A reversible Carnot engine operates on the following four-step cycle $(T_2 > T_1)$:

<table>
<thead>
<tr>
<th>Step (reversible)</th>
<th>Temperature</th>
<th>Work</th>
<th>Heat</th>
<th>Entropy change of engine</th>
<th>Energy change of engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Isothermal (expansion)</td>
<td>$A \rightarrow B$</td>
<td>$T_2$</td>
<td>$w_2$</td>
<td>$q_2$</td>
<td>$q_2 + w_2$</td>
</tr>
<tr>
<td>(b) Adiabatic (expansion)</td>
<td>$B \rightarrow C$</td>
<td>$T_2 \rightarrow T_1$</td>
<td>$w_{21}$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>(c) Isothermal (compression)</td>
<td>$C \rightarrow D$</td>
<td>$T_1$</td>
<td>$w_1$</td>
<td>$q_1$</td>
<td>$q_1 + w_1$</td>
</tr>
<tr>
<td>(d) Adiabatic (compression)</td>
<td>$D \rightarrow A$</td>
<td>$T_1 \rightarrow T_2$</td>
<td>$w_{12}$</td>
<td>$0$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

The terms in parentheses in the steps above refer to the case of pressure-volume work for a gas. However, in general, a Carnot engine can operate with systems involving other types of work as well, for example, magnetic work.

The efficiency $\varepsilon$ of the engine is defined as the ratio of the work done by the engine on the surroundings to the heat taken in at the high temperature; that is,

$$\varepsilon = \frac{-w}{q_2}$$  \hspace{1cm} (4-35)

where

$$-w = -(w_2 + w_{21} + w_1 + w_{12})$$

The engine operates in a cyclic manner; that is, it returns to its original state at the end of each cycle. Application of the first law to one complete cycle of the engine yields

$$\Delta U_{\text{eng}} = 0 = w + q_2 + q_1$$

Thus the work done by the engine ($-w$) per cycle is

$$-w = q_2 + q_1$$  \hspace{1cm} (4-36)

Application of the second law to one complete cycle of the engine yields (see page 88)

$$\Delta S_{\text{eng}} = 0 = \Delta S_2 + \Delta S_1 = \frac{q_2}{T_2} + \frac{q_1}{T_1}$$  \hspace{1cm} (4-37)

Given that the engine takes in energy as heat ($q_2 > 0$) from the high-temperature reservoir and therefore must undergo an entropy increase $\Delta S_2$,

$$\Delta S_2 = \frac{q_2}{T_2} > 0$$

we conclude that to return to its initial state the engine must discharge energy as heat to produce an entropy decrease that will offset the entropy increase in the heat intake step. However, because the engine puts out energy as work, the amount of energy discharged as heat must be less than the amount of energy taken in as heat (Eq. 4-36). From Eq. 4-37 we have

$$\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$  \hspace{1cm} (4-38)

but $-q_1$ is less than $q_2$ and thus $T_1$ must be less than $T_2$. In other words, a heat engine requires a temperature difference to take in energy as heat and to do work on the surroundings.

The efficiency of the Carnot engine is given by

$$\varepsilon = \frac{-w}{q_2} = \frac{q_2 + q_1}{q_2} = 1 + \frac{q_1}{q_2}$$  \hspace{1cm} (4-39)

but from Eq. 4-38

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

and thus

$$\frac{-w}{q_2} = \frac{T_2 - T_1}{T_2}$$  \hspace{1cm} (4-40)

Equation 4-40 is a truly remarkable result; it says that the efficiency of a reversible Carnot engine depends only on the temperatures of the two heat reservoirs. The efficiency is independent of the nature of the engine, the engine working substance, or the type of work performed. If any irreversibility enters into the operation of the engine, then the work done must be less than for the reversible case, and thus we can write Eq. 4-40 as

$$\frac{-w}{q_2} \leq \frac{T_2 - T_1}{T_2}$$  \hspace{1cm} (4-41)
where the inequality sign applies if any irreversibility is involved in the operation of the engine. Equation 4-41 can be obtained directly from Eq. 4-39 by noting that if any irreversibility is involved, then \( q_2 = T_2 \Delta S_2 \) and \( q_1 < T_1 \Delta S_1 \), but in any event \( \Delta S_1 = -\Delta S_2 \).

