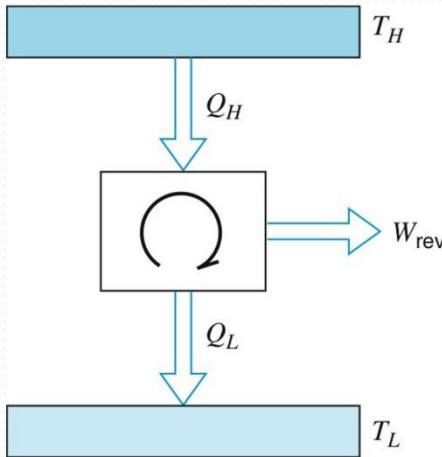


# Chapter 8 Entropy For a Control Mass

## 8.1. The Inequality of Clausius



Reversible heat engine cycle for demonstration of the inequality of Clausius.

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

Clausius inequality

Consider first a reversible (Carnot) heat engine cycle operating between reservoirs at temperatures  $T_H$  and  $T_L$

The cyclic integral of the heat transfer  $\oint \delta Q$  is greater than zero  $\oint \delta Q = Q_H - Q_L > 0$

Since  $T_H$  and  $T_L$  are constant, from the definition of the absolute temperature scale and from the fact this is a reversible cycle

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

If  $T_H$  approaches  $T_L$ , the cyclic integral of  $\delta Q$ , approaches zero (by making  $T_H$  approach  $T_L$ ) and the cycle remains reversible, the cyclic integral of  $\delta Q/T$  remains zero. Thus, we conclude that for all reversible heat engine cycles

$$\oint \delta Q \geq 0 \quad \text{and} \quad \oint \frac{\delta Q}{T} = 0$$

Consider an irreversible cyclic heat engine operating between the same  $T_H$  and  $T_L$

$$W_{\text{irr}} < W_{\text{rev}}$$

$$\text{Since } Q_H - Q_L = W$$

$$Q_H - Q_{L \text{ irr}} < Q_H - Q_{L \text{ rev}}$$

and therefore

$$Q_{L \text{ irr}} > Q_{L \text{ rev}}$$

Consequently, for the irreversible cyclic engine,

$$\oint \delta Q = Q_H - Q_{L \text{ irr}} > 0$$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{L \text{ irr}}}{T_L} < 0$$

Suppose that we cause the engine to become more and more irreversible but keep  $Q_H$ ,  $T_H$ , and  $T_L$  fixed. The cyclic integral of  $\delta Q$  then approaches zero, and that for  $\delta Q/T$  becomes a progressively larger negative value

Thus, we conclude that for all irreversible heat engine cycles

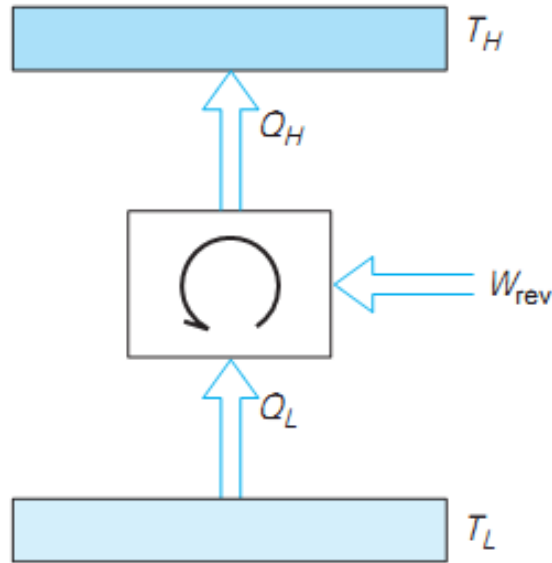
$$\oint \delta Q \geq 0$$

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

## For the reversible refrigeration cycle

## For the irreversible Refrigerator cycle

To complete the demonstration of the inequality of Clausius, we must perform similar analyses for both reversible and irreversible refrigeration cycles



Reversible refrigeration cycle for demonstration of the inequality of Clausius.

$$\oint \delta Q = -Q_H + Q_L < 0$$

$$\oint \frac{\delta Q}{T} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

As the cyclic integral of  $\delta Q$  approaches zero reversibly ( $T_H$  approaches  $T_L$ ), the cyclic integral of  $\delta Q/T$  remains at zero.

$$\oint \delta Q = 0$$

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

Thus, for all reversible refrigeration cycles,

$$\oint \delta Q \leq 0$$

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

$$W_{\text{irr}} > W_{\text{rev}}$$

$$Q_{H \text{ irr}} - Q_L > Q_{H \text{ rev}} - Q_L$$

$$Q_{H \text{ irr}} > Q_{H \text{ rev}}$$

$$\oint \delta Q = -Q_{H \text{ irr}} + Q_L < 0$$

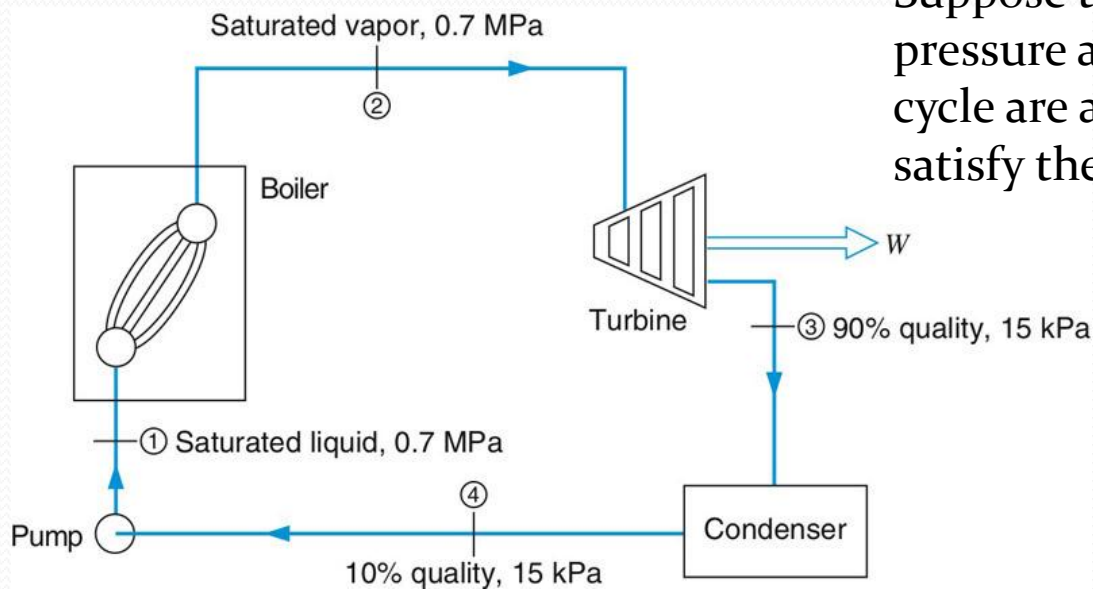
$$\oint \frac{\delta Q}{T} = -\frac{Q_{H \text{ irr}}}{T_H} + \frac{Q_L}{T_L} < 0$$

Thus, for all irreversible refrigeration cycles,

$$\oint \delta Q < 0$$

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

Thus, for all cycles we can write  $\oint \frac{\delta Q}{T} \leq 0$



Suppose that someone reports that the pressure and quality at various points in the cycle are as given in Figure. Does this cycle satisfy the inequality of Clausius?

