

## **Chapter 7: Implications of The Second Law**

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This chapter will investigate the effects of the second law on life, and then show why the law makes it so difficult to explain the origin of life. Finally, the claim made by some authors that the second law makes evolution after life exists impossible will be investigated.

### **How Does Life Exist So Far From Equilibrium?**

The answer lies with proteins. A specific kind of protein called an enzyme lowers the activation energy of chemical reactions. Reactions that would normally take years happen in seconds. Figure 7.1 shows how this effect alters chemical equilibrium. Consider a set of chemicals that have two paths to interact as shown in figure 7.1. One reaction is a side reaction that is undesirable. The other is desirable.

The enzyme lowers the activation energy for the desirable reaction making it happen quickly. The undesirable reaction does not have a chance. Also notice that the entropy of the universe is maximized by the undesirable reaction. Thus, from thermodynamic considerations, one might think that the undesirable reaction is always dominant, but because the laws of thermodynamics have no way to deal with time, this observation is seldom true. The enzyme is not violating the second law by forcing the reaction in the preferred direction. Its reaction is also spontaneous because it also increases the entropy of the universe. By making the desired reaction happen faster, the enzyme does not give the undesirable reaction time to happen.

Figure 7.1: Enzymes and the Second Law

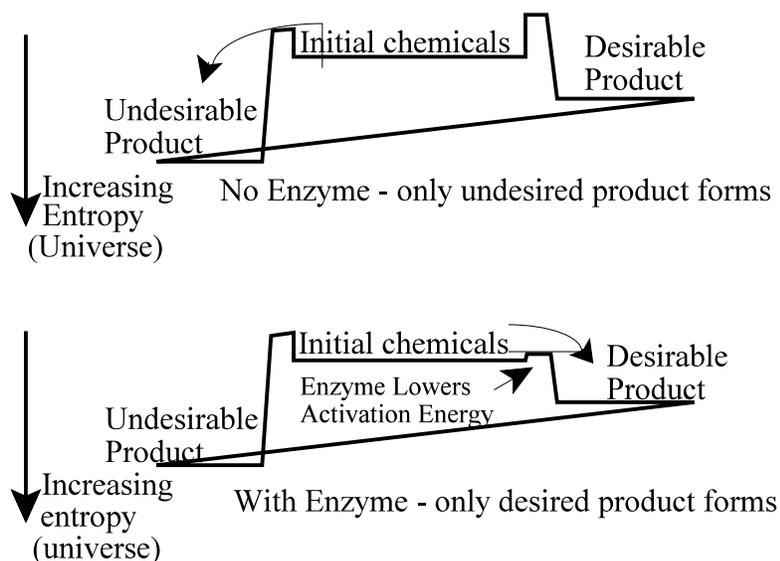
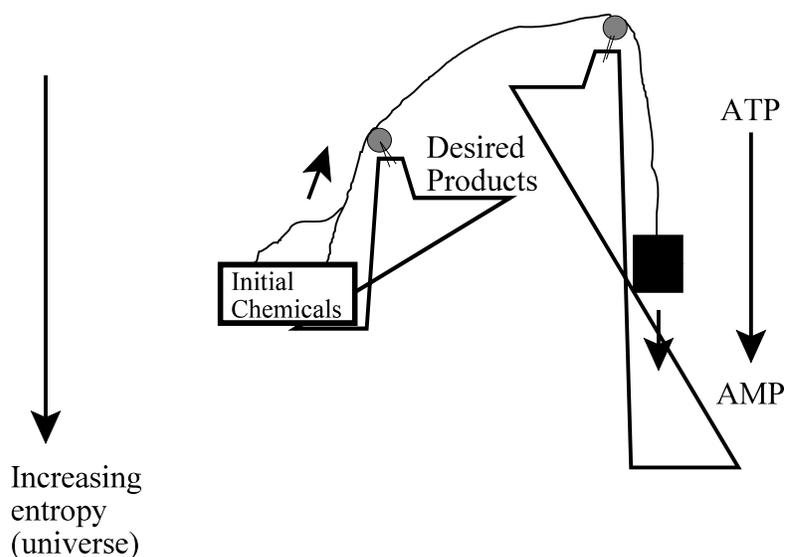


Figure 7.1 illustrates a powerful technique, but this trick alone does not enable life. Enzymes have another much more impressive trick. They can force chemical reactions that should never take place to happen and happen quickly. They do this by coupling a favorable chemical reaction to an unfavorable one.

Lowering the activation energy will not help a reaction go forward if the entropy of the final state is lower than the initial. In figure 7.1, the final state of the desired products is a higher entropy state than the initial state (in these diagrams moving down hill represents increasing entropy). Thus, the chemical reaction is spontaneous as it increases the entropy of the universe. Figure 7.2 considers the case in which the opposite is true.

Figure 7.2: Enzymes Couple Reactions

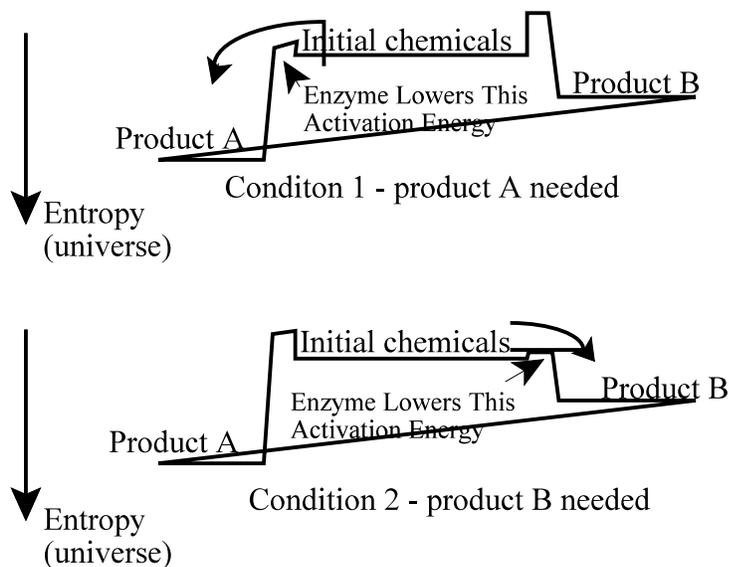


In figure 7.2, a chemical reaction that increases the entropy of the universe is coupled to one that decreases it. The favorable chemical reaction turns the chemical, ATP into AMP. This reaction is represented by the falling weight. It is attached by a rope to the unfavorable reaction. The rope and pulleys represent the enzyme.

