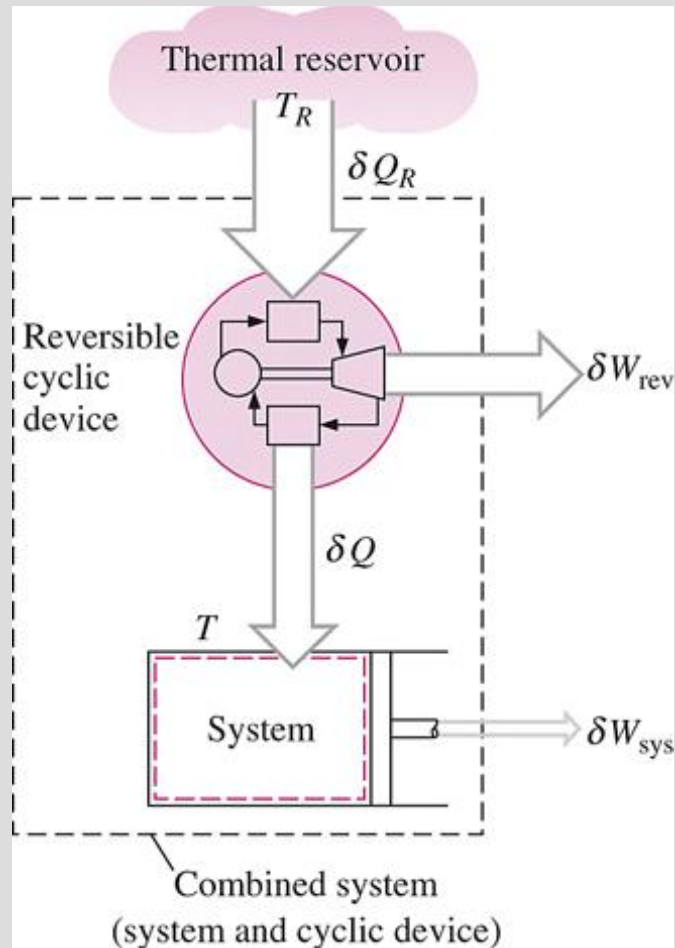


# Objectives

- 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.
- Derive the reversible steady-flow work relations.
- Develop the isentropic efficiencies for various steady-flow devices.
- Introduce and apply the entropy balance to various systems.

# ENTROPY



The system considered in the development of the Clausius inequality.

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

$$\delta W_C = \delta Q_R - dE_C$$

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

$$\delta W_C = T_R \frac{\delta Q}{T} - dE_C$$

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

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

Clausius inequality

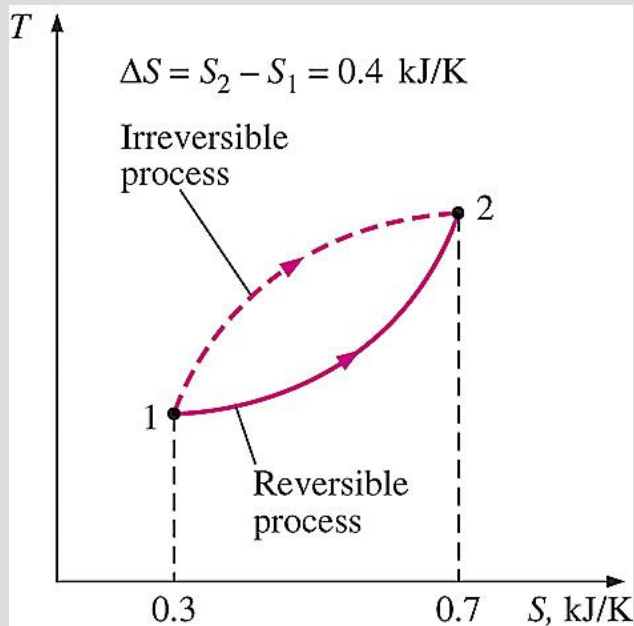
$$\oint \left( \frac{\delta Q}{T} \right)_{int rev} = 0$$

$$dS = \left( \frac{\delta Q}{T} \right)_{int rev} \quad (\text{kJ/K})$$

Formal definition of entropy

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

The equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones.



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

A quantity whose cyclic integral is zero (i.e., a property like volume)

Entropy is an extensive property of a system.

The entropy change between two specified states is the same whether the process is reversible or irreversible.

