

8.3: Evaluating Entropy and Entropy Changes

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 8.3.1). 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.

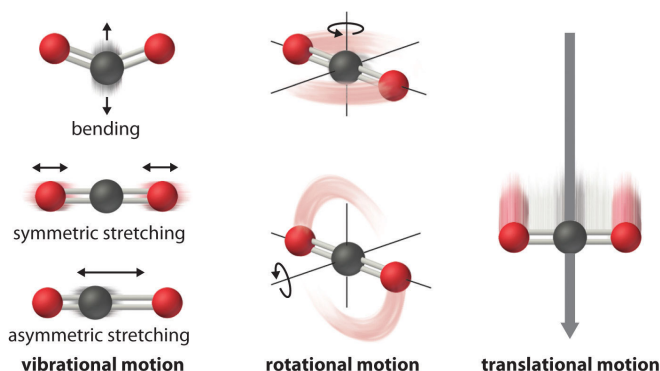


Figure 8.3.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

Third Law of Thermodynamics

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

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 ΔS 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 ΔS from Standard Molar Entropy Values

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° are $J/(mol \cdot K)$. 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 $S = 0 J/(mol \cdot K)$] and 298 K.

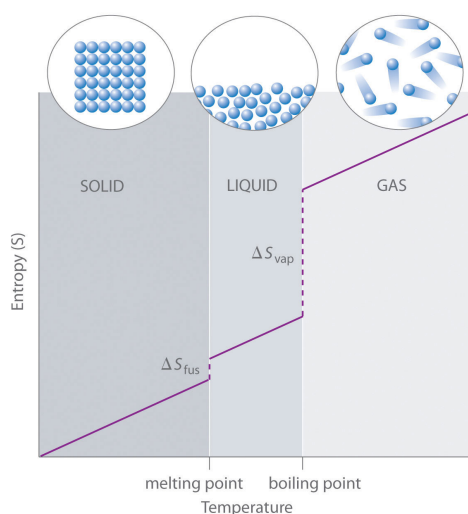


Figure 8.3.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{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 (ΔS_{vap}).

As shown in Table 8.3.1, for substances with approximately the same molar mass and number of atoms, S° values fall in the order $S^\circ(\text{gas}) > S^\circ(\text{liquid}) > S^\circ(\text{solid})$. For instance, S° for liquid water is $70.0 \text{ J}/(\text{mol}\cdot\text{K})$, whereas S° for water vapor is $188.8 \text{ J}/(\text{mol}\cdot\text{K})$. Likewise, S° is $260.7 \text{ J}/(\text{mol}\cdot\text{K})$ for gaseous I_2 and $116.1 \text{ J}/(\text{mol}\cdot\text{K})$ for solid 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 8.3.2, which is a generalized plot of the entropy of a substance versus temperature.

Table 8.3.1: Standard Molar Entropy Values of Selected Substances at 25°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	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	$\text{CH}_3\text{CH}_2\text{OH}$	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			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 8.3.1 also reveals that substances with similar molecular structures tend to have similar S° 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° [$5.7 \text{ J}/(\text{mol}\cdot\text{K})$] 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° 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° , which reflects a more ordered structure.

Note

ΔS° for a reaction can be calculated from absolute entropy values using the same “products minus reactants” rule used to calculate ΔH° .

To calculate ΔS° 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 8.3.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18} ; 2,2,4-trimethylpentane).

✓ Example 8.3.1

Use the data in Table 8.3.1 to calculate ΔS° 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

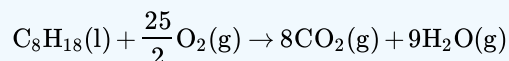
Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 8.3.1. 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 ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:



We calculate ΔS° for the reaction using the “products minus reactants” rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\Delta S^\circ_{\text{rxn}} = \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \quad (8.3.1)$$

$$= [8S^\circ(\text{CO}_2) + 9S^\circ(\text{H}_2\text{O})] - [S^\circ(\text{C}_8\text{H}_{18}) + \frac{25}{2}S^\circ(\text{O}_2)] \quad (8.3.2)$$

$$= \{[8 \text{ mol CO}_2 \times 213.8 \text{ J}/(\text{mol} \cdot \text{K})] + [9 \text{ mol H}_2\text{O} \times 188.8 \text{ J}/(\text{mol} \cdot \text{K})]\} \quad (8.3.3)$$

$$- \left\{ [1 \text{ mol C}_8\text{H}_{18} \times 329.3 \text{ J}/(\text{mol} \cdot \text{K})] + \left[\frac{25}{2} \text{ mol O}_2 \times 205.2 \text{ J}/(\text{mol} \cdot \text{K}) \right] \right\} \quad (8.3.4)$$

$$= 515.3 \text{ J/K} \quad (8.3.5)$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

? Exercise 8.3.1

Use the data in Table 8.3.1 to calculate ΔS° for the reaction of $\text{H}_2(\text{g})$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: -361.1 J/K

Calculating ΔS 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°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°C at constant volume. The increase in entropy with increasing temperature in Figure 8.3.2 is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow (q_{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:

$$\Delta S = \frac{q_{\text{rev}}}{T} = nC_p \frac{\Delta T}{T} \quad (\text{constant pressure}) \quad (8.3.6)$$

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.

$$\Delta S = nC_p \ln \frac{T_2}{T_1} \quad (\text{constant pressure}) \quad (8.3.7)$$

Similarly,

$$\Delta S = nC_v \ln \frac{T_2}{T_1} \quad (\text{constant volume}) \quad (8.3.8)$$

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 8.3.3): an orthorhombic form with a highly ordered structure (S_α) and a less-ordered monoclinic form (S_β). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure 8.3.3, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{\text{fus}(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the overall entropy change (ΔS_t) for the S_α - S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β , $\Delta H_{\text{fus}(\alpha)}$, and the melting point of S_α .)

