CHAPTER 25
SYNTHETIC AND NATURAL ORGANIC POLYMERS
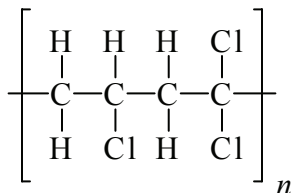
25.7 The reaction is initiated be a radical, R•

$$R• + CF_2=CF_2 \rightarrow R-CF_2-CF_2•$$
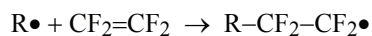
The product is also a radical, and the reaction continues.

$$R-CF_2-CF_2• + CF_2=CF_2 \rightarrow R-CF_2-CF_2-CF_2-CF_2• \quad etc...$$
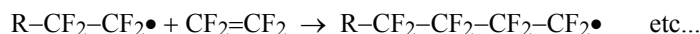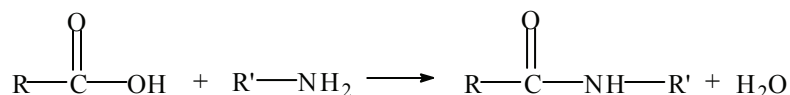
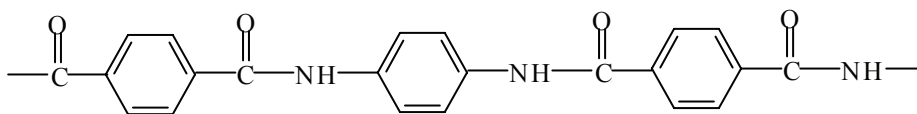**25.8** The repeating structural unit of the polymer is:

Does each carbon atom still obey the octet rule?

25.9 The general reaction is a condensation to form an amide.

The polymer chain looks like:

Note that both reactants are disubstituted benzene derivatives with the substituents in the para or 1,4 positions.

25.10 Polystyrene is formed by an addition polymerization reaction with the monomer, styrene, which is a phenyl–substituted ethylene. The structures of styrene and polystyrene are shown in Table 25.1 of your text.

25.11 The structures are as shown.

(a) $CH_2=CF_2$ **(b)** $HO_2C-$$-CO_2H$ $H_2N-$$-NH_2$
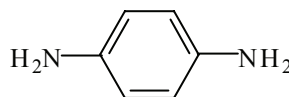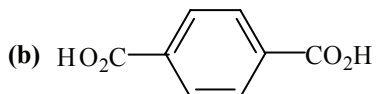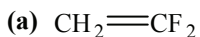
25.12   The structures are shown.

(a)
$$H_2C=CH-CH=CH_2$$

(b)

$$
\begin{array}{c}
\quad\quad\quad O \\
\quad\quad\quad \| \\
\quad\quad\quad C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2 \\
HO
\end{array}
$$
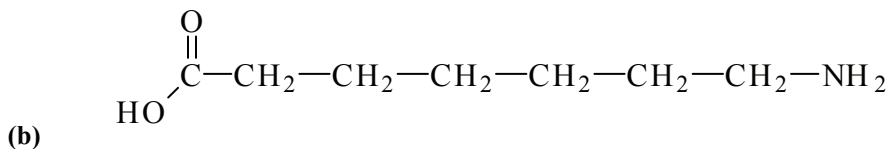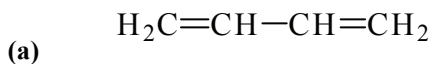
25.19   alanylglycine and glycylalanine are shown in Figure 25.8.

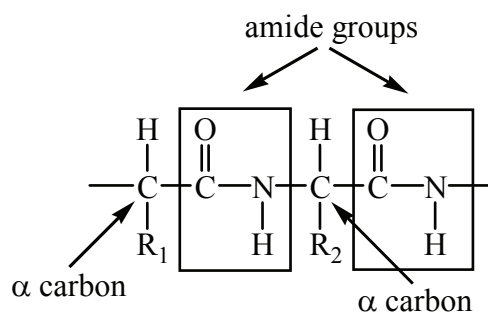**25.20**   The main backbone of a polypeptide chain is made up of the α carbon atoms and the amide group repeating alternately along the chain.

