



## Chapter Seven

### Entropy

- Apply the second law of thermodynamics to processes.
- Define a new property called *entropy* to quantify the second-law effects.
- Establish the increase of entropy principle.
- Calculate the entropy changes that take place during processes for pure substances, incompressible substances, and ideal gases.
- Examine a special class of idealized processes, called *isentropic* processes, and develop the property relations for these processes.
- Introduce and apply the entropy balance to various systems.

#### 7.1 Introduction

It is necessary to specify the amount of the heat added to or rejected from the system by estimating the work done and adding it to the change in the internal energy. From the second law of thermodynamics, entropy is a function of a quantity of heat which shows the possibility of conversion of heat into work.

**Entropy** can be viewed as *a measure of molecular disorder, or molecular randomness*. As a system becomes more disordered, the positions of the molecules become less predictable and the entropy increases. Thus, it is not surprising that the entropy of a substance is lowest in the solid phase and highest in the gas phase.

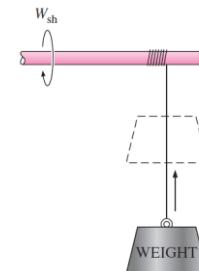
In the solid phase, the molecules of a substance continually oscillate about their equilibrium positions, but they cannot move relative to each other, and their position



at any instant can be predicted with good certainty. In the gas phase, however, the molecules move about at random, collide with each other, and change direction, making it extremely difficult to predict accurately the microscopic state of a system at any instant. Associated with this molecular chaos is a high value of entropy.

There is no entropy transfer associated with energy transfer as work.

In the absence of friction, raising a weight by a rotating shaft does not create any disorder (entropy), and thus energy is not degraded during this process.

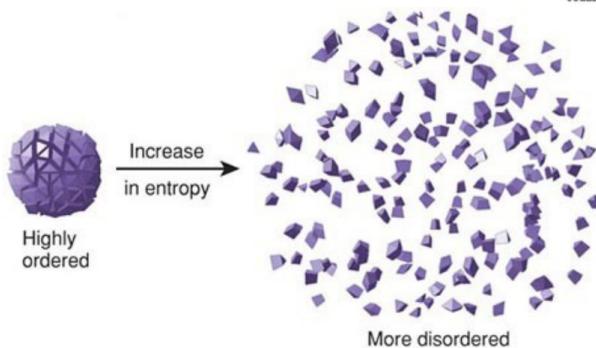


The second law of thermodynamics often leads to expressions that involve inequalities. An irreversible heat engine (or irreversible refrigerator or heat pump), for example, is less efficient than a reversible one operating between the same two thermal energy reservoirs. Another important inequality that has major consequences in thermodynamics is the **Clausius** inequality. Historically, the name of entropy was first introduced by **Clausius**. It was first stated by the German physicist R. J. E. **Clausius** (1822–1888), one of the founders of thermodynamics, and is expressed as

$$\oint \frac{\delta Q}{T} \leq 0 \quad (1)$$

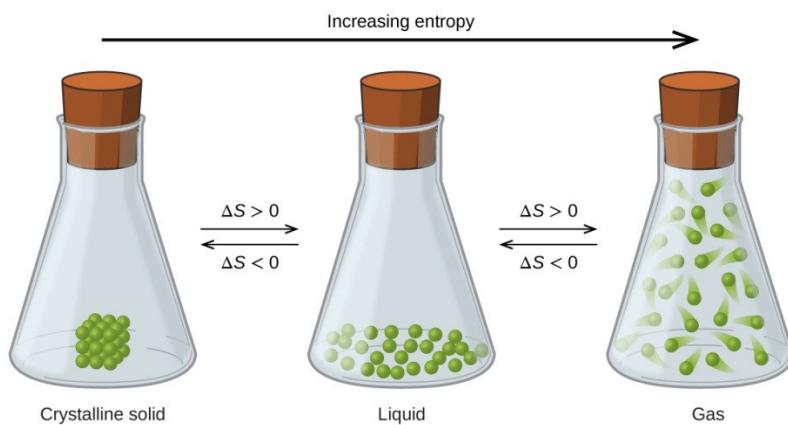
This inequality is valid for all cycles, reversible or irreversible.

The increase in entropy is small when heat is added at a high-temperature and is greater when heat addition is done at lower-temperature. Thus, for maximum entropy, there is minimum availability for conversion into work and vice versa.



$$S_{\text{final}} - S_{\text{initial}} \geq 0, \text{ or } S_{\text{final}} \geq S_{\text{initial}}$$

The entropy of any substance increases when the phase is changed from the solid to the liquid and to the gas.