Heat is transferred in two places, the boiler and the condenser. Therefore, Heat is transferred in two places, the boiler and the condenser. Therefore,

$$\oint \frac{\delta Q}{T} = \frac{1}{T_1} \int_1^2 \delta Q + \frac{1}{T_3} \int_3^4 \delta Q = \frac{{}_1Q_2}{T_1} + \frac{{}_3Q_4}{T_3}$$

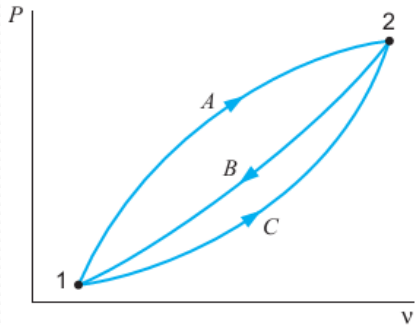
$${}_1q_2 = h_2 - h_1 = 2066.3 \text{ kJ/kg}, \quad T_1 = 164.97^\circ\text{C}$$

$${}_3q_4 = h_4 - h_3 = 463.4 - 2361.8 = -1898.4 \text{ kJ/kg}, \quad T_3 = 53.97^\circ\text{C}$$

$$\oint \frac{\delta Q}{T} = \frac{2066.3}{164.97 + 273.15} - \frac{1898.4}{53.97 + 273.15} = -1.087 \text{ kJ/kg K}$$

## 8.2. Entropy – A Property of a System

The second law of thermodynamics leads to a property of a system that we call entropy.



Let a system (control mass) undergo a reversible process from state 1 to state 2 along a path A, and let the cycle be completed along path B, which is also reversible.

a reversible process from state 1 to state 2 along a path A

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \frac{\delta Q}{T} \right)_B$$

a reversible process from state 1 to state 2 along a path C

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left( \frac{\delta Q}{T} \right)_C + \int_2^1 \left( \frac{\delta Q}{T} \right)_B$$

Subtracting the second equation from the first

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

Since  $\oint \delta Q/T$  is the same for all reversible paths between states 1 and 2, we conclude that this quantity is independent of the path and is a function of the end states only; it is therefore a property. This property is called entropy and is designated S.

Entropy may be defined as a property of a substance in accordance with the relation

$$dS \equiv \left( \frac{\delta Q}{T} \right)_{\text{rev}}$$

Entropy is an extensive property, and the entropy per unit mass is designated  $s$ . It is important to note that entropy is defined here in terms of a reversible process.

The change in the entropy of a system as it undergoes a change of state may be found by

$$S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_{\text{rev}}$$



## 8.3. The Entropy of a Pure Substance

Values of specific entropy (entropy per unit mass) are given in tables of thermodynamic properties in the same manner as specific volume and specific enthalpy.

SU VE SU BUHARI TABLOLARI

TABLO 2.5.3 Sıkıştırılmış Sıvı ve Kızgın Buhar

P=50 kPa $T_d=81.35^\circ\text{C}$				T ( $^\circ\text{C}$ )	P=100 kPa $T_d=99.63^\circ\text{C}$			
$v_b$	$u_b$	$h_b$	$s_b$		$v_b$	$u_b$	$h_b$	$s_b$
3,240	2484.0	2646.00	7.5947		1,694	2675.3	2675.4	7.3598
$v$ $\text{m}^3/\text{kg}$	$u$ $\text{kJ/kg}$	$h$ $\text{kJ/kg}$	$s$ $\text{kJ/kg}\cdot\text{K}$		$v$ $\text{m}^3/\text{kg}$	$u$ $\text{kJ/kg}$	$h$ $\text{kJ/kg}$	$s$ $\text{kJ/kg}\cdot\text{K}$
0.0010002	-0.1	0.00	-0.0002	0	0.0010002	0.0	0.1	-0.0001
0.0010017	83.8	83.90	0.2963	20	0.0010017	83.9	84.0	0.2963
0.0010078	167.4	167.50	0.5721	40	0.0010078	167.4	167.5	0.5721
0.0010171	251.0	251.10	0.8310	60	0.0010171	251.1	251.2	0.8309
0.0010292	334.8	334.90	1.0753	80	0.0010292	334.9	335.0	1.0752
3.418	2511.7	2682.60	7.6953	100	1.696	2506.6	2676.2	7.3618
3.607	2541.3	2721.60	7.7972	120	1.793	2537.2	2716.5	7.4670
3.796	2570.8	2760.60	7.8940	140	1.889	2567.5	2756.4	7.5662
3.983	2600.5	2799.60	7.9861	160	1.984	2597.8	2796.2	7.6601
4.170	2630.1	2838.60	8.0742	180	2.078	2628.0	2835.8	7.7495

Above the line, the properties are given for the compressed liquid or subcooled region

Below the line, the properties are given for the superheated region

A partial listing of Table 2.5.3.

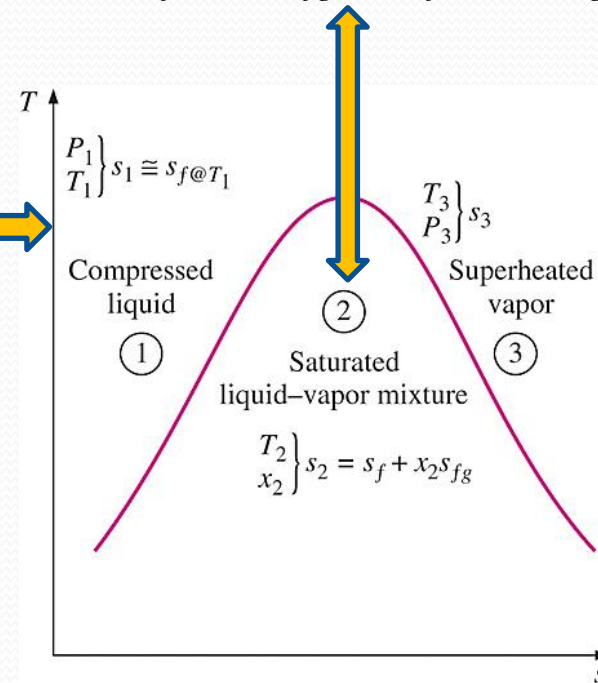
The units of specific entropy in the steam tables, refrigerant tables, and ammonia tables are  $\text{kJ/kg}\cdot\text{K}$ , and the values are given relative to an arbitrary reference state.

In general, we use the term entropy to refer to both total entropy and entropy per unit mass, since the context or appropriate symbol will clearly indicate the precise meaning of the term.

In the **saturation region** the entropy may be calculated **using the quality**. The relations are similar to those for specific volume, internal energy and enthalpy.