amide groups

$$
\begin{array}{ccccccc}
 & H & O & & H & O & \\
 & | & \| & & | & \| & \\
-\!\!&C&\!-\!\!C\!-\!N\!-\!&C&\!-\!\!C\!-\!N\!-\!\!\!\! \\
 & | & | & & | & | & \\
 & R_1 & H & & R_2 & H &
\end{array}
$$

α carbon α carbon

For each R group shown above, substitute the distinctive side groups of the two amino acids. Their are two possible dipeptides depending on how the two amino acids are connected, either glycine–lysine or lysine–glycine. The structures of the dipeptides are:

$$
\begin{array}{c}
NH_2 \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
CH_2 \\
\quad\quad\quad\quad\quad\quad\quad CH_2\ O \\
H\ \ \ O \quad\quad\quad | \ \ \ \| \\
| \ \ \ \| \quad\quad\quad | \ \ \ \\
H_2N-CH-C-NH-CH-C-OH \\
\end{array}
$$

glycine   lysine

and

$$
\begin{array}{c}
NH_2 \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
CH_2\ O \quad\quad\quad H \ \ \ O \\
| \ \ \ \| \quad\quad\quad | \ \ \ \| \\
H_2N-CH-C-NH-CH-C-OH \\
\end{array}
$$

lysine   glycine
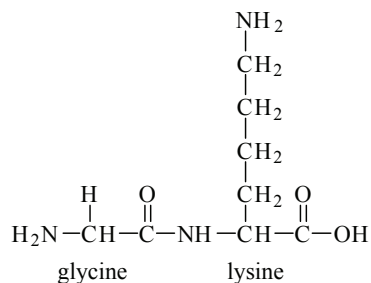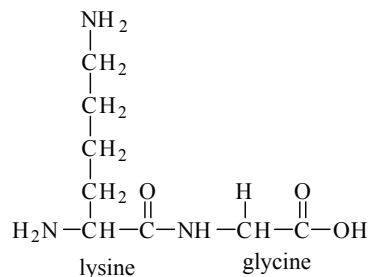
25.21   The structure of the polymer is:
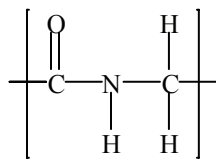
25.22   The rate increases in an expected manner from 10°C to 30°C and then drops rapidly. The probable reason for this is the loss of catalytic activity of the enzyme because of denaturation at high temperature.

25.27   There are two common structures for protein molecules, an α helix and a β–pleated sheet. The α–helical structure is stabilized by intramolecular hydrogen bonds between the NH and CO groups of the main chain, giving rise to an overall rodlike shape. The CO group of each amino acid is hydrogen-bonded to the NH group of the amino acid that is four residues away in the sequence. In this manner all the main-chain CO and NH groups take part in hydrogen bonding. The β–pleated structure is like a sheet rather than a rod. The polypeptide chain is almost fully extended, and each chain forms many intermolecular hydrogen bonds with adjacent chains. In general, then, the hydrogen bonding is responsible for the three dimensional geometry of the protein molecules.

In nucleic acids, the key to the double-helical structure is the formation of hydrogen bonds between bases in the two strands. Although hydrogen bonds can form between any two bases, called base pairs, the most favorable couplings are between adenine and thymine and between cytosine and guanine.

More information concerning the importance of hydrogen bonding in biological systems is in Sections 25.3 and 25.4 of the text.

25.28   Nucleic acids play an essential role in protein synthesis. Compared to proteins, which are made of up to 20 different amino acids, the composition of nucleic acids is considerably simpler. A DNA or RNA molecule contains only four types of building blocks: purines, pyrimidines, furanose sugars, and phosphate groups. Nucleic acids have simpler, uniform structures because they are primarily used for protein synthesis, whereas proteins have many uses.

