Chapter 20
Entropy and the Second Law of Thermodynamics

20.2 Irreversible Processes and Entropy:

**Entropy Postulate:**

*If an irreversible process occurs in a closed system, the entropy S of the system always increases; it never decreases.*

Changes in energy within a closed system do not set the direction of irreversible processes.

For example, if you were to wrap your hands around a cup of hot coffee, you would be astonished if your hands got cooler and the cup got warmer. That is obviously the wrong way for the energy transfer, but the total energy of the closed system (hands + cup of coffee) would be the same as the total energy if the process had run in the right way.
20.3 Change in Entropy: Irreversible Process

\[
\Delta S = S_f - S_i = \int \frac{dQ}{T} \quad \text{(change in entropy defined)}.
\]

Here \( Q \) is the energy transferred as heat to or from the system during the process, and \( T \) is the temperature of the system in kelvins.

20.3 Change in Entropy: Reversible Process

To find the entropy change for an irreversible process occurring in a closed system, replace that process with any reversible process that connects the same initial and final states, and calculate the entropy change for this reversible process.

\[
\Delta S = S_f - S_i = \frac{1}{T} \int dQ.
\]

\[
\Delta S = S_f - S_i = \frac{Q}{T} \quad \text{(change in entropy, isothermal process)}.
\]

Fig. 20-3 The isothermal expansion of an ideal gas, done in a reversible way. The gas has the same initial state \( i \) and same final state \( f \) as in the irreversible process.

Fig. 20-4 A \( p-V \) diagram for the reversible isothermal expansion of Fig. 20-3. The intermediate states, which are now equilibrium states, are shown.
20.3 Change in Entropy: Entropy is a State Function

Suppose that an ideal gas is taken through a reversible process, with the gas in an equilibrium state at the end of each step.

For each small step, the energy transferred as heat to or from the gas is $dQ$, the work done by the gas is $dW$, and the change in internal energy is $dE_{\text{int}}$.

We have: 
$$dE_{\text{int}} = dQ - dW.$$

Since the process is reversible, $dW = p \, dV$ and $dE_{\text{int}} = nC_v \, dT$.

Therefore, 
$$dQ = p \, dV + nC_v \, dT.$$

Using ideal gas law, we obtain: 
$$\frac{dQ}{T} = nR \frac{dV}{V} + nC_v \frac{dT}{T}.$$

Integrating, 
$$\int \frac{dQ}{T} = \int nR \frac{dV}{V} + \int nC_v \frac{dT}{T}.$$

Finally, 
$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_v \ln \frac{T_f}{T_i}.$$

Therefore, the change in entropy $\Delta S$ between the initial and final states of an ideal gas depends only on properties of the initial and final states; $\Delta S$ does not depend on how the gas changes between the two states.

Example, Change of Entropy:

Figure 20.5a shows two identical copper blocks of mass $m = 1.5$ kg: block L at temperature $T_L = 60^\circ C$ and block R at temperature $T_R = 20^\circ C$. The blocks are in a thermally insulated box and are separated by an insulating shutter. When we lift the shutter, the blocks eventually come to the equilibrium temperature $T_f = 40^\circ C$ (Fig. 20.5b). What is the net entropy change of the two-block system during this irreversible process? The specific heat of copper is 386 J/kg K.

Calculations: For the irreversible process, we need a thermal reservoir whose temperature can be changed slowly (say, by turning a knob). We then take the blocks through the following two steps, illustrated in Fig. 20.6.

**Step 1:** With the reservoir’s temperature set at $60^\circ C$, put block L on the reservoir. (Since block and reservoir are at the same temperature, they are already in thermal equilibrium.) Then slowly lower the temperature of the reservoir and the block to $40^\circ C$. As the block’s temperature changes by each increment $dT$ during this process, energy $dQ$ is transferred as heat from the block to the reservoir. Using Eq. 18-14, we can write this transferred energy as $dQ = mc \, dT$, where $c$ is the specific heat of copper. According to Eq. 20-1, the entropy change $\Delta S_L$ of block L during the full temperature change from initial temperature $T_L$ ($= 60^\circ C = 333 K$) to final temperature $T_f$ ($= 40^\circ C = 313 K$) is
$$\Delta S_L = \frac{\int mc \, dT}{T_L} = \frac{mc}{T_L} \int_{T_L}^{T_f} dT = mc \ln \frac{T_f}{T_L}.$$

