

Chapter 10: Entropy, Temperature, and Heat Transfer

When an aqueous solution of a protein is heated above the melting point of the protein, hydrogen bonds in the folded, native structure are disrupted. Above the melting point the protein exists in a random coil geometry. This process is called denaturation. Discuss denaturation from the prospective of energy dispersal and the change in entropy of the protein.

10.1 What is the Criterion for Spontaneity?

Spontaneous processes are often exothermic. However, endothermic processes can also be spontaneous. For example, a salt dissolving in water is often endothermic:



and the protonation of weak bases is also often endothermic:



Both of these processes are certainly spontaneous. So, if the enthalpy or internal energy change for a process doesn't predict the spontaneous direction for a process, what does?

Our experience is that nature is very "economical and efficient." Nature doesn't have different sets of rules for rocks, trees, people, and chemical reactions. All physical systems are governed by a very few laws. In searching for the criterion for the spontaneity of chemical reactions, we can look to simple processes, since at a fundamental level simple processes behave according to the same principles as complex processes. Enzymatically catalyzed reactions and bouncing balls have much in common. Consider a bouncing ball at height h , Figure 10.1.1. Initially, the ball has mechanical potential energy, $V = mgh$. When the ball is released, it falls and bounces on the table top. After each successive bounce, the ball loses some kinetic energy and eventually comes to rest on the surface of the table. Energy must be conserved, the First Law of thermodynamics will hold, but still a spontaneous process occurs. What happens to the total energy of this system? After the ball is released, the mechanical potential energy is converted into kinetic energy of the ball. During each bounce some of the kinetic energy is converted into thermal energy in the ball and the table. Energy is transferred into the rubber of the ball and the surface of the table in the form of heat; the ball and table increase slightly in temperature. This process shows that the initial potential energy of the system is dispersed spontaneously into thermal energy. The natural tendency is for energy to spread out, or disperse.

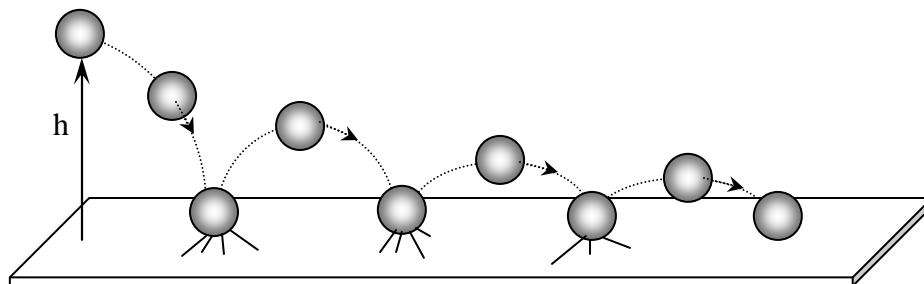


Figure 10.1.1: Potential energy is converted into kinetic energy which is dispersed into thermal energy. A spontaneous process increases energy dispersal.

We can take a more molecular view of the bouncing ball. Potential energy is the stored ability to do work or transfer heat. After release, the potential energy of the ball is converted into kinetic energy of motion of the whole ball. All the molecules in the ball are moving in the same direction. The initial potential energy of the ball is converted into work, which is localized and organized motion. After each bounce some of this kinetic energy is converted into heat, which disperses through all the molecules of the ball and table top as random thermal motion. We will see that there is a useful relationship between energy dispersal and the statistical distribution of energy among the degrees of freedom of the system.

Another common example to illustrate energy dispersal is the isothermal expansion of an ideal gas. Consider a monatomic gas at high pressure confined to a small region of a vessel by a temporary internal wall and a stop, Figure 10.1.2. The region outside of the temporary wall is at vacuum. When the stop is removed the gas expands spontaneously to fill the full available volume. The internal energy of the gas remains the same, $\frac{3}{2} nRT$. Energy is conserved. However, the energy of the gas is now spread out over a larger volume. Once again, the natural tendency is for energy to disperse.

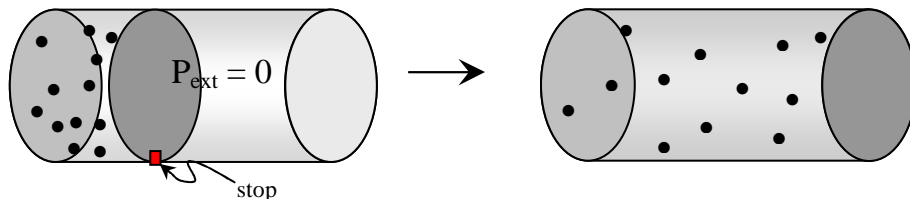


Figure 10.1.2: An isothermal expansion of an ideal gas into a vacuum increases energy dispersal. When the stop is removed, the gas undergoes a free expansion.

