## **Chapter 13: Entropy and Applications**

Hydrogen is a clean burning fuel that decreases the local pollution of hydrogen-powered automobiles. However, hydrogen is a secondary fuel; it must be produced using other energy sources. The reaction for the production of hydrogen using water as a cheap starting material is:

 $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ Calculate the entropy change for the system, surroundings, and the total for the production of one mole of  $H_2(g)$ .

Entropy is one of the most useful concepts that we can use to study chemical processes. In this chapter we define the entropy change for a process and carefully develop the relationship between entropy and spontaneous, irreversible processes. We then apply the definition of entropy to simple processes, phase transitions, and chemical reactions. To determine the entropy change for chemical reactions, we introduce the Third Law of thermodynamics.

## 13.1 Entropy and Spontaneous, Irreversible Processes

*Definition of Entropy*: Energy in the form of heat is transferred from a hotter body to a colder body. This transfer of energy corresponds to dispersal, or spreading out, of the available energy. Energy dispersal is a spontaneous process. This observation is a summary of our experience, and is a form of the Second Law of thermodynamics. The dispersal of energy governs all spontaneous processes including chemical reactions. Energy dispersal is measured by the **entropy** change for a process, dS. The definition of the entropy change for an infinitesimal process at temperature T for a closed system is:

$$dS = \frac{dq_{rev}}{T}$$
 (closed) 13.1.1

This equation shows that transfer of thermal energy to a system increases the entropy of the system. Entropy is an extensive property. The units of entropy are J K<sup>-1</sup>. In older texts you may find the entropy given in cal K<sup>-1</sup>. Remember that 1 cal = 4.184 J to convert from the older units. In addition, 1 cal K<sup>-1</sup> is often called 1 eu, where eu stands for "entropy unit." To show the utility of the concept of entropy we need to prove that entropy always increases for a spontaneous process in an isolated system. We begin by taking a closer look at the definition of entropy.

*Entropy and Temperature*: Consider the definition of entropy. Why does temperature occur in the definition of entropy and why is the temperature in the denominator of the expression? Consider, first, a process at constant volume. The temperature is a measure of the internal energy of the system through  $dU = C_v dT$ . A hotter system has higher energy. A hot system becomes hot because of heat transfer to the system, so through Eq. 13.1.1 a hot system must also have higher entropy. So T, dU, and dS all increase together. The temperature can be taken as representative of all three system properties. The temperature can be considered as a measure of the entropy already present in the system. Consider the following analogy.

Let's say you have two friends, one very neat and one very messy. Being a prankster, you want to play a trick on both friends by throwing an old stinky pair of sneakers into both rooms, Figure 13.1.1. When your friends return to their rooms, the neat friend is greatly perturbed, while the

messy friend doesn't even know that you played a prank on them. The neat room is characterized by a small initial entropy and a low initial temperature, and the messy room is characterized by a large initial entropy and a large initial temperature. So for the same transfer, one pair of sneakers, the change in entropy for the neat room is bigger than the messy room. The change in entropy for a given heat transfer is greater for cold initial temperatures:

$$dS_{neat} = \frac{dq_{rev}}{T_{low}} = \frac{one \ pair \ sneakers}{T_{low}} > dS_{messy} = \frac{dq_{rev}}{T_{high}} = \frac{one \ pair \ sneakers}{T_{high}}$$

The effect of the transfer is greater if the transfer takes place at low temperature.



(a) Low temperature: low initial entropy



Figure 13.1.1: The transfer of one pair of sneakers into a neat room produces a bigger change in entropy than the same transfer into a messy room. For  $dS = dq_{rev}/T$ , the transfer,  $dq_{rev}$ , is the same for both rooms. (a) The neat room is characterized by a low temperature, giving low initial entropy. (b) The messy room is characterized by a high temperature, giving high initial entropy.

Analogies can be useful in understanding new topics, but it is also important to note any shortcomings. The objects represent energy packets. This analogy would be improved if the messy items in the rooms were indistinguishable and able to move from place-to-place.

The definition of the entropy shows that reversible heat transfer and entropy changes are directly related. Thermal energy transfer is governed by the First Law. How does entropy relate to the First Law of thermodynamics?

*Combined First and Second Laws of Thermodynamics*: Spontaneous and non-spontaneous processes conserve energy. So, internal energy alone is not sufficient to determine the spontaneous direction for a process. Energy dispersal as measured by entropy changes determines the spontaneous direction. How do energy conservation and energy dispersal interrelate? Consider heat transfer and PV work for a general closed system. The heat transferred is dq and the internal energy change is given by the First Law of thermodynamics:

$$dU = dq + dw = dq - P_{ext} dV$$
 (closed, PV work) 13.1.2

To evaluate the entropy, we need to specify a reversible process. For a reversible process, substituting  $P = P_{ext}$  into Eq. 13.1.2 gives:

$$dU = dq_{rev} + dw_{rev} = dq_{rev} - P dV$$
 (reversible, closed, PV work) 13.1.3

From the definition of the entropy, Eq. 13.1.1, rearranging to find the reversible heat transfer:

$$dq_{rev} = T dS$$
 (closed) 13.1.4

Substituting Eq. 13.1.4 into Eq. 13.1.3 we find:

$$dU = T dS - P dV$$
 (closed, PV work) 13.1.5

This equation combines the First and Second Laws of thermodynamics and is central to the theory and applications of thermodynamics. This equation is also a good source of understanding of the meaning of temperature and entropy. Notice that the TdS term gives the heat transfer and the –PdV term gives the work available from a reversible process. Both terms have the units of energy, joules. Each term is the product of an intensive variable with the change in an extensive variable. The pressure is the force for expansion work, and by analogy we can consider the temperature as the force for heat transfer. To do work, you need a pressure gradient, and to transfer heat you need a temperature gradient. The fact that temperature is the effective force for thermal energy transfer agrees with our original observations that heat is transferred from a hotter to a colder body. The combined First and Second Laws of thermodynamics succinctly combines our knowledge about the flow of energy through consideration of both energy conservation and energy dispersal. This combination provides the key to understanding spontaneous processes.

*Entropy and Spontaneity–The Clausius Inequality*: The entropy change for a process must be evaluated using a reversible process. At first, this requirement may seem to be very restrictive. However, entropy is a state function, which is independent of the path. So as long as we know the initial and final states for an irreversible process, we are free to construct a corresponding reversible process to evaluate the entropy change. The fact that both internal energy and entropy are state functions is the reason why Eq. 13.1.5 is <u>not</u> restricted to reversible processes only. But, you may wonder, how does dq/T compare to  $dq_{rev}/T$ ? How does the real heat transfer for a spontaneous process compare to the reversible heat transfer for the comparable process that matches the initial and final states? This relationship is the key to predicting the spontaneous direction for chemical processes. We can calculate the entropy change for a process from the internal energy change by solving Eq. 13.1.5 for the entropy:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$
 (closed, PV work) 13.1.6

For any process, with PV work only, the internal energy change is given by Eq. 13.1.2, which upon substitution into the last equation gives:

$$dS = \frac{dq}{T} - \frac{P_{ext}}{T} dV + \frac{P}{T} dV$$
 (closed, PV work) 13.1.7

Distributing out dV gives:

$$dS = \frac{dq}{T} + \left(\frac{P - P_{ext}}{T}\right) dV \qquad (closed, PV work) \qquad 13.1.8$$

This equation holds for any closed process with PV work, whether reversible or irreversible. The second term involving P, P<sub>ext</sub> and V relates the pressure of the system, P, to the external pressure, P<sub>ext</sub>. In other words, this term shows the relationship of the system to its surroundings when expansion work is done. The difference in pressure,  $P - P_{ext}$ , is the pressure gradient between the system and the surroundings. This PV term has an important property; it is always positive for a spontaneous process. To see this fact, consider an adiabatic process so that dq = 0. Then assume the pressure of the system is greater than the external pressure. The pressure gradient is then positive,  $P - P_{ext} > 0$ . Our experience shows that the system will expand in a spontaneous process giving dV > 0. The product of  $(P - P_{ext})/T$  and dV is positive. Now, consider a process with the system pressure less than the external pressure,  $P < P_{ext}$ . The system will contract in a spontaneous process giving dV < 0. However, the pressure gradient is also negative,  $P - P_{ext} < 0$ , so the product of  $(P - P_{ext})/T$  and dV is still positive. In either case, the entropy increases for these spontaneous adiabatic processes, dS > 0. On the other hand, if the system pressure and the external pressure are equal, the pressure gradient is zero and the entropy change is zero, dS = 0, for an adiabatic process. With no pressure gradient, the system is at equilibrium and no process occurs. Remember that an equilibrium process is a reversible process. For a reversible adiabatic process, maximal work, in magnitude, is done on expansion and dS = 0. For an irreversible, spontaneous adiabatic expansion less work is done than a reversible process, but then dS > 0.

The second term, involving P,  $P_{ext}$ , and dV, in Eq. 13.1.8 is often called the **lost work** term.<sup>1,2</sup> The PdV portion gives the work done by a reversible process. The  $P_{ext}dV$  portion gives the actual work done by the spontaneous process. The difference,  $PdV - P_{ext}dV$ , is always positive. The difference is the lost work between the reversible and real process. In other words, to "pay" for an increase in entropy, some work is lost.

