

**CHM 3400 – Fundamentals of Physical Chemistry**  
**Chapter 3 - Handout**

**1. Entropy and the Second Law of Thermodynamics**

The First Law of Thermodynamics is a powerful general statement about the behavior of systems. However, it is clear that there is more to thermodynamics than the First Law. To see this, consider the system in Fig 1. On the left side of the figure is an insulated container with an ice cube floating in hot water. Over time, the ice will melt and the hot water will cool to form a container of warm water at a uniform temperature, as shown on the right side of the figure. This process is consistent with the First Law. However, the reverse process, where warm water spontaneously forms hot water and ice, is never observed to occur, even though that process would also be consistent with the First Law. This suggests there must be at least one additional law of thermodynamics that allows us to predict whether or not processes that obey the First Law will actually happen.

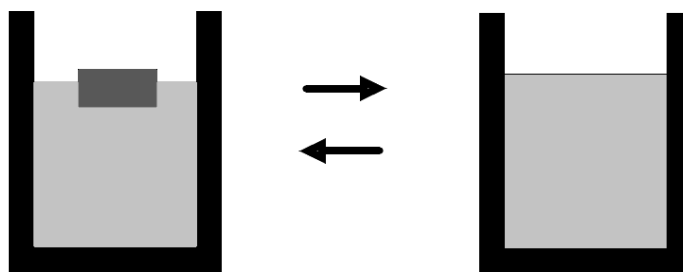


Figure 1. left – an insulated container holding ice and hot water  
right – an insulated container holding warm water

To develop this additional thermodynamic law we need to introduce a new thermodynamic function, called entropy ( $S$ ). By definition, the entropy change for a process is defined as:

$$\Delta S = \int_i^f \frac{(dq)_{\text{rev}}}{T} \quad (3.1.1)$$

The integral in eq 3.1.1 moves from an initial state  $i$  to a final state  $f$  along a reversible pathway. Since heat ( $q$ ) is not a state function, we would normally expect entropy to also not be a state function. However, restricting calculations of changes in entropy to movement along reversible pathways results in entropy being a state function. This is similar to what was observed in Chapter 2 for heat capacity ( $C$ ), which in general is not a state function but which becomes a state function when the restriction of constant volume or constant pressure is applied.

Equation 3.1.1 tells us that changes in entropy can only be found for reversible pathways. However, the fact that entropy is a state function has an important consequence. Consider an irreversible process moving from some initial state  $i$  to some final state  $f$ , as in Fig 2 on the next page. If we can find a reversible pathway connecting the same initial and final state, the value for  $\Delta S$  can be found for the reversible pathway using eq 3.1.1. Since entropy is a state function, we then know that the entropy change for the irreversible process will be the same as that found for the reversible process, since both processes have the same initial and final state and since the change in a state function is path independent. It turns out that for any irreversible process we can always find a reversible pathway connecting the initial and final state, and so can always (in principle) find the value for  $\Delta S$ .

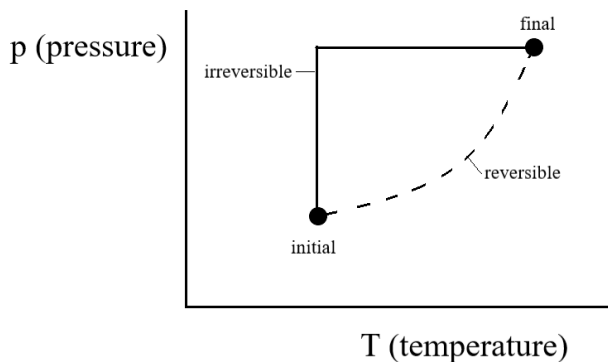


Figure 2. Schematic diagram indicating an initial and final state for a system. The change in entropy for an irreversible pathway (solid line) and a reversible pathway (dashed line) will be the same, since entropy is a state function.