It is impossible to construct an engine that operates in a cycle that is more efficient than a reversible Carnot engine, because such a device would violate Eq. 4-41 and therefore would violate the laws of thermodynamics. A real engine necessarily involves some degree of irreversibility in its operation and therefore the efficiency of any real engine is less than that of a Carnot engine operating between the same two temperatures.

A reversible Carnot cycle for a Carnot engine with a gas as working substance is sketched in Figure 4-3 on \( P-V \) and \( T-S \) coordinate systems. The enclosed area on \( P-V \) coordinates is the net work output \( (-w) \) of the engine, and the enclosed area on \( T-S \) coordinates is the net heat intake \( (q_2 + q_1) \).

The maximum amount of work that can be obtained \( (-w_{rev}) \) from a given input of energy as heat \( (q_2) \) is given by Eq. 4-41 as

\[
-w_{rev} = q_2 \left( \frac{T_2 - T_1}{T_2} \right)
\]

Thus for a given value of \( q_2 \), the value of \( -w_{rev} \) is greater the greater the temperature difference \( T_2 - T_1 \); this conclusion has important practical consequences, as we shall soon see.

A Carnot engine can be run in reverse and used to extract energy as heat from a low-temperature reservoir and discharge energy as heat to a high-temperature reservoir (see Figure 4-4). In such a case the device is called a heat pump, if it is used as a heat source, or a refrigerator, if it is used to remove energy as heat. From the second law we know that work must be done on the engine to accomplish the transfer of energy as heat from the low- to the high-temperature reservoir (reverse Carnot cycle). If the process is cyclic \((A U_{cyc} = 0)\),

\[
T_2 > T_1
\]

Figure 4-3. Reversible Carnot cycle on \( P-V \) and \( T-S \) coordinates for a gas as working fluid. The area enclosed by the \( P-V \) path is equal to the net work done on the surroundings by the gas in one cycle. The area enclosed by the \( T-S \) path is equal to the net intake of energy as heat by the gas in one cycle. Further, \(-w = q_2 + q_1\).

Figure 4-4. Schematic of a Carnot engine used as a refrigerator or a heat pump. Compare with Figure 4-2.
then the amount of energy deposited as heat in the high-temperature reservoir \((q_2)\) will be equal to the amount of heat taken from the low-temperature reservoir \((q_1)\) plus an amount of heat equal to the work done on the system.

Just as for a Carnot engine running in the forward direction we have for the engine running in the reverse direction

\[
\Delta U_{\text{eng}} = q_1 + q_2 + w = 0
\]

The coefficient of performance (cop) of a heat pump is defined as

\[
\text{cop} = \frac{q_1}{w}
\]

and thus

\[
\text{cop} = \frac{q_1}{w} = \frac{-q_1}{q_1 + q_2}
\]

Application of the second law to the cycle \((q_1 \leq T_1 \Delta S_1\) and \(q_2 \leq T_2 \Delta S_2)\) yields

\[
q_1 \leq \frac{T_1 \Delta S_1}{T_1 \Delta S_1 + T_2 \Delta S_2}
\]

but the process is cyclic and therefore \(\Delta S_1 = -\Delta S_2\); hence

\[
\text{cop} = \frac{q_1}{w} \leq \frac{T_1}{T_2 - T_1}
\]

Note that \(q_1/w\) can be greater than unity, and \(q_1/w\) is greater the smaller the temperature difference, \(T_2 - T_1\). In other words, the work required to pump a given amount of energy as heat out of your refrigerator box is greater the difference in temperature between the refrigerator and the room into which the heat is pumped. It costs more to run your refrigerator in the summer.

4-10 The Second-Law Efficiency Rates the Performance of a Device Relative to the Ideal

A primary consideration in the thermodynamic analysis of energy utilization is the efficiency with which the energy is utilized. Unfortunately, there are several definitions of efficiency in use and this situation can lead to ambiguities, unless the definition in use is stated clearly. The definition of efficiency can be based on either the First Law or the Second Law of Thermodynamics.