The entropy of a compressed liquid is tabulated in the same manner as the other properties. These properties are primarily a function of the temperature and are not greatly different from those for saturated liquid at the same temperature.

$$s = s_f + x s_{fg} = s_f + x(s_g - s_f)$$

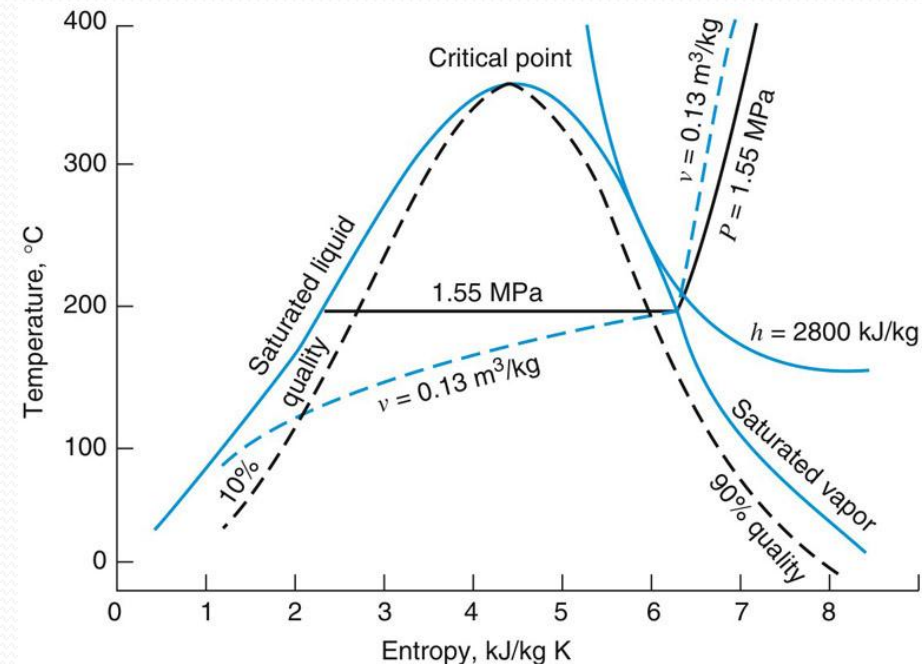


The entropy of a pure substance is determined from the tables (like other properties).

**Table 2.5.3** of the steam tables give the entropy of compressed liquid water in the same manner as for other properties.

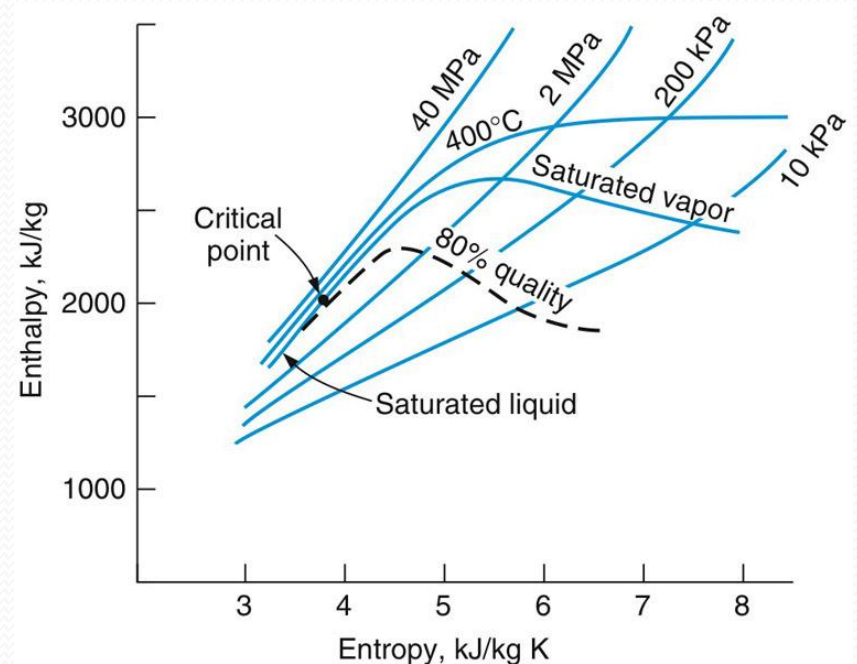


The thermodynamic properties of a substance are often shown on a **temperature entropy diagram** and on an **enthalpy entropy diagram**, which is also called a **Mollier diagram**,



Temperature–Entropy diagram for steam

These **diagrams** are **valuable** both **because** they **present thermodynamic data** and **because** they **enable us to visualize the changes of state that occur in various processes**.



Enthalpy–Entropy diagram for steam

## 8.4 Entropy Change in Reversible Processes

In this section we will limit ourselves to **systems that undergo reversible processes and consider the Carnot cycle, reversible heat-transfer processes, and reversible adiabatic processes.**

### Carnot cycle

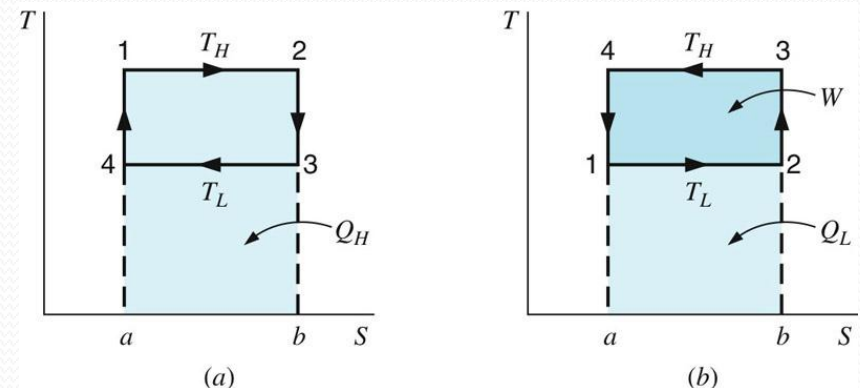
The **first process (1-2)** is the isothermal transfer of heat to the working fluid from the high-temperature reservoir.

$$S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_{rev}$$

Since this is a **reversible process** in which the **temperature** of the working fluid **remains constant**, the equation can be integrated to give

$$S_2 - S_1 = \frac{1}{T_H} \int_1^2 \delta Q = \frac{Q_{12}}{T_H}$$

This process is shown in Figure, and the area under line 1-2, area 1-2-b-a-1, represents the heat transferred to the working fluid during the process ( $Q_H$ ).



### The Carnot cycle on the temperature-entropy diagram

The **second process** (2-3) of a Carnot cycle is a reversible adiabatic one. From the definition of entropy,

$$dS = \left( \frac{\delta Q}{T} \right)_{rev}$$

the **entropy** remains **constant** in a **reversible adiabatic process**. A **constant entropy process** is called an **isentropic process**. Line 2-3 represents this process, and this process is concluded at state 3 when the temperature of the working fluid reaches  $T_L$ .