One difference between entropy and other thermodynamic functions is that is useful to calculate entropy changes for both the system and the surroundings. We can do this using eq 3.1.1 as a starting point. The entropy change for the system is

$$\Delta S = \Delta S_{\text{syst}} = \int_i^f \frac{(\dot{dq})_{\text{rev,syst}}}{T} \quad (3.1.2)$$

and that for the surroundings is

$$\Delta S_{\text{surr}} = \int_i^f \frac{(\dot{dq})_{\text{rev,surr}}}{T} \quad (3.1.3)$$

The entropy change for the universe is then

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} \quad (3.1.4)$$

Note the following:

- 1) If no subscript is given, it is assumed that  $\Delta S = \Delta S_{\text{syst}}$ , as is true for other thermodynamic quantities.
- 2) A process that is irreversible from the point of view of the system may be reversible from the point of view of the surroundings. The exchange of heat between a system and its surroundings, for example, is usually reversible from the point of view of the surroundings, even if the process taking place is irreversible from the point of view of the system.

Before proceeding, it is useful to calculate  $\Delta S_{\text{syst}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for some specific examples. We will use the same examples previously discussed in Handout 2, where 1.00 mol of an ideal gas is expanded isothermally (at  $T = 300.0 \text{ K}$ ) from an initial pressure  $p_i = 4.00 \text{ atm}$  to a final pressure  $p_f = 2.00 \text{ atm}$ , either reversibly, or irreversibly against a constant external pressure  $p_{\text{ex}} = p_f = 2.00 \text{ atm}$ . The results that were found for these two processes are summarized in Table 1 below (Note  $\Delta H = 0$  for both processes, but we did these examples before defining enthalpy).

Table 1. Results for the isothermal expansion of an ideal gas (see Handout 2, Section 1)

process	$\Delta U$	q	w
reversible pathway	0. J	1729. J	- 1729. J
irreversible pathway	0. J	1247. J	- 1247. J

For the reversible process, we can use the process that actually takes place, and so

$$\Delta S_{\text{sys}} = \int_i^f \frac{(\delta q)_{\text{rev,sys}}}{T} = \frac{1}{T} \int_i^f (\delta q)_{\text{rev,sys}} = \frac{q_{\text{rev,sys}}}{T} = \frac{1729. \text{ J}}{300.0 \text{ K}} = + 5.76 \text{ J/K} \quad (3.1.5)$$

where we have made use of the fact that the process was isothermal to take T outside of the integral. From the point of view of the surroundings all that happens is that 1729. J of heat is transferred into the system. This transfer of heat is a reversible process, and so

$$\Delta S_{\text{surr}} = \int_i^f \frac{(\delta q)_{\text{rev,surr}}}{T} = \frac{1}{T} \int_i^f (\delta q)_{\text{rev,surr}} = \frac{q_{\text{rev,surr}}}{T} = - \frac{q_{\text{sys}}}{T} = - \frac{1729. \text{ J}}{300.0 \text{ K}} = - 5.76 \text{ J/K} \quad (3.1.6)$$

where we have used the fact that  $q_{\text{rev,surr}} = - q_{\text{sys}}$ . Since providing heat by the surroundings is, from the point of view of the surroundings, something that can be done reversibly, we can drop the subscript "rev" from  $q_{\text{sys}}$ .

The entropy change for the universe is then

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = + 5.76 \text{ J/K} + (- 5.76 \text{ J/K}) = 0.00 \text{ J/K} \quad (3.1.7)$$

For the irreversible process, we cannot use eq 3.1.2 directly, as that equation can only be used for reversible pathways. We instead need a reversible process with the same initial and final state as the isothermal irreversible expansion. We can then find  $\Delta S_{\text{sys}}$  for the reversible process, and use the fact that entropy is a state function to say the entropy change for the irreversible process is the same as for the reversible process. But the isothermal reversible process in our example has the same initial and final state as the isothermal irreversible process, and so has the same value for the change in entropy. Therefore, for the irreversible process,  $\Delta S_{\text{sys}} = + 5.76 \text{ J/K}$ .