Life requires both the techniques shown in 7.1 and 7.2 to maintain its state so far from equilibrium, and the technique shown in 7.2 requires a continual input of energy. This is why life requires food. Sugar is required by animals to create chemicals like ATP. ATP is a very high energy chemical, and when it reacts with water to form AMP, the entropy of the universe is greatly increased. This reaction is coupled by enzymes to many unfavorable chemical reactions.

The two previous examples show how enzymes implement procedural knowledge. The knowledge may also be conditional (figure 7.3).

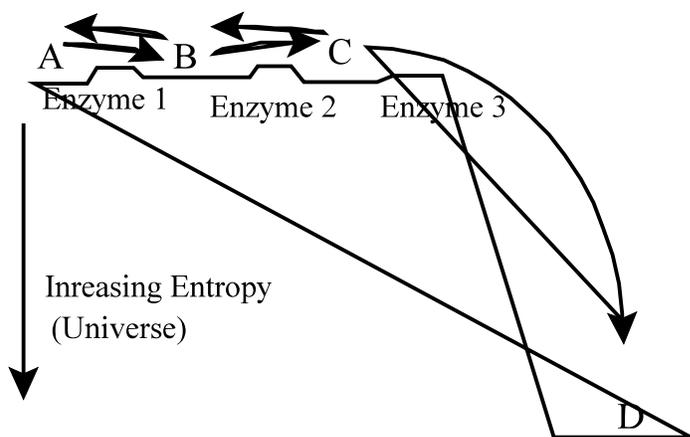
Figure 7.3: Enzymes Can Make Decisions



Conditional knowledge is very powerful. It allows life to change when the environment changes. Life does not have to think about how to do this. The decision making is preprogramed just like a computer. Conditional knowledge is not limited to enzymes. Often proteins interact with sections of DNA to promote or repress gene expression. The effects of conditional knowledge can be seen in any higher form of life. Conditional knowledge determines whether a cell becomes a skin, liver, muscle, lung, kidney, or stomach cell.

The last trick used by life is the most subtle, but yet at the same time the most powerful. Life uses teams of enzymes that work together to create desired products, and in many cases, the enzymes that do this do not even need an energy source to accomplish their goal, see figure 7.4.

Figure 7.4: Team of Enzymes Working Together



In figure 7.4, enzyme 1 lowers the barrier enabling A to form B, but because the change in entropy is small, the reaction proceeds in both directions. The same is true for enzyme 2, and product C, but these first two reactions are coupled to a third, in which C changes into D. This reaction only proceeds in the forward direction because of the large increase in entropy; as a result, the chemicals, A, B and C, will all eventually be converted to D, and only D will exist. Figures 7.1 to 7.4 illustrate how proteins (enzymes) implement the knowledge contained in DNA.

To avoid violating the second law, life requires quite a bit of complexity. Hundreds of enzymes work together with DNA to decide which chemical reactions take place and then make sure that only the desired chemical reactions happen. Enzymes alter equilibrium by speeding up desirable reaction pathways compared to undesirable ones, and if they need to, they will couple unfavorable reactions to favorable ones forcing the unfavorable reactions to happen and happen quickly, and all of this is subject to the built in ability to make decisions as to which chemical reactions are appropriate at any given time.

Hundreds of enzymes make it possible for life to exist in a state of very low entropy. Most origin of life theories concentrate on a single self replicating chemical. What is not clear is how such a chemical can self replicate without violating the second law. Such a chemical does not have a hundred enzymes working in concert on its behalf to help it self replicate. Before the second law was understood, many scientists tried to build machines that would run forever (perpetual motion machines). They all failed because the second law does not allow such machines to exist. A self replicating molecule is very similar to a perpetual motion machine. If one day, a self replicating molecule is created in a lab, it will replicate itself for a very short period of time and then cease.

Life is possible because life can control and direct the flow of entropy. In other words, life uses energy sources to perform work. When sunlight hits a black pavement, most of its energy is converted into heat. This process greatly increases the entropy of the universe. When sunlight strikes a plant something else happens. Plants know how to harness the energy in sunlight to do work. While much of the sunlight is still converted to heat, some of it is used to make sugar in a process called photosynthesis. Photosynthesis also increases the entropy of the universe. So the second law does not prohibit the process. The entropy increase in photosynthesis is certainly less than that if the sunlight had struck a black pavement, but both processes are allowed because both create more entropy. Plants possess molecular knowledge, and this knowledge enables them to harness the energy of the sun to do work.

Fire is a chemical reaction in which oxygen combines with complex organic chemicals to create carbon dioxide and water. The heat released by a burning bush increases the entropy of the universe, and it does so very quickly, but something else happens when a deer eats the bush. The leaves are eventually converted into carbon dioxide and water, but the energy released by this process is harnessed to perform work. It is used to create ATP. ATP is then used to drive many unfavorable chemical reactions (figure 7.2). The deer does not have to think about how to do this. The knowledge is built into the molecules that make up the deer.

### **Is Life Really Different from Non-life?**

Proponents of a naturalistic explanation routinely appeal to the fact that the earth is an open system. Thus, the sun provides the energy for systems to maintain their distance from equilibrium (existing in a low entropy state indefinitely). While this argument is certainly true for life, it is not true for the chemicals residing in a puddle somewhere on earth 4 billion years ago. *Without a team of enzymes working together with the common goal of self replication, energy sources do not help. There is simply no way to harness the energy to achieve the goal.*

Consider a man and his car with no gas in the desert. The man is not concerned. He knows that he is in an open system and that he has an unlimited supply of energy in sunlight. He theorizes that after the car absorbs enough sunlight, it will suddenly start and he can drive home. His theory is flawed because his car does not know how to use the energy from the sun to perform useful work, and 5 billion years will not solve his problem.