The first-law efficiency \(\varepsilon_1\) is defined as

\[
\varepsilon_1 = \frac{\text{desired energy transfer achieved by the device}}{\text{energy input to the device}}
\]

If the maximum possible value of \(\varepsilon_1 = 1\), then \(\varepsilon_1\) is called an efficiency; whereas if necessarily \(\varepsilon_1 > 1\), then \(\varepsilon_1\) is referred to as a coefficient of performance.

The second-law efficiency \(\varepsilon_2\) is defined as

\[
\varepsilon_2 = \frac{\text{minimum amount of energy required to perform a given task}}{\text{amount of energy actually used to perform the task}} < 1
\]

The value of \(\varepsilon_2\) cannot exceed unity. The numerator in the definition of \(\varepsilon_2\) is a task minimum, not a device minimum. The second-law efficiency rates the performance of a device relative to the ideal, and thus \(\varepsilon_2\) is more useful than \(\varepsilon_1\) in assessing the possibility for reducing the amount of energy used to perform a given task. The first-law efficiency measures how much of the energy used actually reaches where it is supposed to go; it ignores alternative ways to accomplish the same task and it is concerned only with how well a particular device works. The second-law efficiency assesses the task and compares the minimum amount of energy required to accomplish the task with the amount of energy actually used to accomplish the task.

A typical furnace providing hot air at 100°F (316 K) to a house when the outside air is 32°F (273 K) has a first-law efficiency of about 0.60, because about 40% of the heat is vented to the outdoors. The second-law efficiency is

\[
\varepsilon_2 = \frac{q_2(T_2 - T_1)}{q} \frac{T_2}{316} = 0.60(316 - 273) = 0.082
\]

where the numerator \(q_2(T_2 - T_1)/T_2\) was obtained from Eq. 4-42 for \(-w\), and where \(q_2/q = 0.60\) (given). A well-designed space heater has \(\varepsilon_1 \approx 0.75\) (25% more first-law efficient than the \(q_2/q = 0.60\) case), because of the reduced amount of heat that is vented. Burning wood in a typical, decorative home fireplace to provide home heat has an \(\varepsilon_1 \approx 0.2\); that is, 80% of the heated air goes up the chimney. Woodburning stoves have \(\varepsilon_1\) values as high as 0.85.

The conversion of electricity to heat by resistance heating (I^2R or Joule heat) has a first-law efficiency of essentially 100%. The second-law efficiency for the 110°F/32°F temperature case is

\[
\varepsilon_2 = \frac{1.0(316 - 273)}{316} = 0.14
\]

If the electricity is generated in a power plant using fossil fuels, then the second-law efficiency of the conversion of chemical energy (fuel) to electricity at the plant is typically about 0.33, and therefore the overall second-law efficiency is 0.14 \times 0.33 = 0.046. Actually the overall efficiency is even less than 0.046, because of energy losses in the transmission of the electricity from the power plant to the home. If the electricity is generated in a hydroelectric plant, then the value of \(\varepsilon_2\) at the power plant is about 0.95 to 0.99, and the overall value of \(\varepsilon_2\) is about 0.14 (neglecting transmission losses).

The use of electricity for space heating by passing current through resistors is much less efficient on a second-law basis than using the electricity to run a heat pump, provided the temperature of the low-temperature reservoir \((T_r)\) is
not too low relative to the desired room temperature \(T_2\). The value of \(T_1\) can be held at, say, 285 K (12°C) by locating the low-temperature heat exchanger in a well. The minimum amount of energy \(w\) that must be expended to “pump” an amount of heat \(q_1\) from \(T_1 = 285\) K to \(T_2 = 293\) K (68°F) is given by Eq. 4.43 as

\[
w = q_1\left(\frac{T_2 - T_1}{T_1}\right) = 0.028q_1
\]

The total amount of energy transferred as heat to the home is \(w + q_1\), and equating this to the production of heat via resistance heating gives

\[
w + q_1 = I^2Rt
\]

or

\[
w + \frac{w}{0.028} = I^2Rt
\]

and thus

\[
w = 0.027I^2Rt
\]

where \(I\) is the current, \(R\) is the resistance, and \(t\) is the time. Even if the heat pump was only 50% efficient (actual value of \(w\) twice the above value), the amount of energy required by the heat pump would only be about 6% of that required by resistance heating. If the heat pump works directly off the outside air (rather than a well) and the outside air is 0°C, then the above 6% figure is increased to 14%. Although the possible energy savings in a particular case obtained by using heat pumps rather than resistance heaters are significant (space heating accounts for 68% of the total average residential energy use), the total possible savings are not large, because most homes are not electrically heated. Also, electrical heating has an advantage over central-forced-air heating in that individual rooms can be thermostated at different temperatures and the heating can be concentrated where it is most needed at any time.