Now consider  $\Delta S_{\text{surr}}$  for the irreversible process. For this process, the surroundings are providing 1247. J of heat to the system. But providing heat to the system from the surroundings (or taking up heat from the system by the surroundings) is, from the point of view of the surroundings, a reversible process, no matter how much heat is involved. This is true even if that heat is used by the system in an irreversible manner. So we can use the result from eq 3.1.6, and say

$$\Delta S_{\text{surr}} = - \frac{q_{\text{sys}}}{T} = - \frac{1247. \text{ J}}{300.0 \text{ K}} = - 4.16 \text{ J/K} \quad (3.1.8)$$

The entropy change for the universe is then

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = + 5.76 \text{ J/K} + (- 4.16 \text{ J/K}) = + 1.60 \text{ J/K} \quad (3.1.9)$$

If we were to look at a large number of examples, we would observe that both  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  can be positive, negative, or zero. However, we would find that  $\Delta S_{\text{univ}}$  is always either positive or zero. In fact we would discover that for process that actually take place, irreversible processes have  $\Delta S_{\text{univ}} > 0$ , while reversible processes  $\Delta S_{\text{univ}} = 0$ . Processes where we find  $\Delta S_{\text{univ}} < 0$  are never observed.

The above results are summarized in the Second Law of Thermodynamics. For a process consistent with the First Law to take place, we require  $\Delta S_{\text{univ}} \geq 0$ . A process where  $\Delta S_{\text{univ}} > 0$  is called a spontaneous process, and, like our original example of ice and hot water in an insulated container forming warm water, will eventually occur (unless a different spontaneous process happens first). Processes where  $\Delta S_{\text{univ}} < 0$ , such as warm water in an insulated container spontaneously forming hot water and ice, never occur. Those processes where  $\Delta S_{\text{univ}} = 0$  are reversible processes, and indicate a system at equilibrium. The observation that  $\Delta S_{\text{univ}} = 0$  for a system at equilibrium leads to a variety of useful results, as we will see in the following few chapters.

The Second Law of Thermodynamics, like the First Law, is a general result, based on the observed behavior of systems. It applies, as far as we know, to all processes, and is particularly important when considering processes where it is not obvious whether the process is a spontaneous process.

## 2. Examples of entropy changes

### Phase transitions

In chemistry, a phase is a state of matter that is uniform in composition and physical state, and separated from other phases by a phase boundary. For pure substances, the common phases are solid, liquid, and gas. Pure substances have only a single gas phase and (except for helium) a single liquid phase, but can have several different solid phases, corresponding to different crystal structures for the solid. The phase or phases that exist for a pure substance at equilibrium are often indicated in a phase diagram, such as in Fig 2 of the Chapter 2 notes.

A phase transition represents the conversion of a substance from one phase to another phase. When the transition occurs under conditions of constant pressure and temperature and where the two phases are at equilibrium (such as the vaporization of water at  $T = 100.0 \text{ }^\circ\text{C}$  and  $p = 1.000 \text{ atm}$ ), the phase transition is a reversible process, and eq 3.1.2 can be used to find the change in entropy.

$$\Delta S = \Delta S_{\text{pt}} = \int_{i}^{f} \frac{(\dot{d}q)_{\text{rev, syst}}}{T} = \frac{n \Delta H_{\text{pt}}}{T_{\text{pt}}} \quad (3.2.1)$$

where "pt" indicates the particular phase transition taking place. When one mole of a substance undergoes a phase transition at the normal transition point (the point where  $p = 1.000 \text{ atm}$ , and the temperature where equilibrium between the two phases occurs) the symbol  $\Delta S^{\circ}_{\text{pt}}$  is used to indicate the change in entropy for the system. For example, for water at  $T = 100.0 \text{ }^\circ\text{C}$  the enthalpy of vaporization is  $\Delta H^{\circ}_{\text{vap}}(\text{H}_2\text{O}) = 40.656 \text{ kJ/mol}$ , and so the corresponding value for the entropy of vaporization is

$$\Delta S^{\circ}_{\text{vap}}(\text{H}_2\text{O}) = \frac{\Delta H^{\circ}_{\text{vap}}(\text{H}_2\text{O})}{T^{\circ}_{\text{vap}}} = \frac{40656 \text{ J/mol}}{373.15 \text{ K}} = 108.95 \text{ J/mol}\cdot\text{K} \quad (3.2.2)$$