Our goal then is to develop a spontaneity criterion for chemical reactions based on our expectations of energy dispersal. As you know from your high school and college General Chemistry courses, this criterion is entropy. You have been working problems on the entropy change for phase transitions and chemical reactions for years. We now specifically want to focus on the careful development of the definition of entropy, so we can better understand the fundamentals of this singularly important concept.

The next four chapters each introduce the definition of entropy from a different perspective. Each chapter is designed to be free standing, so you can choose which approach to use. Each chapter assumes that you have not previously learned about the concept of entropy.

- Chapter 10, this chapter, takes a direct thermodynamic approach based on the development of a new extensive state function that measures energy dispersal. We also introduce the thermodynamic definition of temperature. This chapter is the most general, complete, and probably the most abstract.
- Chapter 11 uses the historical perspective, which is based on the evaluation of the efficiency of cyclic thermal processes. Chapter 11 will be a good starting point if you are interested in energy resource issues. A focus of Chapter 11 is solar energy conversion and other alternative energy sources.
- Chapter 12 takes a molecular point of view by considering statistical measures of energy dispersal. Chapter 12 is valuable if you are interested in structural biology and biochemistry.

- Chapter 13 starts with the statement of the definition of entropy and then develops the understanding and applications of the definition. If you prefer to see applications and practical examples before you jump into the theory, you can start with Chapter 13.

You can read Chapters 10-13 in any order. Your lecturer will probably not cover all these chapters in extensive detail. However, entropy is a tricky concept and having multiple ways of learning about entropy is helpful. Eventually, you will probably want to read all four.

If you are continuing on in this chapter, then, we begin by considering energy dispersal in general and from that understanding we construct the concept of entropy to mirror our observations concerning energy transfer in simple systems.

10.2 Energy is Transferred from a Hotter to a Colder Body

When you heat a pot of water on a stove, the energy from the hot heating element is transferred to the cold water in the form of heat. When you and your friends are gathered around a campfire, the hot burning logs transfer energy, in the form of heat, to everyone standing around the fire. When you touch a hot object, energy is transferred to your fingertips. These observations are so common that we often simply take them for granted. However, these experiences are a universal expectation that we have for all physical processes; energy is transferred from a hotter to a colder body. The transfer of energy from a hotter to a colder object is a spontaneous process. In our experience, the opposite process never happens spontaneously. Energy is never transferred from a colder to a hotter body, without having to do work. The inside of a refrigerator doesn't spontaneously become colder by transferring energy to the surroundings. Such a process wouldn't violate the First Law of thermodynamics, since energy is conserved. However, we know that we need to supply energy to the refrigerator to do the work necessary to cool the refrigerator. For another example, water at room temperature doesn't spontaneously cool to form ice. There is a natural direction for energy flow.

Considering the flow of energy in each of these cases, we note that energy is dispersed from a hot object to colder objects. By dispersed, we mean that the energy in hot objects spreads to colder objects. Energy dispersal is a spontaneous process. This observation is a summary of our experience, and is a qualitative form of the Second Law of thermodynamics. Our goal is to find a general mathematical statement to determine spontaneous heat transfer that holds for all systems and that encapsulates this very simple observation about heat transfer.

Something Is Missing: To find the general statement to determine spontaneous heat transfer, consider heat transfer and PV work for a general closed system. The heat transferred is δq and the internal energy change is:

$$dU = \delta q + \delta w = \delta q - P_{\text{ext}} dV \quad (\text{closed, PV work}) \quad 10.2.1$$

We know that U is a state function, so the change in U will not depend on the path of the process. We can then get a general equation for a process by choosing any path we like. The most convenient path is a reversible process. It doesn't matter what kind of process we choose, but choosing a reversible path gives $P = P_{\text{ext}}$:

$$dU = \delta q_{\text{rev}} + \delta w_{\text{rev}} = \delta q_{\text{rev}} - P dV \quad (\text{reversible, closed, PV work}) \quad 10.2.2$$

Most importantly, by specifying a reversible path, the work term, $-PdV$, only depends on the properties of the system. We don't need any additional information about the pressure change for

the path, we just need the initial and final states. Let's review what we know about heat transfer. We can obtain the heat transferred for a constant volume process from the heat capacity at constant volume, $\delta q_v = C_v dT$. Assuming a constant volume process, then Eq. 10.2.2 reduces to:

$$dU = \delta q_{\text{rev},V} = C_v dT \quad (\text{closed, constant V, PV work}) \quad 10.2.3$$

However, this equation isn't valid if we have a constant pressure process, where $\delta q_p = C_p dT$. So Eq. 10.2.2 doesn't keep track of heat transfer for any general process, without additionally specifying the path. The problem is that reversible heat transfer is still a path function. Internal energy is a state function so it should be independent of the path, but to use Eq. 10.2.2, we still need to specify a specific path. Something is missing.