Inserting the given data yields
$$\Delta S_L = (1.5 \text{ kg})(386 \text{ J/kg K}) \ln \frac{313 K}{333 K} = -35.86 \text{ J/K}.$$

**Step 2:** With the reservoir’s temperature now set at $20^\circ C$, put block R on the reservoir. Then slowly raise the temperature of the reservoir and the block to $40^\circ C$. With the same reasoning used to find $\Delta S_L$, you can show that the entropy change $\Delta S_R$ of block R during this process is
$$\Delta S_R = (1.5 \text{ kg})(386 \text{ J/kg K}) \ln \frac{313 K}{293 K} = +38.23 \text{ J/K}.$$

The net entropy change $\Delta S_{\text{net}}$ of the two-block system undergoing this two-step irreversible process is then
$$\Delta S_{\text{net}} = \Delta S_L + \Delta S_R = -35.86 \text{ J/K} + 38.23 \text{ J/K} = 2.4 \text{ J/K}.$$

Thus, the net entropy change $\Delta S_{\text{net}}$ for the two-block system undergoing the actual irreversible process is
$$\Delta S_{\text{net}} = 2.4 \text{ J/K}.$$

(Answer)
Example, Change of Entropy, Free Expansion of Gas:

Suppose 1.0 mol of nitrogen gas is confined to the left side of the container of Fig. 20-1a. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process? Treat the gas as ideal.

**Calculations:** From Table 19-4, the energy $Q$ added as heat to the gas as it expands isothermally at temperature $T$ from an initial volume $V_i$ to a final volume $V_f$ is

$$Q = nRT \ln \frac{V_f}{V_i}.$$ 

Here $n$ is the number of moles of gas present. The entropy change for this reversible process in which the temperature is held constant is

$$\Delta S_{rev} = \frac{Q}{T} = nRT \ln \frac{V_f}{V_i} = nR \ln \frac{V_f}{V_i} = nR \ln \frac{V_f}{V_i} = (1.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(\ln 2) = +5.76 \text{ J/K}.$$

$$\Delta S_{irrev} = \Delta S_{rev} = +5.76 \text{ J/K}.$$ 

20.4 The Second Law of Thermodynamics

*If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.*

$$\Delta S \geq 0 \quad \text{(second law of thermodynamics)}$$

Here the greater-than sign applies to irreversible processes and the equals sign to reversible processes. This relation applies only to closed systems.
20.4 The Second Law of Thermodynamics: Force due to Entropy

To understand why rubber resists being stretched:
First Law of Thermodynamics: \(dE = dQ - dW\)

The force from the rubber band has magnitude \(F\),
is directed inward, and does work \(dW = -F \, dx\)
during length increase \(dx\). \(dE = T \, dS + F \, dx\). \((\Delta S = Q/T)\)

To good approximation, the change \(dE\) in the
internal energy of rubber is 0 if the total stretch of
the rubber band is not very much.

Therefore, \(F = -T \frac{dS}{dx}\).

20.5 Entropy in the Real World: Carnot Engine

Figure 20-9 shows if we place the cylinder in contact with the
high temperature reservoir at temperature \(T_H\) heat \(|Q_H|\) is
transferred to the working substance from this reservoir as the gas
undergoes an isothermal expansion from volume \(V_a\) to volume
\(V_b\). With the working substance in contact with the low-
temperature reservoir at temperature \(T_L\) heat \(|Q_L|\) is transferred
from the working substance to the low-temperature reservoir as
the gas undergoes an isothermal compression from volume \(V_c\) to
volume \(V_d\) (Fig. 20-9b).
20.5 Entropy in the Real World: Carnot Engine

Heat:
\[ \Delta E_{\text{int}} = 0 \]
\[ W = |Q_H| - |Q_L| \]

Entropy Changes:
\[ \Delta S = \Delta S_H + \Delta S_L = \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L} = 0 \]
\[ \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L} \]

Efficiency:
\[ \varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|} \] (efficiency, any engine)
\[ \varepsilon_C = \frac{|Q_H| - |Q_L|}{Q_H} = 1 - \frac{|Q_L|}{|Q_H|} \]
\[ \varepsilon_C = 1 - \frac{T_L}{T_H} \] (efficiency, Carnot engine)

Fig. 20-10  The Carnot cycle of Fig. 20-9 plotted on a temperature–entropy diagram. During processes ab and cd the temperature remains constant. During processes bc and da the entropy remains constant.

