

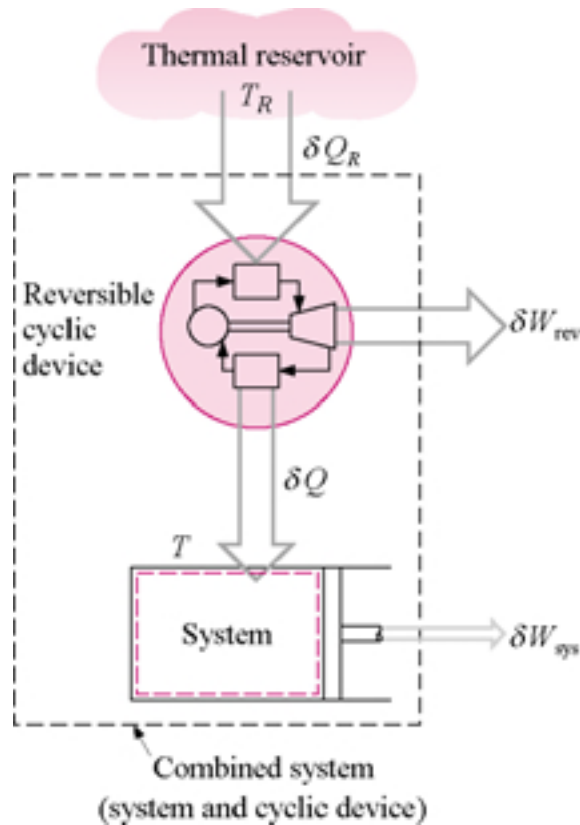
Chapter 6

Entropy: A Measure of Disorder

Entropy and the Clausius Inequality

The second law of thermodynamics leads to the definition of a new property called entropy, a quantitative measure of microscopic disorder for a system. Entropy is a measure of energy that is no longer available to perform useful work within the current environment. To obtain the working definition of entropy and, thus, the second law, let's derive the Clausius inequality.

Consider a heat reservoir giving up heat to a reversible heat engine, which in turn gives up heat to a piston-cylinder device as shown below.



We apply the first law on an incremental basis to the combined system composed of the heat engine and the system.

$$E_{in} - E_{out} = \Delta E_c$$

$$\delta Q_R - (\delta W_{rev} + \delta W_{sys}) = dE_c$$

where E_c is the energy of the combined system. Let W_c be the work done by the combined system. Then the first law becomes

$$\delta W_c = \delta W_{rev} + \delta W_{sys}$$

$$\delta Q_R - \delta W_c = dE_c$$

If we assume that the engine is totally reversible, then

$$\frac{\delta Q_R}{T_R} = \frac{\delta Q}{T}$$

$$\delta Q_R = T_R \frac{\delta Q}{T}$$

The total net work done by the combined system becomes

$$\delta W_c = T_R \frac{\delta Q}{T} - dE_c$$

Now the total work done is found by taking the cyclic integral of the incremental work.

$$W_c = T_R \oint \frac{\delta Q}{T} - \oint dE_c$$

If the system, as well as the heat engine, is required to undergo a cycle, then

$$\oint dE_c = 0$$

and the total net work becomes

$$W_c = T_R \oint \frac{\delta Q}{T}$$

If W_c is positive, we have a cyclic device exchanging energy with a single heat reservoir and producing an equivalent amount of work; thus, the Kelvin-Planck statement of the second law is violated. But W_c can be zero (no work done) or negative (work is done on the combined system) and not violate the Kelvin-Planck statement of the second law. Therefore, since $T_R > 0$ (absolute temperature), we conclude

$$W_c = T_R \oint \frac{\delta Q}{T} \leq 0$$

or

$$\oint \frac{\delta Q}{T} \leq 0$$

Here Q is the net heat added *to* the system, Q_{net} .

$$\oint \frac{\delta Q_{net}}{T} \leq 0$$

This equation is called the Clausius inequality. The equality holds for the reversible process and the inequality holds for the irreversible process.

Example 6-1

For a particular power plant, the heat added and rejected both occur at constant temperature and no other processes experience any heat transfer. The heat is added in the amount of 3150 kJ at 440°C and is rejected in the amount of 1950 kJ at 20°C. Is the Clausius inequality satisfied and is the cycle reversible or irreversible?

$$\begin{aligned}
\oint \frac{\delta Q_{net}}{T} &\leq 0 \\
\int \left(\frac{\delta Q_{net}}{T} \right)_{in} + \int \left(\frac{\delta Q_{net}}{T} \right)_{out} &\leq 0 \\
\left(\frac{Q_{net}}{T} \right)_{in} + \left(\frac{Q_{net}}{T} \right)_{out} &\leq 0 \\
\left(\frac{Q_{in}}{T_{in}} \right) + \left(\frac{-Q_{out}}{T_{out}} \right) &\leq 0 \\
\left(\frac{3150 \text{ kJ}}{(440 + 273) \text{ K}} \right) + \left(\frac{-1950 \text{ kJ}}{(20 + 273) \text{ K}} \right) &\leq 0 \\
(4.418 - 6.655) \frac{\text{kJ}}{\text{K}} &\leq 0 \\
-2.237 \frac{\text{kJ}}{\text{K}} &\leq 0
\end{aligned}$$

Calculate the net work, cycle efficiency, and Carnot efficiency based on T_H and T_L for this cycle.

$$\begin{aligned}
W_{net} &= Q_{in} - Q_{out} = (3150 - 1950) \text{ kJ} = 1200 \text{ kJ} \\
\eta_{th} &= \frac{W_{net}}{Q_{in}} = \frac{1200 \text{ kJ}}{3150 \text{ kJ}} = 0.381 \text{ or } 38.1\% \\
\eta_{th, Carnot} &= 1 - \frac{T_L}{T_H} = 1 - \frac{(20 + 273) \text{ K}}{(440 + 273) \text{ K}} = 0.589 \text{ or } 58.9\%
\end{aligned}$$

The Clausius inequality is satisfied. Since the inequality is less than zero, the cycle has at least one irreversible process and the cycle is irreversible.

Example 6-2

For a particular power plant, the heat added and rejected both occur at constant temperature; no other processes experience any heat transfer. The heat is added in the amount of 3150 kJ at 440°C and is rejected in the amount of 1294.46 kJ at 20°C. Is the Clausius inequality satisfied and is the cycle reversible or irreversible?

$$\oint \frac{\delta Q_{net}}{T} \leq 0$$

$$\int \left(\frac{\delta Q_{net}}{T} \right)_{in} + \int \left(\frac{\delta Q_{net}}{T} \right)_{out} \leq 0$$

$$\left(\frac{Q_{in}}{T_{in}} \right) + \left(\frac{-Q_{out}}{T_{out}} \right) \leq 0$$

$$\left(\frac{3150 \text{ kJ}}{(440 + 273) \text{ K}} \right) + \left(\frac{-1294.46 \text{ kJ}}{(20 + 273) \text{ K}} \right) \leq 0$$

$$(4.418 - 4.418) \frac{\text{kJ}}{\text{K}} = 0$$

The Clausius inequality is satisfied. Since the cyclic integral is equal to zero, the cycle is made of reversible processes. What cycle can this be?