A modern fossil-fuel power plant using steam turbines operates between 811 K (1000°F) (steam from the boiler) and 311 K (100°F) (ejection of heat into the cooling water). The maximum possible second-law efficiency \(\varepsilon_2\) is

\[
\varepsilon_2 = \frac{-w}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{811\text{ K} - 311\text{ K}}{811\text{ K}} = 0.62
\]

However, the actual operational efficiency is only about 0.41 owing to irreversibility. The power output of a heat engine is given by

\[
\text{power output} = p = \frac{-w}{t}
\]

where \(-w\) is the work done in one complete cycle of duration \(t\). For reversible operation, \(t\) is infinite and \(p\) is zero. The major limiting factor on the value of \(p\) is the rate at which heat is transferred from the heat source \(T_2\) to the engine and from the engine to the heat sink \(T_1\). Frictional losses are of less importance.

To transfer a finite amount of energy as heat in a finite time requires a finite temperature difference. That is, at the high temperature \(T_2\) where heat is absorbed, the temperature of the engine working fluid \(T_2\) must be less than \(T_2\); whereas at the low temperature where heat is ejected, the temperature of the engine working fluid \(T_1\) must be greater than \(T_1\). The transfer of energy as heat down a temperature gradient is an irreversible process that leads to entropy production and a lowering of the amount of work obtainable. The rate of nonradiative heat transfer is proportional to the temperature difference between the two bodies (Newton’s law of cooling):

\[
\frac{dT}{dt} = k(T - T_0) \quad T > T_0
\]

In such a case the engine efficiency for maximum power output \(\varepsilon_2(p\text{ max})\) can be shown to be given by (J. Ross)

\[
\varepsilon_2(p\text{ max}) = 1 - \left(\frac{T_1}{T_2}\right)^{1/2}
\]

For the 811 K/311 K power plant, \(\varepsilon_2(p\text{ max}) = 0.38\). The practical operation of a power plant involves a compromise between maximum power and maximum efficiency.
The data in Table 6-2 also show that Eq. 6.20 holds within the experimental error. Using the third law for $S_f(\Delta) = 0$ and $\frac{\Delta S_r}{\Delta G}$, we have

$$\Delta S_r = \Delta S_r(\beta - \beta_e) + \int_{\beta_e}^{\beta} \Delta S_r \, d\beta$$

$$\Delta S_r = \Delta S_e(\beta - \beta_e)$$

or

$$\Delta S_r(\beta - \beta_e) = \Delta S_e(\beta - \beta_e)$$

Another experimental check on the third law is provided by the entropies of two allotropic modifications of a substance to very low temperatures. Let us suppose that $\Delta S_r(\beta - \beta_e)$ is also determined in separate experiments from $\Delta S_r$ at both $\alpha$ and $\beta$ and that the transition temperature $T_a$ is the stable modification. Suppose also that the transition temperature at $T_a$ is determined. Then, if the third-law entropy of both the $\alpha$ and $\beta$ forms are determined separately, we can check whether or not $\Delta S_r(\beta - \beta_e) = 0$, as required by the third law. At the transition temperature $T_a$, the third-law entropy $\Delta S_r$ is zero.

6.5 Internal Metastability Can Lead to Froen-In-Entropy at $T = 0$

The Third Law of Thermodynamics as originally stated by Nernst had a serious defect in that it did not specify that the phases must be in a state of internal equilibrium. This defect was removed by G.N. Lewis who qualified the Nernst statement of the third law by restricting it to substances that did not involve internal metastability (frozen-in entropy) in the limit $T = 0$. Any state in which the arrangement of atoms or molecules is disorder will have a higher entropy than a perfectly ordered arrangement. If the disorder persists in the condensed phase down to the lowest temperatures of the calorimetric measurements, then the third-law entropy of the substance will be lower than the correct third-law entropy of the form of the substance stable above $T_a$.