Heat is a form of disorganized energy, and some disorganization (entropy) flows with heat. As a result, the entropy and the level of molecular disorder or randomness of the hot body decreases with the entropy, and the level of molecular disorder of the cold body increases. The second law requires that the increase in entropy of the cold body be greater than the decrease in entropy of the hot body, and thus the net entropy of the combined system (the cold body and the hot body) increases. That is, the combined system is at a state of greater

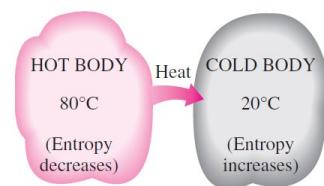
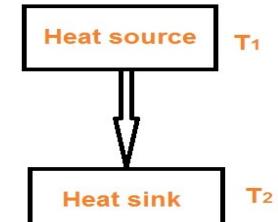


Figure 7-1. The increase in the entropy of the cold body is more than the decrease in the entropy of the hot body.



disorder at the final state. Thus we can conclude that processes can occur only in the direction of increased overall entropy or molecular disorder. That is, the entire universe is getting more and more chaotic every day.

Simply, for the same heat rejection, the cold reservoir receives entropy greater than the entropy lost from the hot reservoir.



$$s = \frac{Q}{T_2} = \frac{Q}{T_1}, \quad T_1 > T_2 \quad (2)$$

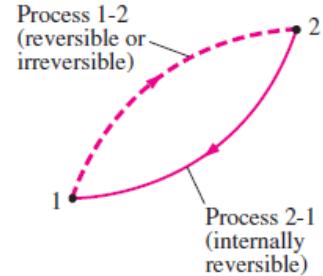
Thus,  $S_{\text{cold}} > S_{\text{hot}}$

## 7.2 Entropy change in a reversible process:

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

or,

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \left( \frac{\delta Q}{T} \right)_{\text{int rev}} \leq 0 \quad (3)$$



$$\int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0 \quad (4)$$

$$S_2 - S_1 \geq \int_1^2 \left( \frac{\delta Q}{T} \right)_{\text{rev}} \gg ds \geq \left( \frac{\delta Q}{T} \right)_{\text{rev}} \quad (5)$$

Or

$$\Delta S = \frac{Q}{T_0} \quad (\text{kJ/K}) \quad (6)$$

where  $T_0$  is the constant temperature and  $\Delta S$  is the entropy change during an internally reversible isothermal heat transfer process. The integrating of equation (5)



is often not available, and the integration can be performed for a few cases only (internally reversible isothermal process). For the majority of cases we have to rely on tabulated data for entropy.

In fact, we usually use the term of change of entropy instead of entropy itself. It should be mentioned that the above relationship between entropy and temperature is derived because the temperature represents the two properties; enthalpy and internal energy, and there is no heat transferred between any two bodies in contact unless there is a difference in their temperatures.

### 7.3 Entropy generation:

Entropy can be viewed as a measure of disorder or disorganization in a system. Likewise, entropy generation can be viewed as a measure of disorder or disorganization generated during a process. It can be concluded that the entropy change of an irreversible process is always greater than the entropy transfer. On another hand, some entropy is generated during the irreversible process due to presence of irreversibility. The entropy generated during a process is called **entropy generation** and denoted as  $S_{gen}$ . It is worth to be noted that the difference between the entropy change of a closed system and entropy transfer is equal to entropy generation. Thus,

$$\Delta S_{sys} = s_2 - s_1 = \int_1^2 \left( \frac{\delta Q}{T} \right) + S_{gen} \quad (7)$$

$$\underbrace{S_{in} - S_{out}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{gen}}_{\text{Entropy generation}} = \underbrace{\Delta S_{system}}_{\text{Change in entropy}} \quad (\text{kJ/K}) \quad (8)$$

$$(s_{in} - s_{out}) + s_{gen} = \Delta s_{system} \quad (\text{kJ/kg} \cdot \text{K}) \quad (9)$$



For a *closed system*;

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = \Delta S_{\text{system}} = S_2 - S_1 \quad (\text{kJ/K}) \quad (10)$$

It can be said that the entropy change of a *closed system* during a process is equal to the sum of the net entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries.

For isolated (adiabatic) system, the heat transfer is zero and the entropy change is due to irreversibility only which causes an increase of entropy.

$$\Delta S_{\text{isolated}} \geq 0 \quad \text{or} \quad S_{\text{gen}} = \Delta S_{\text{adiabatic system}} \quad (11)$$

This equation can be expressed as the ***entropy of an isolated system*** during a process always **increases** or, in the limiting case of a reversible process, remains constant. In other words, ***it never decreases***. This is known as the ***increase of entropy principle***. Note that in the absence of any heat transfer, entropy change is due to irreversibility only, and its effect is always to increase entropy.

