

## 18.4: Entropy Changes and the Third Law of Thermodynamics

### Learning Objectives

- To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 18.4.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

### Third Law of Thermodynamics

The entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

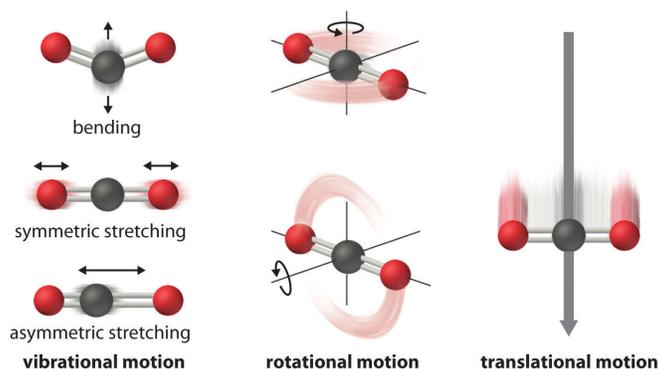


Figure 18.4.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity ( $C_p$ ) as a function of temperature and then plotting the quantity  $C_p/T$  versus  $T$ . The area under the curve between 0 K and any temperature  $T$  is the absolute entropy of the substance at  $T$ . In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms. In this section, we examine two different ways to calculate  $\Delta S$  for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

### Calculating $\Delta S$ from Standard Molar Entropy Values

One way of calculating  $\Delta S$  for a reaction is to use tabulated values of the standard molar entropy ( $S^\circ$ ), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of  $S^\circ$  are  $J/(\text{mol}\cdot\text{K})$ . Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to  $S = 0 J/(\text{mol}\cdot\text{K})$ ] and 298 K.

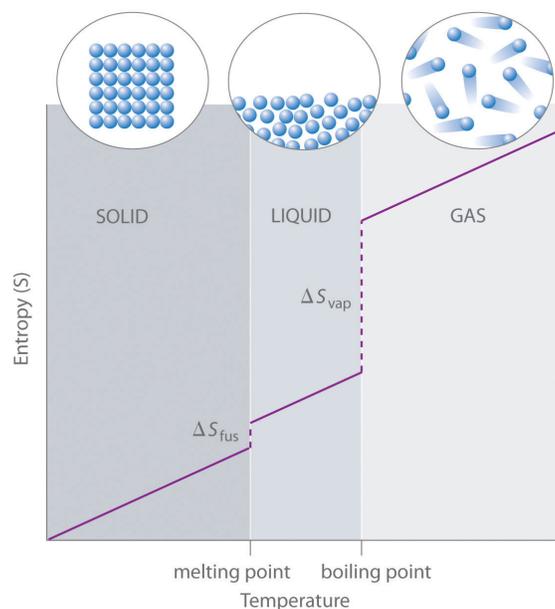


Figure 18.4.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid ( $\Delta S_{\text{fus}}$ ). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas ( $\Delta S_{\text{vap}}$ ).

As shown in Table 18.4.1, for substances with approximately the same molar mass and number of atoms,  $S^\circ$  values fall in the order  $S^\circ(\text{gas}) > S^\circ(\text{liquid}) > S^\circ(\text{solid})$ . For instance,  $S^\circ$  for liquid water is  $70.0 \text{ J}/(\text{mol}\cdot\text{K})$ , whereas  $S^\circ$  for water vapor is  $188.8 \text{ J}/(\text{mol}\cdot\text{K})$ . Likewise,  $S^\circ$  is  $260.7 \text{ J}/(\text{mol}\cdot\text{K})$  for gaseous  $\text{I}_2$  and  $116.1 \text{ J}/(\text{mol}\cdot\text{K})$  for solid  $\text{I}_2$ . This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 18.4.2 which is a generalized plot of the entropy of a substance versus temperature.

Table 18.4.1: Standard Molar Entropy Values of Selected Substances at  $25^\circ\text{C}$

Gases		Liquids		Solids	
Substance	$S^\circ [\text{J}/(\text{mol}\cdot\text{K})]$	Substance	$S^\circ [\text{J}/(\text{mol}\cdot\text{K})]$	Substance	$S^\circ [\text{J}/(\text{mol}\cdot\text{K})]$
He	126.2	$\text{H}_2\text{O}$	70.0	C (diamond)	2.4
$\text{H}_2$	130.7	$\text{CH}_3\text{OH}$	126.8	C (graphite)	5.7
Ne	146.3	$\text{Br}_2$	152.2	LiF	35.7
Ar	154.8	$\text{CH}_3\text{CH}_2\text{OH}$	160.7	$\text{SiO}_2$ (quartz)	41.5
Kr	164.1	$\text{C}_6\text{H}_6$	173.4	Ca	41.6
Xe	169.7	$\text{CH}_3\text{COCl}$	200.8	Na	51.3
$\text{H}_2\text{O}$	188.8	$\text{C}_6\text{H}_{12}$ (cyclohexane)	204.4	$\text{MgF}_2$	57.2
$\text{N}_2$	191.6	$\text{C}_8\text{H}_{18}$ (isooctane)	329.3	K	64.7
$\text{O}_2$	205.2			NaCl	72.1
$\text{CO}_2$	213.8			KCl	82.6
$\text{I}_2$	260.7			$\text{I}_2$	116.1