Now consider a general process in a closed system. Since the lost work term is always positive for an irreversible process, we can then conclude that dS > dq/T, since dropping the lost work term from the equality necessarily decreases the right-hand side of the equation. If the process under study happens to be a reversible process,  $dq = dq_{rev}$  and then  $dS = dq_{rev}/T$ . Putting these two relationships together we have:

$$dS \ge \frac{dq}{T}$$
 > for irreversible process = for reversible process (closed) 13.1.9

This relationship is called the **Clausius inequality**, after Rudolph Clausius who developed the concept of entropy.<sup>3-5</sup> If you have read Chapter 11, you will also remember the development of the Clausius inequality from the perspective of work production from thermodynamic cycles. We began this section by asking how  $dq_{rev}/T$  relates to dq/T. Substitution of the definition of the entropy on the left-hand side of this last equation gives for a spontaneous, irreversible process:

$$\frac{dq_{rev}}{T} > \frac{dq}{T}$$
 (irreversible, closed) 13.1.10

This relationship is quite remarkable, because it shows that for any spontaneous process the reversible heat transfer is always greater than the actual heat transfer, which is not at all obvious. However, the real power of the Clausius inequality is seen when Eqs. 13.1.9 and 13.1.10 are applied to the specific case of an isolated system. For a process in an isolated system dq = 0 and Eq. 13.1.9 reduces to:

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 $dS \ge 0$  > for irreversible process = for reversible process (isolated)13.1.11

Putting this important statement into words we find that:

Entropy always increases for a spontaneous process in an isolated system.

This statement is the most useful form of the **Second Law of thermodynamics**, especially for chemical systems. The requirement of an isolated system may seem to be restrictive. However, many kinds of processes can occur in isolated systems, including chemical reactions. We will shortly see that the specification of an isolated system is not at all restrictive for closed systems.

Let's recap our progress. We began by defining a new state function, the entropy. The entropy was designed to show the dispersal of energy. However, our goal is to find the criterion for the spontaneous direction for any process, especially chemical reactions. The Clausius inequality applied to an isolated system shows that the entropy is, indeed, a useful criterion. The entropy always increases for a spontaneous process. However, we need to remember the restriction of the Second Law to isolated systems. Thermodynamics is a very practical science. If a new concept is useful, we keep it, and if not we discard it. The guarantee that the entropy will always increase for a spontaneous process in an isolated system is a "signpost" for spontaneous change. In General Chemistry you learned how to calculate the entropy change for phase transitions and chemical reactions. Hopefully now you have a deeper understanding of why entropy is important. Let's move on to some examples.

## 13.2 Applying the Thermodynamic Definition of Entropy

Now that we have motivated the thermodynamic definition of entropy, we need to understand the formulation and justify the definition by applying the concept to a variety of chemical problems. Thermodynamics is based on the ability of concepts to clarify our understanding of physical processes and to predict the behavior of systems. First, we look for a deeper understanding of the concept of entropy and its definition.

Entropy and the Ideal Gas for Closed Systems: Let's first consider ideal gas expansions to see if we can get a feel for entropy changes for simple processes. The easiest process to start with is an isothermal reversible expansion. For an isothermal expansion of an ideal gas, dH = dU = 0 and dq = -dw. Consider a closed system for a change in volume from V<sub>1</sub> to V<sub>2</sub>. For a reversible isothermal ideal gas expansion,  $P = P_{ext}$ ,  $dw_{rev} = -PdV$ , and  $w_{rev} = -nRT \ln(V_2/V_1)$  giving the reversible heat transfer as:

$$q_{rev} = nRT \ln \frac{V_2}{V_1}$$
 (isothermal reversible, closed, ideal gas) 13.2.1°

From the definition of the entropy, Eq. 13.1.1, for a constant temperature process:

$$\int_{S_1}^{S_2} dS = \frac{1}{T} \int dq_{rev} \qquad (isothermal reversible, closed) \qquad 13.2.2$$

Entropy is a state function so that integration with respect to dS gives:

$$\Delta S = \frac{q_{rev}}{T}$$
 (isothermal reversible, closed) 13.2.3

We need to use a reversible process to evaluate  $\Delta S$ . Eq. 13.2.3 is <u>only applicable</u> for isothermal reversible processes. Substituting Eq. 13.2.1° into Eq. 13.2.3 gives the entropy change for an isothermal reversible expansion of an ideal gas:

$$\Delta S = nR \ln \frac{V_2}{V_1}$$
 (isothermal, closed, ideal gas) 13.2.4°

What happens if the expansion is not reversible? Since entropy is a state function, the change in entropy is independent of the path. We can choose any path we like between the same starting and ending points. For an irreversible isothermal expansion from  $V_1$  to  $V_2$ , we just choose to evaluate the entropy using an equivalent reversible expansion from  $V_1$  to  $V_2$ . Therefore, Eq. 13.2.4° holds for any isothermal expansion of an ideal gas, reversible or not.

For more general processes with changes in temperature, using  $dU = dq + dw = dq_{rev} - PdV$  for a reversible process and solving for the reversible heat transfer:

$$dq_{rev} = dU + PdV$$
 (reversible) 13.2.5

Remember that  $dU = C_v dT$  for all processes for an ideal gas. Therefore, substituting  $dU = C_v dT$  into Eq. 13.2.5 holds for all processes for an ideal gas:

$$dq_{rev} = C_v dT + P dV$$
 (reversible, closed, ideal gas) 13.2.6°

The entropy change for any process in an ideal gas is given by dividing the last equation by T:

$$dS = \frac{dq_{rev}}{T} = \frac{C_v}{T} dT + \frac{P}{T} dV$$
 (reversible, closed, ideal gas) 13.2.7°

We can solve the ideal gas equation of state for the second term, P/T = nR/V:

$$dS = \frac{dq_{rev}}{T} = \frac{C_v}{T} dT + \frac{nR}{V} dV$$
 (reversible, closed, ideal gas) 13.2.8°

For a process that has a reversible change in volume from  $V_1$  to  $V_2$  and a change in temperature from  $T_1$  to  $T_2$ :

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT + \int_{V_1}^{V_2} \frac{nR}{V} dV \qquad (closed, ideal gas) \qquad 13.2.9^{\circ}$$

Assuming that the heat capacity is constant over the temperature range gives:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \qquad (cst. C_v, closed, ideal gas) \quad 13.2.10^{\circ}$$

This last equation holds for any process in an ideal gas, reversible or not, since entropy is a state function. Notice that specifically for an isothermal process, Eq. 13.2.10° reduces to Eq. 13.2.4°.

Eq. 13.2.9° is handy if you know the change in volume for a process. However, if you are given the change in pressure instead, you can work through the enthalpy,  $H \equiv U+PV$ , and substituting in  $dU = dq_{rev} - PdV$ :

$$dH = dU + PdV + VdP = dq_{rev} - PdV + PdV + VdP$$

(closed, reversible, PV work) 13.2.11

Cancelling terms and solving for dq<sub>rev</sub>:

$$dq_{rev} = dH - VdP$$
 (closed, reversible, PV work) 13.2.12

For an ideal gas,  $dH = C_p dT$  holds for any process in a closed system and substitution into the last equation gives:

$$dq_{rev} = C_p dT - VdP$$
 (closed, reversible, PV work, ideal gas) 13.2.13°

Dividing by T gives the entropy change and using the ideal gas equation of state for V/T = nR/P gives:

$$dS = C_p \frac{dT}{T} - \frac{nR}{P} dP \qquad (closed, PV work, ideal gas) \quad 13.2.14^{\circ}$$

Once again, this last equation holds for irreversible and reversible processes, since entropy is a state function. All we need to specify is the initial and final states for the system. Integrating Eq.  $13.2.14^{\circ}$  gives the analogous expression to Eq.  $13.2.9^{\circ}$ :

$$\Delta S = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} \qquad (cst. C_p, closed, PV work, ideal gas) \quad 13.2.15^{\circ}$$

Either Eq. 13.2.10° or 13.2.15° may be used for any closed process for an ideal gas, with PV-work only.

#### **Example** 13.2.1:

Calculate the change in entropy for one mole of a monatomic ideal gas for a process that doubles (a) the temperature at constant V, (b) the volume at constant T, (c) the temperature at constant P, and (d) the pressure at constant T.

Answer: For one mole ideal monatomic gas:

$$C_v = \frac{3}{2} nR = 12.5 \text{ J K}^{-1}$$
, and  $C_p = C_v + nR = 20.8 \text{ J K}^{-1}$ .

Using Eq. 13.2.10°:

(a) double T at cst.V,  $\Delta S = (12.5 \text{ J K}^{-1}) \ln 2 = 8.6 \text{ J K}^{-1}$ (b) double V at cst. T,  $\Delta S = (8.314 \text{ J K}^{-1}) \ln 2 = 5.8 \text{ J K}^{-1}$ 

Using Eq. 13.2.15°:

(c) double T at cst. P ,  $\Delta S = (20.8 \text{ J K}^{-1}) \ln 2 = 14.4 \text{ J K}^{-1}$ (d) double P at cst. T ,  $\Delta S = -(8.314 \text{ J K}^{-1}) \ln 2 = -5.8 \text{ J K}^{-1}$ 

Notice that entropy changes are typically in the J  $K^{-1}$  range, while internal energies and enthalpies are often in the kJ range. Therefore, we almost always report entropies in J  $K^{-1}$  and internal energy and enthalpies in kJ. Notice also that doubling the temperature or doubling the volume has about the same effect on the entropy. Doubling the pressure has a negative change in entropy because the system volume correspondingly decreases by a factor of two.

*Temperature as an Integrating Factor*: We are now in a position to learn more about the definition of entropy by using an ideal gas as a model. Let's revisit the isothermal expansion of

an ideal gas problem from Section 9.4, Figure 9.3.1. We showed that enthalpy was a state function for the two paths specified. Path 1 is a single step isothermal reversible process. Path 2 is a two-step process, the first step at constant P and the second step at constant V. Figure 9.3.1 is repeated below as Figure 13.2.2. Assume that both steps for path 2 are done reversibly.



Figure 13.2.2: An isothermal process from  $V_1$ ,  $P_1$  to  $V_2$ ,  $P_2$  can be done by two different paths. Path 1 is an isothermal reversible process, and Path 2 is a constant pressure step followed by a constant volume step.