### Constant pressure heating

Except at the points where phase transitions occur, adding heat to a substance under conditions of constant pressure leads to an increase in the temperature of the substance. If heat is added slowly (and therefore reversibly) the change in entropy is

$$\Delta S = \Delta S_{\text{syst}} = \int_{T_i}^{T_f} \frac{(\dot{d}q)_{\text{rev, syst}}}{T} = \int_{T_i}^{T_f} \frac{n C_{p,m} dT}{T} \quad (3.2.3)$$

For the special case where  $C_{p,m}$  is assumed independent of temperature, both  $n$  and  $C_{p,m}$  can be taken outside the integral in eq 3.2.3, to give

$$\Delta S = n C_{p,m} \int_{T_i}^{T_f} \frac{dT}{T} = n C_{p,m} \ln(T_f/T_i) \quad (3.2.4)$$

Equation 3.2.4 only applies if  $C_{p,m}$  can be assumed constant. For cases where the value for  $C_{p,m}$  changes with temperature, and where the temperature dependence is known, eq 3.2.3 must be used to find the change in entropy for heating a pure substance at constant pressure.

### 3. The Third Law of Thermodynamics

Using the results from the previous section and experimental data, we can find the entropy change for the process of changing the temperature of a pure substance from an initial temperature  $T_1$  to a final temperature  $T_2$  under conditions of constant pressure. When heat is slowly added to the substance only two processes will occur, as shown in Figure 3. Most of the time the addition of heat will lead to an increase in the temperature of the substance (curved lines in Fig 3). However, at temperatures where phase transitions take place, entropy will increase while temperature remains constant (vertical lines in Fig 3). Using the results from the last section for the entropy change for constant pressure heating of a substance and for a phase transition, we can obtain the following expression for the entropy of a pure substance at temperature  $T_2$ :

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{n C_{p,m}}{T} dT + \sum_{pt} \frac{n \Delta H_{pt}}{T_{pt}} \quad (3.3.1)$$

In the above expression,  $S(T_1)$  and  $S(T_2)$  are the values for the entropy of the substance at temperatures  $T_1$  and  $T_2$ . The integral in eq 3.3.1 accounts for the entropy change in going from  $T_1$  to  $T_2$  due to the constant pressure heating of the substance, and the summation term accounts for the additional entropy change for any phase transitions that occur.

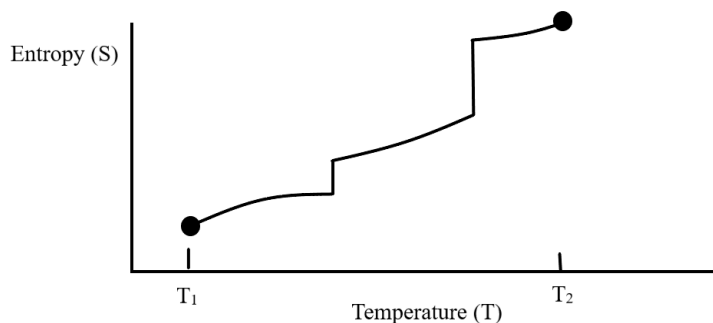


Figure 3. Entropy as a function of temperature for a pure chemical substance.