![Figure 6.2](image-url)
that obtained for the substance as a liquid or gas from equilibrium measurements. In other words, if that amount of entropy due to the disorder remains in the crystal at low T, then it will not show up in the calorimetrically determined \( S_T \). The first experimental work to show this effect was that of G. E. Gibson and W. F. Giauque on glycerin. It is possible to supercool glycerin to very low temperatures, and thus it is possible to obtain and compare third-law entropies for glycerin that (1) has been taken as a crystalline solid from a few degrees Kelvin up through the normal melting point to the normal liquid at, say, 25°C and (2) has been taken as a supercooled (glassy) liquid from a few degrees Kelvin up to the normal liquid at 25°C. The entropy between 0 K and the lowest temperature of the measurements can be obtained in either case by extrapolation. Proceeding in this manner, Gibson and Giauque found that \( S_{298} - S_0 \) for the crystalline case exceeded \( S_{298} - S_0 \) for the glassy case by 23.4 ± 0.4 J·K⁻¹·mol⁻¹. Thus the entropy of glassy glycerin at 0 K must exceed that of crystalline glycerin at 0 K by 23.4 J·K⁻¹·mol⁻¹. That is,

\[
[S_{298}(\text{liquid}) - S_0(\text{crystal})] - [S_{298}(\text{liquid}) - S_0(\text{glass})] = S_0(\text{glass}) - S_0(\text{crystal}) = 23.4 \text{ J·K}^{-1}\text{·mol}^{-1}
\]

The higher entropy in the glassy state at 0 K is due to the more disordered arrangement of the glycerin molecules in the glassy state relative to the crystalline state. We conclude that because a glassy material is internally metastable, its conventional absolute entropy at 0 K is greater than zero (see Figure 6-3).

Frozen-in entropy can arise for magnetic crystals, if the calorimetric measurements are not carried to sufficiently low temperatures (sometimes 1 K or less) to remove the magnetic entropy that arises from a random arrangement of the individual magnetic moments (spin disorder). If the measurements are taken down through the magnetic-ordering transition region in which the spins become aligned, then the third-law entropy should agree with that determined from equilibrium data; whereas if the measurements are not carried to sufficiently low temperature such that the magnetic entropy is removed (spins aligned), then the third-law value of \( S_T \) will be lower than the “equilibrium” value by as much as \( R \ln(2J + 1) \).

Another type of configurational randomness that has been found arises when a molecule can enter a position in the crystal lattice in more than one physically distinguishable, but approximately energetically equivalent, orientation. If \( N \) is the maximum number of such possible orientations per molecule, then the entropy per mole arising from this configurational randomness in the crystal is \( R \ln N \). For example, J. O. Clayton and W. F. Giauque found that the calorimetrically determined third-law entropy of CO(g) at 298.15 K was about 4.2 J·K⁻¹·mol⁻¹ less than the entropy of CO(g) at 298.15 K determined from equilibrium data. They ascribed the discrepancy to end-for-end disorder (CO versus OC) of the CO molecules in the crystal lattice. In other words, CO cannot tell its O end from its C end when it goes into the crystal lattice. The discrepancy predicted from configuration considerations is \( R \ln 2 = 5.76 \text{ J·K}^{-1}\text{·mol}^{-1} \). The actual residual entropy is about 73% of this value, which presumably indicates that the molecular orientation is not completely random, as required to give \( S_0 = 5.76 \text{ J·K}^{-1}\text{·mol}^{-1} \). The case of NO is different than CO because NO goes into the crystal lattice as a dimer. The dimers evidently are oriented randomly in the manner

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{N}
\end{align*}
\]

including appropriate resonance forms. The observed residual entropy of NO(s) is 3.01 ± 0.12 J·K⁻¹·mol⁻¹, and the predicted value is \( \frac{1}{2} R \ln 2 = 2.89 \text{ J·K}^{-1}\text{·mol}^{-1} \), because 1 mol of NO yields 2 mol of (NO)₂.