Calculate the net work and cycle efficiency for this cycle.

$$W_{net} = Q_{in} - Q_{out} = (3150 - 1294.46) \text{ kJ} = 1855.4 \text{ kJ}$$

$$\eta_{th} = \frac{W_{net}}{Q_{in}} = \frac{1855.4 \text{ kJ}}{3150 \text{ kJ}} = 0.589 \text{ or } 58.9\%$$

Definition of Entropy

Let's take another look at the quantity

$$\oint \frac{\delta Q_{net}}{T} \leq 0$$

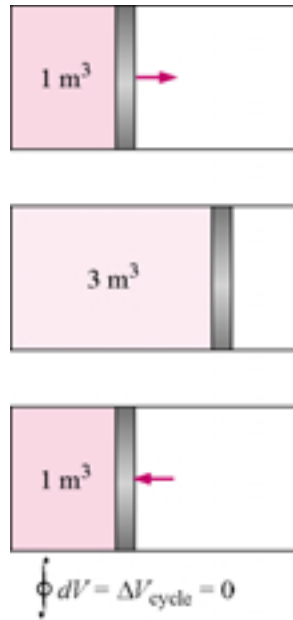
If no irreversibilities occur within the system as well as the reversible cyclic device, then the cycle undergone by the combined system will be internally reversible. As such, it can be reversed. In the reversed cycle case, all the quantities will have the same magnitude but the opposite sign. Therefore, the work W_C , which could not be a positive quantity in the regular case, cannot be a negative quantity in the reversed case. Then it follows that $W_{C,int rev} = 0$ since it cannot be a positive or negative quantity, and therefore

$$\oint \left(\frac{\delta Q_{net}}{T} \right)_{int rev} = 0$$

for internally reversible cycles. Thus we conclude that *the equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones.*

To develop a relation for the definition of entropy, let us examine this last equation more closely. Here we have a quantity whose cyclic integral is zero. Let us think for a moment what kind of quantities can have this characteristic. We know that the cyclic integral of *work* is not zero. (It is a good thing that it is not. Otherwise, heat engines that work on a cycle such as steam power plants would produce zero net work.) Neither is the cyclic integral of heat.

Now consider the volume occupied by a gas in a piston-cylinder device undergoing a cycle, as shown below.



When the piston returns to its initial position at the end of a cycle, the volume of the gas also returns to its initial value. Thus the net change in volume during a cycle is zero. This is also expressed as

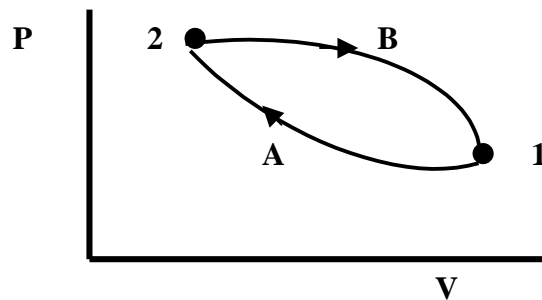
$$\oint (dV) = 0$$

We see that the cyclic integral of a property is zero. A quantity whose cyclic integral is zero depends only on the *state* and not on the process path; thus it is a property. Therefore the quantity $(\delta Q_{\text{net}}/T)_{\text{int rev}}$ must be a property.

In-class Example

Consider the cycle shown below composed of two reversible processes A and B. Apply the Clausius inequality for this cycle. What do you conclude about these two integrals?

$$\underbrace{\int_1^2 \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}}}_{\text{along path A}} \quad \text{and} \quad \underbrace{\int_1^2 \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}}}_{\text{along path B}}$$



A cycle composed of two reversible processes.

Apply the Clausius inequality for the cycle made of two internally reversible processes:

$$\oint \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}} = 0$$

You should find:

$$\underbrace{\int_1^2 \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}}}_{\text{along path A}} = \underbrace{\int_1^2 \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}}}_{\text{along path B}}$$

Since the quantity $(\delta Q_{net}/T)_{\text{int rev}}$ is independent of the path and must be a property, we call this property the entropy S .

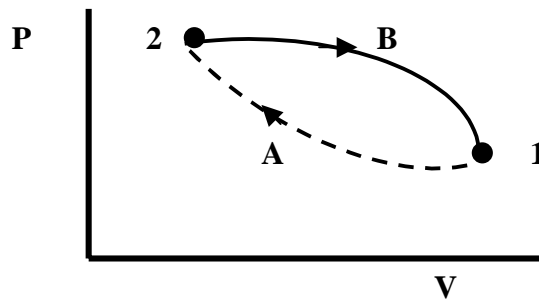
The entropy change occurring during a process is related to the heat transfer and the temperature of the system. The entropy is given the symbol S (kJ/K), and the specific entropy is s (kJ/kg·K).

The entropy change during a reversible process, sometimes called an internally reversible process, is defined as

$$dS = \frac{\delta Q_{net}}{T} \Big|_{\text{int rev}}$$

$$S_2 - S_1 = \int_1^2 \frac{\delta Q_{net}}{T} \Big|_{\text{int rev}}$$

Consider the cycle 1-A-2-B-1, shown below, where process A is arbitrary that is, it can be either reversible or irreversible, and process B is internally reversible.



A cycle composed of reversible and irreversible processes.

$$\oint \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}} \leq 0$$

$$\underbrace{\int_1^2 \frac{\delta Q_{net}}{T}}_{\text{along A}} + \underbrace{\int_2^1 \left(\frac{\delta Q_{net}}{T} \right)_{\text{int rev}}}_{\text{along B}} \leq 0$$

The integral along the internally reversible path, process B, is the entropy change $S_1 - S_2$. Therefore,

$$\int_1^2 \frac{\delta Q_{net}}{T} + S_1 - S_2 \leq 0$$

or

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q_{net}}{T}$$

In general the entropy change during a process is defined as

$$dS \geq \frac{\delta Q_{net}}{T}$$

where $=$ holds for the internally reversible process
 $>$ holds for the irreversible process

Consider the effect of heat transfer on entropy for the internally reversible case.

$$dS = \frac{\delta Q_{net}}{T}$$

Which temperature T is this one? If

$$\delta Q_{net} > 0, \quad \text{then } dS > 0$$

$$\delta Q_{net} = 0, \quad \text{then } dS = 0$$

$$\delta Q_{net} < 0, \quad \text{then } dS < 0$$

This last result shows why we have kept the subscript *net* on the heat transfer Q . It is important for you to recognize that Q has a sign depending on the direction of heat transfer. The *net* subscript is to remind us that Q is positive when added to a system and negative when leaving a system. Thus, the entropy change of the system will have the same sign as the heat transfer in a reversible process.

From the above, we see that for a reversible, adiabatic process

$$dS = 0$$

$$S_2 = S_1$$

The *reversible, adiabatic process* is called an *isentropic process*.

Entropy change is caused by heat transfer and irreversibilities. Heat transfer to a system increases the entropy; heat transfer from a system decreases it. The effect of irreversibilities is always to increase the entropy. In fact, a process in which the heat transfer is out of the system may be so irreversible that the actual entropy change is positive. Friction is one source of irreversibilities in a system.