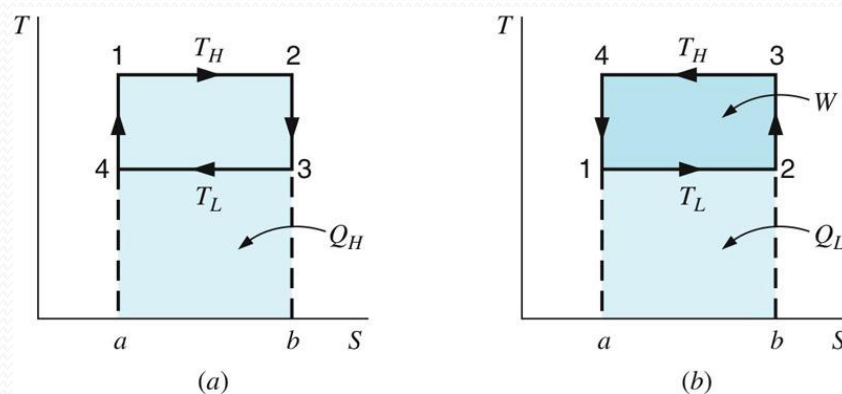
The **third process** (3-4) is the **reversible isothermal** process in which heat is transferred from the working fluid to the low temperature reservoir

$$S_4 - S_3 = \int_3^4 \left( \frac{\delta Q}{T} \right)_{rev} = \frac{Q_{34}}{T_L}$$

During this process the **heat transfer is negative**, So the **entropy** of the working fluid **decreases**.

The **final process** (4-1), which completes the cycle, is a reversible adiabatic process (and therefore isentropic)

**Entropy decrease** in process 3-4 must exactly **equal** the entropy increase in process 1-2

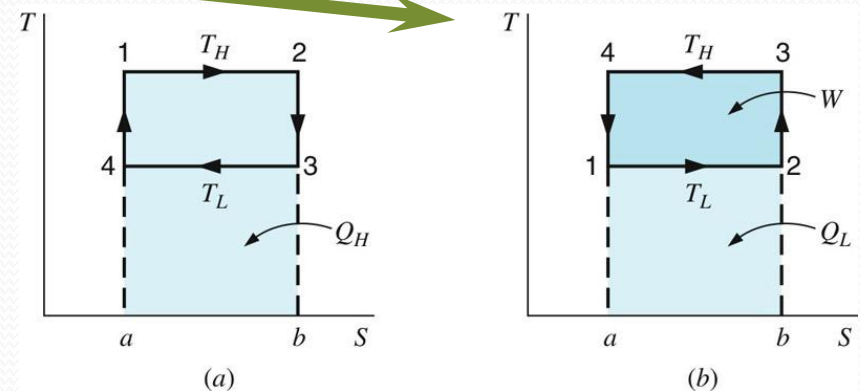


The area under line 3-4, area 3-A-a-b-3, represents the heat transferred from the working fluid to the low-temperature reservoir.

Since the net work of the cycle is equal to the net heat transfer, then area 1-2-3-4-1 must represent the net work of the cycle. The efficiency of the cycle may also be expressed in terms of areas

$$\eta_{th} = \frac{W_{net}}{Q_H} = \frac{\text{area } 1-2-3-4-1}{\text{area } 1-2-b-a-1}$$

If the cycle is reversed, we have a **refrigerator** or **heat pump**. The Carnot cycle for a refrigerator is shown in Figure (b).



The heat transfer to or from a system can be shown as an area on a temperature–entropy diagram

Consider the change of state from saturated liquid to saturated vapor at constant pressure  
The **process 1–2** on the T–s diagram of Figure

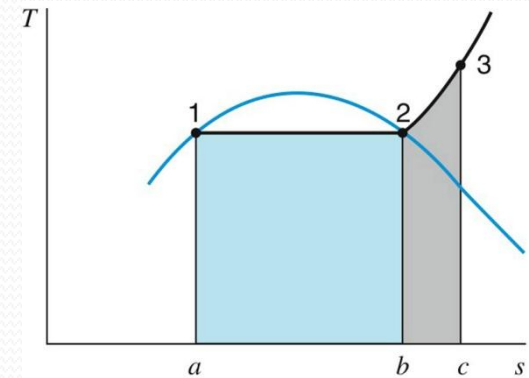
The **area 1–2–b–a–1** represents the **heat transfer**. Since this is a constant–pressure process, the heat transfer per unit mass is equal to  $h_{fg}$ . Thus,

$$s_2 - s_1 = s_{fg} = \frac{1}{m} \int_1^2 \left( \frac{\delta Q}{T} \right)_{rev} = \frac{1}{mT} \int_1^2 \delta Q = \frac{q_{12}}{T} = \frac{h_{fg}}{T}$$

If heat is transferred to the saturated vapor at constant pressure, the steam is superheated along line **2–3**

Since **T is not constant**, this equation **cannot be integrated** unless **we know a relation between temperature and entropy**.

However, we do realize that the **area under line 2–3**, area 2–3–c–b–2, represents  $\int_2^3 T ds$  and therefore **represents the heat transferred during this reversible process**.

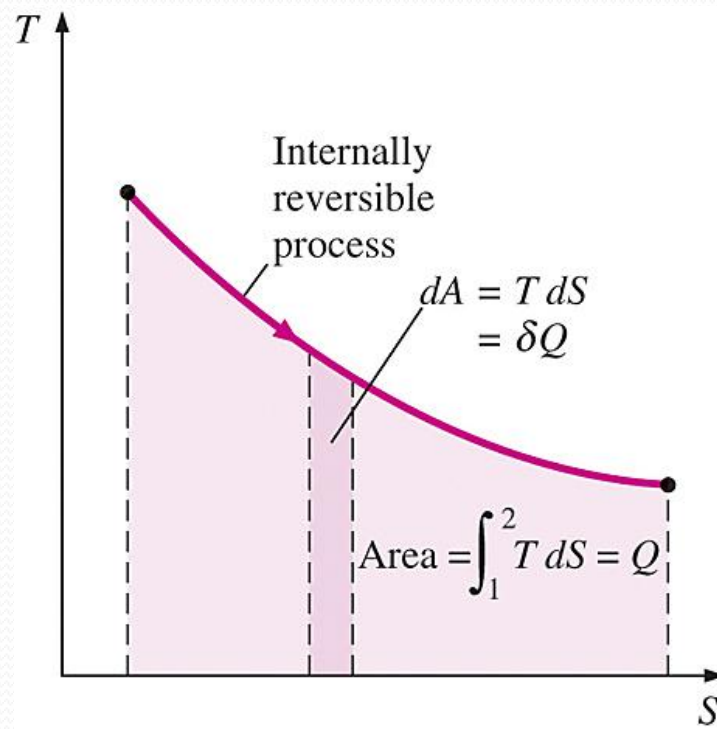


A temperature–entropy diagram to show areas that represent heat transfer for an internally reversible process

$$q_{23} = \frac{1}{m} \int_2^3 \delta Q = \int_2^3 T ds$$



The important conclusion to draw here is that for processes that are internally reversible, the area underneath the process line on a temperature–entropy diagram represents the quantity of heat transferred. This is not true for irreversible processes



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

$$Q_{\text{int rev}} = \int_1^2 T dS$$

$$\delta q_{\text{int rev}} = T ds$$

$$q_{\text{int rev}} = \int_1^2 T ds$$

$$Q_{\text{int rev}} = T_0 \Delta S$$

$$q_{\text{int rev}} = T_0 \Delta s$$

On a  $T$ - $S$  diagram, the area under the process curve represents the heat transfer for internally reversible processes.