## **Do Energy Sources Really Help?**

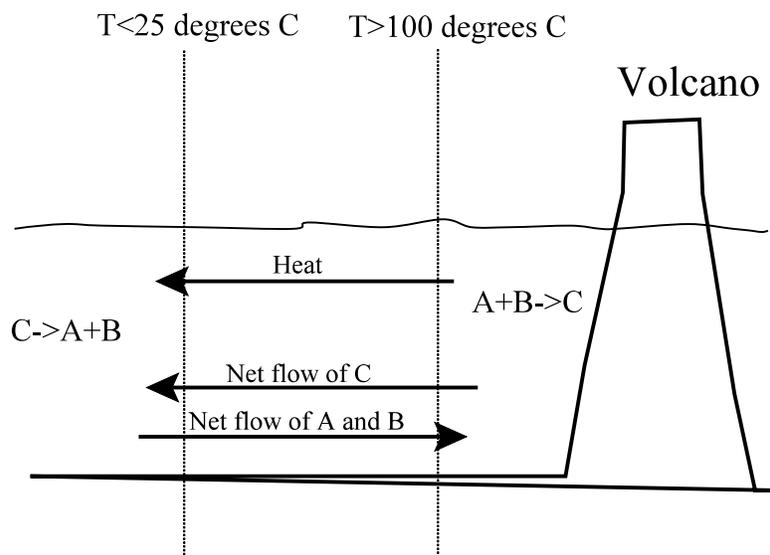
Both experimental and theoretical evidence suggests that sunlight and other energy sources make it harder for chemicals to exist far from equilibrium. This is easily understood in terms of activation energies. A low entropy state may exist indefinitely as long as the chemicals involved never obtain enough energy to cross the activation barrier, but such states are very hard to maintain when energy is plentiful. Energy sources make the origin of life even more difficult to explain. Why so many authors continue to point out their benefits is hard to understand.

In order for a self replicating molecule to replicate indefinitely, it must possess a mechanism to harness and use energy. Self replication decreases the entropy of the universe, and as such, it always requires a source of energy. Therefore, unless a self replicator possesses both the knowledge and ability to drive its replication with a plentiful energy source, the molecule's very existence violates the second law.

## **Non-Equilibrium Thermodynamics**

The idea that energy sources can somehow solve the origins problem is so prevalent that a few detailed examples are required. A flow of energy can maintain a living or a non-living system in a state of non-equilibrium. Consider a chemical reaction that proceeds as follows: if the temperature is less than 25 degrees Celsius, then  $C \rightarrow A + B$ . If the temperature is above 100 degrees Celsius, then the reaction proceeds in the opposite direction,  $A+B \rightarrow C$ . Now consider a body of water that is warmed by volcanic activity (figure 7.5).

Figure 7.5: A Non-Equilibrium System



In figure 7.5, there is a flow of heat from the volcano into the ocean around it. This sets up a temperature gradient. The water is very hot near the volcano and very cool away from it. Heat flows in the water as indicated by the arrow. The chemical reaction under consideration proceeds in the direction to create chemical C near the volcano. Away from the volcano, it proceeds to create the chemicals, A and B.

Since this creates much more of chemical C near the volcano, C tends to move away toward the colder water (see arrows). Much more of the chemicals A and B exist in cold water. So these tend to travel toward the warmer water near the volcano (see arrows). This creates a cycle in which some chemicals are continually transported from warm water to cold water, and others from cold to warm.

If the desired chemical is C, then it would be beneficial to heat the entire body of water to a temperature greater than 100 degrees. If the desired chemical is A or B, then it would be beneficial to have the entire ocean at a temperature less than 25 degrees Celsius. The flow of energy allows the chemicals to exist away from equilibrium, but they exist in an intermediate state between the two extremes. There is less of the chemical C than if the entire body of water is heated to 100 degrees Celsius, but there is more C than if the entire ocean is at 25 degrees Celsius. The same argument applies to A and B.

The relevance of such a system to the origin of life is questionable at best. How this flow of energy and matter can create a complex biological molecule is not clear. Figure 7.4 is certainly a form of order. C flows to the left, and A and B flow to the right. The cycle is maintained by the flow of heat, but there is nothing in figure 7.4 that performs the function of an enzyme. There is no mechanism to couple an unfavorable reaction to a favorable one. Furthermore, there is no mechanism to preferentially create only the desired chemicals. But most importantly, there is no way to store information. So there is no way for such a system to evolve.

Experimental evidence supports this theoretical conclusion because most if not all experiments designed to investigate the origin of complex chemicals make extensive use of non-equilibrium conditions. The most famous, Miller's electric discharge experiment, will be discussed in chapter 9.

So in this case, both theory and experiment converge to the same answer. Under plausible prebiotic conditions, without molecular knowledge, it is very difficult (if not impossible) to create the complex chemicals used by life today.

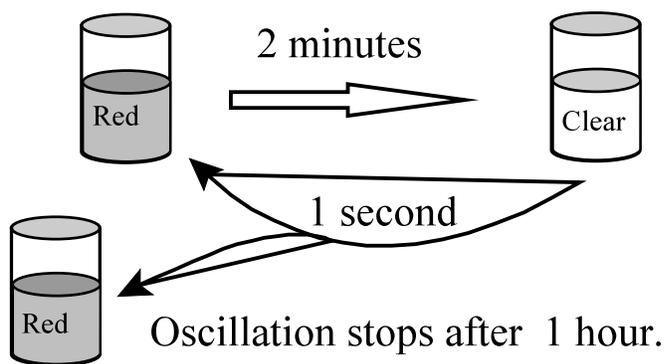
## Chemical Oscillators

Chemical oscillators are systems of chemicals that exhibit very interesting time-based fluctuations when they are far from equilibrium. These fluctuations may cause a solution of chemicals to change colors in a periodic fashion or create complex spatial patterns (figure 7.6).

It would be incorrect to suggest that these systems possess molecular knowledge because their behavior does not benefit any of the chemicals involved. They do not self replicate. Nevertheless, they are interesting anomalies. On their way toward chemical equilibrium, these systems take a detour and veer off course. They eventually reach equilibrium, and the oscillation stops.

These systems do not help explain the origin of life. They have never been implicated in the prebiotic synthesis of proteins, DNA or RNA. *The chemicals in these oscillators cannot evolve because they have no mechanism to store information, and they do not self replicate.* These systems are like a man-made machine. For example, a battery powered watch is a chemical oscillator. The watch hands move in a periodic fashion, and the hands stop when the battery dies. The knowledge that enables the watch to do this is built into it by engineers. In a similar fashion, chemists bring together the necessary chemicals for chemical oscillators.

Figure 7.6: A Chemical Oscillator



The popularity of chemical oscillators in the origins field rests largely on the shoulders of two authors, Kauffman and Prigogine. Both dedicated an entire book to this one subject. Despite their enthusiasm, chemical oscillators do not solve any of the problems related to the origin of life. While they do tap an energy source to perform work, the energy source is limited, and once it runs out, the oscillation ceases. Furthermore, because these systems have no way to store molecular knowledge, they cannot evolve, and perhaps most importantly, the systems do not self replicate. A chemical oscillator has about as much chance of evolving into a living organism as does a watch. Neither possesses the knowledge or has the ability to acquire the knowledge required for self replication. So natural selection cannot optimize these systems, and evolution cannot take place.