Another way of seeing our dilemma is to work from the general form of the exact differential. Since U is a state function, considering U as a function of T and V , the total differential is:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (\text{closed, PV work}) \quad 10.2.4$$

Using the definition of the constant volume heat capacity:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \quad (\text{constant V}) \quad 10.2.5$$

and substituting into Eq. 10.2.4 gives:

$$dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (\text{closed, PV work}) \quad 10.2.6$$

This equation is still not what we are looking for, because we don't know what $(\partial U/\partial V)_T$ is. The last term can't be just $-PdV$, since $-PdV$ is only the reversible work done against an external force. $(\partial U/\partial V)_T$ includes all changes in the internal energy for a given volume change, which include forces between molecules. Intermolecular forces are strong for liquids, solids, and solutions. Also, the heat capacity appears in the equation, and the heat capacity in general is a path function. Something is missing. We still haven't gotten a completely general description of our system. We need a better way of describing reversible heat transfer for a general process.

Energy is transferred from a Hotter to a Colder Body: Eq. 10.2.6 shows that T and V don't work out well as the independent variables to describe a system in the most general case. However, Eq. 10.2.2 still looks like it might be a good place to start. We need to find a new variable that allows us to predict the direction of reversible heat transfer. We want this new variable to measure energy dispersal. For the lack of a better symbol, choose S to represent this new variable. We want S to be a state function, so it is independent of the path of the process. We should be able to express the total differential of the internal energy in the form of Eq. 7.11.13 with S and V chosen as the independent variables, $U(S,V)$, since U is a state function:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad (\text{closed, PV work}) \quad 10.2.7$$

If our new variable S works out, it will be really fortunate since all the tricks that we learned in the last chapter for exact differentials will work for the new equation and we will be able to predict the outcome for processes where energy is transferred in the form of heat and work. For example, if $dV = 0$ then no work will be done, alternatively if $dS = 0$, no reversible heat will be

transferred. To find out more about our new variable, S , we first need to establish the sign convention. If the system transfers heat to the surroundings, $\dot{dq}_{\text{rev}} < 0$, and then we choose the sign convention so that $dS < 0$ as well. Having \dot{dq}_{rev} and dS have the same sign make it easier to keep track of the direction of energy transfer. The big difference between \dot{dq}_{rev} and dS is that dS will be a state function, which is independent of the path. To learn more about dS we need to consider a typical general process. We need to consider a hotter system and a colder system so that we can monitor the direction of energy transfer and the corresponding change in S .

A simple model for considering energy transfer is to consider two blocks of metal labeled A and B as an isolated system, Figure 10.2.1. We consider the two blocks as an isolated system, so that the only transfers of energy are between the two blocks. We then allow energy transfer from the hotter block to the colder block in a reversible process.

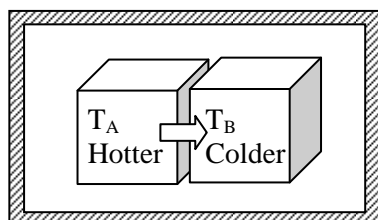


Figure 10.2.1: Energy transfer in the form of heat from a hotter to a colder body. The system is isolated from the surroundings, so no energy is exchanged with the surroundings.

However, to keep the transfer reversible, we set the temperature T_A just slightly higher than T_B . If we can understand this simple system, then we can understand all heat transfer processes. The heat flow for block A is $\dot{dq}_{A,\text{rev}}$ and the energy change for block A is dU_A , and similarly for block B. The thermal energy transferred for A and B is necessarily equal in magnitude but opposite in sign, $\dot{dq}_{B,\text{rev}} = -\dot{dq}_{A,\text{rev}}$. The change in internal energy from Eq. 10.2.2 for the two blocks is:

$$dU_A = \dot{dq}_{A,\text{rev}} + \dot{dw}_{A,\text{rev}} = \dot{dq}_{A,\text{rev}} - P dV_A \quad (\text{closed, PV work}) \quad 10.2.8$$

$$dU_B = \dot{dq}_{B,\text{rev}} + \dot{dw}_{B,\text{rev}} = \dot{dq}_{B,\text{rev}} - P dV_B \quad (\text{closed, PV work}) \quad 10.2.9$$

Internal energy is conserved for this isolated overall process and $dU_{\text{tot}} = dU_A + dU_B = 0$. These equations hold for heat transfer in either direction: both $\dot{dq}_{A,\text{rev}} > 0$ and $\dot{dq}_{A,\text{rev}} < 0$ conserve energy. However, assume block A is hotter than block B. Based on our experience, the spontaneous direction for energy dispersal is for the hotter block to transfer heat to the colder block so that $\dot{dq}_{\text{rev},A} < 0$. Comparing Eqs. 10.2.8 and 10.2.9 with Eq. 10.2.7 for each block, term by term, we find that:

$$-P dV_A = \left(\frac{\partial U_A}{\partial V_A} \right)_S dV_A \quad -P dV_B = \left(\frac{\partial U_B}{\partial V_B} \right)_S dV_B \quad (\text{closed}) \quad 10.2.10$$

which leaves the remaining term for each block:

$$\dot{dq}_{A,\text{rev}} = \left(\frac{\partial U_A}{\partial S_A} \right)_V dS_A \quad \dot{dq}_{B,\text{rev}} = \left(\frac{\partial U_B}{\partial S_B} \right)_V dS_B \quad (\text{closed}) \quad 10.2.11$$