While  $\Delta U$  and  $\Delta H$  are state functions, the heat transferred is path dependent. To show the path dependence, consider path 1. The heat transfer for this isothermal reversible path is given by Eq. 13.2.1°,  $q_{rev} = nRT \ln(V_2/V_1)$ . For path 2, assume the intermediate state is at temperature  $T_i$ . The heat transfer for step 1 is then given by Eq. 13.2.6° at constant pressure P<sub>1</sub>:

 $dq_{rev,1} = C_v dT + P_1 dV$  (cst. P, reversible, closed, ideal gas) 13.2.16°

and integrating from the initial temperature T to the intermediate temperature  $T_i$  assuming a constant heat capacity:

$$q_{rev,1} = C_v (T_i - T) + P_1 (V_2 - V_1)$$
 (cst. P & C<sub>v</sub>, reversible, closed, ideal gas) 13.2.17°

The second step is at constant volume, so Eq. 13.2.6° reduces to:

$$dq_{rev,2} = C_v dT$$
 (cst. V, reversible, closed, ideal gas) 13.2.18°

and integrating from the intermediate temperature back to the initial temperature gives:

$$q_{rev,2} = C_v (T - T_i)$$
 (cst. V &  $C_v$ , reversible, ideal gas) 13.2.19<sup>c</sup>

The total heat transferred for path 2 is the sum for the two steps from Eqs. 13.2.17° and 19°:

$$q_{rev} = C_v (T_i - T) + P_1 \Delta V + C_v (T - T_i)$$
 (cst. C<sub>v</sub>, reversible, ideal gas) 13.2.20°

The temperature dependent terms cancel giving:

$$q_{rev} = P_1 \Delta V$$
 (ideal gas) 13.2.21°

Comparing Eq. 13.2.1° for the isothermal process to Eq. 13.2.21° shows the heat transferred is different for the two paths, even though both paths are reversible. As we have mentioned many times,  $\Delta U$  and  $\Delta H$  are independent of the path, while heat and work transfer are path dependent.

Now consider the <u>entropy</u> change for the two paths. If entropy is a state function,  $\Delta S$  should be the same for both paths, even though the heat transfers differ. For isothermal reversible path 1 the entropy change, using Eq. 13.2.4°, is  $\Delta S = nR \ln (V_2/V_1)$ . For path 2, we need to calculate the entropy change for each step and then add. For the first step from Eq. 13.2.10°:

$$\Delta S_1 = C_v \ln \frac{T_i}{T} + nR \ln \frac{V_2}{V_1} \qquad (cst. P \& C_v, closed, ideal gas) \quad 13.2.22^\circ$$

For the second step at constant volume, applying Eq.  $13.2.10^{\circ}$  from T<sub>i</sub> to back to the original temperature T, gives:

$$\Delta S_2 = C_v \ln \frac{T}{T_i} \qquad (cst. V \& C_v, reversible, closed) \qquad 13.2.23$$

The total change in entropy for path 2 is the sum of the last two equations:

$$\Delta S = \Delta S_1 + \Delta S_2 = C_v \ln \frac{T_i}{T} + nR \ln \frac{V_2}{V_1} + C_v \ln \frac{T}{T_i} \qquad (cst. C_v, closed, ideal gas) \quad 13.2.24^{\circ}$$

The temperature dependent terms cancel to give:

$$\Delta S = nR \ln \frac{V_2}{V_1}$$
 (closed, ideal gas) 13.2.25°

This equation is the same result as for isothermal path 1, showing that entropy is independent of the path. The trick lies in the division of  $dq_{rev}$  by T in Eq. 13.2.3 and 13.2.7°. The temperature is called an **integrating factor**. Even though  $dq_{rev}$  is a path function,  $dq_{rev}/T$  is a state function, independent of the path. The definition of  $dS = dq_{rev}/T$  is then seen to be necessary to make the entropy a state function. The advantage, of course, is that we no longer need to know the details of the actual path of a process. The equations that we derive hold for irreversible as well as reversible paths, even though we need a reversible path to actually evaluate the entropy change.

The original definition of entropy by Rudolf Clausius was based on a careful analysis of the Carnot cycle (see Chapter 11) with the additional realization that 1/T served as an integrating factor for heat transfer.<sup>6,7</sup> The role of 1/T as an integrating factor played a critical role in the foundations of thermodynamics.

*General System at Constant Volume or Pressure*: What about changes in entropy for real gases, liquids, and solids? For a constant volume process for any system, not just ideal gases,  $dU = C_v dT$  and Eq. 13.2.5 becomes:

$$dq_{rev} = C_v dT$$
 (cst. V, closed) 13.2.26

The entropy change is then:

$$dS = \frac{dq_{rev}}{T} = \frac{C_v}{T} dT \qquad (cst. V, closed) \qquad 13.2.27$$

For a change in temperature from  $T_1$  to  $T_2$ :

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT \qquad (cst. V, closed) \qquad 13.2.28$$

Assuming that the heat capacity is constant over the temperature range gives:

$$\Delta \mathbf{S} = \mathbf{C}_{\mathbf{v}} \ln \frac{\mathbf{T}_2}{\mathbf{T}_1} \qquad (\text{cst. V \& C_{\mathbf{v}}, \text{closed}}) \qquad 13.2.29$$

which is the same as we derived for an ideal gas at constant volume, as expected. For a constant pressure process for any system,  $dH = C_p dT$  and Eq. 13.2.12 reduces to:

$$dq_{rev} = C_p dT$$
 (cst. P, closed) 13.2.30

The entropy change is then:

$$dS = \frac{dq_{rev}}{T} = \frac{C_p}{T} dT \qquad (cst. P, closed) \qquad 13.2.31$$

Integrating at constant pressure gives:

$$\Delta S = \int \frac{C_p}{T} dT \qquad (cst. P, closed) \qquad 13.2.32$$

This integral is very important for determining the absolute entropies for substances, and is often evaluated numerically using experimental heat capacities as a function of temperature. We will return to this equation when we discuss the Third Law of thermodynamics. However, integrating assuming a constant heat capacity:

$$\Delta S = C_p \ln \frac{T_2}{T_1} \qquad (cst. P \& C_p, closed) \qquad 13.2.33$$

which is the same as we derived for an ideal gas for a constant pressure process.

#### **Example** 13.2.2

Heat capacities have strong temperature dependence for large changes in temperature. Evaluate the change in entropy for a change in temperature from  $T_1$  to  $T_2$  at constant pressure for a substance that has a heat capacity given by  $C_p = a + bT + cT^2$ .

Answer: From Eq. 13.2.33, substituting the heat capacity expression:

$$\Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T} = \int_{T_1}^{T_2} (a + bT + cT^2) \frac{dT}{T} = \int_{T_1}^{T_2} \left(\frac{a}{T} + b + cT\right) dT$$

The power series coefficients are rigorously temperature independent and so factor out in front of the integrals. Integrating term-by-term:

$$\Delta S = a \left[ \ln T \right]_{T_1}^{T_2} + b \left[ T \right]_{T_1}^{T_2} + \frac{c}{2} \left[ T^2 \right]_{T_1}^{T_2}$$
  
$$\Delta S = a \ln \frac{T_2}{T_1} + b \left( T_2 - T_1 \right) + \frac{c}{2} \left( T_2^2 - T_1^2 \right)$$
(cst. P, closed) 13.2.34

Notice that the leading term is the same as we obtained for the case of a constant heat capacity (In other words, if b = c = 0,  $a = C_p$ ). The remaining two terms can be thought of as "correction terms" for the temperature dependence of the heat capacity.

# **13.3 Entropy Changes for Phase Transitions**

*At the Equilibrium Phase Transition Temperature*: A phase transition at the equilibrium phase transition temperature is a reversible process. For examples, melting ice at the normal melting point and boiling water at the normal boiling point are reversible at 1 atm. Phase transitions are also isothermal processes, as long as the two phases are in contact. To show the reversibility, consider the solid to liquid phase transition:

$$H_2O(s) \stackrel{\rightarrow}{\leftarrow} H_2O(l)$$
 (reversible at 273.15 K) 13.3.1

At 273.15 K if a small amount of heat is added to the system, some of the ice melts. If the same small amount of heat is then transferred back out of the system, some ice freezes and the system returns to it original state. Another way to see the reversibility is to note that at 273.15 K and 1 atm the ice and liquid water are in equilibrium. Specifically, if ice and water are held in a well-insulated container, the net amounts of ice and water stay constant, since the system is at equilibrium. We are usually interested in phase transitions at constant pressure. The corresponding heat transfer is the enthalpy change for the process,  $\Delta_{tr}H$ , at the equilibrium phase transition temperature. Then using the definition of entropy from Eq. 13.2.3 for these isothermal reversible processes gives the entropy change for the phase transition,  $\Delta_{tr}S$ , as:

$$\Delta_{\rm tr} S = \frac{\Delta_{\rm tr} H}{T_{\rm tr}}$$
 (reversible phase transition at cst. T<sub>tr</sub> & P) 13.3.2

where  $T_{tr}$  is the equilibrium phase transition temperature at the constant pressure of interest. Eq. 13.3.2 holds for melting, vaporization, and sublimation (any first-order phase transition). For melting transitions, the terms melting and fusion are synonymous:  $\Delta_{fus}S = \Delta_{fus}H/T_{melt} = \Delta_{melt}S = \Delta_{melt}H/T_{melt}$ . For vaporization:  $\Delta_{vap}S = \Delta_{vap}H/T_{b}$ .

# **Example** 13.3.1

Calculate the change in entropy for the solid to liquid phase transition for water. The enthalpy of fusion is  $6.00 \text{ kJ mol}^{-1}$  at 273.15 K.

Answer: Using Eq. 13.3.2 at the normal phase transition temperature:

$$\Delta_{\rm fus} S = \frac{\Delta_{\rm fus} H}{T_{\rm melt}} = \frac{6.00 \times 10^3 \text{J mol}^{-1}}{273.15 \text{ K}} = 22.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

Entropies are almost always given in J K<sup>-1</sup> units rather than kJ K<sup>-1</sup>.