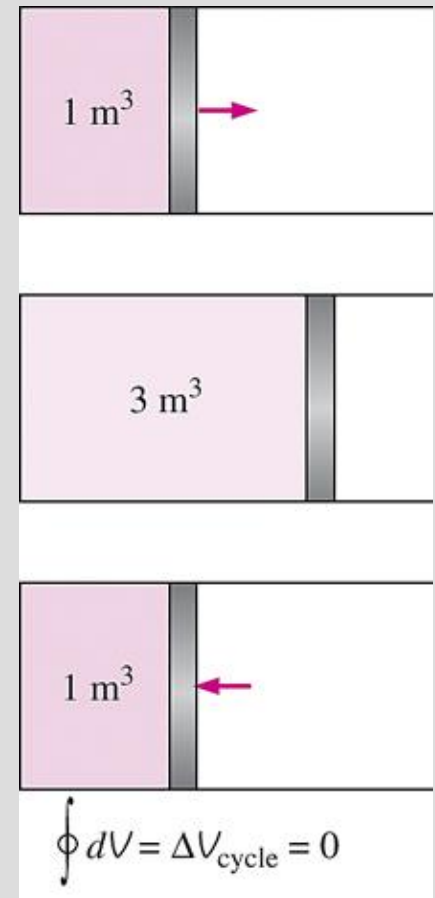
## A Special Case: Internally Reversible Isothermal Heat Transfer Processes

$$\Delta S = \int_1^2 \left( \frac{\delta Q}{T} \right)_{\text{int rev}} = \int_1^2 \left( \frac{\delta Q}{T_0} \right)_{\text{int rev}} = \frac{1}{T_0} \int_1^2 (\delta Q)_{\text{int rev}}$$

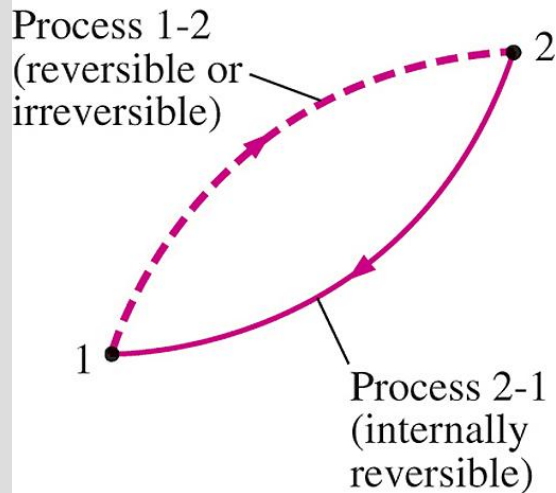
$$\Delta S = \frac{Q}{T_0}$$

This equation is particularly useful for determining the entropy changes of thermal energy reservoirs.

The net change in volume (a property) during a cycle is always zero.



# THE INCREASE OF ENTROPY PRINCIPLE



A cycle composed of a reversible and an irreversible process.

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

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

$$dS \geq \frac{\delta Q}{T}$$

The equality holds for an internally reversible process and the inequality for an irreversible process.

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

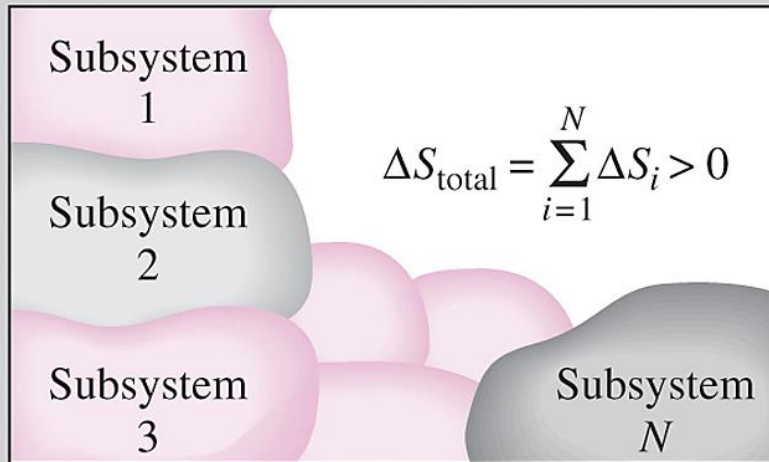
$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

Some entropy is *generated* or *created* during an irreversible process, and this generation is due entirely to the presence of irreversibilities.

The entropy generation  $S_{\text{gen}}$  is always a *positive* quantity or zero.

Can the entropy of a system during a process decrease?