25.29   When proteins are heated above body temperature they can lose some or all of their secondary and tertiary structure and become denatured. The denatured proteins no longer exhibit normal biological activity.
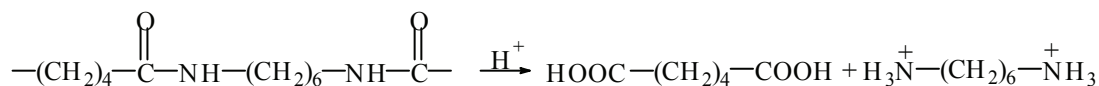
25.30   The sample that has the higher percentage of C–G base pairs has a higher melting point because C–G base pairs are held together by three hydrogen bonds. The A–T base pair interaction is relatively weaker because it has only two hydrogen bonds. Hydrogen bonds are represented by dashed lines in the structures below.
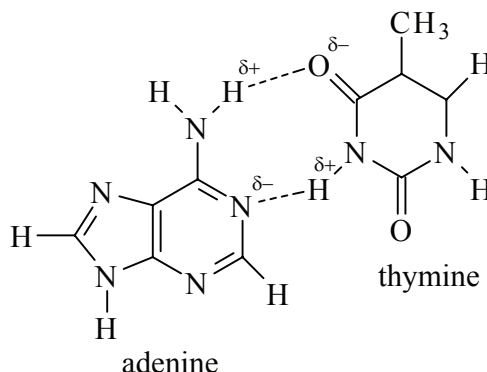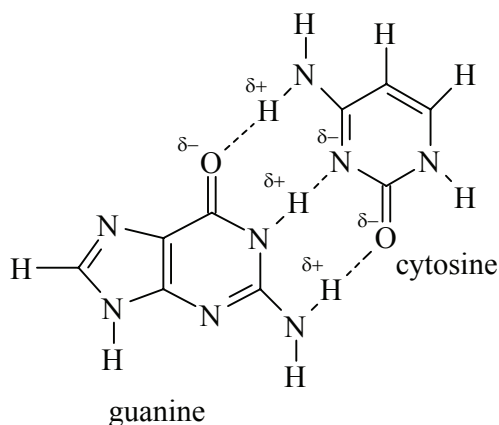
25.31 As is described in Section 25.3 of the text, acids *denature* enzymes. The citric acid in lemon juice denatures the enzyme that catalyzes the oxidation so as to inhibit the oxidation (browning).

25.32 Leg muscles are active having a high metabolism, which requires a high concentration of myoglobin. The high iron content from myoglobin makes the meat look dark after decomposition due to heating. The breast meat is "white" because of a low myoglobin content.

25.33 The cleavage reaction is:

$$-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}- \xrightarrow{H^+} HOOC-(CH_2)_4-COOH + H_3\overset{+}{N}-(CH_2)_6-\overset{+}{N}H_3$$

25.34 Insects have blood that contains no hemoglobin. Thus, they rely on simple diffusion to supply oxygen. It is unlikely that a human-sized insect could obtain sufficient oxygen by diffusion alone to sustain its metabolic requirements.

25.35 The best way to attack this type of problem is with a systematic approach. Start with all the possible tripeptides with three lysines (one), then all possible tripeptides with two lysines and one alanine (three), one lysine and two alanines (three also −−Why the same number?), and finally three alanines (one).

Lys–Lys–Lys

Lys– Lys–Ala	Lys–Ala– Lys	Ala– Lys– Lys
Lys–Ala–Ala	Ala–Lys–Ala	Ala–Ala–Lys

Ala–Ala–Ala

Any other possibilities?

25.36 From the mass % Fe in hemoglobin, we can determine the mass of hemoglobin.

$$\% \text{ Fe} = \frac{\text{mass of Fe}}{\text{mass of compound (hemoglobin)}} \times 100\%$$

$$0.34\% = \frac{55.85 \text{ g}}{\text{mass of hemoglobin}} \times 100\%$$

minimum mass of hemoglobin = 1.6×10^4 g

Hemoglobin must contain **four Fe atoms per molecule** for the actual molar mass to be four times the minimum value calculated.

25.37 The main interaction between water molecules and the amino acid residues is that of hydrogen bonding. In water the polar groups of the protein are on the exterior and the nonpolar groups are on the interior.

25.38 The type of intermolecular attractions that occur are mostly attractions between nonpolar groups. This type of intermolecular attraction is called a **dispersion force**.