The case of frozen-in entropy in water is particularly interesting. In this case the observed residual entropy at 0 K is 3.43 ± 0.21 J·K⁻¹·mol⁻¹. Ice (Figure 6-4) consists of tetrahedral units of O atoms, with a fifth O atom in the center of the tetrahedron; the whole structure is held together by hydrogen bonds. If we consider the H₂O molecule in the center of the tetrahedron, then each one of its protons can be directed at any one of three different apical O.

\[\text{Figure 6-3. Comparison of the entropy of crystalline and glassy glycerine. Note that the entropy of glassy glycerin is 23.4 J·K}^{-1}\text{·mol}^{-1} \text{ higher than the entropy of crystalline glycerin at absolute zero. The difference in entropies at absolute zero arises from the frozen-in disorder (entropy) of glassy glycerin at absolute zero.}\]
EXAMPLE 6-3

Nitrous oxide, NNO, a linear molecule, has a frozen-in (residual) entropy at 0 K of 4.77 J·K⁻¹·mol⁻¹. That is, for N₂O(g) at 25°C and 1 atm,

$$\bar{S}_{\text{equilibrium data}} - \bar{S}_{\text{heat capacity data}} = 4.77 \text{ J·K}^{-1}\cdot\text{mol}^{-1}$$

Suggest an explanation for the above discrepancy based on configurational disorder in N₂O(s) at 0 K.

Solution: If the linear NNO molecules are randomly oriented in the crystal lattice, that is, if each NNO molecule can enter the crystal in either of the two orientations

NNO or ONN

then the residual entropy per mole in the crystal at absolute zero would be

$$\bar{S} = R \ln N = R \ln 2 = 5.76 \text{ J·K}^{-1}\cdot\text{mol}^{-1}$$

The fact that the observed residual entropy is less than 5.76 J·K⁻¹·mol⁻¹ suggests that the end-for-end disorder of N₂O in the crystal is not completely random.

6-6 The Entropy of a Molecule Depends on the Type, Number, and Arrangement of the Atoms in the Molecule

In Chapter 4, we described the dependence of the entropy of a substance on configurational and thermal randomness factors. We shall now describe briefly the dependence of the entropy of a molecule on the type, the number, and the arrangement of the atoms in a molecule. The entropy increases with increasing mass of the atoms. For example, at 1 atm and 25°C we have the following:

<table>
<thead>
<tr>
<th>Substance</th>
<th>ΔS/ΔJ·K⁻¹·mol⁻¹</th>
<th>Substance</th>
<th>ΔS/ΔJ·K⁻¹·mol⁻¹</th>
<th>Substance</th>
<th>ΔS/ΔJ·K⁻¹·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(g)</td>
<td>126.0</td>
<td>F₂(g)</td>
<td>202.7</td>
<td>CH₄(g)</td>
<td>186.2</td>
</tr>
<tr>
<td>Ne(g)</td>
<td>146.2</td>
<td>Cl₂(g)</td>
<td>223.0</td>
<td>CH₂Cl(g)</td>
<td>234.5</td>
</tr>
<tr>
<td>Ar(g)</td>
<td>154.7</td>
<td>Br₂(g)</td>
<td>245.4</td>
<td>CCl₂(g)</td>
<td>309.7</td>
</tr>
<tr>
<td>Kr(g)</td>
<td>164.0</td>
<td>I₂(g)</td>
<td>260.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The entropy of a diamagnetic (no unpaired electrons) gaseous species arises from the absorption of energy into the translational, rotational, vibrational, and electronic motions of the molecule. At a given temperature and pressure, the contributions to the entropy of a gaseous species arising from the...
various motions in the molecule depend on the following factors: atomic masses, bond strengths, and molecular structure. In general, the more complex the molecule, the higher the entropy. Thus a molecule like F₂(g) (molecular mass of 38) has a higher entropy than Ar(g) (molecular mass of 40) because the F₂(g) molecules rotate as well as translate. The vibrational contributions to the entropy are small, relative to the contributions from translation and rotation, around 25°C.