## 8.5 The Thermodynamic Property Relation

Two important thermodynamic relations for a simple compressible substance  
the first  $T ds$ , or *Gibbs equation*

$$T ds = du + P dv$$

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

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

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

$$T ds = du + P dv \quad (\text{kJ})$$

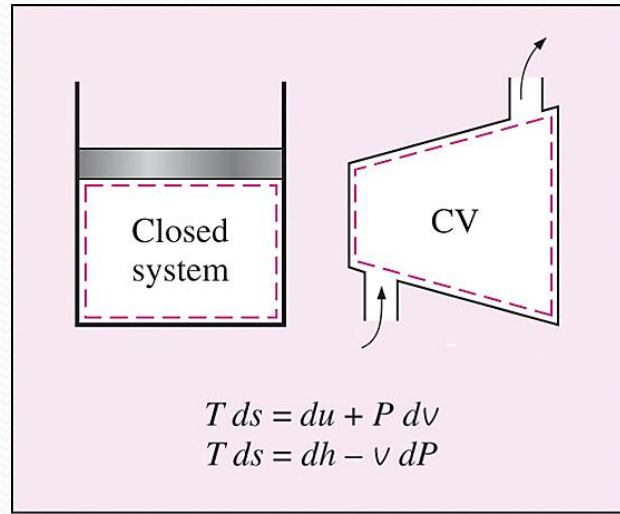
$$T ds = du + P dv \quad (\text{kJ/kg})$$

the second  $T ds$  equation

$$T ds = dh - v dp$$

$$h = u + Pv$$

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



Two forms of the thermodynamic property relation and are frequently called Gibbs equations

surface effects, magnetic effects, and electrical effects are insignificant when dealing with the substances

substances of fixed composition other than a simple compressible substance

$$\delta W = p dv - \mathfrak{T} dL - \wp dA - \zeta dZ$$

$$T ds = du + P dv - \mathfrak{T} dL - \wp dA - \zeta dZ$$



## 8.6 Entropy Change of a Solid or Liquid

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

Since  $dv \cong 0$  for liquids and solids

$$ds = \frac{du}{T} = \frac{c dT}{T}$$

since  $c_p = c_v = c$  and  $du = c dT$

Liquids and solids can be approximated as incompressible substances since their specific volumes remain nearly constant during a process.

$$\text{Liquids, solids:} \quad s_2 - s_1 = \int_1^2 c(T) \frac{dT}{T} \cong c_{\text{avg}} \ln \frac{T_2}{T_1} \quad (\text{kJ/kg} \cdot \text{K})$$

For an isentropic process (a reversible + adiabatic ( $dq = 0$ )) of an incompressible substance

$$\text{Isentropic:} \quad s_2 - s_1 = c_{\text{avg}} \ln \frac{T_2}{T_1} = 0 \quad \rightarrow \quad T_2 = T_1$$



## 8.7 Entropy Change of an Ideal Gas

$$\begin{aligned}P\nu &= RT \\ du &= C_\nu dT \\ dh &= C_p dT\end{aligned}$$

From the first  $T ds$  relation

$$ds = \frac{du}{T} + \frac{P d\nu}{T} \quad \begin{aligned} du &= c_\nu dT \\ P &= RT/\nu \end{aligned}$$

$$ds = c_\nu \frac{dT}{T} + R \frac{d\nu}{\nu}$$

$$s_2 - s_1 = \int_1^2 c_\nu(T) \frac{dT}{T} + R \ln \frac{\nu_2}{\nu_1}$$

From the second  $T ds$  relation

$$ds = \frac{dh}{T} - \frac{\nu dP}{T}$$

$$dh = c_p dT \quad \nu = RT/P$$

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

The second possibility for the specific heat is to use an analytical equation for  $C_{po}$  in the below equation as a function of temperature

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1}$$

We choose absolute zero as the reference temperature  $T_o$  and define a function  $s^\circ$  as

$$s_T^\circ = \int_1^2 \frac{C_{po}}{T} dT \quad \text{standard entropy}$$

$$\int_1^2 c_p(T) \frac{dT}{T} = s_2^\circ - s_1^\circ$$

$T, K$	$s^\circ, \text{kJ/kg} \cdot K$
.	.
.	.
.	.
300	1.70203
310	1.73498
320	1.76690
.	.
.	.
.	.
(Table A-17)	

On a unit-mass basis

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

On a unit-mole basis

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

The entropy of an ideal gas depends on both  $T$  and  $P$ . The function  $s^\circ$  represents only the temperature-dependent part of entropy.

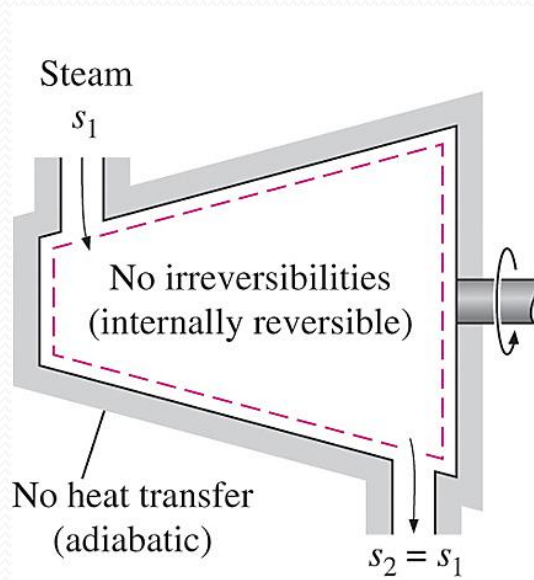
**For air in Table 2.4.3 or For other gases in Table 2.12.21** **Tables 2.4.3 and 2.12.2, would give the most accurate results, and the equations listed in Table 2.4.1 would give a close empirical approximation.**



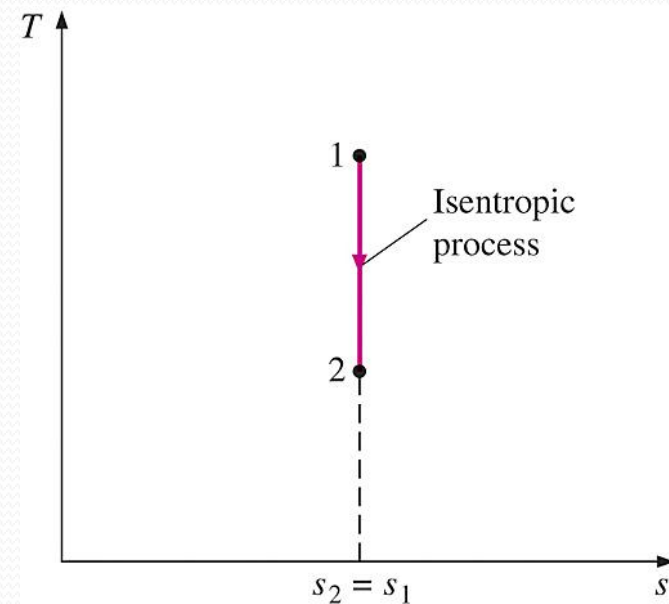
Let us now consider the case of an **ideal gas undergoing an isentropic process**

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

$$\Delta s = 0 \quad \text{or} \quad s_2 = s_1 \quad (\text{kJ/kg} \cdot \text{K})$$



During an internally reversible, adiabatic (isentropic) process, the entropy remains constant.