Table 13.3.1 gives some typical results for the entropy of fusion and vaporization. The entropy changes are all positive since the transitions are all endothermic, which agrees with the notion that entropy changes measure the extent of energy dispersal. Liquids are less localized than solids and gases are less localized than liquids. Notice that the entropy of fusion increases with molecular size. This increase is caused by increased intermolecular forces. For example, Van der Waals forces scale with the volume of the molecule. Notice also that the entropy of fusion for

each substance is smaller than the entropy of vaporization. This observation leads to the conclusion that the structure of a liquid is closer to a solid than it is to a gas. Liquids are very "solid-like" with extensive short-range order.

Notice, however, that the entropy of fusion for water is larger than that for  $O_2$ , even though  $O_2$  has a larger molar mass. Why is the entropy of fusion for water greater than  $O_2$ ? The large value of the entropy of vaporization of water is more striking. To further explore the unique behavior of water, Table 13.3.2 lists the entropy of vaporization for molecules with a large range of sizes.

able 15.5.1.	Endopy of Fusion vers	us Endopy of vaporiza
	$\Delta_{\rm f} S (J  {\rm K}^{-1}  {\rm mol}^{-1})$	$\Delta_{\rm vap} S (J K^{-1} mol^{-1})$
He	6.0	19.9
$O_2$	8.17	75.63
$H_2O$	22.0	108.95
$C_6H_6$	38.0	87.19

Table 13.3.1: Entropy of Fusion versus Entropy of Vaporization<sup>8</sup>

Tuble 15.5.2. Entropy of Auponzuton Versus Size					
	$\Delta_{\rm vap} S (J  {\rm mol}^{-1} {\rm K}^{-1})$	$\mathcal{M}(g \text{ mol}^{-1})$			
$H_2S$	87.9	33.08			
Benzene C <sub>6</sub> H <sub>6</sub>	87.19	78.08			
Cyclohexane	85.1	84.16			
Toluene C <sub>7</sub> H <sub>9</sub>	87.30	92.14			
$\text{CCl}_4$	85.8	153.82			
HF	66.94	20.0			
HCl	78.32	36.5			
HBr	84.64	80.9			
HI	87.19	127.9			
NH <sub>3</sub>	97.40	17.00			
$H_2O$	108.95	18.02			
$PH_3$	78.20	32.0			
$H_2S$	87.9	33.08			

Table 13.3.2: Entropy of Vaporization versus Size<sup>8</sup>

The first group of molecules shows that the entropy of vaporization is remarkably constant for a wide range of liquids, with an average value near  $87.3 \text{ J K}^{-1} \text{ mol}^{-1}$  (10.5 R). This generalization is called **Trouton's Rule**. The next group of hydrogen halides shows that very small molecules like HF and also O<sub>2</sub> (Table 13.3.1) and can be exceptions to Trouton's Rule, giving small entropies of vaporization. The next group of second and third period binary hydrides shows that water and to a lesser extent ammonia are also exceptions, with unusually large entropies of vaporization, especially in respect to their small size. The large value for water was historically the first solid evidence for the unusual hydrogen bonding ability of water. Liquids with strong intermolecular hydrogen bonding are called **associated liquids**. Trouton's Rule holds for non-associated liquids.

*Irreversible Phase Transitions*: At 1 atm, above the normal melting point, ice spontaneously melts. Below the normal melting point, liquid water spontaneously freezes. Eq. 13.3.2 only holds

if the phase transition is reversible. How do we calculate the change in entropy for an irreversible phase transition? Entropy is a state function, so entropy changes are independent of the path. We construct a thermodynamic cycle that has the same effect as the irreversible process, but by a series of reversible processes. Consider the irreversible freezing of ice at  $-5^{\circ}$ C. Let the normal melting point be T<sub>1</sub>, where Eq. 13.2.3 holds for the change in entropy. Let T<sub>2</sub> be the temperature of the irreversible process.

$$\Delta_{tr}S_{T1} = \frac{\Delta_{tr}H}{T_{1}}$$

$$T_{1} = 0^{\circ}C \qquad H_{2}O(s) \stackrel{\rightarrow}{\leftarrow} \qquad H_{2}O(l)$$

$$\Delta S = \int_{T_{2}}^{T_{1}} C_{p}^{\text{solid}}/T \, dT \qquad \Delta S = \int_{T_{1}}^{T_{2}} C_{p}^{\text{liq}}/T \, dT$$

$$T_{2} = -5^{\circ}C \qquad H_{2}O(s) \xrightarrow{\rightarrow} \qquad H_{2}O(l) \qquad 13.3.3$$

We first start with solid ice at  $-5^{\circ}$ C, T<sub>2</sub>, and heat it up to the normal melting point, T<sub>1</sub>. We then allow the ice to melt reversibly at T<sub>1</sub> and then cool the liquid water back down to T<sub>2</sub>. The initial and final points are the same, so the entropy change for the three step process is equivalent to the irreversible process at T<sub>2</sub>:

$$\Delta_{tr} S_{T2} = \int_{T_2}^{T_1} \frac{C_p^{\text{solid}}}{T} dT + \Delta_{tr} S_{T1} + \int_{T_1}^{T_2} \frac{C_p^{\text{liq}}}{T} dT$$
13.3.4

Assuming constant heat capacities for this narrow temperature range:

$$\Delta_{tr} S_{T2} = C_p^{\text{solid}} \ln \frac{T_1}{T_2} + \Delta_{tr} S_{T1} + C_p^{\text{liq}} \ln \frac{T_2}{T_1} \qquad (\text{cst } P \& C_p^{\text{solid}}) = 13.3.5$$

Combining the two log terms using  $\ln(T_1/T_2) = -\ln(T_2/T_1)$ :

$$\Delta_{tr} S_{T_2} = \Delta_{tr} S_{T_1} + (C_p^{\ liq} - C_p^{\ solid}) \ln \frac{T_2}{T_1} \qquad (\text{cst } P \& C_p^{\ s}) \qquad 13.3.6$$

Defining the difference in heat capacities as  $(C_p^{liq} - C_p^{solid}) \equiv \Delta_{tr}C_p$  gives the final result:

$$\Delta_{tr} S_{T_2} = \Delta_{tr} S_{T_1} + \Delta_{tr} C_p \ln \frac{T_2}{T_1}$$
 (cst P & C<sub>p</sub>'s ) 13.3.7

Notice if we think of the phase transition as a chemical reaction, then  $\Delta_{tr}C_p$  corresponds to the heat capacities of the products minus the reactants, as is the normal custom for expressing thermodynamic changes for chemical reactions. There is no difference at this fundamental level between phase transitions and chemical reactions; Eqs. 13.3.4-13.3.7 apply to all chemical reactions and phase transitions (first-order).

We commented in Chapter 8 that it is easy and automatic to convert a thermodynamic formula for a simple system to a chemical reaction by inserting the  $\Delta_r$  for every extensive term, which is

general pattern  $\wp 8$ . Starting with Eq. 13.2.33,  $\Delta S = (S_2 - S_1) = C_p \ln(T_2/T_1)$  or equivalently  $S_2 = S_1 + C_p \ln(T_2/T_1)$ , inserting the  $\Delta_r$  for every term gives Eq. 13.3.7.

## 13.4 Absolute Entropies and the Third Law of Thermodynamics

The entropy of a substance is a variable like P, V, and T. As long as we have a suitable reference point, as we do for absolute temperature at  $0 \text{ K} = -273.15^{\circ}\text{C}$ , we can calculate the absolute entropy of a substance at any temperature. In other words, we are not restricted to calculating only changes in S as we are for the thermodynamic potentials,  $\Delta U$  and  $\Delta H$ . The reference point for the entropy is established by the Third Law of thermodynamics:

The absolute entropy of a pure, perfect crystalline substance is zero at absolute zero.

This assignment is reasonable, since at absolute zero there is no quenchable energy so there is no energy to disperse. No quenchable energy means that all molecules are in their lowest energy states. The Third Law is like all laws; it is a summary of our communal experience. As such it cannot be proven. We can however, use the concept repeatedly in a variety of circumstances to verify that the law agrees with our experience. After decades of agreement, we accept the law as a statement of the underlying form of nature.

Once we set  $S_0 \equiv 0$  at 0 K we can calculate the entropy of a substance at any temperature. We use Eq. 13.2.32 for each phase and take into account any phase transitions using Eq. 13.3.2. For example, for a substance that is a gas at the temperature of interest, T:

$$S_{T} = S_{o} + \int_{0}^{T_{melt}} \frac{C_{p}^{solid}}{T} dT + \frac{\Delta_{fus}H}{T_{melt}} + \int_{T_{melt}}^{T_{b}} \frac{C_{p}^{liq}}{T} dT + \frac{\Delta_{vap}H}{T_{b}} + \int_{T_{b}}^{T} \frac{C_{p}^{gas}}{T} dT$$

$$13.4.1$$

where  $T_{melt}$  is the equilibrium melting point of the substance,  $T_b$  is the equilibrium boiling point of the substance at the pressure of interest, and  $S_o \equiv 0$ . Since the temperature ranges for the integrals are so large, the heat capacities are strong functions of temperature and the integrals must be evaluated numerically. A plot of  $C_p/T$  versus T is constructed for the determination of the integrals. A plot of the heat capacity data for benzene is given in Figure 13.4.1a and for  $C_p/T$ in Figure 13.4.1b. The value of each integral is the area under the curve for each phase. Alternatively, the heat capacity data can be fit to power series expansions and the resulting expressions integrated analytically (see the homework problems). Entropies calculated from Eq. 13.4.1 with  $S_o = 0$  are often called Third Law entropies or absolute entropies. There are extensive tabulations of absolute entropies in many reference sources and in the Appendix Data Section.<sup>7</sup>

Many substances have solid-state phase transitions, so the solid-phase portion of the integration in Eq. 13.4.1 is split above and below the phase transition temperature. The entropy change for the phase transition is also added in:

$$\int_{0}^{T_{melt}} \frac{C_p^{solid}}{T} dT \quad \text{is replaced by} \quad \int_{0}^{T_c} \frac{C_p^{stal 1}}{T} dT + \frac{\Delta_{tr}H}{T_c} + \int_{T_c}^{T_{melt}} \frac{C_p^{stal 2}}{T} dT \qquad 13.4.2$$

where  $T_c$  is the solid phase transition temperature and  $C_p^{xtal 1}$  and  $C_p^{xtal 2}$  are the heat capacities for the difference crystalline forms below and above the phase transition, respectively. Solid-state phase transitions often result from a change in crystal structure or a sudden change in the motions of the molecules.