Kauffman has also put forth several other ideas concerning the origin of life and self organization. For example, in order to create a self organizing system, he envisions a set of chemicals that perform the many functions of enzymes described in this chapter. So he defines a self organizing system as life, and it stands to reason that life can self replicate. He just assumes that the molecular knowledge and a method to implement the knowledge already exist, and once these two are in place, life is inevitable. Unfortunately, his ideas do not explain how the knowledge arose in the first place. He also fails to consider the need to tap a plentiful energy source to perform work. So most of his ideas give rise to perpetual motion machines.

Furthermore, he continually confuses order with knowledge. Because most of his thought experiments and computer simulations actually give rise to order, many of the ideas that he proposes are not relevant to the origin of life. For example, he simulates the order that arises when many logic gates are connected together in a random fashion. He observes large sections of these arrays oscillating at the same frequency. Any electrical engineer would immediately recognize his system as nothing more than a collection of ring oscillators, and the order that results contains no useful information.

## **Entropy and Biological Evolution**

Several authors have suggested that the second law works against evolution. While this is certainly true for chemical evolution, the second law does not prevent existing biological systems from evolving. If anything the contrary is true. Evolution is possible because life does not seem to be able to copy its DNA without making an occasional mistake. If DNA was replicated faithfully in every generation, then chance would never create new useful information, and natural selection would never have the opportunity to preserve anything new.

The second law is often stated as the disorder of the universe must always increase. This statement is not true, because entropy is a measure of uncertainty not disorder. Several authors have used the entropy as disorder definition, to justify the conflict between the second law and evolution. Since life is not disordered, it is possible to see the conflict when entropy is defined in this way. Nevertheless, entropy and disorder are not the same.

The second law stipulates that the uncertainty of the universe will increase with time. This uncertainty is reflected in all physical systems. Mutations increase uncertainty. Thus, changes to existing genes and proteins are fully expected and consistent with the second law.

The direction toward increasing complexity that life displays with time may be attributed to the preserving power of natural selection. If chance creates useful information that confers a selective advantage, then natural selection will preserve it. This process has nothing to do with the second law, and authors who suggest that the second law and evolution are somehow mutually exclusive do not understand the nature of entropy.

### **References:**

- 1) Morowitz, Energy Flow in Biology, Ox Bow Press, 1979.
- 2) Brillouin, Science and Information Theory, 1956.
- 3) Prigogine, Stengers, Order Out of Chaos, Bantam Books, 1984.
- 4) Kauffman, At Home in The Universe, Oxford University Press, 1995.

## **Chapter 8: The Structure of DNA, RNA and Proteins**

This chapter will explore the structure of nucleic acids and proteins.

### **DNA Structure**

DNA is composed of several different subunits. The backbone of the molecule is made of a sugar called deoxyribose. The deoxyribose is held together by phosphate groups. Deoxyribose also forms bonds with the four bases, adenine (A), cytosine (C), thymine (T) and guanine (G). Figures 8.1-8.6 depict how the subunits are assembled in a DNA molecule. In these figures, black represents adenine, white thymine, dark gray guanine, and light gray cytosine.

Figure 8.1: Rasmol Image of DNA Double Helix Segment

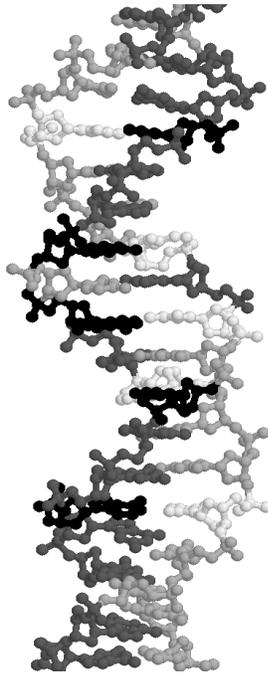


Figure 8.2: Closer View of DNA

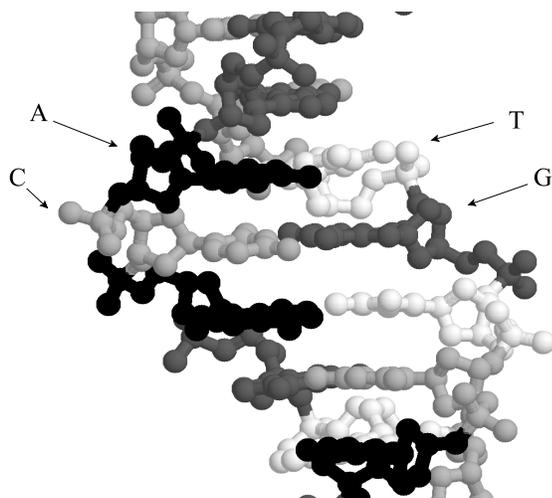


Figure 8.3: Conceptual DNA Model

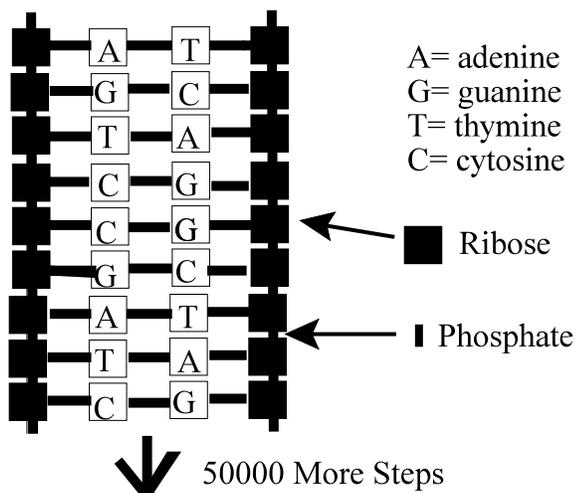
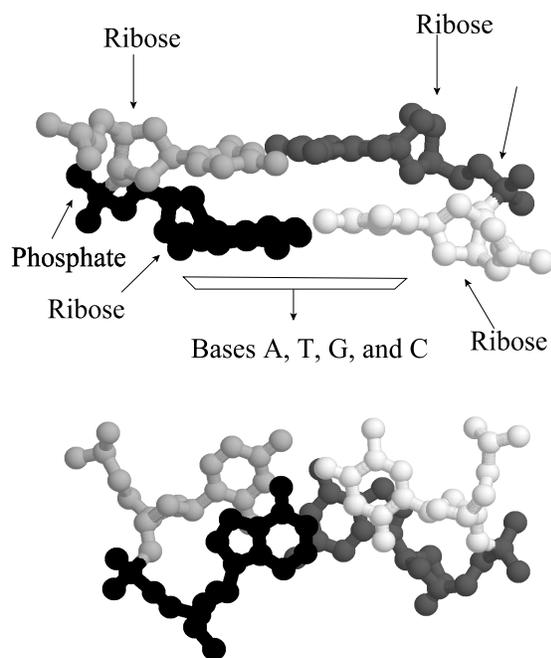


