Chapter 6

Entropy

6.1 Clausius Inequality and Definition of Entropy

The Clausius inequality states that for any thermodynamic cycle

\[ \oint \left( \frac{\delta Q}{T} \right)_b \leq 0 \]  \hspace{1cm} (6.1-1)

In this expression \( \delta Q \) is the heat transfer and \( T \) is the temperature at the system boundary. The equality applies when there are no (internal) irreversibilities as the system execute the cycle. Consider two cycles executed by a closed system shown in Figure 6.1. One cycle follows a reversible path A from state 1 to state 2, followed by a reversible path C from state 2 to state 1. The other cycle follows a reversible path B from state 1 to state 2, followed by the same reversible path C from state 2 to state 1 as in the first cycle.

![Figure 6.1-1 Two reversible cycles.](image)

Applying Clausius inequality to the first cycle 1A2C1 gives

\[ \left( \int_1^2 \frac{\delta Q}{T} \right)_A + \left( \int_2^1 \frac{\delta Q}{T} \right)_C = 0 \]  \hspace{1cm} (6.1-2a)

The right hand side of Clausius inequality is set to zero since the cycle is composed of reversible processes. Similarly for the second cycle 1B2C1 we have

\[ \left( \int_1^2 \frac{\delta Q}{T} \right)_B + \left( \int_2^1 \frac{\delta Q}{T} \right)_C = 0 \]  \hspace{1cm} (6.1-2b)

Comparing Eq. (6.1-2a) and Eq. (6.1-2b) we obtain

\[ \left( \int_1^2 \frac{\delta Q}{T} \right)_A = \left( \int_1^2 \frac{\delta Q}{T} \right)_B \]

Since the paths A and B are arbitrary, the value of the integral depends only on the end states.
The integral therefore represents the change in some property of the system. We call this property *entropy*, and the change in entropy is given by

\[ \Delta S = S_2 - S_1 = \left( \int_{T_1}^{T_2} \frac{\delta Q}{T} \right)_{rev} \]  

(6.1-3)

On differential form, the definition of entropy is given by

\[ dS = \frac{\delta Q_{rev}}{T} \]  

(6.1-4)

Since entropy is a property, the change in entropy of a system in going from one state to another state is independent of the processes, reversible or irreversible. The entropy value might be obtained from software, table, or chart as shown in Table 6.1-1 and Figure 6.1-1.

**Table 6.1-1** Entropy values for water at 212°F

<table>
<thead>
<tr>
<th>Temp F</th>
<th>Pressure psia</th>
<th>Specific Volume ft3/lbm</th>
<th>Internal Energy Btu/lbm</th>
<th>Specific Enthalpy Btu/lbm</th>
<th>Specific Entropy Btu/lbm/R</th>
<th>Quality</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>212</td>
<td>14.7</td>
<td>0.01672</td>
<td>180.1</td>
<td>180.1</td>
<td>0.3121</td>
<td>0 Saturated Liquid</td>
</tr>
<tr>
<td>2</td>
<td>212</td>
<td>14.7</td>
<td>26.8</td>
<td>1078</td>
<td>1150</td>
<td>1.757</td>
<td>1 Saturated Vapor</td>
</tr>
<tr>
<td>3</td>
<td>212</td>
<td>14.7</td>
<td>10.73</td>
<td>539.1</td>
<td>568.3</td>
<td>0.8899</td>
<td>0.4 Liquid Vapor Mixture</td>
</tr>
</tbody>
</table>

**Figure 6.1-1** Temperature-entropy diagram for water.
6.2 Fundamental Property Relations

The first law for a closed system undergoing reversible process with only $PV$ work is given by

$$dU = \delta Q_{rev} + \delta W_{rev}$$

From the second law, $\delta Q_{rev} = TdS$, the first law can be written as

$$dU = TdS - pdV$$

(6.2-1)

We can write the change in internal energy in terms of two independent variables $S$ and $V$, that is, $U = U(S, V)$:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

(6.2-2)