25.39   (a)   deoxyribose and cytosine
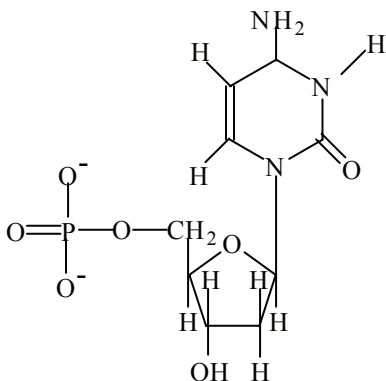
(b)   ribose and uracil
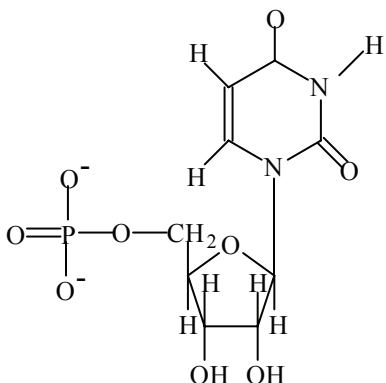
25.40   This is as much a puzzle as it is a chemistry problem. The puzzle involves breaking up a nine-link chain in various ways and trying to deduce the original chain sequence from the various pieces. Examine the pieces and look for patterns. Remember that depending on how the chain is cut, the same link (amino acid) can show up in more than one fragment.

Since there are only seven different amino acids represented in the fragments, at least one must appear more than once. The nonapeptide is:

Gly−Ala−Phe−Glu−His−Gly−Ala−Leu−Val

Do you see where all the pieces come from?

25.41 $pH = pK_a + \log \dfrac{[\text{conjugate base}]}{[\text{acid}]}$

At pH = 1,

$-\text{COOH}$ $1 = 2.3 + \log \dfrac{[-\text{COO}^-]}{[-\text{COOH}]}$

$\dfrac{[-\text{COOH}]}{[-\text{COO}^-]} = 20$

$$-\text{NH}_3{}^+ \qquad 1 = 9.6 + \log\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}$$

$$\frac{[-\text{NH}_3^+]}{[-\text{NH}_2]} = 4 \times 10^8$$

Therefore the **predominant species** is: $^+\text{NH}_3 - \text{CH}_2 - \text{COOH}$

At pH = 7,

$$-\text{COOH} \qquad 7 = 2.3 + \log\frac{[-\text{COO}^-]}{[-\text{COOH}]}$$

$$\frac{[-\text{COO}^-]}{[-\text{COOH}]} = 5 \times 10^4$$

$$-\text{NH}_3{}^+ \qquad 7 = 9.6 + \log\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}$$

$$\frac{[-\text{NH}_3^+]}{[-\text{NH}_2]} = 4 \times 10^2$$

Predominant species: $^+\text{NH}_3 - \text{CH}_2 - \text{COO}^-$

At pH = 12,

$$-\text{COOH} \qquad 12 = 2.3 + \log\frac{[-\text{COO}^-]}{[-\text{COOH}]}$$

$$\frac{[-\text{COO}^-]}{[-\text{COOH}]} = 5 \times 10^9$$

$$-\text{NH}_3{}^+ \qquad 12 = 9.6 + \log\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]}$$

$$\frac{[-\text{NH}_2]}{[-\text{NH}_3^+]} = 2.5 \times 10^2$$

Predominant species: $\text{NH}_2 - \text{CH}_2 - \text{COO}^-$

25.42   No, the milk would *not* be fit to drink. Enzymes only act on one of two optical isomers of a compound.

25.43   **(a)**   The repeating unit in nylon 66 is

$$-(\text{CH}_2)_4-\overset{\displaystyle O}{\overset{\displaystyle \|}{\text{C}}}-\underset{\underset{\displaystyle H}{|}}{\text{N}}-(\text{CH}_2)_6-\underset{\underset{\displaystyle H}{|}}{\text{N}}-\overset{\displaystyle O}{\overset{\displaystyle \|}{\text{C}}}-$$
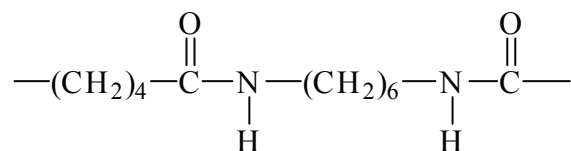
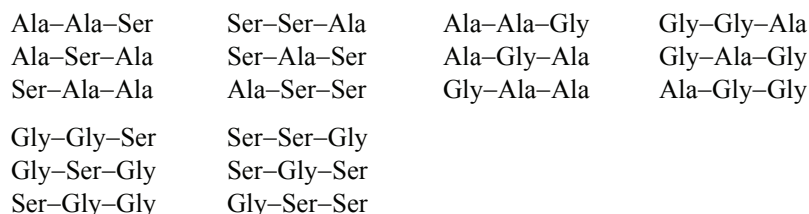and the molar mass of the unit is 226.3 g/mol. Therefore, the number of repeating units (n) is

