

3.6.7. Entropy

Recall from Eq. (3.124) that the Clausius Inequality is given by,

$$\left(\int_b \frac{\delta Q_{\text{into}}}{T} \right)_{\text{cycle}} = -\sigma_{\text{cycle}}, \quad (3.133)$$

where,

$$\sigma_{\text{cycle}} > 0 \quad \text{internally irreversible system,} \quad (3.134)$$

$$\sigma_{\text{cycle}} = 0 \quad \text{internally reversible system,} \quad (3.135)$$

$$\sigma_{\text{cycle}} < 0 \quad \text{impossible (violates the Second Law).} \quad (3.136)$$

Consider a system undergoing a cycle in which two different internally reversible cycles are considered: path A then C and path B then C. From Eq. (3.133),

$$\left(\int_b \frac{\delta Q_{\text{into}}}{T} \right)_{\text{cycle}} = 0, \quad (3.137)$$

since the cycle is internally reversible. Expanding the integral along the cycle's two paths,

$$\int_{A,b} \frac{\delta Q_{\text{into}}}{T} + \int_{C,b} \frac{\delta Q_{\text{into}}}{T} = 0, \quad (3.138)$$

and,

$$\int_{B,b} \frac{\delta Q_{\text{into}}}{T} + \int_{C,b} \frac{\delta Q_{\text{into}}}{T} = 0. \quad (3.139)$$

Combining the previous two equations,

$$\int_{A,b} \frac{\delta Q_{\text{into}}}{T} = \int_{B,b} \frac{\delta Q_{\text{into}}}{T}. \quad (3.140)$$

Thus, the result of the integral is independent of the (reversible) path, which means that the integral can be considered a change in properties between the end points. Recall that property values are independent of path. This system property is defined as the entropy and is defined as,

$$S_2 - S_1 := \int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T} \Big|_{\text{internally reversible}}, \quad (3.141)$$

or in differential form,

$$dS := \frac{\delta Q_{\text{into}}}{T} \Big|_{\text{internally reversible}}. \quad (3.142)$$

Note that the integrals in Eqs. (3.139) - (3.142) are performed over the system boundary while traversing the path from state 1 to state 2.

Notes:

- (1) Entropy S is an extensive property. The specific entropy s is the entropy per unit mass, i.e., $s = S/m$. The dimensions of entropy are [energy]/[temperature], e.g., kJ K^{-1} or $\text{Btu } ^\circ\text{R}^{-1}$. Typical units for specific entropy are $\text{kJ}/(\text{kg} \cdot \text{K})$ or $\text{Btu}/(\text{lb}_m \cdot ^\circ\text{R})$.
- (2) Since entropy is a property, the change in entropy between two states is independent of the path between the two states. The internally reversible path in Eq. (3.141) is used just to define entropy. Even if a process path between two states isn't reversible, as shown in Figure 3.35, we can still calculate the entropy at each of the endpoints since we can imagine reversible paths from some reference state to each endpoint. A later note discusses irreversible process paths in more detail.
- (3) From Eq. (3.141), adding heat in an internally reversible manner into a system increases its entropy. Removing heat in an internally reversible manner reduces its entropy.
- (4) The change in entropy for a process can be positive, negative, or zero; it just depends on the heat transfer (which occurs reversibly).

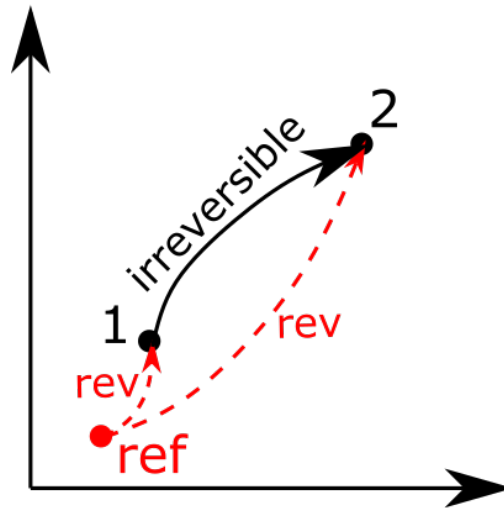


FIGURE 3.35. An illustration showing how the path for defining the property of entropy involves a reversible path from a reference point to a given state, but the entropy difference between two end states in an irreversible process can still be calculated.