Note; the entropy change can be negative during a process but entropy generation cannot. The principle of entropy increase is detailed as

$$S_{\text{gen}} = \begin{cases} > 0 & \text{irreversible process} \\ = 0 & \text{reversible process} \\ < 0 & \text{impossible} \end{cases}$$

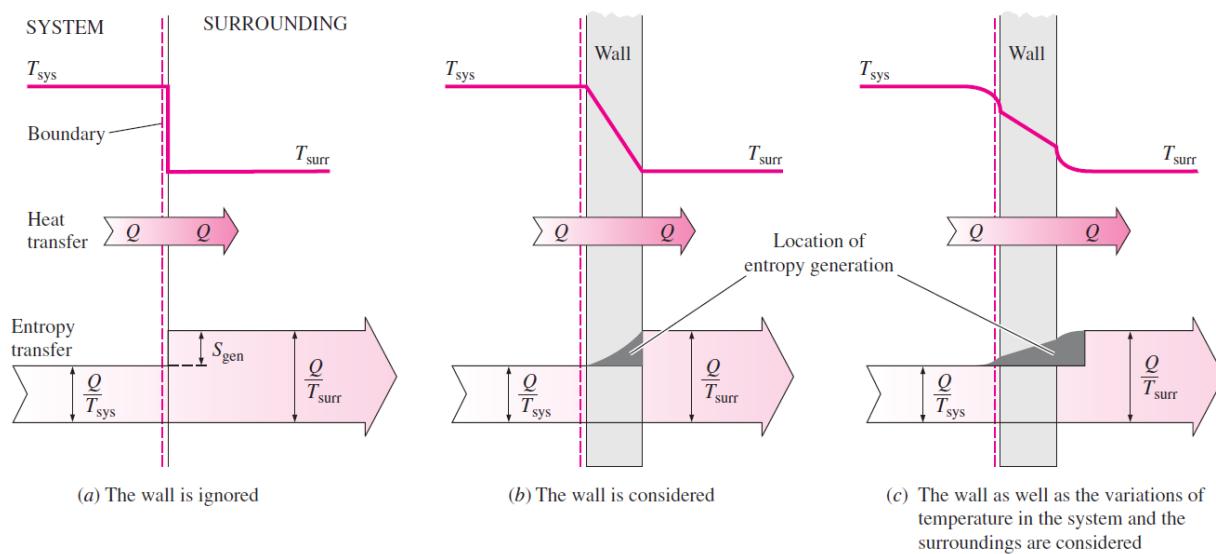


Figure 7-2. entropy generation during a heat transfer process through a finite temperature difference.

## 7.4 Remarks about entropy:

- $(-s)$  means that heat is rejected, and  $(+s)$  means heat is added.
- Processes can occur in a certain direction only, not in any direction.
- Entropy is a ***non-conserved property***, and there is no such thing as the conservation of entropy principle. Entropy is conserved during the idealized reversible processes only and increases during all actual processes.
- The performance of engineering systems is degraded by the presence of irreversibilities, and *entropy generation* is a measure of the magnitude of the *irreversibilities* present during that process. The greater the extent of irreversibilities, the greater the entropy generation. Therefore, entropy generation can be used as a *quantitative* measure of *Irreversibilities* associated with a process.



## 7.5 The T ds relations

Recall that the quantity  $(\delta Q/T)_{\text{int,rev}}$  corresponds to a differential change in the property *entropy*. The entropy change for a process can be evaluated by integrating  $\delta Q/T$  along some imaginary internally reversible path between the actual end states. But when the temperature varies during the process, we have to have a relation between  $\delta Q$  and  $T$  to perform this integration. The differential form of the conservation of energy equation for a closed stationary system (a fixed mass) containing a simple compressible substance can be expressed for an internally reversible process as

$$\delta Q_{\text{int rev}} - \delta W_{\text{int rev,out}} = dU \quad (12)$$

But

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

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

Thus

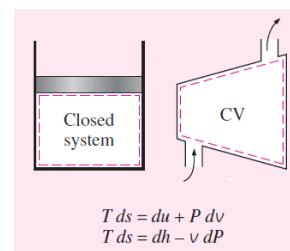
$$T \, dS = dU + P \, dV \quad (\text{kJ}) \quad \text{Or} \quad T \, ds = du + P \, dv \quad (\text{kJ/kg}) \quad (13)$$

This equation is known as the first T ds, or *Gibbs equation*.