**EXAMPLE 6-4**

Make a prediction about the relative values of the molar entropies at 25°C and 1 atm of the following compounds:

\[
\text{NH}_3(g) \quad \text{H}_2\text{O}(g) \quad \text{CH}_4(g)
\]

**Solution:** The molecular masses of the three molecules are about the same, and all the molecules have three rotational degrees of freedom; thus we predict that the molar entropies of the three molecules will have roughly the same values. The actual S values at 25°C follow:

<table>
<thead>
<tr>
<th>Species</th>
<th>(S/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(g)</td>
<td>188.7</td>
</tr>
<tr>
<td>NH₃(g)</td>
<td>192.3</td>
</tr>
<tr>
<td>CH₄(g)</td>
<td>186.2</td>
</tr>
</tbody>
</table>

The interpretation of entropy as a measure of disorder or randomness can be applied to chemical reactions. For a reaction involving only phases of a given type, be they solid, liquid, or gas, we expect \(\Delta S_{\text{rxn}} > 0\), if the number of moles of products exceeds the number of moles of reactants, and we expect \(\Delta S_{\text{rxn}} < 0\), if the reverse is true; whereas we expect \(\Delta S \approx 0\) if the number of moles of reactants and products are the same. The foregoing predictions are generally, though not always, observed, because we are restricting our entropy considerations to configurational factors. If the reaction involves both gaseous and condensed phases, then we expect \(\Delta S_{\text{rxn}} > 0\) if there are more moles of gas in the products than in the reactants and \(\Delta S_{\text{rxn}} < 0\) if the reverse is true. Recall that the entropy of a gaseous species is generally much greater than the entropy of a condensed-phase species of similar mass.

**EXAMPLE 6-5**

Arrange the following reactions in order of increasing \(\Delta S_{\text{rxn}}\) values (all species at 25°C, 1 atm).

(a) \(\text{C}(s) + \text{O}_2(g) \rightleftharpoons \text{CO}_2(g)\)
(b) \(\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}(g)\)
(c) \(\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2 \text{CO}(g)\)
(d) \(2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g)\)

**Solution:** The change in the number of moles of gas (products minus reactants) for the four cases are

(a) 0  (b) +1  (c) +1  (d) −1

Thus we predict

\[
\Delta S_a < \Delta S_c < \Delta S_b \approx \Delta S_e
\]

which is the actual order of the \(\Delta S_{\text{rxn}}\) values found experimentally.

The practical absolute entropy scale enables us to specify a number for the molar entropy of a substance at a particular temperature and pressure. Although practical absolute entropies are not true absolute entropies, in that they do not include the nuclear spin entropy or the entropy of isotope mixing, practical absolute entropies are unambiguously defined and they can be used to compute \(\Delta S_{\text{rxn}}\) values for chemical reactions. The nuclear spin entropies and isotope-mixing entropies both cancel out for chemical reactions. The calorimetrically determined value of the practical absolute entropy of a substance may be less than the actual value, if there is any unaccounted for frozen-in entropy (disorder) at the lowest temperature of the calorimetric measurements.

**6-7 Very Low Temperatures Can Be Obtained by Adiabatic Demagnetization**

Liquid helium has the lowest normal boiling point (4.2 K at 1 atm) of any known substance. Liquid helium is produced from gaseous helium by a Joule-Thomson expansion at 14 K (the boiling point of liquid hydrogen). Temperatures as low as 0.7 K can be obtained by evaporative cooling of He(\(\ell\)), using large, high-speed pumps to evaporate the He(\(\ell\)). The temperature of the evaporating liquid helium drops as a result of the utilization of internal energy in the liquid to supply the energy necessary to vaporize the liquid (\(\Delta H_{\text{vap}}\)). Temperatures below about 0.7 K cannot be attained by evaporative cooling of He(\(\ell\)), because the equilibrium vapor pressure of He(\(\ell\)) is less than 0.1 torr at 0.7 K and the rate of evaporation of He(\(\ell\)) becomes too low to overcome the flow of heat into the system from the surroundings. Also, below 2.17 K, He(\(\ell\)) becomes a superfluid (Chapter 9) and superfluid He(\(\ell\)) flows up and out of the low-temperature containment vessel to higher-temperature regions where the He(\(\ell\)) evaporates and then recondenses, thereby releasing heat (\(-\Delta H_{\text{vap}}\)) in the low-temperature containment vessel.

Temperatures below 0.7 K are produced by adiabatic demagnetization. The possibility of using adiabatic demagnetization to achieve very low temperatures was proposed independently by W. F. Giauque (pronounced "joke") and P. Debye in 1926. The basic idea is as follows. Moving charges give rise to a magnetic field. The electrons in matter move about the nucleus (orbital motion) and also rotate about their own axes (electron spin). A substance with unpaired