- (5) The specific entropy for a two-phase mixture may be found using the quality,

$$s = xs_v + (1 - x)s_l. \quad (3.143)$$

- (6) The specific entropy for a compressed liquid may be approximated as the specific entropy of a saturated liquid at the same temperature,

$$s_{CL}(T, p) \approx s_l(T). \quad (3.144)$$

- (7) As with p - v and T - v diagrams, T - s and h - s (aka Mollier) diagrams are often helpful in visualizing processes (Figure 3.36).

- (8) For a process that is both adiabatic and internally reversible, Eq.(3.141) indicates that the process is also isentropic, i.e., $S_2 - S_1 = 0$ or $dS = 0$. Many real processes are often idealized as being isentropic. An isentropic process need not be adiabatic and internally reversible, however. It's possible to have internally irreversible processes in which heat is removed that end up producing no net entropy. We'll discuss this scenario a little later in the notes.

- (9) We can re-arrange Eq. (3.141) to give,

$$\delta Q_{\substack{\text{into,} \\ \text{internally} \\ \text{reversible}}} = TdS, \quad (3.145)$$

$$Q_{\substack{\text{into,12,} \\ \text{internally} \\ \text{reversible}}} = \int_1^2 TdS. \quad (3.146)$$

Thus, the area under an *internally reversible* process path on a T - S diagram is equal to the energy entering a system via heat transfer (Figure 3.37).

- (10) Now let's consider the possibility of processes that may not be internally reversible. Let's consider a cycle that consists of a process from state 1 to state 2, and a return process from state 2 to state 1. The return process (2 to 1) will be assumed to be internally reversible. The first process (from 1 to 2) can be either internally reversible or internally irreversible. Combining Eqs. (3.133) and

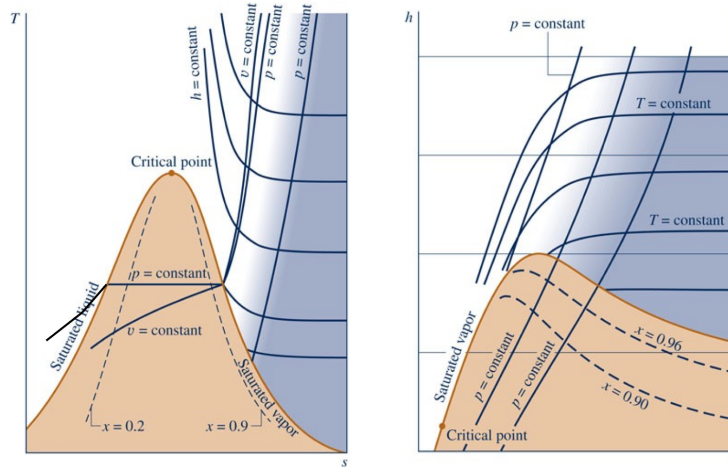


FIGURE 3.36. Example $T-s$ and $h-s$ (aka Mollier) diagrams. Figures are from Moran et al., 7th ed.

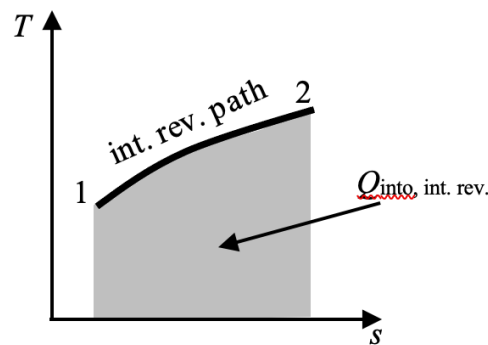


FIGURE 3.37. A schematic showing that the area under an *internally reversible* process path in a $T-S$ plot is equal to the energy added to the system via heat transfer.

(3.141) gives,

$$\left(\int_b^1 \frac{\delta Q_{\text{into}}}{T} \right)_{\text{cycle}} = -\sigma_{\text{cycle}} \implies \underbrace{\int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T} + \int_{2,b}^1 \frac{\delta Q_{\text{into}}}{T}}_{\text{the cycle}} \Big|_{\text{internally reversible}} = -\sigma_{\text{cycle}}, \quad (3.147)$$

$$\int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T} + \sigma_{\text{cycle}} = - \int_{2,b}^1 \frac{\delta Q_{\text{into}}}{T} \Big|_{\text{internally reversible}} = \int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T} \Big|_{\text{internally reversible}} = S_2 - S_1, \quad (3.148)$$

$$\boxed{\begin{array}{l} \underbrace{S_2 - S_1}_{\text{change in system}} \\ \text{entropy between states} \end{array} = \underbrace{\int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T}}_{\text{entropy transferred}} + \underbrace{\sigma_{12}}_{\text{entropy produced}} \quad (3.149)}_{\text{into the system through the boundary via heat transfer} \quad \text{in the system during the process from 1 to 2}}$$

where,

$$\sigma_{12} > 0 \quad \text{irreversibilities in the system in going from 1 to 2,} \quad (3.150)$$

$$\sigma_{12} = 0 \quad \text{reversible system in going from 1 to 2,} \quad (3.151)$$

$$\sigma_{12} < 0 \quad \text{impossible in going from 1 to 2.} \quad (3.152)$$

Note that $\sigma_{12} = 0$ since we assumed that the return process was internally reversible.