The isentropic process appears as a *vertical* line segment on a  $T-s$  diagram.

$$s_2 - s_1 = 0 = C_{po} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad \text{left side equal to zero for isentropic process}$$

Setting this equation equal to zero, we get

$$\ln \frac{T_2}{T_1} = \frac{R}{C_{po}} \ln \frac{P_2}{P_1} \quad \text{or} \quad \frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{R/C_p} \quad \text{However} \quad \frac{R}{C_{po}} = \frac{C_{po} - C_{vo}}{C_{po}} = \frac{k-1}{k}$$

where k, the ratio of the specific heats  $k = \frac{C_{po}}{C_{vo}}$  and thus  $\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{(k-1)/k}$

From this expression and the ideal gas equation of state

$$\frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{(k-1)} \quad \frac{P_2}{P_1} = \left( \frac{v_1}{v_2} \right)^k \quad Pv^k = \text{constant}$$

$$\left( \frac{T_2}{T_1} \right)_{s=\text{const.}} = \left( \frac{P_2}{P_1} \right)^{(k-1)/k} = \left( \frac{v_1}{v_2} \right)^{k-1}$$

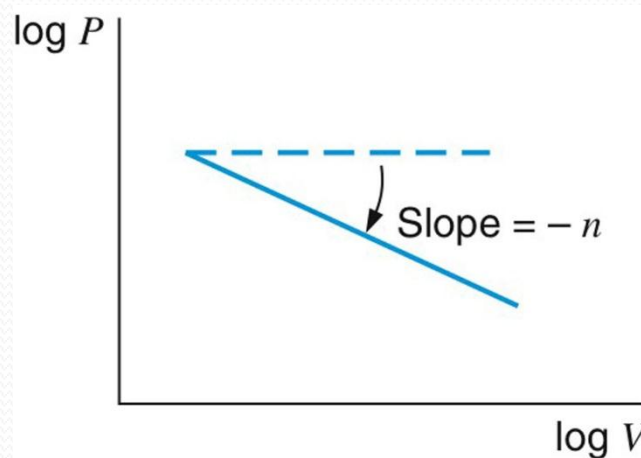
VALID FOR  
 \*ideal gas  
 \*isentropic process  
 \*constant specific heats

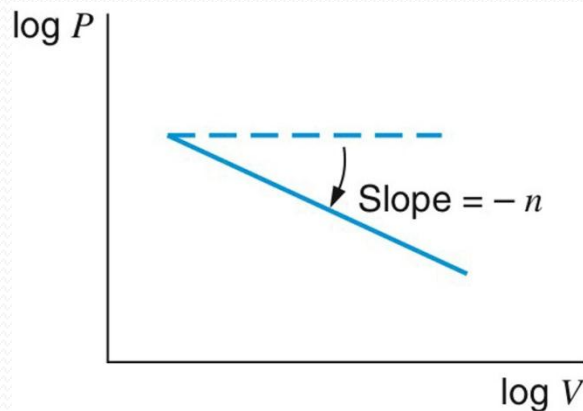
The isentropic relations of ideal gases are valid for the isentropic processes of ideal gases only.

## 8.8 The Reversible Polytropic Process for an Ideal Gas

When a gas undergoes a reversible process in which there is heat transfer, the process frequently takes place in such a manner that a plot of  $\log P$  versus  $\log V$  is a straight line, as shown in Figure. For such a process  $PV^n$  is a constant.

A process having this relation between pressure and volume is called a **polytropic process**. An example is the expansion of the combustion gases in the cylinder of a water-cooled reciprocating engine.





From this figure it follows that

$$\frac{d \ln P}{d \ln V} = -n \quad d \ln P + n d \ln V = 0$$

If  $n$  is a constant, this equation can be integrated to give the following relation

$$Pv^n = \text{constant} = P_1 v_1^n = P_2 v_2^n$$

From this equation the following relations can be written for a polytropic process

$$\frac{P_2}{P_1} = \left( \frac{V_1}{V_2} \right)^n \quad \frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{(n-1)/n} = \left( \frac{V_1}{V_2} \right)^{(n-1)}$$

For a control mass consisting of an **ideal gas**, the work done at the moving boundary during a reversible polytropic process can be derived,

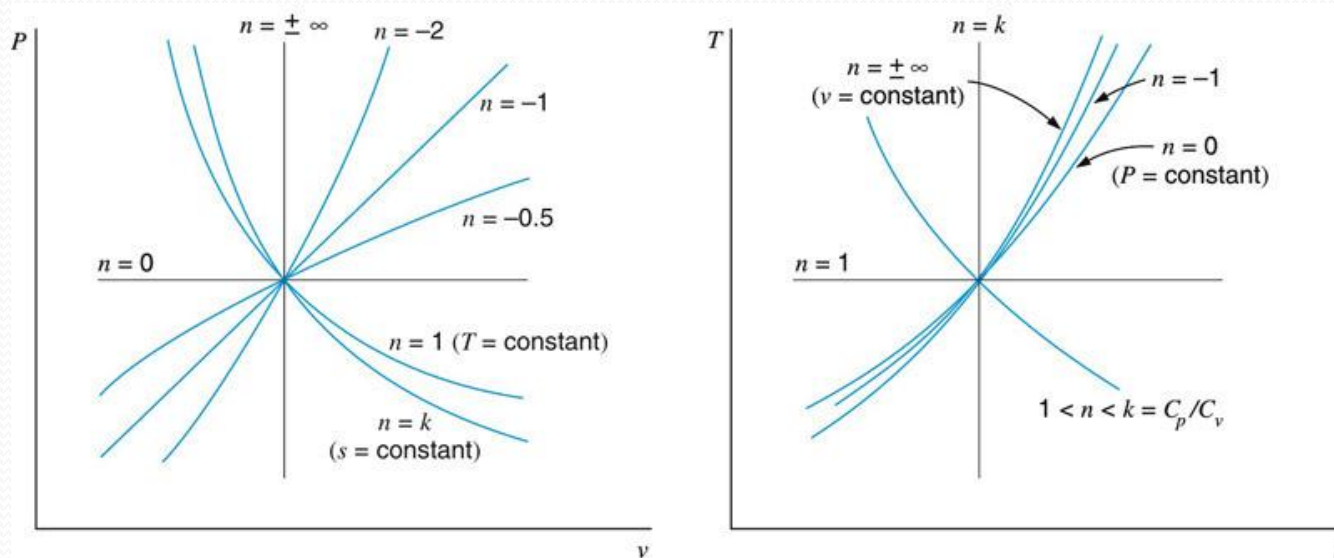
$${}_1W_2 = \int_1^2 P dV \quad \text{and} \quad PV^n = \text{cons}$$

$${}_1W_2 = \text{cons} \int_1^2 V^{-n} dV = \frac{P_2 V_2 - P_1 V_1}{1-n} = \frac{mR(T_2 - T_1)}{1-n}$$

for any value of  $n$  **except  $n = 1$**

The polytropic processes for various values of  $n$  are shown in Figure on  $P$ - $v$  and  $T$ - $s$  diagrams. The values of  $n$  for some familiar processes are