Comparing equations (6.2-1) and (6.2-2) we have

$$T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } p = -\left(\frac{\partial U}{\partial V}\right)_S$$

(6.2-3)

The four functions $U$, $H$, $A$, and $G$ are collectively called thermodynamic potentials. The expression represented by $U = U(S, V)$ results in the partial derivatives of the thermodynamic potentials corresponding to thermodynamic properties $T$ and $p$ as defined in Eq. (6.2-3). While $U$ can be a function of any two properties, no other grouping of independent properties $x$ and $y$, $U = U(x, y)$, allows us to write partial derivatives in terms of thermodynamic properties as given by Eq. (6.2-3). The three properties $\{U, S, V\}$ form a fundamental grouping.

Similarly, the change in enthalpy ($H = U + pV$) is given by

$$dH = dU + d(pV) = TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp$$

(6.2-4)

The change in enthalpy in terms of two independent variables $S$ and $p$ is

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

(6.2-5)

Comparing equations (6.2-4) and (6.2-5) we have

$$T = \left(\frac{\partial H}{\partial S}\right)_p \text{ and } V = \left(\frac{\partial H}{\partial p}\right)_S$$

(6.2-6)
We have two more relations for the change in *Helmholtz free energy*, $dA$, and the change in *Gibbs free energy*, $dG$,

\[
dA = -SdT - pdV 
\]

\[
dG = -SdT + Vdp 
\]

(6.2-7)

(6.2-8)

The fundamental groupings \( \{A, T, V\} \) and \( \{G, T, p\} \) result in

\[
S = \left( \frac{\partial A}{\partial T} \right)_V \quad \text{and} \quad p = \left( \frac{\partial A}{\partial V} \right)_T 
\]

(6.2-9)

\[
S = \left( \frac{\partial G}{\partial T} \right)_p \quad \text{and} \quad V = \left( \frac{\partial G}{\partial p} \right)_T 
\]

(6.2-10)

The grouping can be obtained from the following diagram where there properties at a corner form a fundamental grouping, for example \( \{A, T, V\} \) and \( \{G, T, p\} \).

\[
\begin{array}{c}
G \\
T \\
A
\end{array}
\quad \begin{array}{c}
p \\
S \\
U
\end{array}
\quad \begin{array}{c}
H \quad \text{Great physicists Have Study} \\
\text{Under Very Able Teachers}
\end{array}
\]

Thermodynamic properties can then be obtained from the partial derivative of the thermodynamics potentials. Temperature can be obtained from the derivative of $H$ or $U$. In both cases, the variable opposite $T$ in the diagram will be in the denominator of the derivative and the remaining variable belong to the grouping will be the variable keeping constant.

\[
T = \left( \frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad T = \left( \frac{\partial H}{\partial S} \right)_P 
\]
Similarly, $p$ can be expressed in terms of the partial derivative of thermodynamic potentials using the following diagram. Note the minus sign since $V$ is in the negative direction of $P$.

\[ p = - \left( \frac{\partial U}{\partial V} \right)_S \quad \text{and} \quad p = - \left( \frac{\partial A}{\partial V} \right)_T \]

Similarly, we have

\[ S = - \left( \frac{\partial A}{\partial T} \right)_V \quad \text{and} \quad S = - \left( \frac{\partial G}{\partial T} \right)_P \]

and

\[ V = \left( \frac{\partial H}{\partial p} \right)_S \quad \text{and} \quad V = \left( \frac{\partial G}{\partial p} \right)_T \]

When we study phase equilibrium, the Gibbs free energy will be use frequently to obtain the relations between the measured properties.
6.3 Entropy Balance for Closed Systems

The entropy balance for a closed system can be written as

\[ S_2 - S_1 = \left( \int_1^2 \frac{\delta Q}{T} \right)_b + \sigma \]  

(6.3-1)

In this equation, \( S_2 - S_1 \) is the change in the amount of entropy contained within the system, \( \left( \int_1^2 \frac{\delta Q}{T} \right)_b \) is the net amount of entropy transferred in across the system boundary, and \( \sigma \) is the amount of entropy produced within the system all during some time interval \( \Delta t \). The entropy production will be zero if no irreversibilities present within the system. In differential form, the entropy balance is given by

\[ dS = \left( \frac{\delta Q}{T} \right)_b + \delta\sigma \]  