Also,

$$\text{Hence, } (h = u + Pv)$$

$$\left. \begin{aligned} dh &= du + P \, dv + v \, dP \\ T \, ds &= du + P \, dv \end{aligned} \right\} T \, ds = dh - v \, dP$$





They are property relations and therefore are independent of the type of the processes. Thus;

$$ds = \frac{du}{T} + \frac{P dv}{T} \quad ds = \frac{dh}{T} - \frac{v dP}{T} \quad (14)$$

## 7.6 Entropy of pure substances:

### 7.6.1 Entropy of liquids:

$$dQ = c_{pl} \cdot dT \quad (15)$$

$c_{pl}$ : specific heat capacity of a liquid at constant pressure (4.187 kJ/kg.K).

$$\frac{dQ}{T} = c_{pl} \cdot \frac{dT}{T} = ds \quad (16)$$

$$\int_{s_1}^{s_2} ds = c_{pl} \cdot \int_{T_1}^{T_2} \frac{dT}{T} \quad (17)$$

$$s_2 - s_1 = c_{pl} \cdot \ln \frac{T_2}{T_1} \quad (18)$$

When the initial temperature of the liquid is 273K,

$$s_2 - 0 = c_{pl} \cdot \ln \frac{T_2}{273} \quad (19)$$

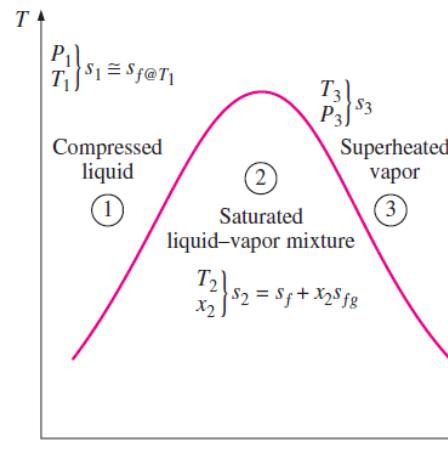


Figure 7-3. The entropy of a pure substance is determined from the tables (like other properties).

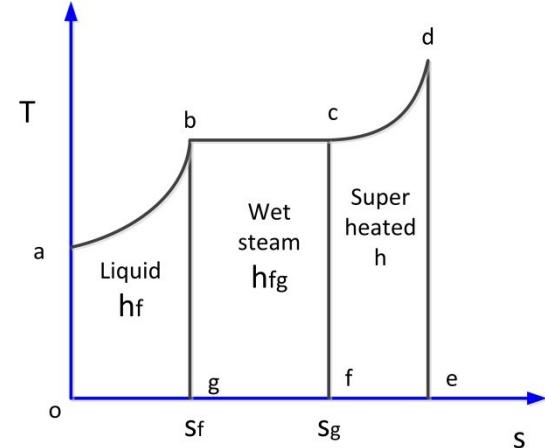


### 7.6.2 Entropy of evaporation

It is shown that liquid temperature increases from *a* to the saturation liquid temperature *b* (boiling). The line (*b*–*c*) represents the conversion of saturated liquid to a saturated steam at *c*, while it is a superheated steam at *d*.

$h_f$ : area (abgo)

$h_{fg}$ : area (bcfg) =  $T_f \cdot (s_g - s_f)$



$$s_g = s_f + \frac{h_{fg}}{T_f} \quad (20)$$

$$s_g = c_{pl} \cdot \ln \frac{T_2}{273} + \frac{h_{fg}}{T_f} \quad \text{dry saturated vapour} \quad (21)$$

$$s_{fg} = c_{pl} \cdot \ln \frac{T_2}{273} + x \frac{h_{fg}}{T_f} \quad \text{wet steam} \quad (22)$$

### 7.6.3 Superheated steam entropy

Area (cdef) =  $c_{pv} \cdot dT$

$c_{pv}$ : specific heat capacity of superheated vapour at constant pressure

$$dQ = c_{pv} \cdot dT \quad (23)$$

$$\frac{dQ}{T} = c_{pv} \cdot \frac{dT}{T} = ds \quad (24)$$

$$s - s_g = c_{pv} \cdot \ln \frac{T}{T_f} \quad (25)$$

Thus,

$$s = c_{pl} \cdot \ln \frac{T_f}{273} + \frac{h_{fg}}{T_f} + c_{pv} \cdot \ln \frac{T}{T_f} \quad (26)$$



Besides, the value of entropy can be estimated from the steam table.