The entropy change during a process is obtained by integrating the dS equation over the process:

$$\Delta S_{sys} = S_2 - S_1 \geq \int_1^2 \frac{\delta Q_{net}}{T} \quad \left(\frac{kJ}{K} \right)$$

Here, the inequality is to remind us that the entropy change of a system during an irreversible process is always greater than $\int_1^2 \delta Q / T$, called the entropy transfer. That is, some entropy is generated or created during an irreversible process, and this generation is due entirely to the presence of irreversibilities. The entropy generated during a process is called **entropy generation** and is denoted as S_{gen} .

We can remove the inequality by noting the following

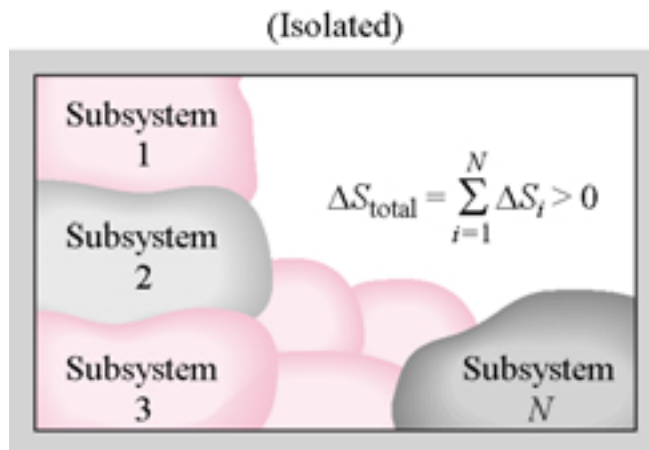
$$\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q_{net}}{T} + S_{gen} \quad \left(\frac{kJ}{K} \right)$$

S_{gen} is always a positive quantity or zero. Its value depends upon the process and thus it is **not** a property. S_{gen} is zero for an internally reversible process.

The integral $\int_1^2 \delta Q / T$ is performed by applying the first law to the process to obtain the heat transfer as a function of the temperature. The integration is not easy to perform, in general.

Definition of Second Law of Thermodynamics

Now consider an isolated system composed of several subsystems exchanging energy among themselves. Since the isolated system has no energy transfer across its system boundary, the heat transfer across the system boundary is zero.



Applying the definition of entropy to the isolated system

$$\Delta S_{isolated} \geq \int_1^2 \frac{\delta Q_{net}}{T} \quad 0, \text{ adiabatic}$$

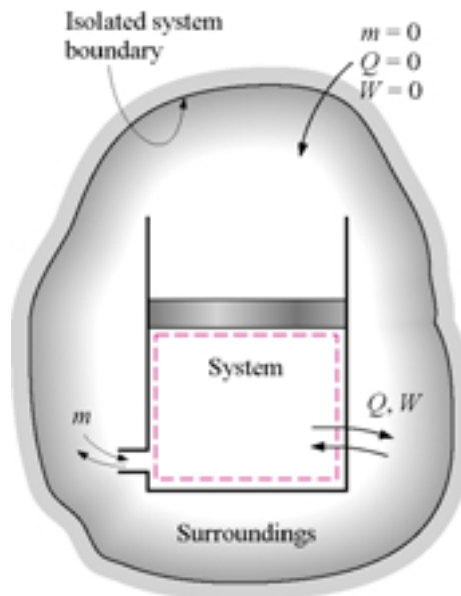
The total entropy change for the isolated system is

$$\Delta S_{isolated} \geq 0$$

This equation is the working definition of the second law of thermodynamics. The second law, known as the principle of increase of entropy, is stated as

The total entropy change of an isolated system during a process always increases or, in the limiting case of a reversible process, remains constant.

Now consider a general system exchanging mass as well as energy with its surroundings.



$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \sum \Delta S_{surr} \geq 0$$

where $=$ holds for the totally reversible process
 $>$ holds for the irreversible process

Thus, the entropy generated or the total entropy change (sometimes called the entropy change of the universe or net entropy change) due to the process of this isolated system is positive (for actual processes) or zero (for reversible processes). The total entropy change for a process is the amount of entropy generated during that process (S_{gen}), and it is equal to the sum of the entropy changes of the system and the surroundings. The entropy changes of the important system (closed system or control volume) and its surroundings do not both have to be positive. The entropy for a given system (important or surroundings) may decrease during a process, but the **sum** of the entropy changes of the system and its surroundings for an isolated system can never decrease.

Entropy change is caused by heat transfer and irreversibilities. Heat transfer to a system increases the entropy, and heat transfer from a system decreases it. The effect of irreversibilities is always to increase the entropy.

The increase in entropy principle can be summarized as follows:

$$S_{gen} = \Delta S_{Total} \begin{cases} > 0 & \text{Irreversible processes} \\ = 0 & \text{Reversible processes} \\ < 0 & \text{Impossible processes} \end{cases}$$

Some Remarks about Entropy

1. Processes can occur in a certain direction only, not in just any direction, such that $S_{\text{gen}} \geq 0$.
2. Entropy is a nonconserved property, and there is no such thing as the conservation of entropy principle. The entropy of the universe is continuously increasing.
3. The performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a measure of the magnitudes of the irreversibilities present during that process.

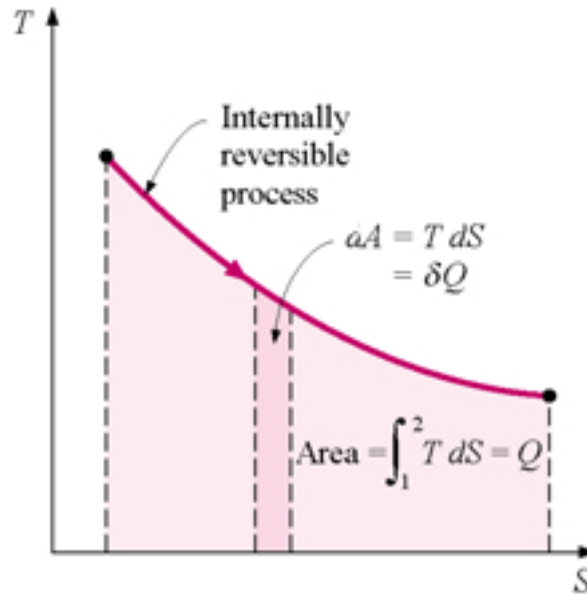
Heat Transfer as the Area under a T - S Curve

For the reversible process, the equation for dS implies that

$$dS = \frac{\delta Q_{\text{net}}}{T}$$
$$\delta Q_{\text{net}} = TdS$$

or the incremental heat transfer in a process is the product of the temperature and the differential of the entropy, the differential area under the process curve plotted on the T - S diagram.

$$Q_{\text{net}} = \int_1^2 TdS$$



In the above figure, the heat transfer in an internally reversible process is shown as the area under the process curve plotted on the T-S diagram.

Isothermal, Reversible Process

For an isothermal, reversible process, the temperature is constant and the integral to find the entropy change is readily performed. If the system has a constant temperature, T_0 , the entropy change becomes

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q_{net}}{T} = \frac{Q_{net}}{T_0}$$

For a process occurring over a varying temperature, the entropy change must be found by integration over the process.