20.5 Entropy in the Real World: Perfect Engines

Perfect engine: total conversion of heat to work

\[ Q_H \]
\[ W = |Q_H| \]
\[ Q_L = 0 \]

Fig. 20-11  The elements of a perfect engine—that is, one that converts heat \( Q_H \) from a high-temperature reservoir directly to work \( W \) with 100% efficiency.

Real engines, in which the processes that form the engine cycle are not reversible, have lower efficiencies.

100% engine efficiency (that is, \( \varepsilon = 1 \)) can only be achieved if \( T_L = 0 \) or \( T_H \rightarrow \infty \), which are impossible requirements.
20.5 Entropy in the Real World: Stirling Engine

The two isotherms of the Stirling engine cycle are connected, not by adiabatic processes as for the Carnot engine but by constant-volume processes.

To increase the temperature of a gas at constant volume reversibly from $T_L$ to $T_H$ (process $da$ in figure) requires a transfer of energy as heat to the working substance from a thermal reservoir whose temperature can be varied smoothly between those limits.

Also, a reverse transfer is required in process $bc$. Thus, reversible heat transfers (and corresponding entropy changes) occur in all four of the processes that form the cycle of a Stirling engine, not just two processes as in a Carnot engine.

Moreover, the efficiency of an ideal Stirling engine is lower than that of a Carnot engine operating between the same two temperatures. Real Stirling engines have even lower efficiencies.

Example, Carnot Engine:

Imagine a Carnot engine that operates between the temperatures $T_H = 850$ K and $T_L = 300$ K. The engine performs 1200 J of work each cycle, which takes 0.25 s.

(a) What is the efficiency of this engine?

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{850} = 0.647 = 64.7\%.$$ (Answer)

(b) What is the average power of this engine?

$$P = \frac{W}{t} = \frac{1200}{0.25} = 4800 \text{ W} = 4.8 \text{ kW}.$$ (Answer)

(c) How much energy $Q_H$ is extracted as heat from the high-temperature reservoir every cycle?

$$Q_H = \frac{W}{\varepsilon} = \frac{1200}{0.647} = 1855 \text{ J}.$$ (Answer)

$$Q_L = Q_H - W = 1855 - 1200 = 655 \text{ J}.$$ (Answer)

(d) By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?

$$\Delta S_H = \frac{Q_H}{T_H} = \frac{1855}{850} = +2.18 \text{ J/K}.$$ (Answer)

Similarly, for the negative transfer of energy $Q_L$ to the low-temperature reservoir at $T_L$, we have

$$\Delta S_L = \frac{Q_L}{T_L} = \frac{-655}{300} = -2.18 \text{ J/K}.$$ (Answer)

Note that the net entropy change of the working substance for one cycle is zero, as we discussed in deriving Eq. 20.10.
Example, Impossible Engine:

An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and freezing points of water. Is this possible?

Calculation: From Eq. 20-13, we find that the efficiency of a Carnot engine operating between the boiling and freezing points of water is

\[ e = 1 - \frac{T_l}{T_H} = 1 - \frac{(0 + 273) K}{(100 + 273) K} = 0.268 \approx 27\%. \]

The efficiency of a real engine must be less than the efficiency of a Carnot engine operating between the same two temperatures.

Thus, for the given temperatures, the claimed efficiency of 75% for a real engine (with its irreversible processes and wasteful energy transfers) is impossible.

20.6 Entropy in the Real World: Refrigerators

Fig. 20-14 The elements of a refrigerator.

In an ideal refrigerator, all processes are reversible and no wasteful energy transfers occur as a result of, say, friction and turbulence.