Equation 3.3.1 also applies when heat is slowly removed from a substance at constant pressure. However, the process of removing heat cannot continue indefinitely, as there is a lowest temperature, absolute zero (0. K). If we use absolute zero as our reference point, assume one mole of substance, and standard pressure, we can then say:

$$S(T) = S(0. K) + \int_0^T \frac{C_{p,m}}{T} dT + \sum_{pt} \frac{\Delta H_{pt}^\circ}{T_{pt}^\circ} \quad (3.3.2)$$

There is experimental evidence that all pure substances in the form of a perfect crystal have the same value for absolute entropy at absolute zero. It is convenient to define this value for entropy as being equal to zero. This is the basis of the Third Law of Thermodynamics. The Third Law states that the absolute entropy of one mole of any pure chemical substance in the form of a perfect crystal and at absolute zero is exactly 0.0 J/mol·K. Based on that definition and experimental data, absolute entropies for any pure chemical substance can be found using eq 3.3.2.

Note the following:

1) Since entropy always increases when heat is added to a substance, the absolute entropy of any pure chemical substance (even elements in their standard state) will be greater than zero for any temperature above absolute zero.

2) The Third Law does not apply in some cases, the most important being ions in aqueous solution. For that case, we define the absolute entropy of hydrogen ion at standard pressure and 25.0 °C as being exactly equal to zero. Based on this, entropies for other aqueous ions can be found from experiment. Since the Third Law is not used to do this, values for the entropy for some aqueous ions will be negative.

#### 4. Entropy changes for chemical reactions

As chemists, we are interested in the change in entropy when a chemical reaction takes place, and whether the reaction will spontaneously occur. Using the Second and Third Laws of Thermodynamics, it is relatively easy to find  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  for standard conditions, and from that,  $\Delta S_{\text{univ}}$ .

For a chemical reaction taking place at standard conditions, the entropy change for the system will simply be the entropy change for the reaction, given by the expression

$$\Delta S^{\circ}_{\text{sys}} = \Delta S^{\circ}_{\text{rxn}} = [ \sum S^{\circ}(\text{products}) ] - [ \sum S^{\circ}(\text{reactants}) ] \quad (3.4.1)$$

where the summations indicate that all of the absolute entropies of the products or reactants are added together. For the entropy change for the surroundings we use the fact that at constant pressure  $q_{\text{sys}} = \Delta H$ . Applying this to a reaction taking place at standard pressure and temperature, the entropy change for the surroundings will be

$$\Delta S_{\text{surr}} = - \frac{q_{\text{sys}}}{T} = - \frac{\Delta H^{\circ}_{\text{rxn}}}{T} \quad (3.4.2)$$

As a specific example, consider the reaction previously used to show how the change in enthalpy for a chemical reaction is calculated.



The values for the entropy and enthalpy of reaction are:

$$\Delta S^{\circ}_{\text{rxn}} = [ 3 S^{\circ}(\text{NO}(\text{g})) ] - [ S^{\circ}(\text{NO}_2(\text{g})) + S^{\circ}(\text{N}_2\text{O}(\text{g})) ] \quad (3.4.4)$$

$$\Delta H^{\circ}_{\text{rxn}} = [ 3 \Delta H^{\circ}_{\text{f}}(\text{NO}(\text{g})) ] - [ \Delta H^{\circ}_{\text{f}}(\text{NO}_2(\text{g})) + \Delta H^{\circ}_{\text{f}}(\text{N}_2\text{O}(\text{g})) ] \quad (3.4.5)$$

Using the data from Table 2 below, we get  $\Delta S^{\circ}_{\text{sys}} = \Delta S^{\circ}_{\text{rxn}} = 172.37 \text{ J/mol}\cdot\text{K}$  and  $\Delta H^{\circ}_{\text{rxn}} = 155.52 \text{ kJ/mol}$ . So  $\Delta S^{\circ}_{\text{surr}} = - \Delta H^{\circ}_{\text{rxn}}/T = - (155520. \text{ J/mol})/(298.15 \text{ K}) = - 521.6 \text{ J/mol}\cdot\text{K}$ .