Figure 13.4.1: (a)  $C_p$  for benzene as a function of temperature. (b) The entropy change of each phase is the area under the plot of  $C_p/T$  versus T. The change in entropy for any phase transitions must also be added in.

*Debye Extrapolation*: One experimental difficulty with the calculation of the solid-phase heat capacity integral is that the lowest experimental temperature for many substances is near liquid helium temperature. Because the integrand is  $C_p$  divided by T, the low temperature region is important. The lowest experimental temperature for benzene is 3.79 K with  $C_{p,lowest} = 0.051463 \text{ J K}^{-1} \text{ mol}^{-1}$ . Considering the lattice vibration normal modes of solids, Peter Debye suggested the low temperature heat capacity of solids should be in the form:

$$C_p = AT^3$$
 13.4.3

The value of A is calculated from the lowest available temperature; solving for A:

$$A = \frac{C_{p,lowest}}{T_{lowest}^3} = \frac{0.051463 \text{ J K}^{-1} \text{ mol}^{-1}}{(3.79 \text{ K})^3} = 9.4532 \text{ x} 10^{-4} \text{ J K}^{-4} \text{ mol}^{-1}$$
(cst. P) 13.4.4

The integral up to this temperature is then:

$$\int_{0}^{T_{\text{lowest}}} \frac{C_p^{\text{solid}}}{T} \, \mathrm{d}T = \int_{0}^{T_{\text{lowest}}} \frac{A \, T^3}{T} \, \mathrm{d}T = \frac{A}{3} \left[ T^3 \right]_{0 \, \text{K}}^{T_{\text{lowest}}} = \frac{A}{3} \, T_{\text{lowest}}^3 = \frac{C_{p,\text{lowest}}}{3} \qquad (\text{cst. P}) \quad 13.4.5$$

For benzene this integral is  $AT_{lowest}^3/3 = C_{p,lowest}/3 = 0.01715 \text{ J K}^{-1} \text{ mol}^{-1}$ .

*Absolute Entropies*: A list of typical absolute entropies is given in Table 13.4.1. What generalizations about the entropies of compounds can we extract from this data? The series methane-acetylene-ethane-propane shows that entropies tend to increase with the number of atoms. The results of an approximate normal mode analysis are shown for comparison in Table 13.4.2 to see the relative contributions of translation, rotation, and vibrations to the overall entropy. The change from acetylene to ethylene is primarily due to the fact that acetylene is a linear molecule and ethylene is not. Therefore, ethylene has one more rotational degree of freedom. The increase from ethylene to ethane is in large part caused by the increase in the

number of low frequency vibrational normal modes. Ethane has an unhindered torsion, giving ethane the highest absolute entropy of the C<sub>2</sub> hydrocarbons. Propane has two low frequency torsional modes and a low frequency bending mode. The smaller value of the absolute entropy of cyclopropane compared to propane again shows the influence of low frequency vibrations. Cyclopropane has no freely-rotating C–C bonds. Propane has higher entropy than benzene again primarily because propane has low frequency torsional vibrations. The benzene examples for different phases remind us that gases have higher entropies than liquids, and liquids have higher entropies than solids, which is in large part caused by the  $\Delta_{tr}S$  for the corresponding phase change. Example 10.3.1 applies these factors to the important problem of protein folding.

Formula	Name	$S_{m,298}^{\circ}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
CH <sub>4</sub> (g)	methane	186.16
$C_2H_2(g)$	acetylene	200.94
$C_{2}H_{4}(g)$	ethylene	219.56
$C_{2}H_{6}(g)$	ethane	229.49
$C_{3}H_{6}(g)$	cyclopropane	237.4
$C_{3}H_{8}(g)$	propane	270.3
$C_6H_6(g)$	benzene (g)	269.2
$C_{6}H_{6}(1)$	benzene (l)	173.3

Table 13.4.1: Absolute Entropies for Some Organic Compounds at 298.15 K.<sup>(DS)</sup>

Table 13.4.2: Contributions to the Entropy for Some Organic Compounds at 298.2 K. Normal mode vibrations less than 500 cm<sup>-1</sup> are listed. Torsions are listed in *italics* and bending vibrations are listed in normal font.

Name	Entropy Contributions (J K <sup>-1</sup> mol <sup>-1</sup> )*				Normal modes
	translation	rotation	vibration	total	$\widetilde{\nu} < 500 \text{ cm}^{-1}$
methane	143.3	42.8	0.4	186.6	
acetylene	149.4	45.4	2.7	197.5	
ethylene	150.3	66.4	2.4	219.1	
ethane	151.2	68.1	10.9	230.3	204
cyclopropane	155.4	75.8	4.8	236.0	
propane	156.0	89.0	32.8	277.7	<i>79, 190,</i> 414
benzene (g)	163.1	86.7	19.1	268.9	371, 371

\* Approximations at the semi empirical AM1 level.

*Does the Third Law Really Work*? The Third Law assigns the absolute entropy at 0 K of any pure perfect crystalline substance a value of zero, no matter how simple or complex. The absolute entropy of perfect crystalline helium and perfect crystalline DNA are both zero. Do these assignments agree with the available experimental data? There have been many tests of the Third Law. We will discuss just one, the solid-state phase transition of rhombic elemental sulfur to monoclinic sulfur. At the equilibrium phase transition temperature, 368.5 K, at 1 bar pressure:

 $S_8$  (rhombic)  $\rightarrow S_8$  (monoclinic)

$$\Delta_{\rm tr} {\rm H}^{\circ} = 401.7 \ {\rm J \ mol}^{-1}$$
 (at 368.5 K) 13.4.6

The entropy change for the phase transition of rhombic to monoclinic sulfur at 368.5 K is:

$$\Delta_{tr}S^{\circ} = \Delta_{tr}H^{\circ}/T_{tr} = 1.09 \pm 0.01 \text{ J K}^{-1} \text{ mol}^{-1}$$
 (reversible at 368.5 K) 13.4.7

If the Third Law is correct, the absolute entropy of rhombic and monoclinic sulfur should both be zero at absolute zero, even though the entropies differ at higher temperatures. Therefore, the entropy for the phase transition should be zero at 0 K. Eq. 13.3.4 shows the relationship between the entropy change for a phase transition at two different temperatures. Setting  $T_2$  at 0 K and  $T_1$ = 368.5 K, we can calculate the entropy change at absolute zero using Eq. 13.3.4. Eq. 13.3.4 applied to this solid-state phase transition gives:

$$\Delta_{\rm tr} S_{0\,\rm K} = \int_{0\,\rm K}^{368.5\,\rm K} C_{\rm p}^{\rm rhomb} \frac{\rm dT}{\rm T} + \Delta_{\rm tr} S_{368.5\,\rm K} + \int_{368.5\,\rm K}^{0\,\rm K} C_{\rm p}^{\rm mono} \frac{\rm dT}{\rm T}$$
13.4.8

Integrating the experimental heat capacity data gives:<sup>9,10</sup>

$$\int_{0 \text{ K}}^{368.5 \text{ K}} C_{p}^{\text{ rhomb}} \frac{dT}{T} = 36.86 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$$
 13.4.9

and  $\int_{368.5 \text{ K}}^{0 \text{ K}} C_p^{\text{mono}} \frac{dT}{T} = -37.82 \pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$ 13.4.10

Substitution of Eqs. 13.4.7, 13.4.9, and 13.4.10 into Eq. 13.4.8 gives:

$$\Delta_{\rm tr} S_{0\rm K} = 36.86 + 1.09 - 37.82 \,\rm J \,\rm K^{-1} \,\rm mol^{-1} = 0.15 \pm 0.65 \,\rm J \,\rm K^{-1} \,\rm mol^{-1} \qquad 13.4.11$$

This result is zero to within experimental uncertainty. The absolute entropies of both rhombic and monoclinic sulfur are zero at 0 K. All known experimental tests, based on phase transitions and chemical reactions, have shown the same result for pure, perfect crystalline substances.

Residual Entropies: Not all substances produce perfect crystalline phases at absolute zero. This randomness results from rapid cooling that locks the substance into a metastable state. At very cold temperatures the reorganization kinetics are very slow. This locked-in randomness results in a residual entropy at 0 K. Two examples of systems showing residual entropies are CO and  $N_2O$ . Both are linear molecules with small dipole moments that show only weak tendencies for orientational alignment in the solid, Figure 13.4.2.

	perfect	crystal				orienta	tional ra	ndomne	SS
C≡O	C≡O	C≡O	C≡O		O≡C	C≡O	O≡C	C≡O	O≡C
C≡O	C≡O	C≡O	C≡O		C≡O	C≡O	O≡C	O≡C	C≡O
C≡O	C≡O	C≡O	C≡O		C≡O	O≡C	C≡O	O≡C	C≡O

Figure 13.4.2: The residual entropy for CO is the result of orientational randomness.

We showed in Chapter 12 that the residual entropy in such cases can be approximated by:

$$S_{o} = R \ln w$$
 13.4.12

where w is the number of energetically equivalent ways that the molecules can be arranged in the solid lattice. For C=O and N=N=O, w = 2, and the residual entropy is approximately  $S_0 = (8.314)$ J mol<sup>-1</sup> K<sup>-1</sup>) ln 2 = 5.76 J K<sup>-1</sup> mol<sup>-1</sup>. The experimental residual entropy for CO is 4.7 J K<sup>-1</sup> mol<sup>-1</sup>.