**Note**

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table 18.4.1 also reveals that substances with similar molecular structures tend to have similar  $S^\circ$  values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [ $S^\circ = 2.4 \text{ J}/(\text{mol}\cdot\text{K})$ ]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher  $S^\circ$  [ $5.7 \text{ J}/(\text{mol}\cdot\text{K})$ ] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the  $S^\circ$  values for  $\text{CH}_3\text{OH}(\text{l})$  and  $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$ . Finally, substances with strong hydrogen bonds have lower values of  $S^\circ$ , which reflects a more ordered structure.

**Note**

$\Delta S^\circ$  for a reaction can be calculated from absolute entropy values using the same “products minus reactants” rule used to calculate  $\Delta H^\circ$ .

To calculate  $\Delta S^\circ$  for a chemical reaction from standard molar entropies, we use the familiar “products minus reactants” rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 18.4.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane ( $\text{C}_8\text{H}_{18}$ ; 2,2,4-trimethylpentane).

**✓ Example 18.4.1**

Use the data in Table 18.4.1 to calculate  $\Delta S^\circ$  for the reaction of liquid isooctane with  $\text{O}_2(\text{g})$  to give  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  at 298 K.

**Given:** standard molar entropies, reactants, and products

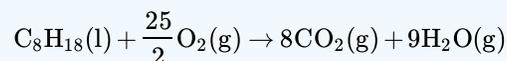
**Asked for:**  $\Delta S^\circ$

**Strategy:**

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 18.4.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain  $\Delta S^\circ$  for the reaction.

**Solution:**

The balanced chemical equation for the complete combustion of isooctane ( $\text{C}_8\text{H}_{18}$ ) is as follows:



We calculate  $\Delta S^\circ$  for the reaction using the “products minus reactants” rule, where  $m$  and  $n$  are the stoichiometric coefficients of each product and each reactant:

$$\Delta S_{\text{rxn}}^\circ = \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \quad (18.4.1)$$

$$= [8S^\circ(\text{CO}_2) + 9S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{C}_8\text{H}_{18}) + \frac{25}{2}S^\circ(\text{O}_2)] \quad (18.4.2)$$

$$= \{[8 \text{ mol CO}_2 \times 213.8 \text{ J}/(\text{mol}\cdot\text{K})] + [9 \text{ mol H}_2\text{O} \times 188.8 \text{ J}/(\text{mol}\cdot\text{K})]\} \quad (18.4.3)$$

$$- \left\{ [1 \text{ mol C}_8\text{H}_{18} \times 329.3 \text{ J}/(\text{mol}\cdot\text{K})] + \left[ \frac{25}{2} \text{ mol O}_2 \times 205.2 \text{ J}/(\text{mol}\cdot\text{K}) \right] \right\} \quad (18.4.4)$$

$$= 515.3 \text{ J/K} \quad (18.4.5)$$

$\Delta S^\circ$  is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

### ? Exercise 18.4.1

Use the data in Table 18.4.1 to calculate  $\Delta S^\circ$  for the reaction of  $\text{H}_2(\text{g})$  with liquid benzene ( $\text{C}_6\text{H}_6$ ) to give cyclohexane ( $\text{C}_6\text{H}_{12}$ ).

**Answer:**  $-361.1 \text{ J/K}$

## Calculating $\Delta S$ from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned previously, the **molar heat capacity** ( $C_p$ ) is the amount of heat needed to raise the temperature of 1 mol of a substance by  $1^\circ\text{C}$  at constant pressure. Similarly,  $C_v$  is the amount of heat needed to raise the temperature of 1 mol of a substance by  $1^\circ\text{C}$  at constant volume. The increase in entropy with increasing temperature in Figure 18.4.2 is approximately proportional to the heat capacity of the substance.

Recall that the entropy change ( $\Delta S$ ) is related to heat flow ( $q_{\text{rev}}$ ) by  $\Delta S = q_{\text{rev}}/T$ . Because  $q_{\text{rev}} = nC_p\Delta T$  at constant pressure or  $nC_v\Delta T$  at constant volume, where  $n$  is the number of moles of substance present, the change in entropy for a substance whose temperature changes from  $T_1$  to  $T_2$  is as follows:

$$\Delta S = \frac{q_{\text{rev}}}{T} = nC_p \frac{\Delta T}{T} \quad (\text{constant pressure}) \quad (18.4.6)$$

As you will discover in more advanced math courses than is required here, it can be shown that this is equal to the following: For a review of natural logarithms, see Essential Skills 6 in Chapter 11.

$$\Delta S = nC_p \ln \frac{T_2}{T_1} \quad (\text{constant pressure}) \quad (18.20)$$

Similarly,

$$\Delta S = nC_v \ln \frac{T_2}{T_1} \quad (\text{constant volume}) \quad (18.21)$$