Isobaric process:	$n = 0$ , $P = \text{constant}$
Isothermal process:	$n = 1$ , $T = \text{constant}$
Isentropic process:	$n = k$ , $s = \text{constant}$
Isochoric process:	$n = \infty$ , $v = \text{constant}$





The reversible isothermal process for an ideal gas is of particular interest. In this process

$$Pv = \text{constant} = P_1 v_1 = P_2 v_2$$

The work done  ${}_1W_2 = \int_1^2 P dV$

$${}_1W_2 = \text{const} \int_1^2 \frac{dV}{V} = P_1 V_1 \ln \frac{V_2}{V_1} = P_1 V_1 \ln \frac{P_1}{P_2} \quad \text{or} \quad {}_1W_2 = mRT \ln \frac{V_2}{V_1} = mRT \ln \frac{P_1}{P_2}$$

Because there is no change in internal energy or enthalpy in an isothermal process, the heat transfer is equal to the work

$$\int_1^2 T ds = q_{12} = \int_1^2 du + \int_1^2 P dv$$

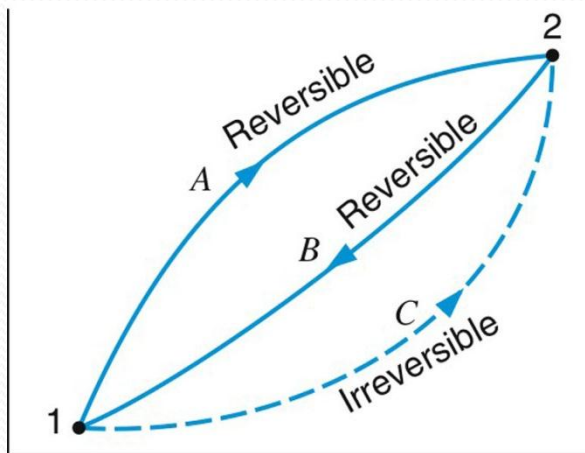
But  $du = 0$  and  $Pv = \text{constant} = P_1 v_1 = P_2 v_2$ , such that

$${}_1q_2 = \int_1^2 P dv = P_1 v_1 \ln \frac{v_2}{v_1}$$



## 8.9 Entropy Change of a Control Mass During an Irreversible Process

Consider a control mass that undergoes the cycles shown in Figure.



The cycle made up of the reversible processes and B is a reversible cycle. Therefore, we can write

$$\oint \frac{\delta Q}{T} = \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \frac{\delta Q}{T} \right)_B = 0$$

The cycle made of the irreversible process C and the reversible process B is an irreversible cycle. Therefore, for this cycle the inequality of Clausius may be applied

$$\oint \frac{\delta Q}{T} = \int_1^2 \left( \frac{\delta Q}{T} \right)_C + \int_2^1 \left( \frac{\delta Q}{T} \right)_B < 0$$

Subtracting the second equation from the first and rearranging

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A > \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

Since path A is reversible, and since entropy is a property

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 dS_A = \int_1^2 dS_C$$

Therefore,

$$\int_1^2 dS_C > \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

As path C was arbitrary, the general result is  $dS \geq \frac{\delta Q}{T}$  or  $S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$

In these equations the equality holds for a reversible process and the inequality for an irreversible process.

If an amount of heat  $\delta Q$  is transferred to a control mass at temperature  $T$  in a reversible process, the change of entropy is given by the relation  $dS = \left( \frac{\delta Q}{T} \right)_{rev}$

If any irreversible effects occur while the amount of heat  $\delta Q$  is transferred to the control mass at temperature  $T$ , however, the change of entropy will be greater than for the reversible process.  $dS > \left( \frac{\delta Q}{T} \right)_{irrev}$

The entropy will tend to decrease as a result of the heat transfer. However, the influence of irreversibilities is still to increase the entropy of the mass, and from the absolute numerical perspective we can still write for  $\delta Q$ :  $dS \geq \frac{\delta Q}{T}$

## 8.10 Entropy Generation

The entropy change for an irreversible process is larger than the change in a reversible process for the same  $\delta Q$  and  $T$ .

$$dS = \frac{\delta Q}{T} + \delta S_{gen}$$

provided the last term is positive,

$$\delta S_{gen} \geq 0$$

The amount of entropy,  $\delta S_{gen}$  is the entropy generation in the process due to irreversibilities occurring inside the system **such as friction, unrestrained expansions, and the internal transfer of energy (redistribution) over a finite temperature difference.** In addition to this internal entropy generation, external irreversibilities are possible by **heat transfer over finite temperature differences as the  $\delta Q$  is transferred from a reservoir or by the mechanical transfer of work.** A control mass for now but later extended to the more general control volume.

Consider a reversible process, for which the entropy generation is zero, and the heat transfer and work terms therefore

$$\delta Q = T dS \quad \text{and} \quad \delta W = P dV$$

For an irreversible process with a nonzero entropy generation

$$\delta Q_{irr} = T dS - T \delta S_{gen}$$



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



$$T dS = dU + P dV$$



$$\delta W_{irr} = P dV - \underbrace{T dS_{gen}}$$

The work is reduced by an amount proportional to the entropy generation. For this reason the term  $T \delta S_{gen}$  is often called "lost work,"



$$dS = \frac{\delta Q}{T} + \delta S_{gen}$$

Integration of left side equation  
between initial and final states

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{12gen}$$

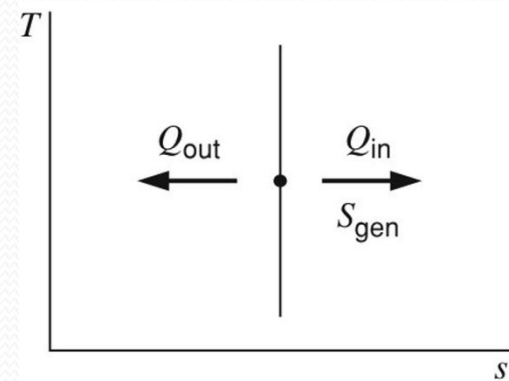
the entropy balance  
equation for a  
control mass

The equation can also be written in the general form  $\Delta Entropy = +in - out + gen$

stating that we can generate but not destroy entropy. This is in contrast to energy, which we can neither generate nor destroy.