Chemical processes don't usually take place in isolation. Chemical processes usually exchange energy with their surroundings. When a system exchanges energy with its surroundings, the entropy of the system changes and the entropy of the surroundings also change, Figure 13.5.1.



Figure 13.5.1: The system and surroundings taken together are specified as an isolated composite.

The Second Law only applies to isolated systems. However, we can take the system and surroundings together as a composite. If the composite is isolated, the Second Law holds.

The entropy change of the surroundings is easy to calculate. The surroundings are assumed to be large in extent so that the surroundings act as a constant temperature reservoir, at temperature  $T_{surr}$ . All transfers of energy to the surroundings are reversible. This reversibility results because the temperature of the surroundings is unchanged and all transfers of energy are essentially infinitesimal from the perspective of the surroundings. Therefore all transfers of energy leave the surroundings in an equilibrium state. As a consequence,  $dq_{surr} = dq_{rev,surr}$ . The reversibility of the thermal transfer for the surroundings is true for any process in the system, reversible or irreversible. If we assume that the composite of the system and surroundings is isolated,  $dq = -dq_{surr}$ , where dq is the thermal energy transfer of the system. We follow the convention that all changes for the system are listed without subscript, but changes for the surroundings are always given with the "surr" subscript. The entropy change for the surroundings is then given as:

$$dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dq}{T_{surr}}$$
13.5.1

For an isothermal process, if the system is held in contact with the surroundings and the surroundings act as a constant temperature reservoir, the temperature of the system is equal to the temperature of the surroundings,  $T = T_{surr}$ . Then, the entropy change for the surroundings is:

$$dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dq}{T}$$
 (isothermal) 13.5.2

If the process for the system occurs at constant volume, then the heat transfer at constant volume is the internal energy change,  $dq_v = dU$  and then:

$$dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dU}{T}$$
(cst. T&V) 13.5.3

If the process for the system occurs at constant pressure, then the heat transfer at constant pressure is the enthalpy change,  $dq_p = dH$  and then:

$$dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dH}{T}$$
(cst. T&P) 13.5.4

The total entropy change for a process must include the system and the surroundings:

$$dS_{tot} = dS + dS_{surr}$$
 13.5.5

In many respects, the entropy change for the surroundings is just as important as the entropy change for the system. If the system and surroundings encompass the whole of the universe, then  $dS_{tot} = dS_{univ}$ . We often use  $S_{tot}$  and  $S_{univ}$  interchangeably. However, Eq. 13.5.5 holds as well if a composite of the system and surroundings is a small part of the universe and is isolated. The interrelationship of the system and its surroundings is particularly important for chemical reactions.

# **13.6 Entropy Changes for Chemical Reactions**

Once the absolute entropy for a substance is known, it is quite straightforward to calculate entropy changes for chemical reactions; see general pattern  $\partial 8$ . As usual  $\Delta_r S = [\Sigma \text{products}] - [\Sigma \text{reactants}]$  and in terms of the stoichiometric coefficients:

$$\Delta_{\mathbf{r}}\mathbf{S} = \sum \mathbf{v}_{\mathbf{i}} \mathbf{S}_{\mathbf{i}} \tag{cst. T\&P} \qquad 13.6.1$$

where  $S_i$  is the molar absolute entropy for each reactant and product. Extensive tabulations of absolute entropies are available in standard reference sources,<sup>7</sup> your General Chemistry text, and in the data section at the back of this text.

The temperature dependence of the entropy change for chemical reactions is given by Eq. 13.3.4 and 13.3.7 with the change in the heat capacity for the reaction given by:

$$\Delta_{\rm r} C_{\rm p} = \sum v_{\rm i} C_{\rm pi} \qquad (\text{cst. T} \& P) \qquad 13.6.2$$

where  $C_{pi}$  is the molar heat capacity for each reactant and product.

#### **Example** 13.6.1:

Hydrogen is a clean burning fuel that decreases the local pollution of hydrogen-powered automobiles. However, hydrogen is a secondary fuel; it must be produced using other energy sources. The reaction for the production of hydrogen using water as a cheap starting material is:

 $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ Calculate the entropy change for the system, surroundings, and the total for the production of one mole of  $H_2(g)$  under standard conditions and 298.15 K.

Answer: Using the data section, the standard entropies are given as:

	$H_2O(l)$	$\rightarrow$	$H_{2}(g) +$	$\frac{1}{2}O_{2}(g)$
S <sup>o</sup> <sub>1</sub> ,298	69.92		130.574	205.029 J K <sup>-1</sup> mol <sup>-1</sup>

 $\Delta_r S = [\Sigma products] - [\Sigma reactants]$ 

$$\Delta_{\rm r} S = \left[1 \ (130.574 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{1}{2} \ (205.029 \text{ J K}^{-1} \text{ mol}^{-1})\right] - \left[1 \ (69.92 \text{ J K}^{-1} \text{ mol}^{-1})\right] \\ = 163.168 \text{ J K}^{-1} \text{ mol}^{-1}$$

The entropy change for the formation of one mole of  $H_2$  is quite favorable. As is often the case, the reaction entropy is dominated by the change in number of moles of gases. Notice that the reaction is the reverse of the standard formation reaction for water,  $\Delta_r H^\circ = -\Delta_f H^\circ(H_2O) = 285.830 \text{ kJ mol}^{-1}$ . The enthalpy change for the production of  $H_2$  is quite endothermic. At constant pressure and temperature the entropy change for the surroundings is:

$$\Delta S_{surr} = \frac{-\Delta_r H}{T_{surr}} = \frac{-285.830 \text{ kJ mol}^{-1} (1000 \text{ J/1 kJ})}{298.15 \text{ K}} = -958.679 \text{ J K}^{-1} \text{ mol}^{-1}$$

which is unfavorable from the perspective of the surroundings. The total change in entropy is:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 163.168 \text{ J K}^{-1} + (-958.679 \text{ J K}^{-1}) = -795.511 \text{ J K}^{-1} \text{ mol}^{-1}$$

We can treat the combined system and surroundings as isolated. The Second Law holds and the production of  $H_2$  is not spontaneous. Of course the reverse of the reaction, the combustion of  $H_2$  is quite spontaneous, which is why  $H_2$  is such a good fuel. The primary fuel for the space shuttle was liquid  $H_2$ .

### 13.7 Entropy Changes for the System and Surroundings and the Total Entropy Change

The previous example illustrates why it is important to keep track of the entropy change for the system and the surroundings. The last example was for a chemical reaction. How do the entropy changes for the system and surroundings interact to determine the overall total entropy change for the other types of processes that we discussed in this chapter? We specify the composite of the system and the surroundings as isolated, which places important restrictions on the entropy changes based on the Clausius inequality, Eq. 13.1.11. Specifically, Eq. 13.5.5 applies to the composite and dS<sub>tot</sub> = dS + dS<sub>surr</sub>  $\geq$  0. In outline:

• For any <u>reversible</u> processes,  $q = q_{rev}$ , and from the Clausius inequality,  $\Delta S_{tot} = 0$ , giving:

 $\Delta S_{surr} = -\Delta S$ 

(reversible, isolated) 13.7.1

For reversible processes the entropy changes for the system and surroundings cancel.

- For any <u>spontaneous</u> process,  $\Delta S_{tot} = \Delta S + \Delta S_{surr} > 0$ .
- For <u>ideal gases</u>, Eqs. 13.1.6, 13.2.10°, and 13.2.15° hold for any process, reversible or irreversible, since entropy is a state function.
- For any <u>adiabatic</u> process, reversible or irreversible, q = 0, giving  $\Delta S_{surr} = 0$ .
- For <u>adiabatic reversible</u> processes,  $q_{rev} = 0$ , giving  $\Delta S = 0$  and  $\Delta S_{surr} = 0$ .

Example 13.7.1: Isothermal Reversible Expansion for an Ideal Gas

The volume of one mole of an ideal gas changes from 1.00 L to 2.00 L in an isothermal reversible expansion. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: For an isothermal expansion of an ideal gas  $T = T_{surr}$  and also Eq. 13.2.4° gives:  $\Delta S = nR \ln(V_2/V_1) = 1 \mod (8.314 \text{ J K}^{-1} \mod^{-1}) \ln 2 = 5.76 \text{ J K}^{-1}$ 

$$\Delta S_{surr} = -\Delta S = -5.76 \text{ J K}$$
$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$$

Note also that  $\Delta U = \Delta H = 0$  for this example.

# Example 13.7.2: Isothermal Irreversible Expansion of an Ideal Gas

The volume of one mole of an ideal gas changes from 1.00 L to 2.00 L in an isothermal expansion against a constant external pressure of 1.00 bar. The temperature is 298.2 K. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: For an isothermal expansion of an ideal gas  $T = T_{surr}$ . The entropy change for the system is the same as a reversible expansion, Eq. 13.2.4°, since entropy is a state function:

$$\Delta S = nR \ln(V_2/V_1) = 1 \mod (8.314 \text{ J K}^{-1} \mod^{-1}) \ln 2 = 5.76 \text{ J K}^{-1}$$

For the surroundings we use Eq. 13.5.2:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q}{T}$$

Since  $\Delta U = 0$  for an isothermal process in an ideal gas:

$$\begin{split} q &= -w = P_{ext} \, \Delta V = 1.00 x \, 10^5 \, \text{Pa} \, (2.00 \, \text{L} - 1.00 \, \text{L}) (1 \, \text{m}^3 / 1000 \, \text{L}) = 100. \, \text{J} \\ \Delta S_{surr} &= \frac{-q}{T} = -\frac{-100. \, \text{J}}{298.2 \, \text{K}} = -0.335 \, \text{J} \, \text{K}^{-1} \\ \Delta S_{tot} &= \Delta S + \Delta S_{surr} = 5.43 \, \text{J} \, \text{K}^{-1} \end{split}$$

The expansion is spontaneous. Note also that  $\Delta U = \Delta H = 0$  for this example.