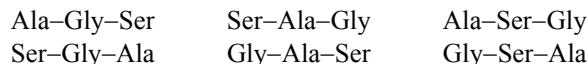$$n = \frac{12000 \text{ g/mol}}{226.3 \text{ g/mol}} = 53$$

(b)   The most obvious feature is the presence of the amide group in the repeating unit. Another important and related feature that makes the two types of polymers similar is the ability of the molecules to form intramolecular hydrogen bonds.

(c)   We approach this question systematically. First, there are three tripeptides made up of only one type of amino acid:

Ala–Ala–Ala   Gly–Gly–Gly   Ser–Ser–Ser

Next, there are eighteen tripeptides made up of two types of amino acids.

Ala–Ala–Ser	Ser–Ser–Ala	Ala–Ala–Gly	Gly–Gly–Ala
Ala–Ser–Ala	Ser–Ala–Ser	Ala–Gly–Ala	Gly–Ala–Gly
Ser–Ala–Ala	Ala–Ser–Ser	Gly–Ala–Ala	Ala–Gly–Gly

Gly–Gly–Ser	Ser–Ser–Gly
Gly–Ser–Gly	Ser–Gly–Ser
Ser–Gly–Gly	Gly–Ser–Ser

Finally, there are six different tripeptides from three different amino acids.

Ala–Gly–Ser	Ser–Ala–Gly	Ala–Ser–Gly
Ser–Gly–Ala	Gly–Ala–Ser	Gly–Ser–Ala

Thus, there are a total of twenty-seven ways to synthesize a tripeptide from three amino acids. In silk, a basic six-residue unit repeats for long distances in the chain.

–Gly–Ser–Gly–Ala–Gly–Ala–
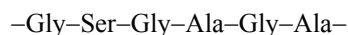
The ability of living organisms to reproduce the correct sequence is truly remarkable. It is also interesting to note that we can emulate the properties of silk with such a simple structure as nylon.

**25.44**   We assume $\Delta G = 0$, so that

$$\Delta G = \Delta H - T\Delta S$$

$$0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{125 \times 10^3 \text{ J/mol}}{397 \text{ J/K} \cdot \text{mol}} = 315 \text{ K} = 42°\text{C}$$

25.45   In deoxyhemoglobin, it is believed that the Fe^{2+} ion has too large a radius to fit into the porphyrin ring (see Figure 25.15 of the text). When O_2 binds to Fe^{2+}, however, the ion shrinks somewhat so that it now fits into the plane of the ring. As the ion slips into the ring, it pulls the histidine residue toward the ring and thereby sets off a sequence of structural changes from one subunit to another. These structural changes occurring from one subunit to the next that cause deoxyhemoglobin crystals to shatter. Myoglobin is only made up of one of the four subunits and thus does not have the structural changes from subunit to subunit described above. Therefore, deoxymyoglobin crystals are unaffected by oxygen.

25.46
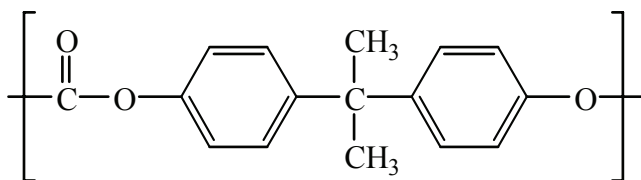
25.47 A DNA molecule has 4 bases (A, C, G, T). A sequence of only two bases to define a particular amino acid has a total of 4^2 or 16 possible combinations. Because there are 20 different amino acids in proteins, we need a sequence of 3 bases or $4^3 = 64$ combinations. Because this number is greater than 20, some of the sequences are redundant; that is, they define the same amino acids.

25.48 **(a)** The $-COOH$ group is more acidic because it has a smaller pK_a.