Adiabatic, Reversible (Isentropic) Process

For an adiabatic process, one in which there is no heat transfer, the entropy change is

$$\Delta S = S_2 - S_1 \geq \int_1^2 \frac{\delta Q_{net}}{T} \quad \nearrow \quad 0, \text{ adiabatic}$$

$$\Delta S = S_2 - S_1 \geq 0$$

If the process is adiabatic and reversible, the equality holds and the entropy change is

$$\Delta S = S_2 - S_1 = 0$$

$$S_2 = S_1$$

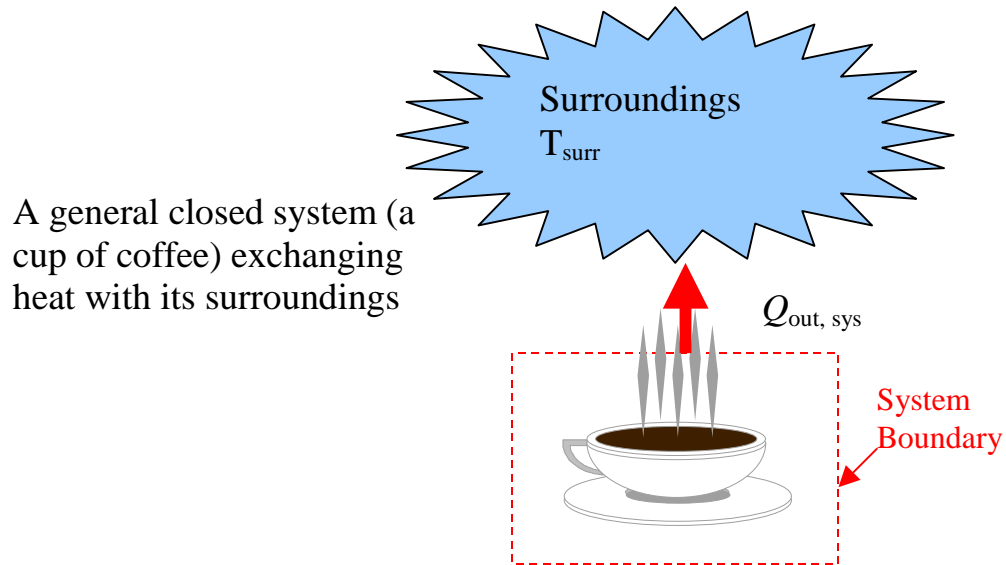
or on a per unit mass basis

$$s = \frac{S}{m}$$

$$s_2 = s_1$$

The *adiabatic, reversible process is a constant entropy process and is called isentropic*. As will be shown later for an ideal gas, the adiabatic, reversible process is the same as the polytropic process where the polytropic exponent $n = k = C_p/C_v$.

The principle of increase of entropy for a closed system exchanging heat with its surroundings at a constant temperature T_{surr} is found by using equation (6.11)



$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \sum \Delta S_{surr} \geq 0$$

$$\Delta S_{sys} = (S_2 - S_1)_{sys}$$

$$\sum \Delta S_{surr} = \frac{Q_{net, surr}}{T_{surr}}$$

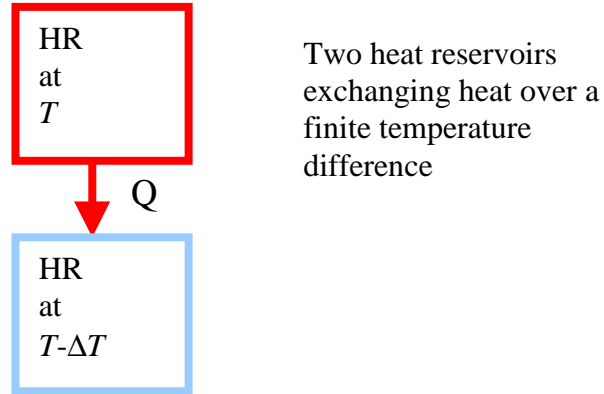
$$S_{gen} = \Delta S_{total} = m(s_2 - s_1)_{sys} + \frac{Q_{net, surr}}{T_{surr}} \geq 0$$

where

$$Q_{net, surr} = -Q_{net, sys} = -(0 - Q_{out, sys}) = Q_{out, sys}$$

Effect of Heat Transfer on Entropy

Let's apply the second law to the following situation. Consider the transfer of heat from a heat reservoir at temperature T to a heat reservoir at temperature $T - \Delta T > 0$ where $\Delta T > 0$, as shown below.



The second law for the isolated system composed of the two heat reservoirs is

$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \sum \Delta S_{surr} \geq 0$$

$$S_{gen} = \Delta S_{total} = \Delta S_{HR@T} + \Delta S_{HR@T-\Delta T}$$

In general, if the heat reservoirs are internally reversible

$$\Delta S_{sys} = \int_1^2 \frac{\delta Q_{net}}{T}$$

$$\Delta S_{HR@T} = \frac{-Q}{T}$$

$$\Delta S_{HR@T-\Delta T} = \frac{+Q}{T - \Delta T}$$

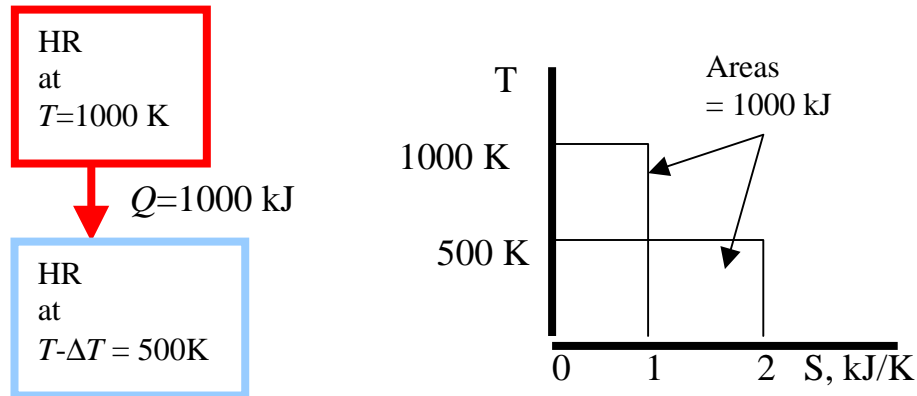
$$S_{gen} = \Delta S_{Total} = \frac{-Q}{T} + \frac{+Q}{T - \Delta T}$$

$$S_{gen} = \Delta S_{Total} = \frac{Q}{T} \left[\frac{\Delta T}{(T - \Delta T)} \right]$$

Now as $\Delta T \rightarrow 0$, $S_{gen} \rightarrow 0$ and the process becomes totally reversible. Therefore, for reversible heat transfer ΔT must be small. As ΔT gets large, S_{gen} increases and the process becomes irreversible.

Example 6-3

Find the total entropy change, or entropy generation, for the transfer of 1000 kJ of heat energy from a heat reservoir at 1000 K to a heat reservoir at 500 K.