(Isolated)



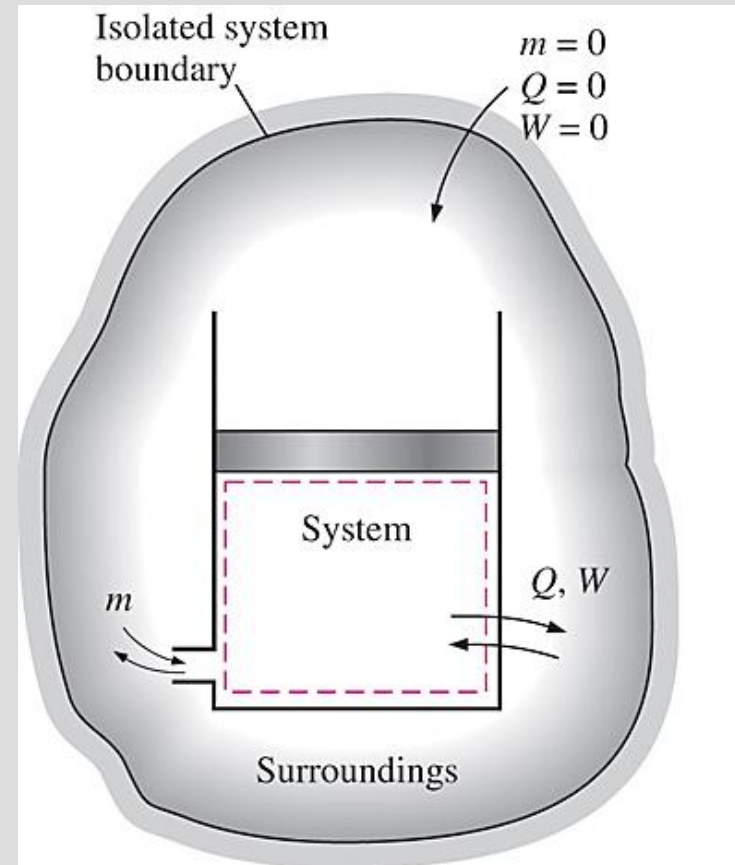
The entropy change of an isolated system is the sum of the entropy changes of its components, and is never less than zero.

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

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

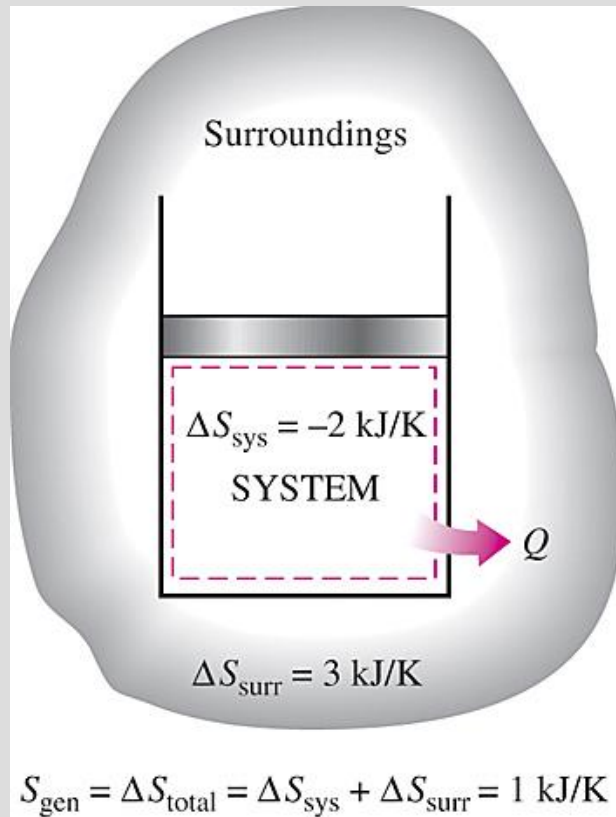
$$S_{\text{gen}} \begin{cases} > 0 & \text{Irreversible process} \\ = 0 & \text{Reversible process} \\ < 0 & \text{Impossible process} \end{cases}$$

The increase of entropy principle



A system and its surroundings form an isolated system.