Eqs. 10.2.11 for the reversible heat flow are particularly interesting. Notice the signs for $(\partial U/\partial S)_V$ and dS in Eq. 10.2.11. Heat is transferred into block B giving $\dot{dq}_{B,\text{rev}} > 0$, $dS_B > 0$, and the internal energy increases, $dU_B > 0$. The ratio of the changes, $(\partial U_B/\partial S_B)_V$, is positive. On the

other hand, for block A heat is transferred out, $\delta q_{A,\text{rev}} < 0$, $dS_A < 0$, and the internal energy decreases, $dU_A < 0$. However, $(\partial U_A / \partial S_A)_V$ is still positive, since it is the ratio of two negative numbers. So the partial derivative $(\partial U / \partial S)_V$ is always positive. However, what is $(\partial U / \partial S)_V$? To make things easier, assume that the volume change of the blocks is negligible so that $dV_A = 0$ and $dV_B = 0$, then for the total internal energy applying Eq. 10.2.7 for each block:

$$dU_{\text{tot}} = dU_A + dU_B = \left(\frac{\partial U_A}{\partial S_A}\right)_V dS_A + \left(\frac{\partial U_B}{\partial S_B}\right)_V dS_B = 0 \quad (\text{isolated, cst. } V_A \& V_B) \quad 10.2.12$$

The sum is equal to zero because of conservation of energy. But, if S shows the direction for energy dispersal as we require, then the sum of the overall change in S should be positive for the spontaneous process:

$$dS_A + dS_B > 0 \quad (\text{isolated, spontaneous}) \quad 10.2.13$$

showing an increase in energy dispersal. Comparing the two changes by subtracting dS_A from both sides of Eq. 10.2.13:

$$dS_B > -dS_A \quad \text{or equivalently} \quad -dS_A < dS_B \quad (\text{isolated, spontaneous}) \quad 10.2.14$$

Note since system A is losing reversible heat, $dS_A < 0$, so that $-dS_A$ is a positive number. In the comparison, $-dS_A < dS_B$, we are comparing two positive numbers; the magnitude of the change for A is smaller than the magnitude for the change in B. Summarizing these relationships, if the overall change in S is to be positive for the dispersal of energy, then the change in the magnitude of S for the hotter block is less than the change for the colder block. However, if $-dS_A < dS_B$, the sum for the internal energy in Eq. 10.2.12 still must equal zero showing that:

$$\left(\frac{\partial U_A}{\partial S_A}\right)_V > \left(\frac{\partial U_B}{\partial S_B}\right)_V \quad (\text{isolated, spontaneous}) \quad 10.2.15$$

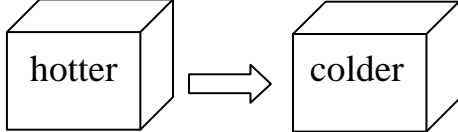
In other words, if the magnitude of dS_A is smaller, the coefficient in front of dS_A must be larger so that the two terms for A and B cancel. This last inequality, Eq. 10.2.15, is just what we would expect for the temperatures of the two bodies. Thermodynamic temperatures are positive as are these partial derivatives. We also assumed that block A was hotter than block B at the beginning, which is the result that we see for the partial derivatives in Eq. 10.2.15. Now let's line up all the changes, Figure 10.2.2.

If we define the **temperature** as the change in internal energy with a change in S, at constant volume:

$$\left(\frac{\partial U}{\partial S}\right)_V \equiv T \quad 10.2.16$$

then our equations result in an increase in S for the transfer of heat from the hotter to the colder body. This definition is important because it determines the temperature of the system using properties of the system that are independent of the equation of state. Our new variable S is making sense as a measure of energy dispersal. S is called the **entropy**. Substitution of the definition of temperature in terms of the partial derivative back into Eq. 10.2.11 gives in general:

$$\delta q_{\text{rev}} = T dS \quad (\text{closed}) \quad 10.2.17$$



$$\dot{d}q_{A,\text{rev}} = -\dot{d}q_{B,\text{rev}}$$

$dU_{\text{tot}} = dU_A + dU_B = 0$	(isolated)
$dS_{\text{tot}} = dS_A + dS_B > 0$	(isolated, spontaneous)
$dS_A < 0$	(energy dispersal)
$dS_B > 0$	(energy dispersal)
$-dS_A < dS_B$	(isolated, spontaneous)
$\left(\frac{\partial U_A}{\partial S_A}\right)_V > \left(\frac{\partial U_B}{\partial S_B}\right)_V$	(isolated, spontaneous)
$\parallel \parallel \parallel$ $T_A > T_B$	(by definition)

Figure 10.2.2: Changes for heat transfer from a hotter to a colder body, $T_A > T_B$.