The second law for the isolated system is

$$\begin{aligned}
 S_{gen} &= \Delta S_{Total} = \frac{-Q}{T} + \frac{+Q}{T - \Delta T} \\
 &= \frac{-1000 \text{ kJ}}{1000 \text{ K}} + \frac{1000 \text{ kJ}}{500 \text{ K}} \\
 &= (-1 + 2) \frac{\text{kJ}}{\text{K}} \\
 &= 1 \frac{\text{kJ}}{\text{K}}
 \end{aligned}$$

What happens when the low-temperature reservoir is at 750 K?

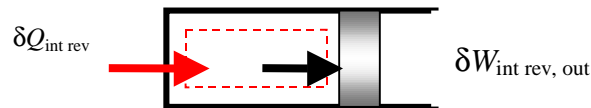
The effect of decreasing the ΔT for heat transfer is to reduce the entropy generation or total entropy change of the universe due to the isolated system and the irreversibilities associated with the heat transfer process.

Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a pure crystalline substance at absolute zero temperature is zero. This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is called absolute entropy.

Entropy as a Property

Entropy is a property, and it can be expressed in terms of more familiar properties (P, v, T) through the Tds relations. These relations come from the analysis of a reversible closed system that does boundary work and has heat added. Writing the first law for the closed system in differential form on a per unit mass basis



System used to find expressions for ds

$$\delta Q_{\text{int rev}} - \delta W_{\text{int rev, out}} = dU$$

$$\delta Q_{\text{int rev}} = T dS$$

$$\delta W_{\text{int rev, out}} = P dV$$

$$T dS - P dV = dU$$

On a unit mass basis we obtain the first Tds equation, or Gibbs equation, as

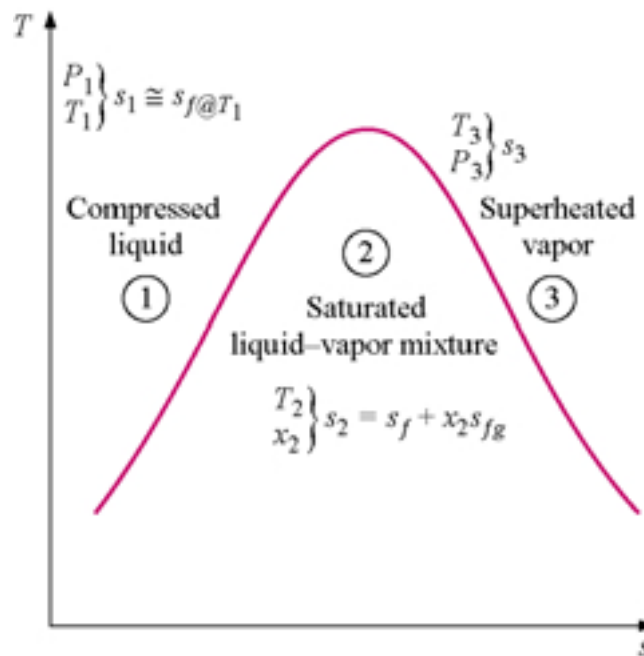
$$Tds = du + Pdv$$

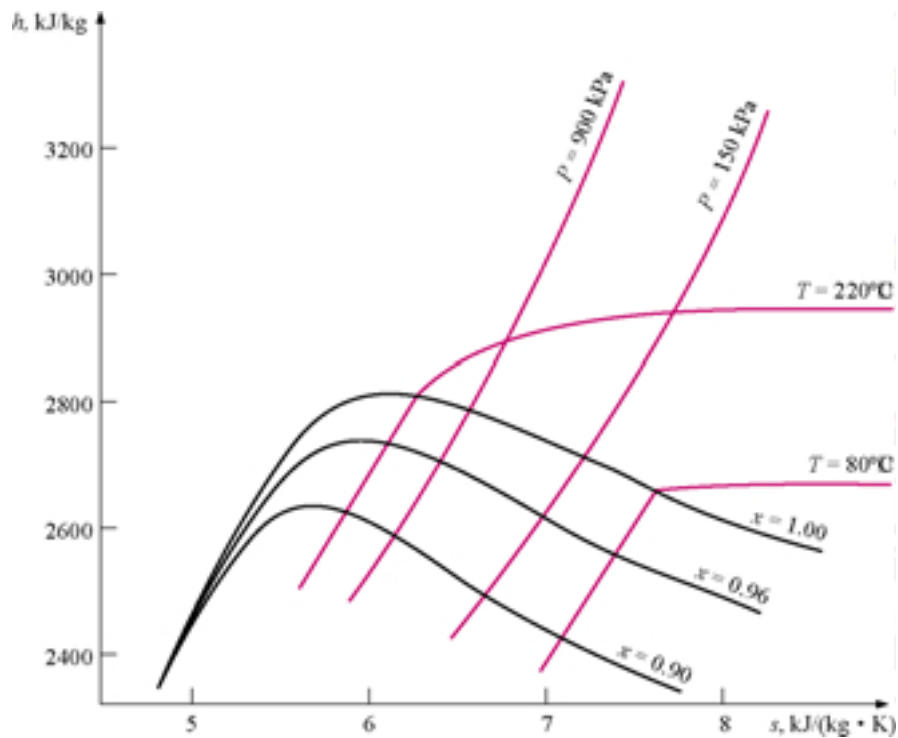
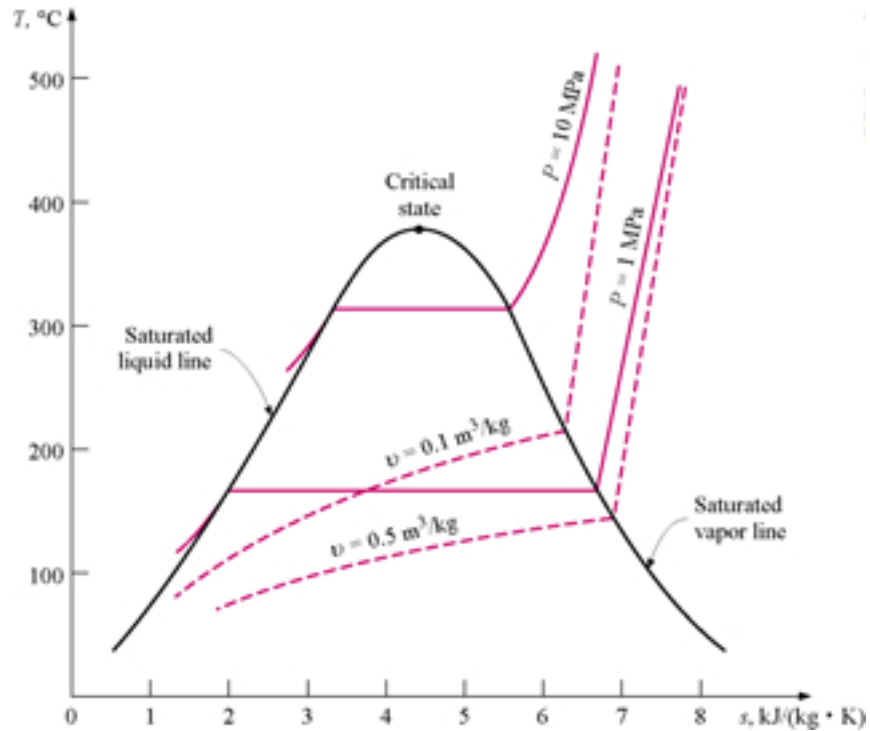
Recall that the enthalpy is related to the internal energy by $h = u + Pv$. Using this relation in the above equation, the second Tds equation is

$$T ds = dh - v dP$$

These last two relations have many uses in thermodynamics and serve as the starting point in developing entropy-change relations for processes. The successful use of Tds relations depends on the availability of property relations. Such relations do not exist in an easily used form for a general pure substance but are available for incompressible substances (liquids, solids) and ideal gases. So, for the general pure substance, such as water and the refrigerants, we must resort to property tables to find values of entropy and entropy changes.