## Some important conclusions can be drawn

**First**, there are two ways in which the entropy of a system can be increased – by transferring heat to it and by having an irreversible process. Since the entropy generation cannot be less than zero, there is only one way in which the entropy of a system can be decreased, and that is to transfer heat from the system. These changes are illustrated in a  $T$ - $s$  diagram in Figure.

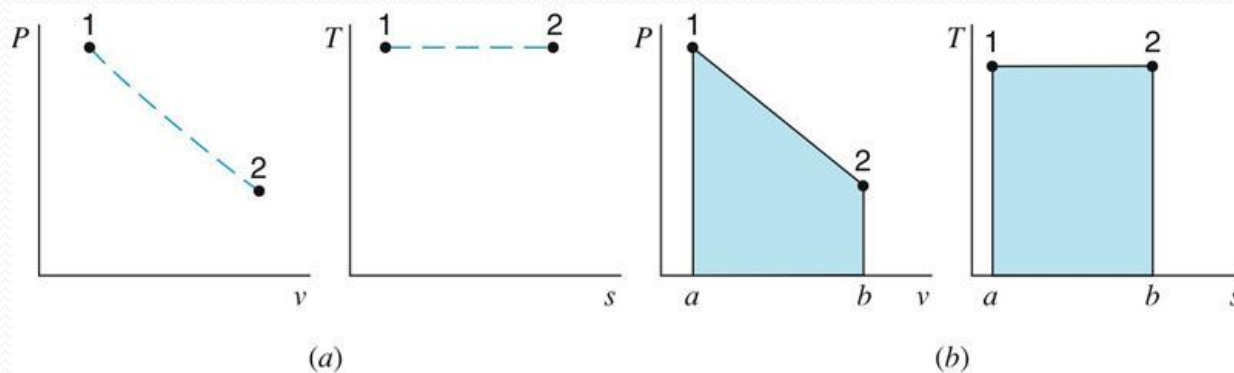


**Second**, as we have already noted for an adiabatic process,  $\delta Q = 0$ , and therefore the increase in entropy is always associated with the irreversibilities.

**Third**, the presence of irreversibilities will cause the work to be smaller than the reversible work. This means less work out in an expansion process and more work into the control mass ( $\delta W < 0$ ) in a compression process.

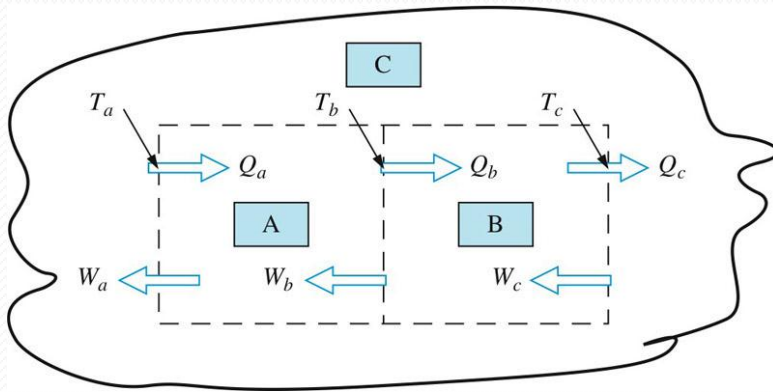
**Finally**, it should be emphasized that the change in  $s$  associated with the heat transfer is a transfer across the control surface, so a gain for the control volume is accompanied by a loss of the same magnitude outside the control volume. This is in contrast to the generation term that expresses all the entropy generated inside the control volume due to any irreversible process.

The work for an irreversible process is not equal to  $\int P dV$ , and the heat transfer is not equal to  $\int T dS$ . Therefore, the area underneath the path does not represent work and heat on the P-V and T-S diagrams in Figure a.



## 8.11 Principle of the Increase of Entropy

The entropy change of a control mass could be either positive or negative, since entropy can be increased by internal entropy generation and either increased or decreased by heat transfer, depending on the direction of that transfer. Now we would like to emphasize the difference between the energy and entropy equations and point out that energy is conserved but entropy is not.



Energy  $(E_2 - E_1)_A = Q_a - W_a - Q_b + W_b$

$$(E_2 - E_1)_B = Q_b - W_b - Q_c + W_c$$

$$(E_2 - E_1)_C = Q_c - W_c - Q_a + W_a$$

Entropy:  $(S_2 - S_1)_A = \int \frac{\delta Q_a}{T_a} - \int \frac{\delta Q_b}{T_b} + S_{gen A}$

$$(S_2 - S_1)_B = \int \frac{\delta Q_b}{T_b} - \int \frac{\delta Q_c}{T_c} + S_{gen B}$$

$$(S_2 - S_1)_C = \int \frac{\delta Q_c}{T_c} - \int \frac{\delta Q_a}{T_a} + S_{gen C}$$

Now we add all the energy equations to get the energy change

$$\begin{aligned}(E_2 - E_1)_{total} &= (E_2 - E_1)_A + (E_2 - E_1)_B + (E_2 - E_1)_C \\ &= Q_a - W_a - Q_b + W_b + Q_b - W_b - Q_c + W_c + Q_c - W_c - Q_a + W_a = 0\end{aligned}$$

For entropy

$$\begin{aligned}(S_2 - S_1)_{total} &= (S_2 - S_1)_A + (S_2 - S_1)_B + (S_2 - S_1)_C \\ &= \int \frac{\delta Q_a}{T_a} - \int \frac{\delta Q_b}{T_b} + S_{gen A} + \int \frac{\delta Q_b}{T_b} - \int \frac{\delta Q_c}{T_c} + S_{gen B} \\ &\quad + \int \frac{\delta Q_c}{T_c} - \int \frac{\delta Q_a}{T_a} + S_{gen C} = S_{gen A} + S_{gen B} + S_{gen C} \geq 0\end{aligned}$$

leaving only the positive entropy generation terms

The total entropy increases and is then not conserved. Only if we have reversible processes in all parts of the world will the right-hand side term becomes zero. This concept is referred to as principle of the increase of entropy.

## 8.12 Entropy as a Rate Equation

The rate form is also the basis for the development of the entropy balance equation in the general control volume analysis for an unsteady situation.

Take the incremental change in  $S$  from  $dS = \frac{\delta Q}{T} + \delta S_{gen}$  and divide by  $\delta t$ . We get

$$\frac{dS}{\delta t} = \frac{1}{T} \frac{\delta Q}{\delta t} + \frac{\delta S_{gen}}{\delta t} \quad \text{or} \quad \frac{dS_{cm}}{dt} = \sum \frac{1}{T} \dot{Q} + \dot{S}_{gen}$$

expressing the rate of entropy change as due to the **flux of entropy** into the control mass from heat transfer and an increase due to irreversible processes inside the control mass.