## Example 13.7.3: Adiabatic Irreversible Expansion of an Ideal Gas

The volume of one mole of an ideal gas changes from 1.00 L to 2.00 L in an adiabatic expansion against a constant external pressure of 1.00 bar. The initial temperature is 298.2 K. The gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: The temperature <u>and</u> volume change for an adiabatic expansion, so Eq. 13.2.10° must be used. However, the change in temperature must first be calculated from  $\Delta U = w$ , Eq. 9.8.23°:

$$C_{v} (T_{2} - T_{1}) = -P_{ext} (V_{2} - V_{1})$$
(9.8.23°)

For a diatomic gas,  $C_v = 5/2$  nR and:

 $5/2 (1 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (\text{T}_2 - 298.2 \text{ K}) = -1.00 \text{x} 10^5 \text{ Pa} (2.00 \text{ L} - 1.00 \text{ L})(1 \text{ m}^3/1000 \text{ L})$ 20.785 J (T<sub>2</sub> - 298.2 K) = -100. J

Solving for T<sub>2</sub> gives 293.4 K. The entropy change is then:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = (1 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})[5/2 \ln(293.4/298.2) + \ln 2]$$
  
= 3.19 J K<sup>-1</sup>

The change in entropy for the system is smaller than Example 13.7.2 because the temperature drops. Since q = 0, then  $\Delta S_{surr} = 0$  and  $\Delta S_{tot} = \Delta S$ ; the system must have a positive change in entropy to have a spontaneous process, since no contribution is available from the surroundings. Note that  $\Delta U = C_v \Delta T = -100 \text{ J}$  and  $\Delta H = C_p \Delta T = -140 \text{ J}$  for this example.

Table 13.7.1 summarizes the change in entropy for the system and the surroundings for ideal gas expansions. Avoid the temptation to memorize these relationships. Rather, this summary is given to help you make sure that you understand the underlying principles. Try not to refer to this table when you are doing the homework problems.

System	Diagram	Surroundings
Isothermal reversible $T = T_{surr}$ $\Delta S = nR ln \frac{V_2}{V_1}$	$P_{ext} = P$ $T_{surr} = T$ $dq$	$\Delta \mathbf{S}_{\mathrm{surr}} = -\Delta \mathbf{S}$
Isothermal irreversible $T = T_{surr}$ $P_{ext} = cst$ $\Delta S = nR ln \frac{V_2}{V_1}$	$P_{ext} = cst$ $T_{surr} = T$ $dq \leftrightarrow$	$q = -w$ $\Delta S_{surr} = -\frac{P_{ext}\Delta V}{T}$
Adiabatic reversible $\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ $= 0$	$\mathbf{P} \cdot \mathbf{T}$ $\mathbf{P} \cdot \mathbf{T}$ $\mathbf{P} \cdot \mathbf{T}$ $\mathbf{P} \cdot \mathbf{T}$	$\Delta S_{surr} = 0$
$\label{eq:additional} \begin{array}{l} \mbox{Adiabatic irreversible} \\ P_{ext} = cst \\ \Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \\ C_v \left(T_2 - T_1\right) = - P_{ext}(V_2 - V_1) \end{array}$	$P_{ext} = cst$ $P, T$ $dq = 0$	$\Delta S_{surr} = 0$
Constant P = P <sub>ext</sub> $\Delta S = C_p \ln \frac{T_2}{T_1}$ $T_1 \neq T_{surr}$	P, T	$\Delta S_{surr} = \frac{-\Delta H}{T_{surr}} = -\frac{C_{p}\Delta T}{T_{surr}}$

Table 13.7.1: Entropy changes of the System and Surroundings for Ideal Gas Expansions.

#### 13.8 Summary – Looking Ahead

Entropy is a state function and therefore independent of the path of the process. Only the initial and final states need be specified. However, to guarantee that entropy is a state function the entropy is calculated using a reversible path. In addition, in the definition of entropy, the factor of 1/T is a necessary integrating factor to ensure that entropy is a state function. Entropy always increases for a spontaneous process in an isolated system. We treat the system and the surroundings as an isolated composite, so that we can apply the Second Law. The entropy change of the surroundings is just as important as the entropy change of the system; neither indicates spontaneity alone. The entropy change of the surroundings is easy to calculate and is independent of whether the process for the system is reversible or irreversible,  $\Delta S_{surr} = -q/T_{surr.}$  All transfers of energy to the surroundings are reversible, because the surroundings remain at equilibrium. The Second Law clearly delineates the interrelationship of the system to the surroundings. Composite systems are discussed further in Sec. 14.3.

The preceding examples illustrate that there is an intimate relationship among q, w,  $\Delta S$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S_{surr}$ . However, according to the Second Law, it is only  $\Delta S_{tot}$  that determines the spontaneity for a process. Our next goal is to relate the internal energy, enthalpy, and entropy changes for chemical reactions to the spontaneity of the reaction.

#### **Chapter Summary**

- 1. Energy dispersal is a spontaneous process.
- 2. Energy dispersal is measured by the entropy change:  $dS \equiv \frac{dq_{rev}}{T}$
- 3. Entropy is an extensive state function. The entropy change for a process must be evaluated using a reversible process that has the same initial and final state as the real process.
- 4. For a closed system with PV work the combined First and Second Laws give:
- dU = T dS P dV
- 5. For a closed system with PV work:  $dS = \frac{1}{T} dU + \frac{P}{T} dV$
- 6. For a closed system with PV work:  $dS = \frac{dq}{T} + \left(\frac{P P_{ext}}{T}\right) dV$
- 7. The Clausius inequality is:  $dS \ge \frac{dq}{T}$  > for irreversible process = for reversible process 8. For an isolated system:  $dS \ge 0$  > for irreversible process = for reversible process 9. Entropy always increases for a spontaneous process in an isolated system.
- 10. For an isothermal reversible process in a closed system:  $\Delta S = \frac{q_{rev}}{T}$
- 11. For an isothermal expansion of an ideal gas:  $\Delta S = nR \ln \frac{V_2}{V_1}$
- 12. For any process in a closed system for an ideal gas and constant  $C_v$ :  $\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$
- 13. For any process in a closed system for an ideal gas and constant  $C_p$ :  $\Delta S = C_p \ln \frac{T_2}{T_1} nR \ln \frac{P_2}{P_1}$

- 14. Temperature is the **integrating factor** for reversible heat transfer.
- 15. For any closed system at constant volume:  $\Delta S = \int_{T_1}^{T_2} C_{v/T} dT$
- 16. For any closed system at constant pressure:  $\Delta S = \int_{T_1}^{T_2} C_{p/T} dT$
- 17. For a reversible phase transition at constant  $T_{tr}$  and P:  $\Delta_{tr}S = \frac{\Delta_{tr}H}{T_{tr}}$
- 18. Assuming constant heat capacities, the change in entropy with temperature for phase transitions and chemical reactions is:  $\Delta_r S_{T2} = \Delta_r S_{T1} + \Delta_r C_p \ln \frac{T_2}{T_1}$ , with  $\Delta_r C_p = \sum \nu_i C_{pi}$ .
- 19. The absolute entropy of a pure, perfect crystalline substance is zero at absolute zero:  $S_0 \equiv 0$
- 20. For a closed system at constant pressure, assuming no solid-state phase transitions::

$$S_{T} = S_{o} + \int_{0}^{T_{melt}} \frac{C_{p}^{solid}}{T} dT + \frac{\Delta_{fus}H}{T_{melt}} + \int_{T_{melt}}^{T_{b}} \frac{C_{p}^{liq}}{T} dT + \frac{\Delta_{vap}H}{T_{b}} + \int_{T_{b}}^{T} \frac{C_{p}^{gas}}{T} dT$$

- 21. The Debye approximation for the low temperature heat capacity of a solid is  $C_p = A T^3$ .
- 22. All transfers of energy to the surroundings are reversible.
- 23. The entropy change for the surroundings is  $dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dq}{T_{surr}}$
- 24. For an isothermal constant volume process, for the system in contact with the surroundings acting as a constant temperature reservoir:  $dS_{surr} = \frac{-dU}{T}$
- 25. For an isothermal constant pressure process, for the system in contact with the surroundings acting as a constant temperature reservoir:  $dS_{surr} = \frac{dq_{surr}}{T_{surr}} = \frac{-dH}{T}$
- 26. For a chemical reaction or phase transition at constant T and P:  $\Delta_r S = \sum v_i S_i$

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### **Further Reading**

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#### **Problems: Entropy and Applications**

<u>1</u>. Eqs. 13.2.10° and 13.2.15° apply for all processes for an ideal gas. Show that the two expressions are equivalent.

<u>2</u>. Eq. 13.2.10° applies for all processes for an ideal gas, assuming a constant heat capacity. However, for an adiabatic reversible process,  $\Delta S = 0$ . Does Eq. 13.2.10° give  $\Delta S = 0$  for an adiabatic reversible process?

<u>3</u>. Calculate the change in entropy for 1.00 mole of ideal gas that is expanded against a constant external pressure of 1.00 atm from an initial pressure of 10.0 atm to a final pressure of 1.00 atm. During this process the temperature also drops from 25.00 °C to 0.00 °C. The heat capacity is  $C_p = 7/2$  nR.

<u>4</u>. For a closed system we know that  $\Delta U = q + w$ ,  $\Delta U = q_{rev} + w_{max}$ , and that a reversible process does maximum work on expansion and minimum work on contraction. Use these statements to derive the Clausius inequality.

<u>5</u>. In the section on "*Temperature as an Integrating Factor*" we derived Eq. 13.2.28° using Eq. 13.2.10°. Repeat the derivation of the entropy change for path 2, Eq. 13.2.28°. However, this time start from the heat transfers directly, Eqs. 13.2.16° and 13.2.18°, find  $dS_1$  and  $dS_2$ . Then do the integrals. Note when path specific information is eliminated.