Solving Eq. 10.2.17 for dS gives the definition of the entropy change as:

$$dS \equiv \frac{\dot{d}q_{\text{rev}}}{T} \quad (\text{closed}) \quad 10.2.18$$

This equation is a statement of the Second Law of thermodynamics. Eq. 10.2.18 shows that transfer of thermal energy to a system increases the entropy of the system. Note that the units of entropy are J K^{-1} . Entropy is extensive because heat transfer is extensive. The entropy of 20 mL of water is twice the entropy of 10 mL of water. The following is a quick initial example, which you will remember from General Chemistry, to help make the entropy more concrete.

Example 10.2.1: Phase Transitions

Melting phase transitions at the equilibrium transition temperature remain at constant temperature and are reversible. Melting transitions are reversible since any amount of solid, finite or infinitesimal, may be converted into liquid and any amount of liquid may be converted to solid by additions or withdrawals of heat. At constant pressure, $\dot{d}q_{\text{rev}} = dH$, giving for the constant temperature and pressure phase transition:

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_m} \quad (\text{reversible phase transition at cst. } T_m \text{ and } P) \quad 10.2.19$$

where T_m is the equilibrium melting point and $\Delta_{\text{fus}}H$ is the enthalpy of fusion at the same temperature. The terms melting and fusion are synonymous. Calculate the molar entropy of fusion for methanol at its normal melting point of -97.53°C ; $\Delta_{\text{fus}}H^\circ$ is $3.215 \text{ kJ mol}^{-1}$.

Answer: We need to convert the melting point to absolute temperature, $T_m^\circ = 175.62 \text{ K}$. Then:

$$\Delta_{\text{fus}}S^{\circ} = \frac{\Delta_{\text{fus}}H^{\circ}}{T_{\text{m}}^{\circ}} = \frac{3.215 \text{ kJ mol}^{-1} (1000 \text{ J/kJ})}{175.62 \text{ K}} = 18.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

Notice that entropy changes are often small values compared to enthalpy changes, so that entropies are usually given in units of J K^{-1} , not kJ K^{-1} . See Appendix Data Section Table 8.1.1.

Thermodynamic Definition of Temperature: The empirical definition of temperature established using an ideal gas thermometer is essentially: temperature is the property that is measured by a thermometer. This empirical definition does little to advance our fundamental understanding of the underlying concepts. The thermodynamic definition of temperature, Eq. 10.2.16, is the most direct and fundamental definition of temperature. From this definition flows all of thermodynamics and the predictive power of this most general theory. However, you might be surprised that such a simple concept as temperature has such an abstract foundation. How can something as simple to measure as temperature have such an abstract interpretation? Remember however, that the measurement of temperature is really not direct at all. We associate the measurement of temperature with thermometers. But, what do thermometers measure? Typical thermometers actually measure the change in volume of a working substance like an alcohol, or mercury, or a piece of metal in a bimetallic strip, or ultimately an ideal gas. Thermometers seem so intuitive because the measurements correlate with our tactile concept of hot and cold. Eq. 10.2.15 puts the concept of hotter and colder on a firm quantitative basis that also correlates with our tactile concept of hot and cold. At this point, we should consider our new definition of temperature so that we can judge its validity and become more comfortable with this powerful new concept.

The internal energy of a system gives the ability of a system to transfer energy in the form of heat and work. In other words, the internal energy relates the ability of a system to do useful things. The change in entropy is a measure of energy dispersal. For the definition of temperature, the change in internal energy for a system appears in the numerator of $(\partial U/\partial S)_{\text{v}}$. That is, $(\partial U/\partial S)_{\text{v}}$ gives the ability of a system to do useful things for a given change in entropy. Consider two blocks of metal, each having the same internal energy but one being much larger than the other. Next, assume that we transfer one joule of energy into each block. The change in entropy for this transfer of energy into the smaller block is small. The input energy stays localized in the small system. The same amount of energy transferred into the large block produces a larger change in energy dispersal. The joule of energy “spreads out” more in the larger block. Because the change in entropy is in the denominator of the derivative, $(\partial U/\partial S)_{\text{v}}$, for the same change in internal energy, the smaller block has a larger value for $(\partial U/\partial S)_{\text{v}}$. The input energy in the smaller system has a greater ability to do useful work because the energy is not as dispersed. Since the smaller block has a larger $(\partial U/\partial S)_{\text{v}}$, by the definition of temperature, the smaller block is at higher temperature. The temperature can be thought of as the “quality” of the available energy. A transfer of energy at higher temperature has a greater ability to do useful things.

Let’s put our new concepts together. For thermal energy to be transferred there must be a temperature difference between the two objects. This temperature difference is the temperature gradient. The temperature gradient drives the transfer of thermal energy (please review the discussion on conductive heat flux in the kinetics chapter). The energy dispersal is measured by the change in entropy for the complete system. The balance of any work done and heat transferred is determined by the conservation of energy through $dU = \delta q + \delta w$.