Equation (3.149) may also be written on a rate basis,

$$\underbrace{\frac{dS}{dt}}_{\text{rate of change in system entropy}} = \underbrace{\int_b \frac{\dot{Q}_{\text{into}}}{T}}_{\text{rate at which entropy is transferred into the system through the boundary via heat transfer}} + \underbrace{\dot{\sigma}}_{\text{rate at which entropy is produced in the system}} \quad (3.153)$$

where,

$$\dot{\sigma} > 0 \quad \text{irreversibilities in the system,} \quad (3.154)$$

$$\dot{\sigma} = 0 \quad \text{reversible system,} \quad (3.155)$$

$$\dot{\sigma} < 0 \quad \text{impossible.} \quad (3.156)$$

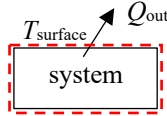
Note that the process in going from 1 to 2 in Eqs. (3.149) and (3.153) need not be internally reversible. If it is internally reversible, then $\sigma_{12} = 0$ and we recover Eq. (3.141). If the process from 1 to 2 is internally irreversible, then $\sigma_{12} > 0$. The change in entropy can be positive, negative, or zero depending on the contributions due to heat transfer and entropy production due to internal irreversibilities; however, the entropy production term must be positive or equal to zero. Note that it is possible to have an isentropic process ($S_2 = S_1$) for an internally irreversible process ($\sigma_{12} > 0$) as long as heat is removed from the system during the process ($\delta Q_{\text{into}} < 0$) and the boundary integral term exactly balances the entropy production term in magnitude.

- (11) An isolated system is one that has no interaction with the surroundings, i.e., no work input/output and no heat transfer with the surroundings. In such a case, the change in total energy of the system must be zero from the first law, i.e., $\Delta E_{\text{sys}} = 0$. In addition, the change in entropy of the system will equal the entropy production within the system due to irreversibilities, i.e., $\Delta S_{\text{sys}} = \sigma \geq 0$. Since all real processes have irreversibilities, the change in entropy for a real, isolated system must be positive.

During a process involving a 1 kg mass of material, 9000 J of heat leaves the system and enters the surroundings. The temperature at the surface of the system is 300 K. Determine if the process is internally reversible, internally irreversible, or impossible for the following conditions:

- The change in the specific entropy of the system is $-30.0 \text{ J}/(\text{kg}\cdot\text{K})$.
- The change in the specific entropy of the system is $-20.0 \text{ J}/(\text{kg}\cdot\text{K})$.
- The change in the specific entropy of the system is $-40.0 \text{ J}/(\text{kg}\cdot\text{K})$.

SOLUTION:



The Entropy Equation applied to the control volume shown in the figure,

$$\Delta S = \int_b \frac{\delta Q_{into}}{T} + \sigma \Rightarrow \frac{\sigma}{m} = \Delta s + \frac{1}{m} \frac{Q_{out}}{T_{surf}}. \quad (1)$$

We're given that $m = 1 \text{ kg}$, $Q_{out} = 9000 \text{ J}$, and $T_{surf} = 300 \text{ K}$. Now consider the different cases,

- $\frac{\sigma}{m} = -30.0 \frac{\text{J}}{\text{kg}\cdot\text{K}} + \frac{1}{(1 \text{ kg})} \frac{(9000 \text{ J})}{(300 \text{ K})} = 0 \Rightarrow$ This process is internally reversible.
- $\frac{\sigma}{m} = -20.0 \frac{\text{J}}{\text{kg}\cdot\text{K}} + \frac{1}{(1 \text{ kg})} \frac{(9000 \text{ J})}{(300 \text{ K})} = 10.0 \frac{\text{J}}{\text{kg}\cdot\text{K}} \Rightarrow$ This process is internally irreversible.
- $\frac{\sigma}{m} = -40.0 \frac{\text{J}}{\text{kg}\cdot\text{K}} + \frac{1}{(1 \text{ kg})} \frac{(9000 \text{ J})}{(300 \text{ K})} = -10.0 \frac{\text{J}}{\text{kg}\cdot\text{K}} \Rightarrow$ This process is impossible.