Table 2. Selected values for thermodynamic data (at T = 25.0 °C)

Substance	$\Delta H^{\circ}_{\text{f}}$ (kJ/mol)	$S^{\circ}$ (J/mol·K)	$\Delta G^{\circ}_{\text{f}}$ (kJ/mol)	$C_{\text{p,m}}$ (J/mol·K)
NO(g)	90.25	210.76	86.55	29.844
NO <sub>2</sub> (g)	33.18	240.06	51.31	37.20
N <sub>2</sub> O(g)	82.05	219.85	104.20	38.45

Using the above results we get  $\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{syst}} + \Delta S^\circ_{\text{surr}} = 172.37 \text{ J/mol}\cdot\text{K} + (-521.6 \text{ J/mol}\cdot\text{K}) = -349.2 \text{ J/mol}\cdot\text{K}$ . Since  $\Delta S^\circ_{\text{univ}} < 0$ , the reaction is not spontaneous for standard conditions and therefore will not occur.

The above procedure is general. This means that if we have data for the absolute entropy and enthalpy of formation for all of the reactants and products of a chemical reaction, we can find  $\Delta S^\circ_{\text{syst}}$ ,  $\Delta S^\circ_{\text{surr}}$ , and  $\Delta S^\circ_{\text{univ}}$  for the reaction and determine whether or not the reaction is spontaneous for standard conditions. In fact, based on the above results we may say

$$\Delta S^\circ_{\text{univ}} = \Delta S^\circ_{\text{syst}} + \Delta S^\circ_{\text{surr}} = \Delta S^\circ_{\text{rxn}} - (\Delta H^\circ_{\text{rxn}}/T) \quad (3.4.6)$$

Based on the Second Law, for a reaction to be spontaneous for standard conditions we therefore require

$$\Delta S^\circ_{\text{rxn}} - (\Delta H^\circ_{\text{rxn}}/T) > 0 \quad (3.4.7)$$

Of course, not all reactions take place under standard conditions. Because of this, we will eventually develop methods for finding out the above information for a chemical reaction for any conditions instead of just standard conditions.

## 5. Free energy

It is tedious, although straightforward, to carry out the calculations discussed in the last section. To make it easier to decide whether or not a chemical reaction will spontaneously occur, we define a new thermodynamic function, called free energy (technically, Gibbs free energy), that is useful for working with processes taking place under conditions of constant temperature and pressure. A second type of free energy, useful for processes taking place under conditions of constant temperature and volume, also exists, but will not be discussed here.

By definition, the Gibbs free energy ( $G$ ) is defined as

$$G = H - TS \quad (3.5.1)$$

Since,  $H$ ,  $T$ , and  $S$  are state functions, free energy is also a state function.

Starting with eq 3.5.1, the change in free energy for a process is

$$\Delta G = \Delta H - \Delta(TS) \quad (3.5.2)$$

If we limit ourselves to processes taking place at constant temperature and pressure, then

$$\Delta G = \Delta H - T \Delta S \quad (3.5.3)$$

Now consider a chemical reaction taking place under standard conditions. We may rewrite eq 3.5.3, to get

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T \Delta S^\circ_{\text{rxn}} \quad (3.5.4)$$

Dividing both sides of this equation by  $(-T)$  gives

$$-(\Delta G^\circ_{\text{rxn}}/T) = \Delta S^\circ_{\text{rxn}} - (\Delta H^\circ_{\text{rxn}}/T) \quad (3.5.5)$$

But the right side of eq 3.5.5 is the same expression given in eq 3.4.7. This means that for a chemical reaction taking place at standard conditions to be spontaneous

$$-(\Delta G^\circ_{\text{rxn}}/T) > 0 \quad (3.5.6)$$

Or, since absolute temperature is always positive (other than at absolute zero)

$$\Delta G^{\circ}_{\text{rxn}} < 0 \quad (3.5.7)$$

for a chemical reaction to take place spontaneously for standard conditions.