The thermodynamic definition of temperature, through $(\partial U/\partial S)_V \equiv T$, is equivalent to the empirical definition of temperature that is established by the ideal gas thermometer. However, this equivalence is not obvious or straightforward. We will accept, for now, that the two temperature definitions are equivalent and leave the proof to your further reading.

10.3 Entropy, Energy Dispersal, and Internal Degrees of Freedom

There are two general ways of increasing energy dispersal. The one we have focused on to this point is providing greater spatial dispersion. Energy dispersal increases by taking the energy in a localized area and spreading it into a larger area or equivalently taking some energy in one object and splitting it between two objects. Another way to increase energy dispersal is to increase the number of ways that the energy can be absorbed into the system. For example, non-linear molecules have one more rotational axis than linear molecules. Chemical reactions that produce non-linear molecules from linear molecules have a favorable increase in energy dispersal because there are more rotational degrees of freedom that can absorb energy. Transferring energy into low frequency vibrations is another good example of energy dispersal. The potential energy curves for a high frequency and a low frequency vibration are shown in Figure 10.3.1.

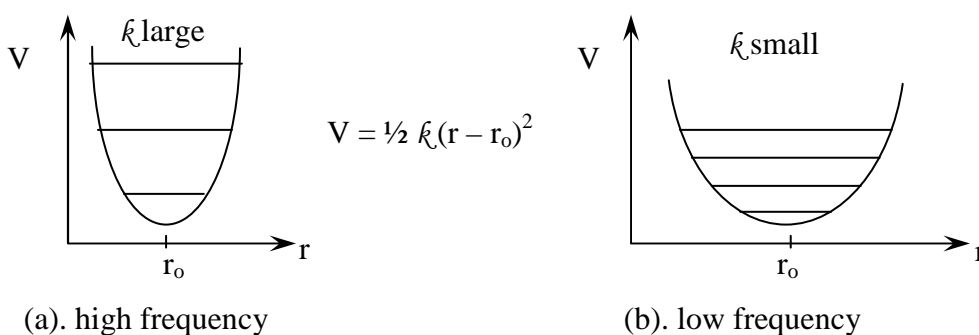


Figure 10.3.1: High frequency vibrations have smaller amplitudes and are harder to excite. Low frequency vibrations contribute more to the entropy of the system.

High frequency vibrations, like very stiff springs, are more difficult to excite than low frequency vibrations. It is easier to transfer energy into low frequency vibrations. Only vibrations with wavenumbers less than 500 cm^{-1} absorb energy at temperatures near room temperature. The greater the number of low frequency vibrations for a system, the greater the number of ways that the system can absorb energy and the greater the energy dispersal. Low frequency vibrations also have larger amplitudes than high frequency vibrations. However, energy dispersal for vibrations is more a function of the degree to which the vibrations may be excited than the increased spatial dispersion through increases in amplitude. Increasing the number of low frequency normal modes increases the number of degrees of freedom that can accept energy, and therefore increases energy dispersal and the entropy.

Example 10.3.1: Protein Folding

When an aqueous solution of a protein is heated above the melting point of the protein, hydrogen bonds in the folded, native structure are disrupted. Above the melting point the protein exists in a random coil geometry. This process is called denaturation. Discuss denaturation from the

perspective of energy dispersal and the change in entropy of the protein. A short segment of alpha-helix is shown in Figure 10.3.2 to illustrate a typical hydrogen-bonding framework.

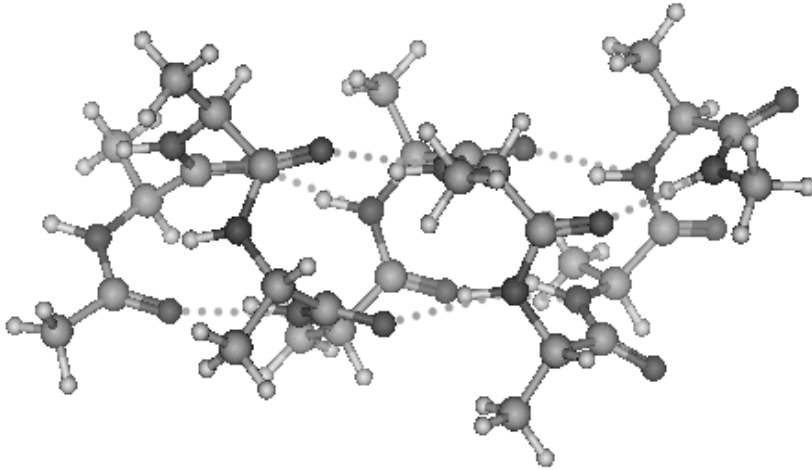


Figure 10.3.2: A short segment of alpha-helical poly-alanylalanine. The hydrogen bonding network that stabilizes the alpha-helix is shown by dotted lines.