The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p-V plot. Energy is transferred as heat \( Q_L \) to the working substance from the low-temperature reservoir. Energy is transferred as heat \( Q_H \) to the high-temperature reservoir from the working substance. Work \( W \) is done on the refrigerator (on the working substance) by something in the environment.

This is reverse of a Carnot engine, and therefore called a Carnot refrigerator. A measure of the efficiency of the refrigerator is \( K \), the coefficient of performance:

\[ K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|} \quad \text{(coefficient of performance, any refrigerator)} \]

\( K_C \), the value for Carnot refrigerator is therefore:

\[ K_C = \frac{|Q_L|}{|Q_H| - |Q_L|} \]

Finally,

\[ K_C = \frac{T_l}{T_H - T_l} \quad \text{(coefficient of performance, Carnot refrigerator)} \]
20.6 Entropy in the Real World: Refrigerators

No series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature.

**Fig. 20-15** The elements of a perfect refrigerator—that is, one that transfers energy from a low-temperature reservoir to a high-temperature reservoir without any input of work.

The entropy change for the cold reservoir is $-\frac{|Q|}{T_L}$, and that for the warm reservoir is $+\frac{|Q|}{T_H}$. Thus, the net entropy change for the entire system is:

$$\Delta S = -\frac{|Q|}{T_L} + \frac{|Q|}{T_H}.$$  

$T_H > T_L$, and the right side of this equation is negative and thus the net change in entropy per cycle for the closed system refrigerator reservoirs is also negative. This violates the second law of thermodynamics, and therefore a perfect refrigerator does not exist.

20.7 The Efficiencies of Real Engines

**Fig. 20-16** (a) Engine X drives a Carnot refrigerator. (b) If, as claimed, engine X is more efficient than a Carnot engine, then the combination shown in (a) is equivalent to the perfect refrigerator shown here. This violates the second law of thermodynamics, so we conclude that engine X cannot be more efficient than a Carnot engine.

Suppose there is an engine $X$, which has an efficiency $\epsilon_X$ that is greater than $\epsilon_C$, the Carnot efficiency.

When the engine $X$ is coupled to a Carnot refrigerator, the work it requires per cycle is just equal to that provided by engine $X$. Thus, no (external) work is performed on or by the combination engine +refrigerator, which we take as our system.

Therefore, $\frac{|W|}{|Q_L|} > \frac{|W|}{|Q_H|}$, where the primed notation refers to the engine $X$.

Therefore, also: $|Q_H| > |Q_L|$, which finally leads to: $|Q_H| - |Q_L| = |Q_L| - |Q_L| = Q$.

This shows that the net effect of engine $X$ and the Carnot refrigerator working in combination is to transfer energy $Q$ as heat from a low-temperature reservoir to a high-temperature reservoir without the requirement of work. This is the perfect refrigerator, whose existence is a violation of the second law of thermodynamics.
20.8 A Statistical View of Entropy

Table 20-1 shows the seven possible configurations of six (N=6) identical molecules, which are contained in the left or right sides of a box. The two sides have equal volumes, and each molecule has the same probability of being in either side. Each configuration is labeled with a Roman numeral. For example, in configuration I, all six molecules are in the left half of the box (n1 = 6) and none are in the right half (n2 = 0). The number of different ways that a given configuration can be achieved are called the molecules' microstates.

The basic assumption is that all microstates are equally probable.

\[ W = \frac{N!}{n_1! n_2!} \]  
(multiplicity of configuration)

### Table 20-1

<table>
<thead>
<tr>
<th>Configuration Label</th>
<th>n1</th>
<th>n2</th>
<th>Multiplicity W (number of microstates)</th>
<th>Calculation of W (Eq. 20-20)</th>
<th>Entropy 10 (^{-22}) J/K (Eq. 20-21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6</td>
<td>0</td>
<td>1</td>
<td>6!/(6! 0!) = 1</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>5</td>
<td>1</td>
<td>6</td>
<td>6!/(5! 1!) = 6</td>
<td>2.47</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
<td>2</td>
<td>15</td>
<td>6!/(4! 2!) = 15</td>
<td>3.74</td>
</tr>
<tr>
<td>IV</td>
<td>3</td>
<td>3</td>
<td>20</td>
<td>6!/(3! 3!) = 20</td>
<td>4.13</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>4</td>
<td>15</td>
<td>6!/(2! 4!) = 15</td>
<td>3.74</td>
</tr>
<tr>
<td>VI</td>
<td>1</td>
<td>5</td>
<td>6</td>
<td>6!/(1! 5!) = 6</td>
<td>2.47</td>
</tr>
<tr>
<td>VII</td>
<td>0</td>
<td>6</td>
<td>1</td>
<td>6!/(0! 6!) = 1</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>64</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Example, Microstates and multiplicity:**