Thus we can use a combination of heat capacity measurements (Equation 18.20 or Equation 18.21) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 18.18) to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure 18.4.3): an orthorhombic form with a highly ordered structure ( $S_\alpha$ ) and a less-ordered monoclinic form ( $S_\beta$ ). The orthorhombic ( $\alpha$ ) form is more stable at room temperature but undergoes a phase transition to the monoclinic ( $\beta$ ) form at temperatures greater than  $95.3^\circ\text{C}$  ( $368.5 \text{ K}$ ). The transition from  $S_\alpha$  to  $S_\beta$  can be described by the thermodynamic cycle shown in part (b) in Figure 18.4.3 in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to  $S_\beta$  ( $-\Delta S_{\text{fus}(\beta)} = \Delta S_3$  in the cycle) cannot be measured directly. Because entropy is a state function, however,  $\Delta S_3$  can be calculated from the overall entropy change ( $\Delta S_1$ ) for the  $S_\alpha$ - $S_\beta$  transition, which equals the sum of the  $\Delta S$  values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of  $S_\alpha$  and  $S_\beta$ ,  $\Delta H_{\text{fus}(\alpha)}$ , and the melting point of  $S_\alpha$ .)

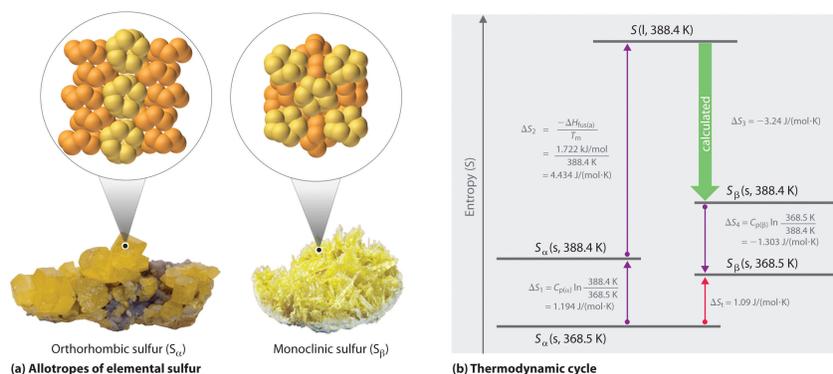


Figure 18.4.3: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other (a) Orthorhombic sulfur ( $S_\alpha$ ) has a highly ordered structure in which the  $S_8$  rings are stacked in a “crankshaft” arrangement. Monoclinic sulfur ( $S_\beta$ ) is also composed of  $S_8$  rings but has a less-ordered structure. (b) At 368.5 K,  $S_\alpha$  undergoes a phase transition to  $S_\beta$ . Although  $\Delta S_3$  cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of  $S_\alpha$  ( $T_m = 115.2^\circ\text{C} = 388.4\text{ K}$ ) and  $\Delta S_t$  for the overall phase transition [calculated to be  $1.09\text{ J/(mol}\cdot\text{K)}$  in the exercise in Example 6], we can calculate  $\Delta S_3$  from the values given in part (b) in Figure 18.4.3 where  $C_{p(\alpha)} = 22.70\text{ J/mol}\cdot\text{K}$  and  $C_{p(\beta)} = 24.77\text{ J/mol}\cdot\text{K}$  (subscripts on  $\Delta S$  refer to steps in the cycle):

$$\Delta S_t = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \quad (18.4.7)$$

$$1.09\text{ J/(mol}\cdot\text{K)} = C_{p(\alpha)} \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{\text{fus}}}{T_m} + \Delta S_3 + C_{p(\beta)} \ln\left(\frac{T_4}{T_3}\right) \quad (18.4.8)$$

$$= 22.70\text{ J/(mol}\cdot\text{K)} \ln\left(\frac{388.4}{368.5}\right) + \left(\frac{1.722\text{ kJ/mol}}{388.4\text{ K}} \times 1000\text{ J/kJ}\right) \quad (18.4.9)$$

$$+ \Delta S_3 + 24.77\text{ J/(mol}\cdot\text{K)} \ln\left(\frac{368.5}{388.4}\right) \quad (18.4.10)$$

$$= [1.194\text{ J/(mol}\cdot\text{K)}] + [4.434\text{ J/(mol}\cdot\text{K)}] + \Delta S_3 + [-1.303\text{ J/(mol}\cdot\text{K)}] \quad (18.4.11)$$

Solving for  $\Delta S_3$  gives a value of  $-3.24\text{ J/(mol}\cdot\text{K)}$ . As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal),  $\Delta S_3$  is negative.

## Summary

- Entropy changes can be calculated using the “products minus reactants” rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

The third law of thermodynamics states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the absolute entropy of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard temperature of 298 K is its standard molar entropy ( $S^\circ$ ). We can use the “products minus reactants” rule to calculate the standard entropy change ( $\Delta S^\circ$ ) for a reaction using tabulated values of  $S^\circ$  for the reactants and the products.

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