Figure 8.4: Top and Side view of Two Steps



Chapter 3 describes how this structure stores information. The order of the four bases (A, T, C and G) read three at a time per table 3.2 determines the amino acid sequence in the final protein.

### RNA Structure

RNA is very similar to DNA, but it normally does not form the characteristic double helix (twisted ladder). RNA is a mixture of single stranded and double stranded segments (figure 8.7). The 3-D structure is often stabilized by complementary base pairing in short regions (boxes in figure 8.7). RNA uses the base uracil in place of thymine. It also uses ribose instead of deoxyribose (figure 8.6).

Figure 8.5: Detailed DNA Structure

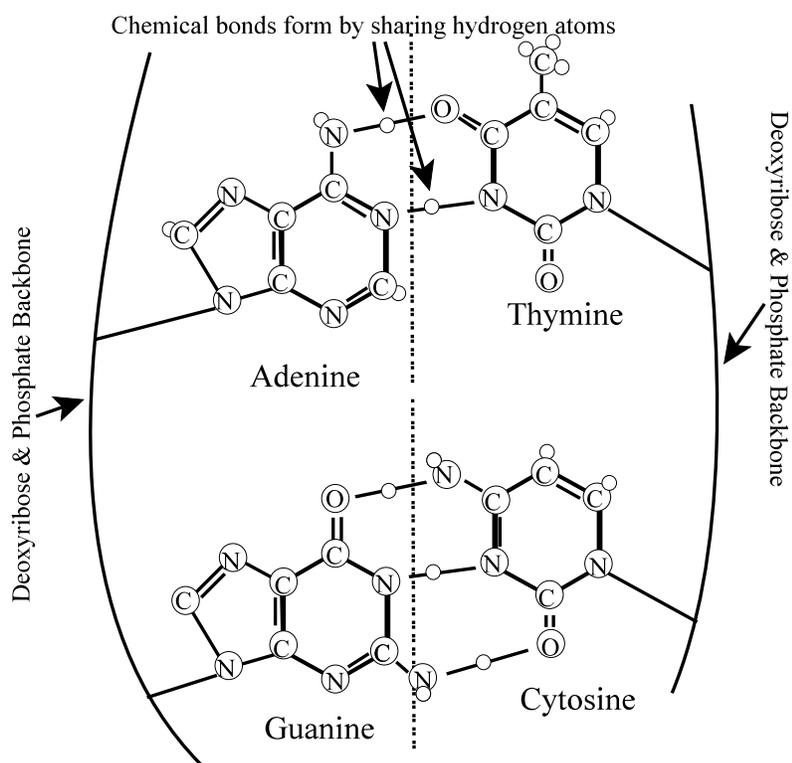
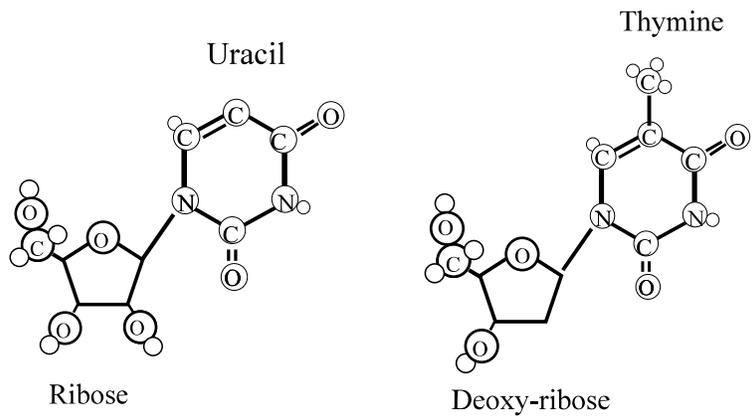


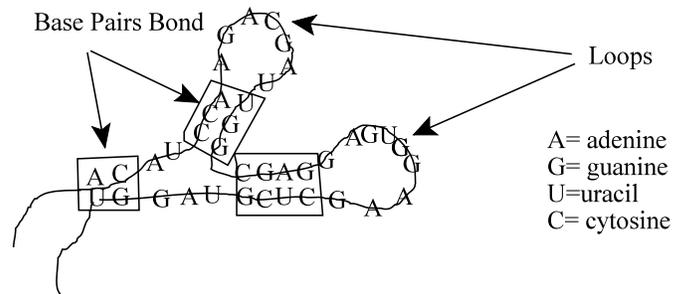
Figure 8.6: Ribose, Deoxyribose, Uracil and Thymine



The 3-D structure is extremely important, because it conveys to RNA some of the properties found in proteins. RNA can regulate chemical reactions just like proteins. This is why RNA has taken center stage in most origin of life theories. RNA can store information and it can regulate chemical reactions. Nevertheless, the initial optimism for self replicating RNA molecules has largely been replaced by doubt. The reasons for the doubt will be discussed in the next two chapters.