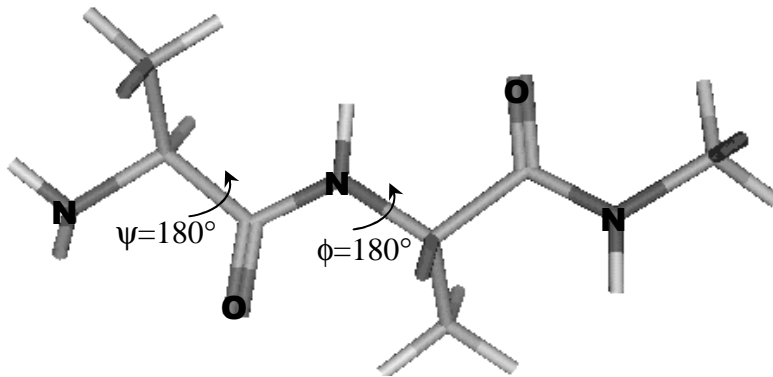


Figure 10.3.3: The backbone dihedral angles in alanylalanine. The peptide is shown in the all-*trans* conformation.

Answer: The backbone dihedral angles for a peptide are shown in Figure 10.3.3. When a protein solution is brought into contact with a hotter object, energy is transferred into the protein solution. When sufficient energy is available, hydrogen bonds are disrupted. The network of backbone hydrogen bonds restricts the motion of the protein. Melting frees the rotation of the backbone dihedrals providing more low frequency torsions and a more open structure. The melting of hydrogen bonds converts high frequency torsions into low frequency torsions, which have higher degrees of excitation and larger amplitudes. This process increases energy dispersal and therefore, the conformational entropy.

However, we should be very careful not to forget the solvent and the tertiary structure of the protein. Globular proteins typically have hydrophobic amino acids on the interior of the folded, native protein and hydrophilic amino acids on the surface. Unfolding exposes the hydrophobic side chains of the amino acids from the interior of the protein to the solvent. On the other hand, the backbone functional groups of amino acids are hydrophilic. Unfolding is aided by favorable

solvation of the backbone functional groups that were interior to the protein. Overall, the change in effective volume of the protein decreases on unfolding, which is surprising. In globular proteins, one big contributor to this decrease is the loss of internal void volume upon denaturation.¹ In summary, conformational entropy is just one component of the total overall change in entropy of denaturation. However, conformational entropy is a good practical example of energy dispersal to help motivate our study of entropy.

10.4 Summary – Looking Ahead

By following the flow of energy for a simple process, we have defined both the temperature of a system and the change in entropy for a process. The concepts of temperature and entropy are deeply intertwined, so understanding one helps us understand the other. We can find a general statement that combines the First and Second Laws of thermodynamics by substituting Eq. 10.2.17 into $dU = \delta q_{\text{rev}} - PdV$, Eq. 10.2.2:

$$dU = TdS - PdV \quad (\text{closed, PV work}) \quad 10.4.1$$

Comparing terms in this last equation with the total differential assuming $U(S,V)$ from Eq. 10.2.7, we find the relationships:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad 10.4.2$$

The temperature relationship is just the definition from Eq. 10.2.16. The pressure relationship is the general form of Eq. 10.2.10. The combined First and Second Laws of thermodynamics, Eq. 10.4.1, will be a central focus as we continue to develop the foundations of thermodynamics. In Chapter 11 and 12 we will find the general relationship between entropy change and spontaneous processes. Chapter 11 presents the arguments that were used historically and also focuses on energy sources for running our society. In Chapter 13 we will also evaluate the entropy change for many different kinds of processes. You may, if you like, skip to Chapter 13 at this point if you would like to see some concrete examples. Using the concepts will build your understanding and also show the utility of entropy for predicting the outcome of different processes, especially chemical reactions. The concept of entropy is the key to understanding chemical reactivity.

10.5 Historical Footnote

There are 30-40 ways of stating the Second Law of thermodynamics. Historically there are three main statements of the definition of entropy. The first was by Rudolph Clausius in 1854.² The Clausius approach is the subject of the next chapter. Ludwig Boltzmann in 1877 and Max Planck in 1900 developed the statistical view of entropy.³⁻⁵ The statistical definition of entropy is presented in Chapter 12. In 1909 Constantin Carathéodory proposed a mathematically rigorous statement of the Second Law:^{6,7}

“In the neighborhood of any prescribed initial state, there are states which cannot be reached by an adiabatic process.”

This approach is the inspiration for the presentation in this chapter. However, the Carathéodory statement is only used tangentially in our discussion. The development of entropy and temperature in this chapter is based on the approach by F. C. Andrews⁸ and H. A. Bent.⁹

Chapter Summary

1. Energy dispersal is a spontaneous process.
2. For a closed system, $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$
3. $\left(\frac{\partial U}{\partial S}\right)_V \equiv T$
4. For a closed system, $\delta q_{\text{rev}} = T dS$
5. For a closed system, $dS \equiv \frac{\delta q_{\text{rev}}}{T}$
6. Entropy is a measure of energy dispersal.
7. The temperature can be thought of as the “quality” of the available energy. A given amount of energy at a higher temperature has a greater ability to do useful things.
8. High frequency vibrations have smaller amplitudes and are harder to excite than low frequency vibrations. Low frequency vibrations contribute to the entropy of the system. Unhindered torsions are examples of low frequency vibrations.