<u>6</u>. Given the total differential for the function z(x,y):

$$dz = \frac{y}{x} dx - dy$$

Show that dz is not an exact differential. The integrating factor for dz is (1/x). Define a new differential as df = dz/x. Show that df is exact. In other words, df is a state function.

<u>7</u>. The lowest temperature heat capacity measurement for benzene is 3.79 K, where  $C_p = 0.051463 \text{ J K}^{-1} \text{ mol}^{-1}$ . The heat capacity data for crystalline and liquid benzene in Figure 13.4.1 can be fit to power series expansions. Because of the complex shape of the curve,

this fitting is best done over three temperature ranges. The breaks between the ranges are arbitrary and are simply chosen to get a good fit to the overall curve. There are no solid-state phase transitions. The enthalpy of fusion for benzene is 10.59 kJ mol<sup>-1</sup> at the normal melting point of 278.6 K. Calculate the absolute entropy of benzene at 298.2 K.

Table Problem	7: Approximate Heat Capacity for Solid and Liquid Benzene
solid	$C_p (J K^{-1} mol^{-1})$
3.79 – 20 K	$C_p = 0.10321 \text{ T} + 0.02431 \text{ T}^2$
20 - 84  K	$C_p = -16.5375 + 1.3854 \text{ T} - 0.00770 \text{ T}^2$
84 -278.6 K	$C_p = 38.2869 + 0.01075 \text{ T} + 1.097 \text{ x} 10^{-3} \text{ T}^2$
liquid	
278.6 – 300 K	$C_p = 81.228 + 0.1794 \text{ T}$

8. Calculate the absolute entropy of methylammonium chloride at 298.15 K. There are three crystalline forms. For the low temperature  $\beta$ -form, the heat capacity is 0.4209 J K<sup>-1</sup> mol<sup>-1</sup> at 12.04 K. The enthalpy of the equilibrium solid-state phase transition from the  $\beta$  to  $\gamma$ -form is 1.7790 kJ mol<sup>-1</sup> at 220.4 K. The enthalpy of the equilibrium solid-state phase transition from the  $\gamma$  to  $\alpha$ -form is 2.8183 kJ mol<sup>-1</sup> at 264.5 K. All values are at standard state. The integrals of C<sub>p</sub>/T, in J  $K^{-1}$  mol<sup>-1</sup>, for the three phases are:<sup>1</sup>

$$\int_{12.04 \text{ K}}^{220.4 \text{ K}} \frac{C_p^{\beta}}{T} dT = 93.412 \qquad \int_{220.4 \text{ K}}^{264.5 \text{ K}} \frac{C_p^{\gamma}}{T} dT = 15.439 \qquad \int_{264.5 \text{ K}}^{298.15 \text{ K}} \frac{C_p^{\alpha}}{T} dT = 10.690 \text{ J K}^{-1} \text{ mol}^{-1}$$

9. One mole of an ideal gas undergoes an isothermal reversible compression from an initial pressure of 1.00 bar to a final pressure of 10.00 bar. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

10. One mole of an ideal gas undergoes an isothermal expansion against a constant external pressure of 1.00 bar. In this process the system does 900.0 J of work from an initial volume of 1.00 L, that is w = -900.0 J. The temperature is 298.2 K. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

11. The volume of one mole of an ideal gas changes from 1.00 L to 2.00 L in an adiabatic reversible expansion. The initial temperature is 298.2 K. The gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

12. The pressure of one mole of an ideal gas drops from 10.0 bar to 1.00 bar in an adiabatic expansion against a constant external pressure of 1.00 bar. The initial temperature is 298.2 K. Assume the gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

13. The pressure inside an inflated balloon filled with helium is 112.0 kPa. Assume the gas expands from the opening in the balloon in an adiabatic expansion. In other words, assume the gas expands quickly and we measure the final temperature of the gas before any thermal energy can be transferred from the surroundings. The initial temperature is 298.2 K. The atmospheric pressure is 101.3 kPa. Calculate the entropy change of the system and the surroundings and the entropy change of the universe.

<u>14</u>. One mole of an ideal gas at 298.2 K triples its volume in an isothermal irreversible expansion against  $P_{ext} = 0$ . Calculate the changes in entropy of the system, the surroundings, and the total entropy change.

<u>15</u>. Calculate the molar entropy change for the phase transition of water to water vapor at room temperature, 298.15 K, and one atmosphere pressure. The difference in heat capacity on vaporization is  $\Delta_{tr}C_p = -41.9 \text{ J K}^{-1} \text{ mol}^{-1}$ . The standard enthalpy of vaporization of water <u>at</u> <u>373.15 K</u> is 40.7 kJ mol<sup>-1</sup>.

<u>16</u>. Consider the reaction: pyruvic acid  $\rightarrow$  acetaldehyde + CO<sub>2</sub> (g)

(which is catalyzed by the enzyme pyruvate decarboxylase.) Calculate  $\Delta_r S^\circ$  for this reaction for the system and the surroundings at 298.2 K. The values in the table below are at 298.2 K.

substance	$\Delta_{\rm f} {\rm H}^{\circ}  ({\rm kJ}  {\rm mol}^{-1})$	$S^{\circ}(J K^{-1} mol^{-1})$
acetaldehyde	-192.8	160.4
$CO_2$	-393.51	213.74
pyruvic acid	-584.5	179.5

<u>17</u>. The chemical reaction that corresponds to the enthalpy of formation of urea,  $(NH_2)_2CO$ , is:

C (graph) + 2 H<sub>2</sub> (g, 1 bar) + N<sub>2</sub> (g, 1 bar)  $\rightarrow$  (NH<sub>2</sub>)<sub>2</sub>CO (s)  $\Delta_{\rm f} {\rm H}^{\circ} = -333.1 \text{ kJ mol}^{-1}$ 

Using the data in the appendix, calculate the reaction entropy, at standard state and at 298.15 K.

18.(a). The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide:

 $(NH_2)_2CO(s) + H_2O(l) \rightarrow 2 NH_3(g, 1 bar) + CO_2(g, 1 bar)$ 

Using the data in the appendix, calculate the reaction enthalpy, at standard state and at 298.15 K. (b). Consider the reaction as an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. Calculate the change in entropy for the surroundings and the total entropy change at 298.15 K. (See Chapter 8 Problem 2b).

<u>19</u>. The aging of marine aerosols produces NaHSO<sub>4</sub> cloud condensation nuclei, CCN. The distribution of CCN determines the formation and reflectivity of clouds, which play an important role in determining the albedo of the atmosphere (see Chapter 8 Problem 3). (a). Using the data in the appendix, calculate the entropy change for the system and for the surroundings for the following reactions separately and in sum, under standard conditions and at 298.15 K.

 $\begin{array}{l} H_2S \ (g, \ 1bar) + 2 \ O_2 \ (g, \ 1bar) \rightarrow SO_3 \ (g, \ 1bar) + H_2O \ (g, \ 1bar) \\ SO_3 \ (g, \ 1 \ bar) + H_2O \ (l) \rightarrow H_2SO_4 \ (l) \\ NaCl \ (s) + H_2SO_4 \ (l) \rightarrow HCl \ (g, \ 1bar) + Na^+ \ (ao) + HSO_4^- \ (ao) \end{array}$ 

(b). Combine the three reactions to show the overall process. Use the single combined reaction to calculate the overall reaction enthalpy. Compare with the result in part (a).

<u>20</u>. Use normal mode analysis to decide whether propane or 2-methylpropane has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

<u>21</u>. Use normal mode analysis to decide whether cyclohexane or benzene has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

 $\underline{22}$ . Give an example for each of the following types of processes. Choose your examples from ideal gas expansions or compressions or phase transitions of pure substances. Specify the difference in the variable, P or T, that is responsible for the spontaneous or non-spontaneous direction of the process:

- (a). a spontaneous adiabatic and isothermal process,
- (b). a spontaneous isothermal process with a decrease in entropy for the system,
- (c). a non-spontaneous isothermal process with an increase in entropy for the system,
- (d). a spontaneous adiabatic process that decreases the temperature of the system.

<u>23</u>. The Clausius inequality relates the entropy changes of the system and surroundings. Consider an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. Use the Clausius inequality, Eq. 13.1.9, to show that  $dS > -dS_{surr}$  for a spontaneous process.

 $\underline{24}$ . Determine if the following statements are true of false. If the statement is false, describe the changes that are required to make the statement true, if possible. Assume that the system and surroundings are an isolated composite. (Hint: three of the following statements are true.)

(a). The heat transfer for the system is equal in magnitude and opposite in sign to the heat transfer for the surroundings ( $dq = -dq_{surr}$ ).

(b). The entropy change of the system is equal in magnitude and opposite in sign to the entropy change of the surroundings ( $dS = -dS_{surr}$ ).

(c). For a spontaneous process, the magnitude of the entropy change of the system is never greater than the magnitude of the entropy change of the surroundings.

(d). Heat transfer to a system at low temperature gives a larger change in the entropy of the system than the transfer of the same amount of heat at high temperature.

(e). Spontaneous processes always result in dispersal of energy to the surroundings.

(f). The entropy of every system is zero at absolute zero.

(g). For a given heat transfer, the entropy change of the surroundings is independent of the details of the process for the system.

(h). One mole of xenon gas at 1 bar and 298.2 K is mixed with another mole of xenon gas at 1 bar and 298.2 K. The total entropy change of the combined systems is positive for the process.

<u>25</u>. Heat capacities are often approximated by a power series:  $C_p = a + b T + c T^{-2}$ , for *a*, *b*, and *c* constants. Find the change in enthalpy and entropy of a substance for a constant pressure process with a temperature change from T<sub>1</sub> to T<sub>2</sub>.

26. Calculate the residual entropy at 0 K for NO, assuming random NO and ON orientations.

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