(6.3-2)

Example 6.3-1

Water initially a saturated liquid at 150°C is contained within a piston–cylinder assembly. The water undergoes a process to the corresponding saturated vapor state, during which the piston moves freely in the cylinder. There is no heat transfer with the surroundings. If the change of state is brought about by the action of a paddle wheel, determine the net work per unit mass, in kJ/kg, and the amount of entropy produced per unit mass, in kJ/kg·K.

Solution

From the energy balance with negligible change in kinetic and potential energies:

---

\[ \Delta U = Q + W \]

Since \( Q = 0 \),
\[
\frac{W}{m} = u_2 - u_1 = 2560 - 631.7 = 1928.3 \text{ kJ/kg}
\]

\[
S_2 - S_1 = \left( \int_{T_1}^{T_2} \frac{\delta Q}{T} \right)_b + \sigma = \sigma
\]

\[
\frac{\sigma}{m} = s_2 - s_1 = 6.838 - 1.842 = 4.996 \text{ kJ/kg·K}
\]

**Example 6.3-2.**

During steady state operation, a gearbox receives 60 kW through the input shaft and delivers power through the output shaft. For the gearbox as the system, the rate of energy transfer by convection is

\[
\dot{Q} = -hA(T_b - T_f), \text{ where } h = 0.171 \text{ kW/m}^2\cdot\text{K}, A = 1.0 \text{ m}^2.
\]

Evaluate the rate of entropy production \( \dot{\sigma} \), in kW/K, for (a) the gearbox as the system and (b) an enlarge system consisting of the gearbox and enough of its surroundings that heat transfer occurs at the temperature of the surroundings away from the immediate vicinity of the gearbox, \( T_f = 293 \text{ K} \).

**Solution**

(a) The rate of entropy production \( \dot{\sigma} \), in kW/K, for the gearbox as the system

The entropy balance is given by

\[
S_2 - S_1 = \left( \int_{T_1}^{T_2} \frac{\delta Q}{T} \right)_b + \sigma
\]

---

For constant temperature, the entropy rate balance for the closed system is

\[ \frac{dS}{dt} = \frac{\dot{Q}}{T_b} + \dot{\sigma} \]

For steady state we have

\[ \dot{\sigma} = -\frac{\dot{Q}}{T_b} \]

\[ \dot{Q} = -hA(T_b - T_i) = -(0.171 \text{ kW/m}^2\cdot\text{K})(1 \text{ m}^2)(300 - 293)\text{K} = -1.2 \text{ kW} \]

\[ \dot{\sigma} = \frac{\dot{Q}}{T_b} = -\frac{(-1.2 \text{ kW})}{300 \text{ K}} = 4\times10^{-3} \text{ kW/K} \]

(b) The rate of entropy production \( \dot{\sigma} \), in kW/K, for an enlarge system consisting of the gearbox and enough of its surroundings that heat transfer occurs at the temperature of the surroundings.

\[ \frac{dS}{dt} = \frac{\dot{Q}}{T_f} + \dot{\sigma} \]

For steady state we have

\[ \dot{\sigma} = -\frac{\dot{Q}}{T_f} = -\frac{(-1.2 \text{ kW})}{293 \text{ K}} = 4.1\times10^{-3} \text{ kW/K} \]

The entropy balance for an isolated system is given by

\[ \Delta S_{iso} = \left( \int_{T_1}^{T_2} \frac{\delta Q}{T} \right)_{p} + \sigma_{iso} \]

Since \( \left( \int_{T_1}^{T_2} \frac{\delta Q}{T} \right)_{p} = 0 \) for an isolated system, we have

\[ \Delta S_{iso} = \Delta S_{sys} + \Delta S_{surr} = \sigma_{iso} \geq 0 \]

The only processes that can occur are those for which the production of entropy for isolated systems is positive.