The temperature-entropy and enthalpy-entropy diagrams for water are shown below.





Shown above are the temperature-entropy and enthalpy-entropy diagrams for water. The $h-s$ diagram, called the Mollier diagram, is a useful aid in solving steam power plant problems.

Example 6-4

Find the entropy and/or temperature of steam at the following states:

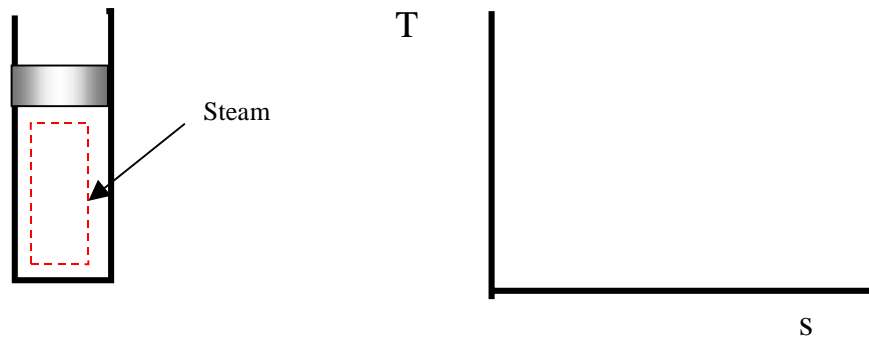
P	T	Region	s kJ/(kg K)
5 MPa	120°C		
1 MPa	50°C		
1.8 MPa	400°C		
40 kPa		Quality, $x = 0.9$	
40 kPa			7.1794

(Answers are on page 6-77)

Example 6-5

Determine the entropy change of water contained in a closed system as it changes phase from saturated liquid to saturated vapor when the pressure is 0.1 MPa and constant. Why is the entropy change positive for this process?

System: The water contained in the system (a piston-cylinder device)



Property Relation: Steam tables

Process and Process Diagram: Constant pressure (sketch the process relative to the saturation lines)

Conservation Principles:

Using the definition of entropy change, the entropy change of the water per mass is

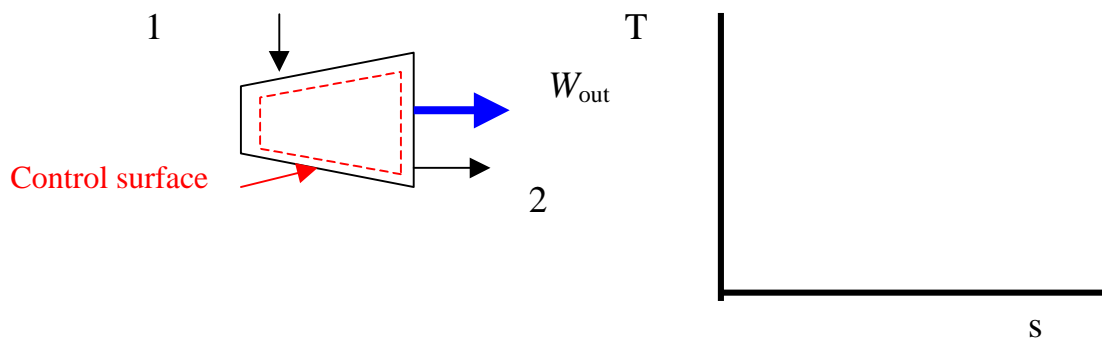
$$\begin{aligned}\Delta s &= s_2 - s_1 = s_g - s_f = s_{fg} \\ &= 6.0568 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}\end{aligned}$$

The entropy change is positive because: (Heat is added to the water.)

Example 6-6

Steam at 1 MPa, 600°C, expands in a turbine to 0.01 MPa. If the process is isentropic, find the final temperature, the final enthalpy of the steam, and the turbine work.

System: The control volume formed by the turbine



Property Relation: Steam tables

Process and Process Diagram: Isentropic (sketch the process relative to the saturation lines on the $T-s$ diagram)

Conservation Principles:

Assume: steady-state, steady-flow, one entrance, one exit, neglect KE and PE

Conservation of mass:

$$\dot{m}_1 = \dot{m}_2 = \dot{m}$$

First Law or conservation of energy:

The process is isentropic and thus adiabatic and reversible; therefore $Q = 0$.
The conservation of energy becomes

$$\begin{aligned}\dot{E}_{in} &= \dot{E}_{out} \\ \dot{m}_1 h_1 &= \dot{m}_2 h_2 + \dot{W}_{out}\end{aligned}$$

Since the mass flow rates in and out are equal, solve for the work done per unit mass

$$\begin{aligned}\dot{E}_{in} &= \dot{E}_{out} \\ \dot{W}_{out} &= \dot{m}_1 h_1 - \dot{m}_2 h_2 \\ &= \dot{m}(h_1 - h_2) \\ w &= \frac{\dot{W}_{out}}{\dot{m}} = h_1 - h_2\end{aligned}$$

Now, let's go to the steam tables to find the h 's.

$$\left. \begin{array}{l} P_1 = 1 \text{ MPa} \\ T_1 = 600^\circ \text{ C} \end{array} \right\} \begin{cases} h_1 = 3697.9 \frac{\text{kJ}}{\text{kg}} \\ s_1 = 8.0290 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \end{cases}$$

The process is isentropic, therefore; $s_2 = s_1 = 8.0290 \text{ kJ/(kg K)}$
 At $P_2 = 0.01 \text{ MPa}$, $s_f = 0.6491 \text{ kJ/kg}\cdot\text{K}$, and $s_g = 8.1510 \text{ kJ/(kg K)}$;
 thus, $s_f < s_2 < s_g$.