Figure 8.7: RNA Structure Stabilized by Base Pair Bonds

RNA Curls up On Itself Form Double and Single Stranded Regions



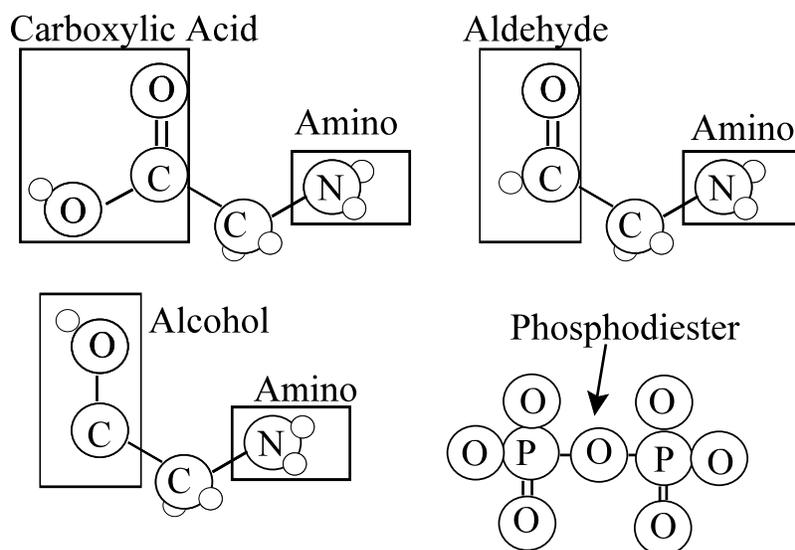
## Proteins

This section explores the structure of proteins and amino acids.

### Organic Chemistry Functional Groups

Organic chemistry is the study of how large chemicals containing carbon interact. Because organic chemicals are very large, the structures of many are overwhelming. Fortunately, the chemicals can only interact with each other in a very limited set of reactions. These reactions are controlled by functional groups. The functional groups relevant to the origin of life are shown in figure 8.8. Carboxylic acid and amino groups are found in all amino acids. P = phosphorous, O = oxygen, N = nitrogen, C = carbon, and unlabeled small spheres = hydrogen.

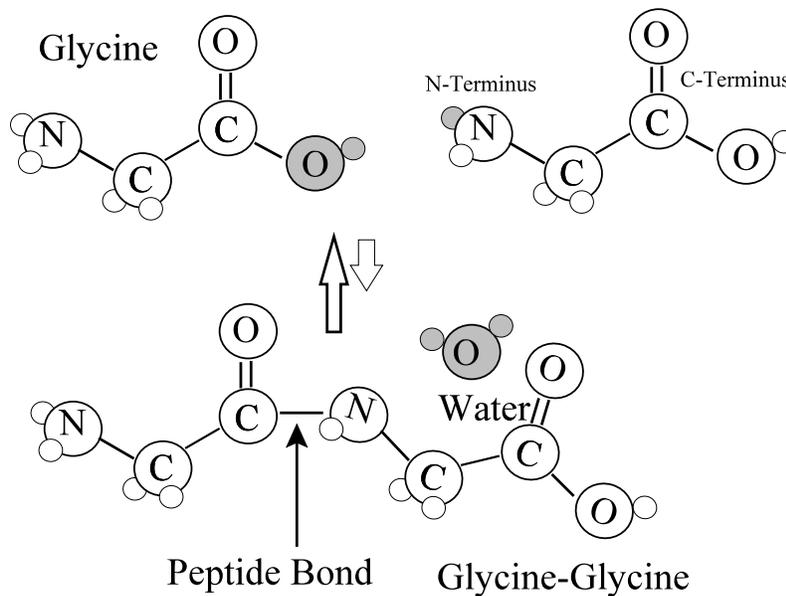
Figure 8.8: Functional Groups



## Structure of Amino Acids

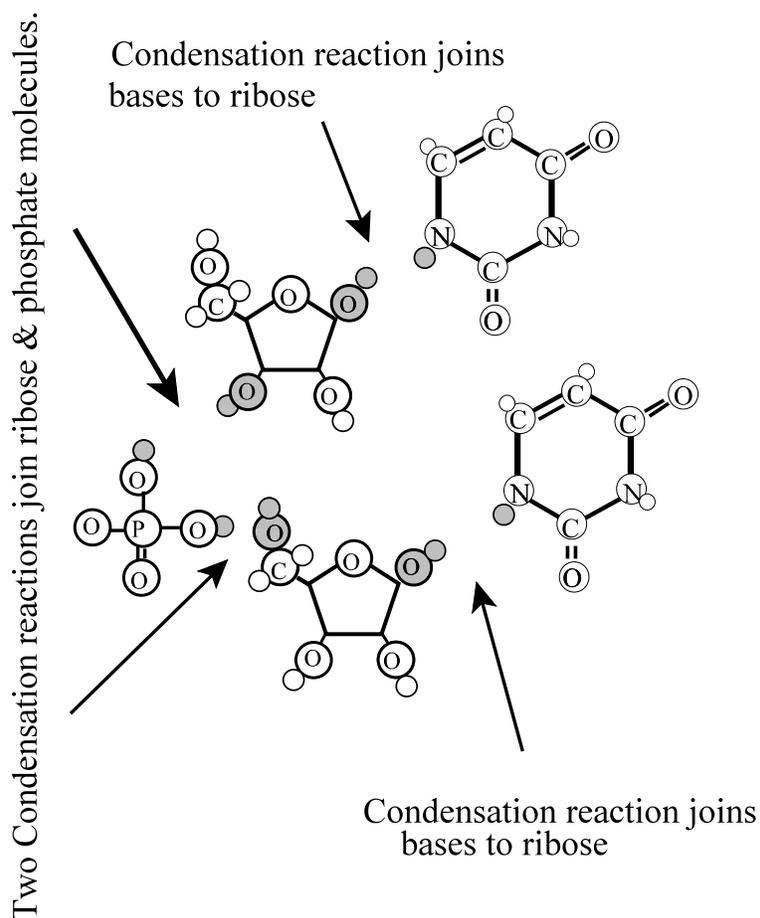
Amino acids are composed of 5 elements - carbon, oxygen, nitrogen, hydrogen and sulfur. It is their chemical structure that permits them to form long chains. These long chains fold up into complex three dimensional patterns forming proteins. Each amino acid can be broken down into three critical parts: the side chain or side group, the N-terminus (amino group) and the C-terminus (carboxylic acid). The N-terminus of one amino acid can attack the C-terminus of another. Under the right conditions, this attack will form a link between the amino acids. This link is called an amide bond or a peptide bond. Figure 8.9 illustrates the key structural components using the amino acid glycine.

Figure 8.9: Glycine and the Peptide Bond



Notice that after the peptide bond forms, and the two glycines are linked by a peptide bond, one C-terminus and one N-terminus still exist. This allows the chain to continue growing. A short chain of amino acids is called a peptide. A peptide may or may not contain information. The dark atoms in figure 8.9 are the atoms that leave forming water when the two glycine molecules join. Because this reaction creates water, it is called a condensation reaction. Condensation reactions do not occur readily in water and are particularly problematic for RNA and DNA prebiotic synthesis.

