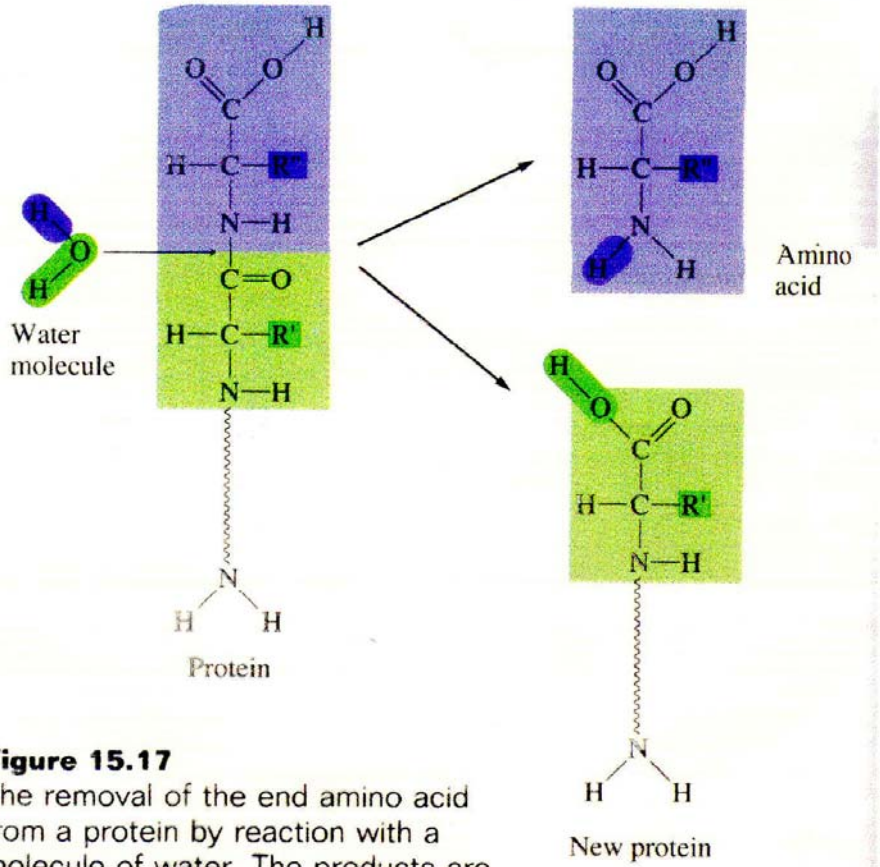
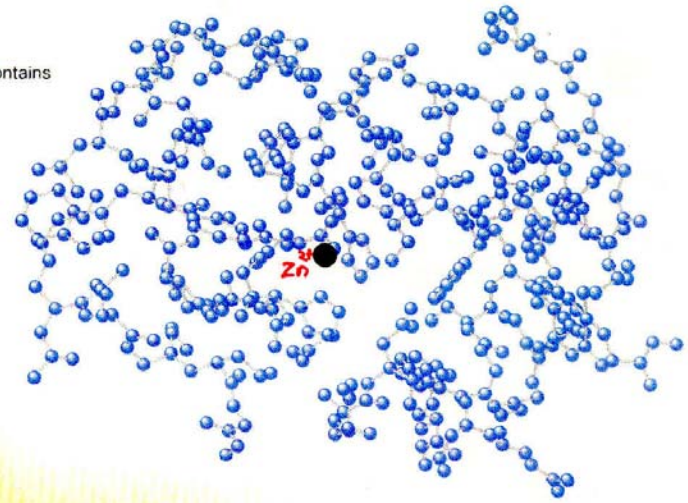


Figure 15.17
The removal of the end amino acid from a protein by reaction with a molecule of water. The products are an amino acid and a new, smaller protein.

PROCESS IS CATALYZED BY THE ZINC-CONTAINING ENZYME CARBOXYPEPTIDASE-A.

Figure 15.18
The structure of the enzyme carboxypeptidase-A, which contains 307 amino acids.



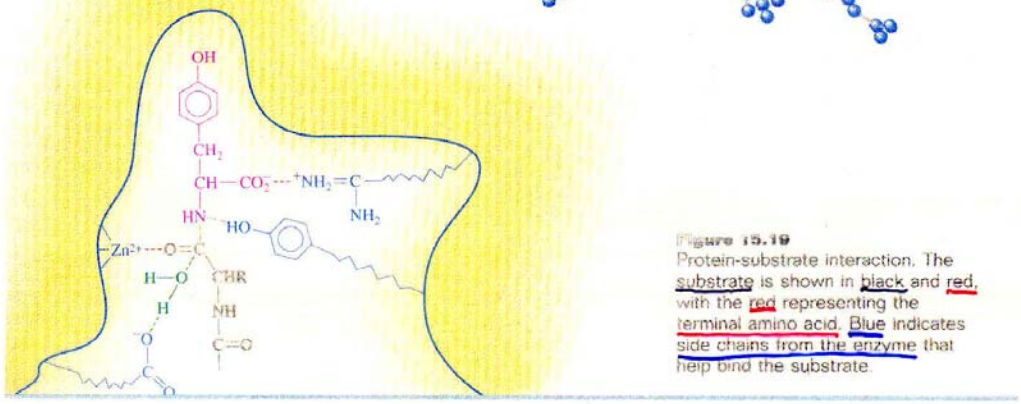


Figure 15.19
Protein-substrate interaction. The substrate is shown in black and red, with the red representing the terminal amino acid. Blue indicates side chains from the enzyme that help bind the substrate.

Zn^{2+} BINDS TO O-ATOM OF CARBONYL GROUP (-C=O), THUS POLARIZING ITS ELECTRON DENSITY AND ALLOWING THE NEIGHBORING C-N BOND TO BE BROKEN MUCH MORE EASILY, RESULTING IN CLEAVAGE OF THE PROTEIN.