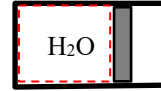
One kilogram of water contained in a piston-cylinder assembly, initially at 160 °C, 150 kPa (abs), undergoes an isothermal compression process to saturated liquid. For the process, the work done by the water is -471.5 kJ. Determine for the process:

- the heat transfer into the water, and
- the change in entropy of the water.

SOLUTION:

The heat transfer into the water may be found from the 1st Law:

$$\Delta E_{\text{sys}} = Q_{\text{into, sys}} - W_{\text{by, sys}} \Rightarrow Q_{\text{into, sys}} = \Delta E_{\text{sys}} + W_{\text{by, sys}}, \quad (1)$$



where $\Delta E_{\text{sys}} = \Delta U$ (neglected changes in kinetic and potential energy) and $W_{\text{by, sys}} = -471.5$ kJ. The change in internal energy is,

$$\Delta U = m(u_2 - u_1), \quad (2)$$

where,

$$m = 1 \text{ kg}$$

$$u_1 = 2595.2 \text{ kJ/kg} \quad (@ 160 \text{ }^\circ\text{C}, 150 \text{ kPa} = 1.5 \text{ bar} \Rightarrow \text{superheated vapor; found from Table A-4 in Moran et al., 7}^{\text{th}} \text{ ed.})$$

$$u_2 = 674.86 \text{ kJ/kg} \quad (\text{saturated liquid at } 160 \text{ }^\circ\text{C; from Table A-2 in Moran et al., 7}^{\text{th}} \text{ ed.})$$

Thus,

$$\Delta U = -1920.34 \text{ kJ/kg,}$$

$$Q_{\text{into}} = -2390 \text{ kJ/kg} \quad (\text{heat leaves the water}).$$

The change in the water's entropy may be found using the thermodynamic tables.

$$s_1 = 7.4665 \text{ kJ/(kg.K)} \quad (@ 160 \text{ }^\circ\text{C}, 150 \text{ kPa} = 1.5 \text{ bar} \Rightarrow \text{superheated vapor; found from Table A-4 in Moran et al., 7}^{\text{th}} \text{ ed.})$$

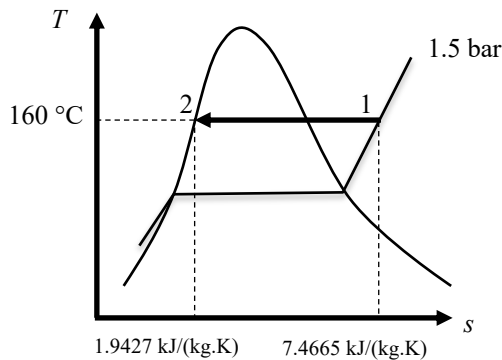
$$s_2 = 1.9427 \text{ kJ/(kg.K)} \quad (\text{saturated liquid at } 160 \text{ }^\circ\text{C; from Table A-2 in Moran et al., 7}^{\text{th}} \text{ ed.})$$

Thus,

$$S_2 - S_1 = m(s_2 - s_1),$$

$$\Rightarrow S_2 - S_1 = -5.5238 \text{ kJ/K.}$$

A plot of the process on a T - s diagram is shown in the following figure.



Although not specifically asked for, we can check to see if this process is internally reversible by checking to see if the entropy production term is zero,

$$S_2 - S_1 = \int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T} + \sigma_{12} \Rightarrow \sigma_{12} = S_2 - S_1 - \int_{1,b}^2 \frac{\delta Q_{\text{into}}}{T}, \quad (3)$$

Since the process is isothermal, T remains constant so that we can write the previous equation as,

$$\sigma_{12} = S_2 - S_1 - \frac{Q_{\text{into},12}}{T} . \quad (4)$$

Substituting the values,

$$S_2 - S_1 = -5.5238 \text{ kJ/K},$$

$$Q_{\text{into},12} = -2392 \text{ kJ},$$

$$T = 160 \text{ }^\circ\text{C} = 433 \text{ K},$$

$$\Rightarrow \sigma_{12} = 4.5 \cdot 10^{-4} \text{ kJ/K},$$

which is close enough to zero (within numerical error) for the process to be considered internally reversible.