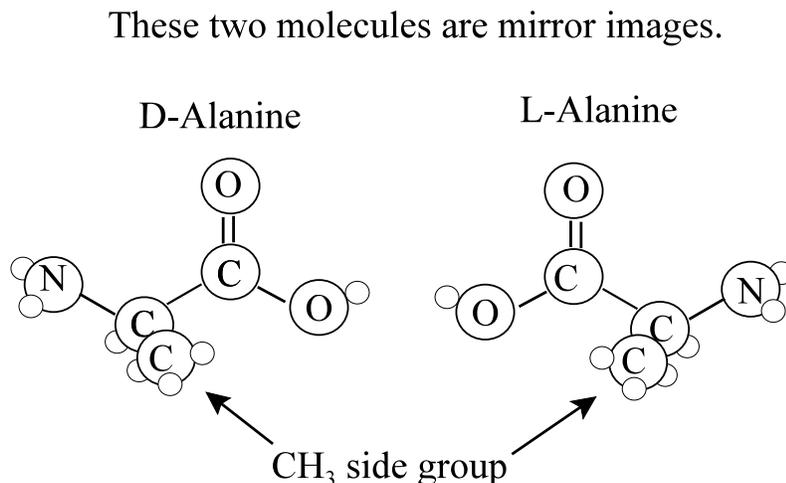
Figure 8.10: RNA and DNA Requires Many Condensation Reactions



A protein is a chain of many amino acids (typically more than 100 amino acids). Proteins have a specific function. Therefore, proteins contain useful information (knowledge). This information is specified by the order of amino acids in the chain. The 20 amino acids used by life differ only in their side chains.

Every amino acid except glycine has two forms, L and D. One form is the mirror image of the other. These forms are called isomers. The L and D isomers of the amino acid alanine are shown in figure 8.11.

Figure 8.11: L and D Isomers of Alanine



L-Alanine is used by life. D-alanine is not.

The L and D isomers can form peptide bonds. But the location of the side group is located in the wrong position when the L isomer is replaced with the D. This of course may influence protein function. One of life's greatest mysteries is why did life chose to only use the L-amino acids? Nineteen of the amino acids used by life are shown in figures 8.12-8.17. Glycine is shown in figure 8.9.

Figure 8.12: Hydrophobic Amino Acids (Do Not Like Water)