Suppose that there are 100 indistinguishable molecules in the box of Fig. 20-17. How many microstates are associated with the configuration n1 = 50 and n2 = 50, and with the configuration n1 = 100 and n2 = 0? Interpret the results in terms of the relative probabilities of the two configurations.

**KEY IDEA**

The multiplicity W of a configuration of indistinguishable molecules in a closed box is the number of independent microstates with that configuration, as given by Eq. 20-20.

**Calculations:** Thus, for the (n1, n2) configuration (50, 50),

\[ W = \frac{N!}{n_1! n_2!} = \frac{100!}{50! 50!} = \frac{9.33 \times 10^{57}}{(3.04 \times 10^{33})(3.04 \times 10^{33})} = 1.01 \times 10^{29}. \]  
(Answer)

Similarly, for the configuration (100, 0), we have

\[ W = \frac{N!}{n_1! n_2!} = \frac{100!}{100! 0!} = \frac{1}{1} = 1. \]  
(Answer)

**The meaning:** Thus, a 50–50 distribution is more likely than a 100–0 distribution by the enormous factor of about \(1 \times 10^{29}\). If you could count, at one per nanosecond, the number of microstates that correspond to the 50–50 distribution, it would take you about \(3 \times 10^{37}\) years, which is about 200 times longer than the age of the universe. Keep in mind that the 100 molecules used in this sample problem is a very small number. Imagine what these calculated probabilities would be like for a mole of molecules, say about \(N = 10^{23}\). Thus, you need never worry about suddenly finding all the air molecules clustering in one corner of your room, with you gasping for air in another corner. So, you can breathe easy because of the physics of entropy.
Here $S$ and $W$ are the entropy of the configuration of a gas and the multiplicity of that configuration respectively.

**Since the relation is logarithmic, the total entropy of two systems is the sum of their separate entropies.**

**Also, therefore, the probability of occurrence of two independent systems is the product of their separate probabilities.**

Sometimes Stirling’s approximation is used for $\ln N!$:

$$\ln N! \approx N \ln N - N$$

(Stirling’s approximation).

**Example, Entropy change:**

When $n$ moles of an ideal gas doubles its volume in a free expansion, the entropy increase from the initial state $i$ to the final state $f$ is $S_f - S_i = nR \ln 2$.

Derive this result with statistical mechanics.

Calculations: The molecules are in a closed container, and the multiplicity $W$ of their microstates can be found by:

$$W_i = \frac{N!}{N! 0!} = 1.$$  

Here $N$ is the number of molecules in the $n$ moles of the gas. Initially, with the molecules all in the left half of the container, their $(n_1, n_2)$ configuration is $(N, 0)$.

Finally, with the molecules spread through the full volume, their $(n_1, n_2)$ configuration is $(N/2, N/2)$.

The initial and final entropies are

$$S_i = k \ln W_i = k \ln 1 = 0$$

$$S_f = k \ln W_f = k \ln (N!) - 2k \ln [(N/2)!]$$

Now,

$$S_f - S_i = nR \ln 2 = k [N \ln(N) - N] - 2k [N/2 \ln(N/2) - (N/2)]$$

$$= k [N \ln(N) - N] - N \ln(N/2) + N$$

$$= k [N \ln(N) - N \ln(N - 1) + N]$$

Therefore,

$$S_f = nR \ln 2.$$  

The change in entropy from the initial state to the final is thus

$$S_f - S_i = nR \ln 2 - 0$$

$$= nR \ln 2,$$

which is what we set out to show.