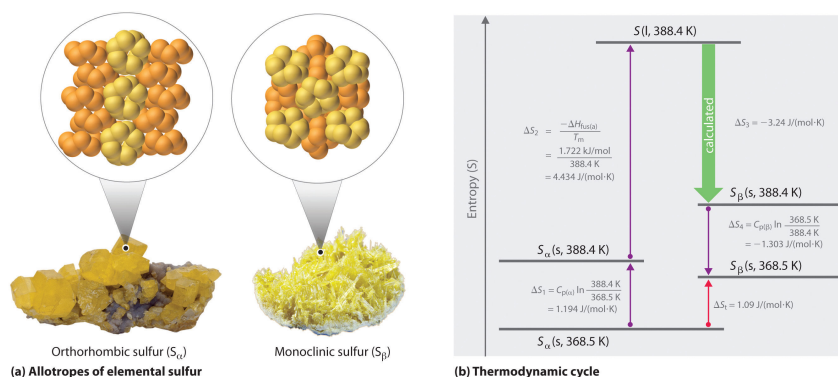


Figure 8.3.3: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other (a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a “crankshaft” arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure. (b) At 368.5 K, S_α undergoes a phase transition to S_β . Although ΔS_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_α ($T_m = 115.2^\circ\text{C} = 388.4 \text{ K}$) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol·K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure 8.3.3 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 ΔS refer to steps in the cycle):

$$\Delta S_t = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \quad (8.3.9)$$

$$1.09 \text{ J}/(\text{mol} \cdot \text{K}) = C_{p(\alpha)} \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{\text{fus}}}{T_m} + \Delta S_3 + C_{p(\beta)} \ln\left(\frac{T_4}{T_3}\right) \quad (8.3.10)$$

$$= 22.70 \text{ J}/(\text{mol} \cdot \text{K}) \ln\left(\frac{388.4}{368.5}\right) + \left(\frac{1.722 \text{ kJ/mol}}{388.4 \text{ K}} \times 1000 \text{ J/kJ}\right) \quad (8.3.11)$$

$$+ \Delta S_3 + 24.77 \text{ J}/(\text{mol} \cdot \text{K}) \ln\left(\frac{368.5}{388.4}\right) \quad (8.3.12)$$

$$= [1.194 \text{ J}/(\text{mol} \cdot \text{K})] + [4.434 \text{ J}/(\text{mol} \cdot \text{K})] + \Delta S_3 + [-1.303 \text{ J}/(\text{mol} \cdot \text{K})] \quad (8.3.13)$$

Solving for ΔS_3 gives a value of $-3.24 \text{ J}/(\text{mol} \cdot \text{K})$. As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

How are Entropies Measured

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat q required to bring the substance from 0 K to the temperature of interest, and then summing the ratios q/T . Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with melting, for example, is just $\Delta H_{\text{fusion}}/T_m$.
2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT , or more precisely, by an infinitesimal amount dT . Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C dT/T$ for each increment of temperature dT . This is of course just the integral

$$S_{0 \rightarrow T^o} = \int_0^{T^o} \frac{C_p}{T} dt \quad (8.3.14)$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the above integral in place of a constant C .

$$S_{0 \rightarrow T^o} = \int_0^{T^o} \frac{C_p(T)}{T} dt \quad (8.3.15)$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve.

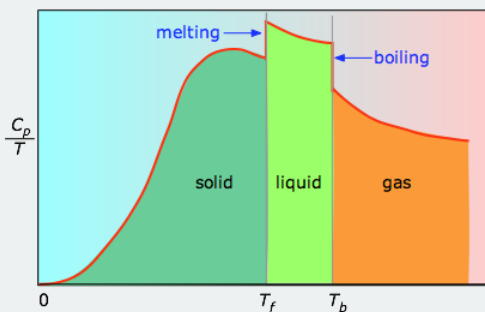


Figure 8.3.4: Heat capacity/temperature as a function of temperature

The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT . To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes. Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory.

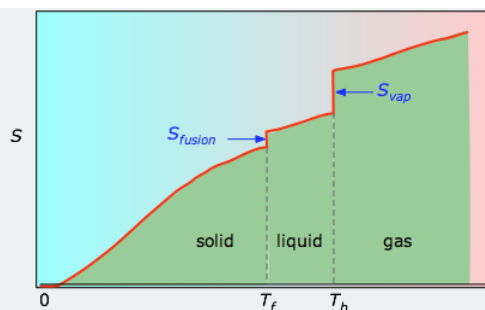


Figure 8.3.5: Molar entropy as a function of temperature

The cumulative areas from 0 K to any given temperature (taken from the experimental plot on the left) are then plotted as a function of T , and any phase-change entropies such as $S_{\text{vap}} = H_{\text{vap}} / T_b$ are added to obtain the absolute entropy at temperature T .

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°). We can use the “products minus reactants” rule to calculate the standard entropy change (ΔS°) for a reaction using tabulated values of S° for the reactants and the products.

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