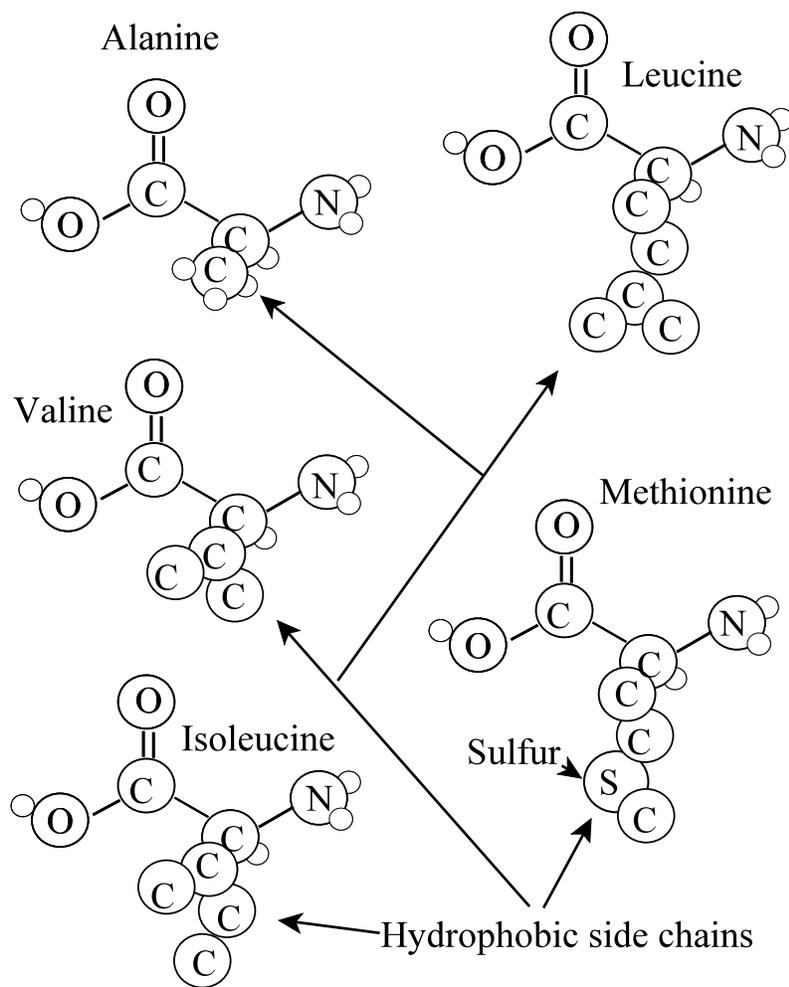


Figure 8.13: Basic Amino Acids

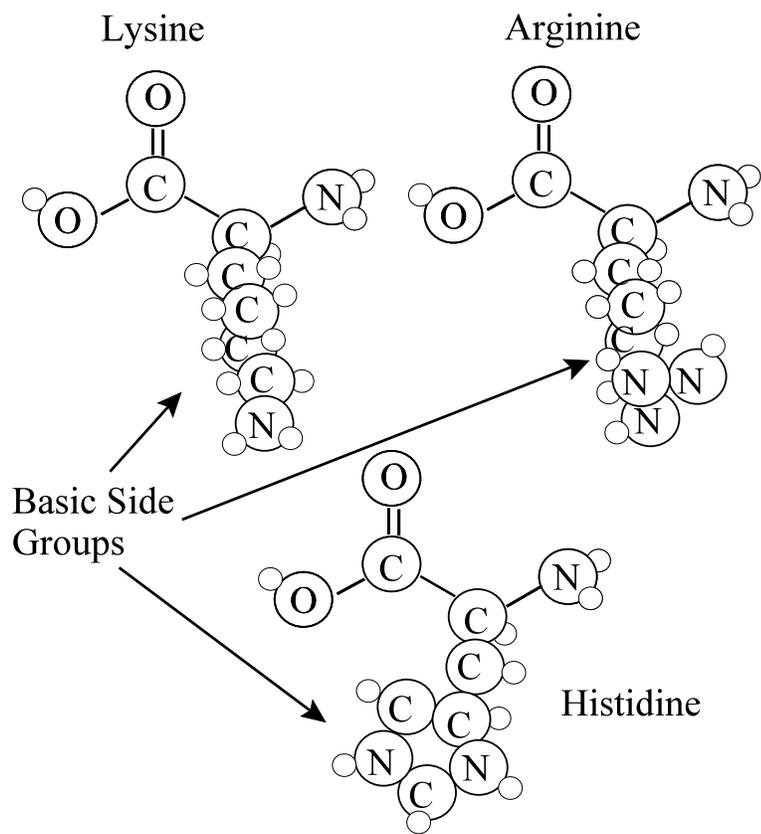


Figure 8.14: Polar Uncharged Amino Acids

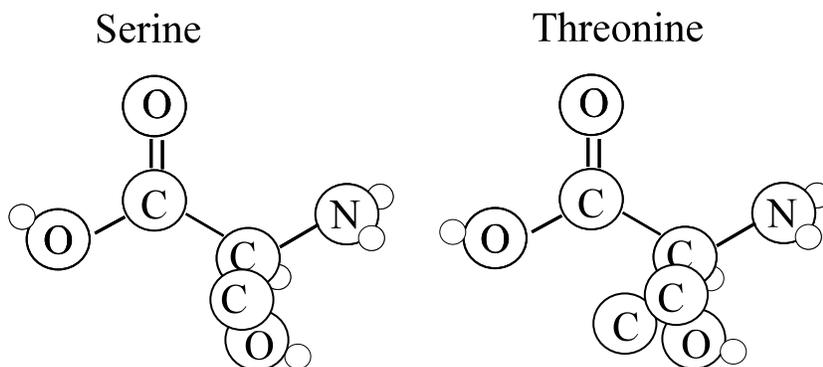


Figure 8.15: Two Unique Amino Acids

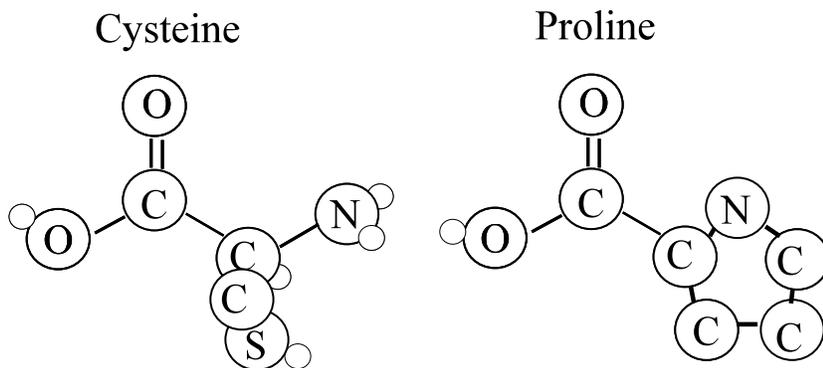


Figure 8.16: Bulky Amino Acids

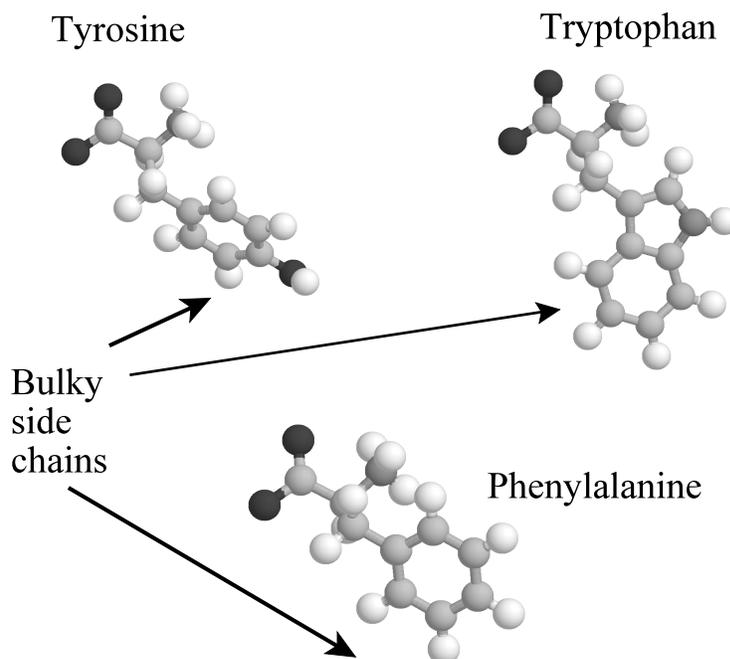
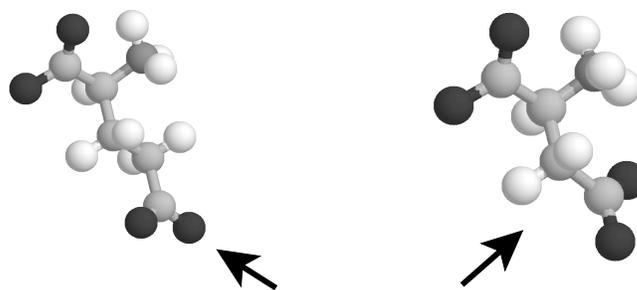


Figure 8.16 was generated using Rasmol. This is a free molecular viewer that allows users to view the 3-D structure of complex molecules. In this view, oxygen is black, hydrogen is white, carbon is gray, and nitrogen is a slightly darker gray. Rasmol was also used to generate the DNA images at the beginning of this chapter.

Figure 8.17: More Rasmol Images of Amino Acids

Glutamate

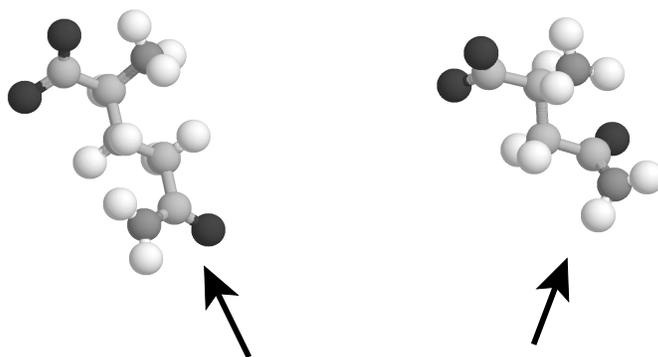
Aspartate



Acidic Side Chains

Glutamine

Asparagine



Charged Polar Side Chains