State 2 is in the saturation region, and the quality is needed to specify the state.

$$s_2 = s_f + x_2 s_{fg}$$

$$\begin{aligned} x_2 &= \frac{s_2 - s_f}{s_{fg}} \\ &= \frac{8.0290 - 0.6491}{7.5019} = 0.984 \end{aligned}$$

$$\begin{aligned} h_2 &= h_f + x_2 h_{fg} \\ &= 191.8 + (0.984)(2392.8) \\ &= 2545.7 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

Since state 2 is in the two-phase region, $T_2 = T_{\text{sat at } P_2} = 45.8^\circ \text{C}$.

$$\begin{aligned}
 w &= h_1 - h_2 \\
 &= (3697.9 - 2545.7) \frac{\text{kJ}}{\text{kg}} \\
 &= 1152.2 \frac{\text{kJ}}{\text{kg}}
 \end{aligned}$$

Entropy Change and Isentropic Processes

The *entropy-change* and *isentropic relations* for a process can be summarized as follows:

1. *Pure substances:*

Any process: $\Delta s = s_2 - s_1$ (kJ/kg·K)

Isentropic process: $s_2 = s_1$

2. Incompressible substances (Liquids and Solids):

$$ds = \frac{du}{T} + \frac{P}{T} dv$$

The change in internal energy and volume for an incompressible substance is

$$du = C dT$$

$$dv \cong 0$$

The entropy change now becomes

$$ds = \frac{C dT}{T} + 0$$

$$\Delta s = \int_1^2 \frac{C(T) dT}{T}$$

If the specific heat for the incompressible substance is constant, then the entropy change is

Any process: $s_2 - s_1 = C_{av} \ln \frac{T_2}{T_1} \quad (\text{kJ/kg} \cdot \text{K})$

Isentropic process: $T_2 = T_1$

3. *Ideal gases:*

a. Constant specific heats (approximate treatment):

Any process: (can you fill in the steps?)

$$s_2 - s_1 = C_{v,av} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad (\text{kJ/kg} \cdot \text{K})$$

and (can you fill in the steps?)

$$s_2 - s_1 = C_{p,av} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (\text{kJ/kg} \cdot \text{K})$$

Or, on a unit-mole basis,

$$\bar{s}_2 - \bar{s}_1 = \bar{C}_{v,av} \ln \frac{T_2}{T_1} + R_u \ln \frac{v_2}{v_1} \quad (\text{kJ/kmol} \cdot \text{K})$$

and

$$\bar{s}_2 - \bar{s}_1 = \bar{C}_{p,av} \ln \frac{T_2}{T_1} - R_u \ln \frac{P_2}{P_1} \quad (\text{kJ/kmol} \cdot \text{K})$$

Isentropic process: (Can you fill in the steps here?)

$$\left(\frac{T_2}{T_1} \right)_{s=const.} = \left(\frac{v_1}{v_2} \right)^{k-1}$$

$$\left(\frac{T_2}{T_1} \right)_{s=const.} = \left(\frac{P_2}{P_1} \right)^{(k-1)/k}$$

$$\left(\frac{P_2}{P_1} \right)_{s=const.} = \left(\frac{v_1}{v_2} \right)^k$$

For an isentropic process this last result looks like $Pv^k = \text{constant}$ which is the polytropic process equation $Pv^n = \text{constant}$ with $n = k = C_p/C_v$.

b. Variable specific heats (exact treatment):

From $Tds = dh - v dP$, we obtain

$$\Delta s = \int_1^2 \frac{C_p(T)}{T} dT - R \ln \frac{P_2}{P_1}$$

The first term can be integrated relative to a reference state at temperature T_{ref} .

$$\begin{aligned} \int_1^2 \frac{C_p(T)}{T} dT &= \int_{T_1}^{T_{\text{ref}}} \frac{C_p(T)}{T} dT + \int_{T_{\text{ref}}}^{T_2} \frac{C_p(T)}{T} dT \\ &= \int_{T_{\text{ref}}}^{T_2} \frac{C_p(T)}{T} dT - \int_{T_{\text{ref}}}^{T_1} \frac{C_p(T)}{T} dT \end{aligned}$$

The integrals on the right-hand side of the above equation are called the standard state entropies, s° , at state 1, T_1 , and state 2, T_2 ; s° is a function of temperature only.

$$\begin{aligned} s_1^\circ &= \int_{T_{\text{ref}}}^{T_1} \frac{C_p(T)}{T} dT \\ s_2^\circ &= \int_{T_{\text{ref}}}^{T_2} \frac{C_p(T)}{T} dT \end{aligned}$$

Therefore, for any process:

$$s_2 - s_1 = s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1} \quad (\text{kJ/kg}\cdot\text{K})$$

or

$$\bar{s}_2 - \bar{s}_1 = \bar{s}_2^o - \bar{s}_1^o - R_u \ln \frac{P_2}{P_1} \quad (\text{kJ/kmol} \cdot \text{K})$$

The standard state entropies are found in Tables A-17 for air on a mass basis and Tables A-18 through A-25 for other gases on a mole basis. When using this variable specific heat approach to finding the entropy change for an ideal gas, remember to include the pressure term along with the standard state entropy terms--the tables don't warn you to do this.

Isentropic process: $\Delta s = 0$

$$s_2^o = s_1^o + R \ln \frac{P_2}{P_1} \quad (\text{kJ/kg} \cdot \text{K})$$

If we are given T_1 , P_1 , and P_2 , we find s_1^o at T_1 , calculate s_2^o , and then determine from the tables T_2 , u_2 , and h_2 .

When air undergoes an isentropic process when variable specific heat data are required, there is another approach to finding the properties at the end of the isentropic process. Consider the entropy change written as

$$\Delta s = \int_1^2 \frac{C_p(T)}{T} dT - R \ln \frac{P_2}{P_1}$$

Letting $T_1 = T_{\text{ref}}$, $P_1 = P_{\text{ref}} = 1 \text{ atm}$, $T_2 = T$, $P_2 = P$, and setting the entropy change equal to zero yield

$$\left(\frac{P}{P_{\text{ref}}} \right)_{s=\text{const}} = \text{EXP} \left(\frac{1}{R} \int_{T_{\text{ref}}}^T \frac{C_p(T')}{T'} dT' \right)$$

We define the relative pressure P_r as the above pressure ratio. P_r is the pressure ratio necessary to have an isentropic process between the reference temperature and the actual temperature and is a function of the actual temperature. This parameter is a function of temperature only and is found in the air tables, Table A-17. The relative pressure is not available for other gases in this text.

$$(P_r)_{s=const} = EXP\left(\frac{1}{R} \int_{T_{ref}}^T \frac{C_p(T')}{T'} dT'\right)$$

The ratio of pressures in an isentropic process is related to the ratio of relative pressures.

$$\left(\frac{P_2}{P_1}\right)_{s=const.} = \left(\frac{P_2 / P_{ref}}{P_1 / P_{ref}}\right)_{s=const.} = \frac{P_{r2}}{P_{r1}}$$

There is a second approach to finding data at the end of an ideal gas isentropic process when variable specific heat data are required. Consider the following entropy change equation set equal to zero.