While we have applied eq 3.5.3 to the specific case of a chemical reaction occurring under standard conditions, there is a more general result. For any process at constant temperature and pressure, we may say

$$\begin{aligned} \Delta G < 0 & \text{ process is spontaneous} \\ \Delta G = 0 & \text{ equilibrium} \\ \Delta G > 0 & \text{ process is not spontaneous (will not occur)} \end{aligned}$$

Unlike the Second Law of Thermodynamics, the above statements are rigorously true only for processes where temperature and pressure do not change. However, since this is common for chemical reactions, free energy can be used in these cases to decide whether a process will spontaneously occur.

There are two ways that  $\Delta G^{\circ}_{\text{rxn}}$  can be found for a chemical reaction. One is by first finding  $\Delta S^{\circ}_{\text{rxn}}$  and  $\Delta H^{\circ}_{\text{rxn}}$ , and then using eq 3.5.4 to find  $\Delta G^{\circ}_{\text{rxn}}$ . The second, and easier, method is to use the general relationship

$$\Delta G^{\circ}_{\text{rxn}} = [ \sum \Delta G^{\circ}_{\text{f}}(\text{products}) ] - [ \sum \Delta G^{\circ}_{\text{f}}(\text{reactants}) ] \quad (3.5.8)$$

and thermodynamic data for the free energy of formation for the reactants and products of the reaction. For example, for the reaction given in eq 3.4.3, the change in free energy for the reaction for standard conditions is

$$\Delta G^{\circ}_{\text{rxn}} = [ 3 \Delta G^{\circ}_{\text{f}}(\text{NO}(\text{g})) ] - [ \Delta G^{\circ}_{\text{f}}(\text{NO}_2(\text{g})) + \Delta G^{\circ}_{\text{f}}(\text{N}_2\text{O}(\text{g})) ] \quad (3.5.9)$$

Using the information in Table 2 gives  $\Delta G^{\circ}_{\text{rxn}} = 104.14$  kJ/mol, indicating that the reaction is not spontaneous for standard conditions, a result previously obtained by calculating  $\Delta S^{\circ}_{\text{univ}}$ . Note that if we find the free energy change using eq 3.5.4, we get  $\Delta G^{\circ}_{\text{rxn}} = 104.13$  kJ/mol, the same result to within roundoff error.

## 6. Temperature dependence of $\Delta H^{\circ}_{\text{rxn}}$ , $\Delta S^{\circ}_{\text{rxn}}$ , and $\Delta G^{\circ}_{\text{rxn}}$

Thermodynamic calculations are commonly carried out at  $T = 25.0$  °C, the temperature at which thermodynamic data are commonly given. It is useful to know how the values for  $\Delta H^{\circ}_{\text{rxn}}$ ,  $\Delta S^{\circ}_{\text{rxn}}$ , and  $\Delta G^{\circ}_{\text{rxn}}$  change when temperature is changed.

We previously gave the following relationship for the enthalpy change for a chemical reaction (eq 2.4.12 in the Chapter 2 handout)

$$\Delta H^{\circ}_{\text{rxn}}(T_2) = \Delta H^{\circ}_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_{\text{p,m}} dT \quad (3.6.1)$$

The derivation for this equation, while not given, is based on the fact that at constant pressure  $dH = n C_{\text{p,m}} dT$ .

In a similar manner, an equation for the temperature dependence of  $\Delta S^{\circ}_{\text{rxn}}$  can also be found, based on the fact that at constant pressure  $dS = (n C_{\text{p,m}}/T) dT$ . The result (not derived) is

$$\Delta S^{\circ}_{\text{rxn}}(T_2) = \Delta S^{\circ}_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} (\Delta C_{\text{p,m}}/T) dT \quad (3.6.2)$$

where  $\Delta C_{\text{p,m}}$  is the difference between the heat capacities of the products and reactants (eq 2.4.13 in the handout for Chapter 2). Note that eq 3.6.1 and 3.6.2 assume that there is no phase change in going from  $T_1$  to  $T_2$ .