## 7.7 Entropy change for gases

The non-flow equation can be written as

$$dQ = du + dW$$

For a gas changed from state 1 to 2,

$$dQ = c_v dT + pdv \quad \text{or} \quad \frac{dQ}{T} = c_v \frac{dT}{T} + \frac{p}{T} dv \quad (27)$$

Where,  $pv = RT$

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v} \quad (28)$$

$$\int_{s1}^{s2} ds = c_v \int_{T1}^{T2} \frac{dT}{T} + R \int_{v1}^{v2} \frac{dv}{v} \quad (29)$$

Thus,

$$s_2 - s_1 = c_v \cdot \ln \frac{T_2}{T_1} + R \cdot \ln \frac{v_2}{v_1} \quad \text{global equation} \quad (30)$$

The above equation represents the relation between  $s$ ,  $T$ , and  $v$ . From the relation of  $(c_p - c_v = R)$ , therefore,

$$\Delta s = c_v \cdot \ln \left( \frac{T_2}{T_1} \cdot \frac{v_1}{v_2} \right) + c_p \cdot \ln \frac{v_2}{v_1} \quad (31)$$

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$$

$$\Delta s = c_v \cdot \ln \left( \frac{p_2}{p_1} \right) + c_p \cdot \ln \frac{v_2}{v_1} \quad (32)$$

The above equation represents the relation between  $s$ ,  $p$ , and  $v$ .

Or  $c_v = c_p - R$ , therefore



$$\Delta s = c_p \cdot \ln\left(\frac{T_2}{T_1}\right) - R \cdot \ln\left(\frac{T_2}{T_1} \cdot \frac{v_1}{v_2}\right) \quad (33)$$

$$\frac{T_2 v_1}{T_1 v_2} = \frac{p_2}{p_1}$$

$$\Delta s = c_p \cdot \ln\left(\frac{T_2}{T_1}\right) - R \cdot \ln\left(\frac{p_2}{p_1}\right) \quad (34)$$

The above equation represents the relation between  $s$ ,  $T$ , and  $p$ .

## 7.8 Processes

### 7.8.1 Isometric process ( $v = \text{constant}$ ):

$$\text{From } \Delta s = c_v \cdot \ln \frac{T_2}{T_1} + R \cdot \ln \frac{v_2}{v_1}, \quad v_1 = v_2 \text{ and } \ln(1) = 0 \quad (35)$$

$$\Delta s = c_v \cdot \ln \frac{T_2}{T_1} \quad (36)$$

$$\text{Or from } \Delta s = c_v \cdot \ln\left(\frac{p_2}{p_1}\right) + c_p \cdot \ln \frac{v_2}{v_1} \quad (37)$$

$$\Delta s = c_v \cdot \ln\left(\frac{p_2}{p_1}\right) \quad (38)$$

$$\text{Thus, } \boxed{\Delta s = c_v \cdot \ln \frac{T_2}{T_1} = c_v \cdot \ln \left(\frac{p_2}{p_1}\right)} \quad (39)$$

### 7.8.2 Isobaric process ( $p = \text{constant}$ ):

$$\text{Or from } \Delta s = c_v \cdot \ln\left(\frac{p_2}{p_1}\right) + c_p \cdot \ln \frac{v_2}{v_1} \quad \text{and} \quad \Delta s = c_p \cdot \ln\left(\frac{T_2}{T_1}\right) - R \cdot \ln\left(\frac{p_2}{p_1}\right)$$

$$\boxed{\Delta s = c_p \cdot \ln \frac{v_2}{v_1} = c_p \cdot \ln \left(\frac{T_2}{T_1}\right)} \quad (40)$$

### 7.8.3 Isothermal process ( $T = \text{constant}$ ):

$$\Delta s = -R \cdot \ln\left(\frac{p_2}{p_1}\right) \quad (41)$$



$$\Delta s = R \cdot \ln\left(\frac{p_1}{p_2}\right) = R \cdot \ln\left(\frac{v_2}{v_1}\right) \quad (42)$$

#### 7.8.4 Polytropic process ( $p v^n = c$ ):

$$\Delta s = c_p \cdot \ln\left(\frac{T_2}{T_1}\right) - R \cdot \ln\left(\frac{p_2}{p_1}\right) = c_v \cdot \ln\left(\frac{p_2}{p_1}\right) + c_p \cdot \ln\frac{v_2}{v_1} = c_v \cdot \ln\frac{T_2}{T_1} + R \cdot \ln\frac{v_2}{v_1}$$

#### 7.8.5 Isentropic process:

A process during which the entropy remains constant is called an *isentropic* process.

$$s_1 = s_2$$

$$\Delta s = 0$$

It is taken place at  $\Delta T_{\max}$ .