(b) We use the Henderson-Hasselbalch equation, Equation (16.4) of the text.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

At pH = 1.0,

$-COOH$
$$1.0 = 2.32 + \log \frac{[-COO^-]}{[-COOH]}$$

$$\frac{[-COOH]}{[-COO^-]} = 21$$

$-NH_3^+$
$$1.0 = 9.62 + \log \frac{[-NH_2]}{[-\overset{+}{N}H_3]}$$

$$\frac{[-\overset{+}{N}H_3]}{[-NH_2]} = 4.2 \times 10^8$$

Therefore the **predominant species** is: $CH(CH_3)_2 - CH(\overset{+}{N}H_3) - COOH$

At pH = 7.0,

$-COOH$
$$7.0 = 2.32 + \log \frac{[-COO^-]}{[-COOH]}$$

$$\frac{[-COO^-]}{[-COOH]} = 4.8 \times 10^4$$

$-NH_3^+$
$$7.0 = 9.62 + \log \frac{[-NH_2]}{[-\overset{+}{N}H_3]}$$

$$\frac{[-\overset{+}{N}H_3]}{[-NH_2]} = 4.2 \times 10^2$$

Predominant species: $CH(CH_3)_2 - CH(\overset{+}{N}H_3) - COO^-$

At pH = 12.0,

$$-\text{COOH} \qquad 12.0 = 2.32 + \log\frac{[-\text{COO}^-]}{[-\text{COOH}]}$$

$$\frac{[-\text{COO}^-]}{[-\text{COOH}]} = 4.8 \times 10^9$$

$$-\text{NH}_3^+ \qquad 12.0 = 9.62 + \log\frac{[-\text{NH}_2]}{[-\overset{+}{\text{N}}\text{H}_3]}$$

$$\frac{[-\text{NH}_2]}{[-\overset{+}{\text{N}}\text{H}_3]} = 2.4 \times 10^2$$

Predominant species: $\qquad \text{CH}(\text{CH}_3)_2 - \text{CH}(\text{NH}_2) - \text{COO}^-$

(c) $\text{pI} = \dfrac{pK_{a_1} + pK_{a_2}}{2} = \dfrac{2.32 + 9.62}{2} = \textbf{5.97}$

25.49 $\Delta G° = \Delta H° - T\Delta S°$

$$\Delta G° = 17 \text{ kJ/mol} - \left[(298 \text{ K})\left(65\frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \right]$$

$$\Delta G° = -2 \text{ kJ/mol}$$

Since $\Delta G° < 0$, the dimerization is favored at standard conditions and 25°C (298 K). As the temperature is lowered, $\Delta G°$ becomes less negative so that the dimerization is less favored. At lower temperatures ($T < 262$ K), the reaction becomes spontaneous in the reverse direction and denaturation occurs. For an enzyme to be cold labile, it must have $\Delta H° > 0$ and $\Delta S° > 0$ for folding to the native state so that below a certain temperature, the enthalpy term dominates, and denaturation occurs spontaneously.

25.50   (a)   All the sulfur atoms will have an octet of electrons and be sp^3 hybridized.

(b)   cysteine

(c)   Denaturation will lead to more disorder (more microstates). ΔS is positive. To break a bond, energy must be supplied (endothermic). ΔH is positive. Consider the equation $\Delta G = \Delta H - T\Delta S$. This type of process with a positive ΔH and a positive ΔS is favored as the temperature is raised. The $T\Delta S$ term will become a larger negative number as the temperature is raised eventually leading to a negative ΔG (spontaneous).

(d)   If we assume that the probability of forming a disulfide bond between any two cysteine residues is the same, then, statistically, the total number of structurally different isomers formed from eight cysteine residues is given by $7 \times 5 \times 3 = 105$. Note that the first cysteine residue has seven choices in forming an S−S bond, the next cysteine residue has only five choices, and so on. This relationship can be generalized to $(N-1)(N-3)(N-5) \cdots 1$, where N is the total (even) number of cysteine residues present. The observed activity of the mixture—the "scrambled protein"—is less than 1% of that of the native enzyme ($1/105 < 0.01$). This finding is consistent with the fact that only one out of every 105 possible structures corresponds to the original state.

(e)   Oxidation causes sulfur atoms in two molecules to link, similar to the cross-linking described in the problem. The new compound formed has less odor compared to compound secreted by the skunk.