From $Tds = du + Pdv$, we obtain for ideal gases

$$\Delta s = \int_1^2 \frac{C_v(T)}{T} dT + R \ln \frac{v_2}{v_1}$$

Letting $T_1 = T_{ref}$, $v_1 = v_{ref}$, $T_2 = T$, $v_2 = v$, and setting the entropy change equal to zero yield

$$\left(\frac{v}{v_{ref}}\right)_{s=const} = EXP\left(-\frac{1}{R} \int_{T_{ref}}^T \frac{C_v(T')}{T'} dT'\right)$$

We define the relative volume v_r as the above volume ratio. v_r is the

volume ratio necessary to have an isentropic process between the reference temperature and the actual temperature and is a function of the actual temperature. This parameter is a function of temperature only and is found in the air tables, Table A-17. The relative volume is not available for other gases in this text.

$$(v_r)_{s=const} = EXP\left(-\frac{1}{R} \int_{T_{ref}}^T \frac{C_v(T')}{T'} dT'\right)$$

$$\left(\frac{v_2}{v_1}\right)_{s=const.} = \left(\frac{v_2 / v_{ref}}{v_1 / v_{ref}}\right)_{s=const.} = \frac{v_{r2}}{v_{r1}}$$

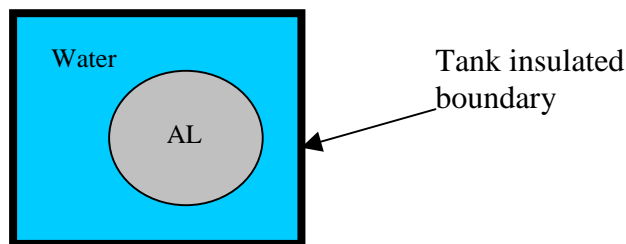
Extra Assignment

For an ideal gas having constant specific heats and undergoing a polytropic process in a closed system, $Pv^n = \text{constant}$, with $n = k$, find the heat transfer by applying the first law. Based on the above discussion of isentropic processes, explain your answer.

Example 6-7

Aluminum at 100°C is placed in a large, insulated tank having 10 kg of water at a temperature of 30°C. If the mass of the aluminum is 0.5 kg, find the final equilibrium temperature of the aluminum and water, the entropy change of the aluminum and the water, and the total entropy change of the universe because of this process. Before we work the problem, what do you think the answers ought to be? Are entropy changes going to be positive or negative? What about the entropy generated as the process takes place?

System: Closed system including the aluminum and water.



Property Relation: ?

Process: Constant volume, adiabatic, no work energy exchange between the aluminum and water.

Conservation Principles:

Apply the first law, closed system to the aluminum-water system.

$$Q - W = \Delta U_{system}$$

$$0 - 0 = \Delta U_{water} + \Delta U_{AL}$$

Using the solid and incompressible liquid relations, we have

$$m_{water} C_{water} (T_2 - T_1)_{water} + m_{AL} C_{AL} (T_2 - T_1)_{AL} = 0$$

But at equilibrium, $T_{2,AL} = T_{2,water} = \underline{T_2}$

$$\begin{aligned}
T_2 &= \frac{m_{\text{water}} C_{\text{water}} (T_1)_{\text{water}} + m_{\text{AL}} C_{\text{AL}} (T_1)_{\text{AL}}}{m_{\text{water}} C_{\text{water}} + m_{\text{AL}} C_{\text{AL}}} \\
&= \frac{10\text{kg}_{\text{water}} (4.18\text{kJ} / \text{kg}_{\text{water}} \cdot \text{K})(303\text{K}) + 0.5\text{kg}_{\text{AL}} (0.941\text{kJ} / \text{kg}_{\text{AL}} \cdot \text{K})(373\text{K})}{10\text{kg}_{\text{water}} (4.18\text{kJ} / \text{kg}_{\text{water}} \cdot \text{K}) + 0.5\text{kg}_{\text{AL}} (0.941\text{kJ} / \text{kg}_{\text{AL}} \cdot \text{K})} \\
&= 303.8\text{K}
\end{aligned}$$

The second law gives the entropy production, or total entropy change of the universe, as

$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{water}} + \Delta S_{\text{AL}} \geq 0$$

Using the entropy change equation for solids and liquids,

$$\begin{aligned}
\Delta S_{\text{AL}} &= m_{\text{AL}} C_{\text{AL}} \ln \frac{T_2}{T_{1,\text{AL}}} \\
&= 0.5\text{kg} (0.941 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}) \ln \left(\frac{303.8\text{K}}{(100 + 273)\text{K}} \right) \\
&= -0.0966 \frac{\text{kJ}}{\text{K}}
\end{aligned}$$

$$\begin{aligned}
\Delta S_{\text{water}} &= m_{\text{water}} C_{\text{water}} \ln \frac{T_2}{T_{1,\text{water}}} \\
&= 10\text{kg} (4.177 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}) \ln \left(\frac{303.8\text{K}}{(30 + 273)\text{K}} \right) \\
&= +0.1101 \frac{\text{kJ}}{\text{K}}
\end{aligned}$$

Why is ΔS_{AL} negative? Why is ΔS_{water} positive?

$$\begin{aligned}
 S_{gen} &= \Delta S_{total} = \Delta S_{water} + \Delta S_{AL} \\
 &= (0.1101 - 0.0966) \frac{kJ}{K} \\
 &= +0.0135 \frac{kJ}{K}
 \end{aligned}$$

Why is S_{gen} or ΔS_{Total} positive?

Example 6-8

Carbon dioxide initially at 50 kPa, 400 K, undergoes a process in a closed system until its pressure and temperature are 2 MPa and 800 K, respectively. Assuming ideal gas behavior, find the entropy change of the carbon dioxide by first assuming constant specific heats and then assuming variable specific heats. Compare your results with the real gas data obtained from the EES software.

- a. Assume the Table A-2(a) data at 300 K are adequate; then $C_p = 0.846$ kJ/kg·K and $R = 0.1889$ kJ/kg·K.

$$\begin{aligned}
 s_2 - s_1 &= C_{p,av} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\
 &= 0.846 \frac{kJ}{kg \cdot K} \ln \left(\frac{800K}{400K} \right) - 0.1889 \frac{kJ}{kg \cdot K} \ln \left(\frac{2000kPa}{50kPa} \right) \\
 &= -0.1104 \frac{kJ}{kg \cdot K}
 \end{aligned}$$

b. For variable specific heat data, use the carbon dioxide data from Table A-20.

$$\begin{aligned}
 s_2 - s_1 &= \left(\frac{\bar{s}_{T_2}^o - \bar{s}_{T_1}^o}{M_{CO_2}} \right) - R \ln \frac{P_2}{P_1} \\
 &= \left(\frac{(257.408 - 225.225) \text{ kJ} / \text{kmol} \cdot \text{K}}{44 \text{ kg} / \text{kmol}} \right) - 0.1889 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \ln \left(\frac{2000 \text{ kPa}}{50 \text{ kPa}} \right) \\
 &= +0.0346 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}
 \end{aligned}$$

c. Using EES for carbon dioxide as a real gas:

$$\begin{aligned}
 \text{Deltas} &= \text{ENTROPY}(\text{CarbonDioxide}, T=800, P=2000) - \\
 &\quad \text{ENTROPY}(\text{CarbonDioxide}, T=400, P=50) \\
 &= +0.03452 \text{ kJ/kg} \cdot \text{K}
 \end{aligned}$$

d. Repeat the constant specific heat calculation assuming C_p is a constant at the average of the specific heats for the temperatures. Then $C_p = 1.054 \text{ kJ/kg} \cdot \text{K}$ (see Table A-2(b)).

$$\begin{aligned}
 s_2 - s_1 &= C_{p,av} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\
 &= 1.054 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \ln \left(\frac{800 \text{ K}}{400 \text{ K}} \right) - 0.1889 \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \ln \left(\frac{2000 \text{ kPa}}{50 \text{ kPa}} \right) \\
 &= +0.0337 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}
 \end{aligned}$$

It looks like the 300 K data give completely incorrect results here.

If the compression process is adiabatic, why is Δs positive for this process?