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Further Reading

Entropy:

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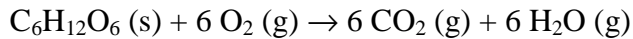
Problems: Entropy, Temperature, and Heat Transfer

1. What is the change in entropy for the system for an adiabatic reversible expansion?
2. Calculate the change in entropy for the isothermal reversible expansion of one mole of an ideal gas from an initial volume of 1.00 m^3 to a final volume of 10.0 m^3 .
3. Evapotranspiration is the process of conversion of liquid water into vapor by the earth's surface. Evapotranspiration is the sum of evaporation and transpiration. Evaporation is the direct vaporization of water from water bodies, plant surfaces, and the soil. Transpiration is the conversion of liquid water into water vapor by movement of water within plants and the subsequent loss of water vapor through stomata in the leaves. Approximately 60% of the energy available from the solar flux in a forest is consumed by evapotranspiration. The solar flux at the equator at midday is about 1000 W m^{-2} . The evaporation of water results in a large increase in entropy in vegetated areas. Evapotranspiration also moderates the surface temperature and maintains the local humidity. To provide a very rough model, consider a flat surface that is heated to the boiling point of water by the sun. Assume that 60% of the solar flux is available for the vaporization of water on this surface. Calculate the rate of the production of entropy from the vaporization of water per second per m^2 at midday at the equator for a forest. The enthalpy of vaporization of water at the normal boiling point is $\Delta_{\text{vap}}H = 40.7 \text{ kJ mol}^{-1}$.
4. The following is a common student question concerning temperature as a measure of the "quality" of the energy in a system. Answer the student's question.

"The higher the temperature of a substance (for example a gas) the higher the quality of the energy in the system to do useful work. But at the same high temperature, the system has high entropy as well, which accounts for energy dispersal and hence less availability of the energy. How is the concept of temperature as a measure of quality and the concept of entropy consistent?"
5. A hot cup of coffee has a temperature of $60\text{-}70^\circ\text{C}$ and a mass of 250 g . Calculate the change in entropy for $250. \text{ g}$ of water when the temperature is increased from 25.0°C to 60.0°C at constant pressure. Assume a constant heat capacity of $4.18 \text{ J K}^{-1} \text{ g}^{-1}$. [Hint: Remember that at constant pressure $dH = C_p dT$ and then you need to integrate the definition of entropy.]
6. Calculate the change in entropy for the isothermal reversible expansion of an ideal gas from an initial volume of V_1 to a final volume of V_2 . This is the same problem as Problem 2. However,

this time, approach the derivation using the combined First and Second Laws of thermodynamics, Eq. 10.4.1. Solve for the change in entropy using Eq. 10.4.1 and then make substitutions appropriate for an isothermal reversible expansion of an ideal gas.

7. Use the concept of energy dispersal to discuss the specific changes in entropy for the combustion of one mole of glucose:



where the water is produced as a gas at high temperature. Do you expect this reaction to be spontaneous?

8. Show that $\left(\frac{\partial S}{\partial V}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V = \frac{P}{T}$

9. Considering that $S(U, V)$, find the total differential of S . From the total differential and the relationship in Problem 8, show that:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

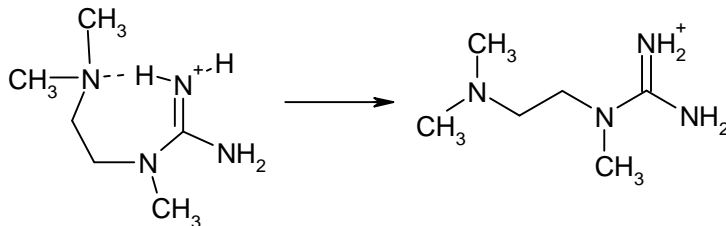
10. We will find that $dH = T dS + V dP$. (see Problem 12) Find the total differential of H assuming that $H(S, P)$. Then determine the values for:

$$\left(\frac{\partial H}{\partial S}\right)_P \text{ and } \left(\frac{\partial H}{\partial P}\right)_S$$

11. Prove that $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$

12. Using the combined First and Second Laws, $dU = T dS - P dV$, and the definition of enthalpy, $H \equiv U + PV$, show that $dH = T dS + V dP$.

13. The N-[2-(dimethylamino)ethyl]-N-methylguanidinium ion has a strong intramolecular hydrogen bond. Describe the change in entropy when this ion is heated sufficiently to break the hydrogen bond.



14. Describe the potential of using the oceans of the world as a source of thermal energy. Explicitly consider changes in the internal energy and entropy of the oceans and extraction of energy from the oceans to do useful work.