We can use the above results to find the free energy change for a reaction at a new temperature

$$\Delta G^{\circ}_{\text{rxn}}(T_2) = \Delta H^{\circ}_{\text{rxn}}(T_2) - T_2 \Delta S^{\circ}_{\text{rxn}}(T_2) \quad (3.6.3)$$

where  $\Delta H^{\circ}_{\text{rxn}}(T_2)$  and  $\Delta S^{\circ}_{\text{rxn}}(T_2)$  are found using eq 3.6.1 and 3.6.2.

For cases where  $T_1$  and  $T_2$  are not too different, the integrals in eq 3.6.1 and 3.6.2 are usually much smaller than the terms they are being added to. Because of this, it is often a good first approximation to say  $\Delta H^{\circ}_{\text{rxn}}$  and  $\Delta S^{\circ}_{\text{rxn}}$  are approximately independent of temperature. Note that since  $\Delta S^{\circ}_{\text{rxn}}$  is multiplied by  $T$  in eq 3.5.4 it is usually not a good assumption to say that the value for  $\Delta G^{\circ}_{\text{rxn}}$  is independent of temperature.

If we assume that the values for  $\Delta H^{\circ}_{\text{rxn}}$  and  $\Delta S^{\circ}_{\text{rxn}}$  are independent of temperature, we can use eq 3.5.4 to find the approximate temperature at which the reactants and products of a chemical reaction are at equilibrium. Since for standard conditions and at equilibrium  $\Delta G^{\circ}_{\text{rxn}} = 0$ , it follows from eq 3.5.4, that

$$\Delta G^{\circ}_{\text{rxn}} = 0 = \Delta H^{\circ}_{\text{rxn}} - T_{\text{eq}} \Delta S^{\circ}_{\text{rxn}} \quad (3.6.4)$$

or

$$T_{\text{eq}} \cong \frac{\Delta H^{\circ}_{\text{rxn}}}{\Delta S^{\circ}_{\text{rxn}}} \quad (3.6.5)$$

where eq 3.6.5 is only approximately correct, since it assumes no temperature dependence for  $\Delta H^{\circ}_{\text{rxn}}$  and  $\Delta S^{\circ}_{\text{rxn}}$ .

Using eq 3.6.5 often results in a value of  $T_{\text{eq}} < 0$ . In those cases, it means the reaction is either always spontaneous or never spontaneous (which can be determined by finding the value for  $\Delta G^{\circ}_{\text{rxn}}$ ), and that there is no temperature where the reactant and products are at equilibrium for standard conditions. When a positive value for  $T_{\text{eq}}$  is obtained, that corresponds to the approximate temperature where the reactants and products are at equilibrium for standard conditions.

One simple example of the use of eq 3.6.5 is in estimating the normal boiling point for a liquid. For example, for the vaporization of water



and using data at  $T = 25.0$  °C, the values for the enthalpy and entropy of vaporization are  $\Delta H^{\circ}_{\text{vap}} = 44.01$  kJ/mol and  $\Delta S^{\circ}_{\text{vap}} = 118.92$  J/mol·K. The value for the normal boiling point for water (the temperature where liquid water and water vapor are at equilibrium at  $p = 1.000$  atm) is then approximately

$$T_{\text{eq}} \cong T^{\circ}_{\text{vap}} = \frac{\Delta H^{\circ}_{\text{rxn}}}{\Delta S^{\circ}_{\text{rxn}}} = \frac{44010 \text{ J/mol}}{118.92 \text{ J/mol}\cdot\text{K}} = 370.1 \text{ K} = 96.9 \text{ }^{\circ}\text{C} \quad (3.6.7)$$

reasonably close to the actual value  $T^{\circ}_{\text{vap}} = 100.0$  °C.

We have now discussed all three laws of thermodynamics, and all of the thermodynamic quantities that we will use in analyzing systems. From this point on, our interest in thermodynamics will be in applications of this basic knowledge to other systems of interest.