# Some Remarks about Entropy

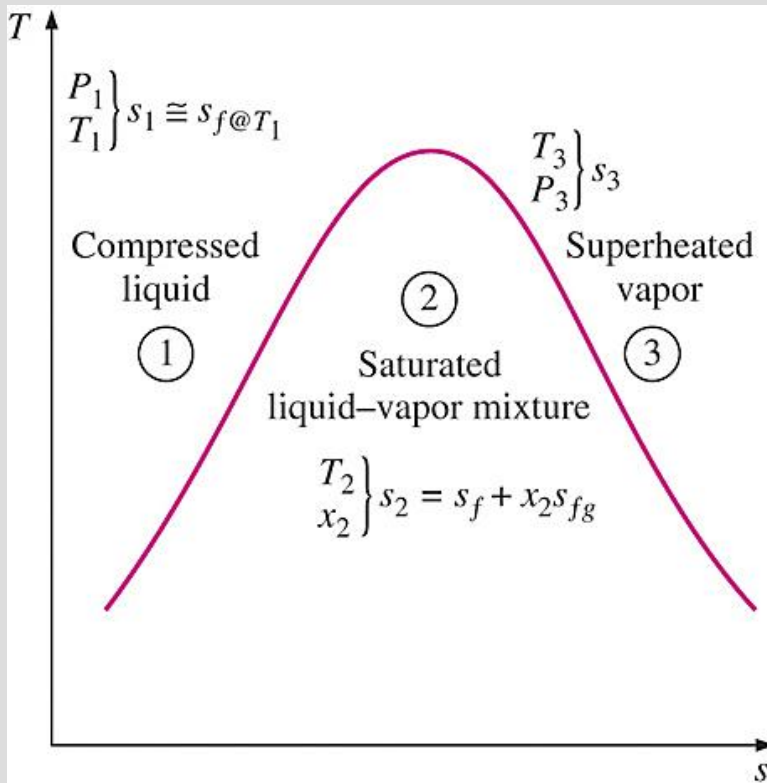


The entropy change of a system can be negative, but the entropy generation cannot.

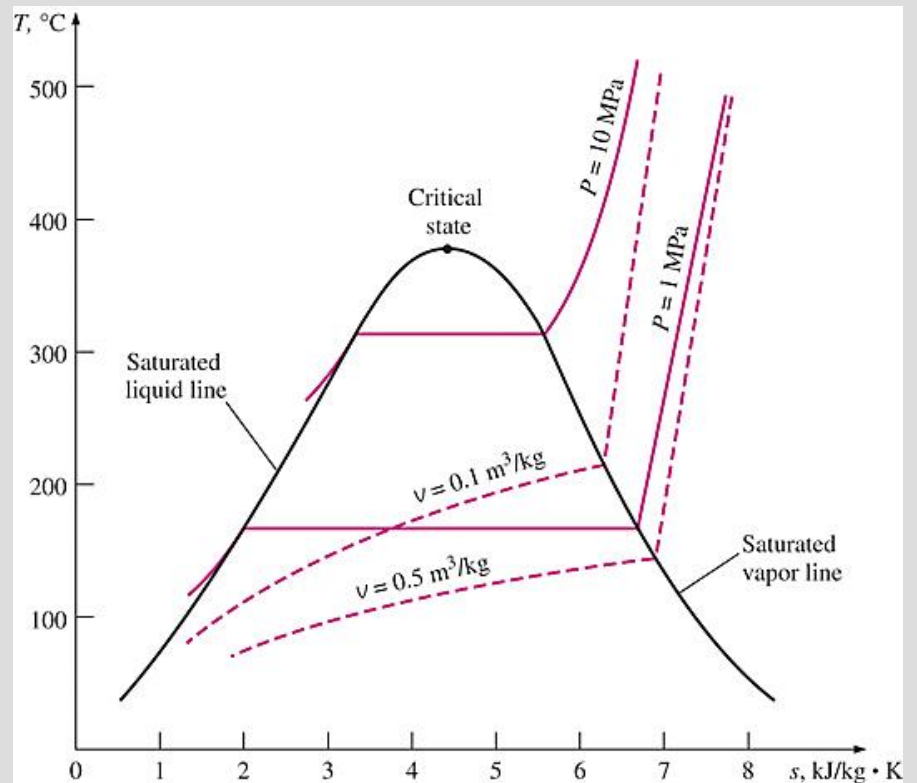
1. Processes can occur in a *certain* direction only, not in *any* direction. A process must proceed in the direction that complies with the increase of entropy principle, that is,  $S_{\text{gen}} \geq 0$ . A process that violates this principle is impossible.
2. Entropy is a *nonconserved property*, 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.
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 during that process. It is also used to establish criteria for the performance of engineering devices.

# ENTROPY CHANGE OF PURE SUBSTANCES

Entropy is a property, and thus the value of entropy of a system is fixed once the state of the system is fixed.



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



Schematic of the  $T-s$  diagram for water.

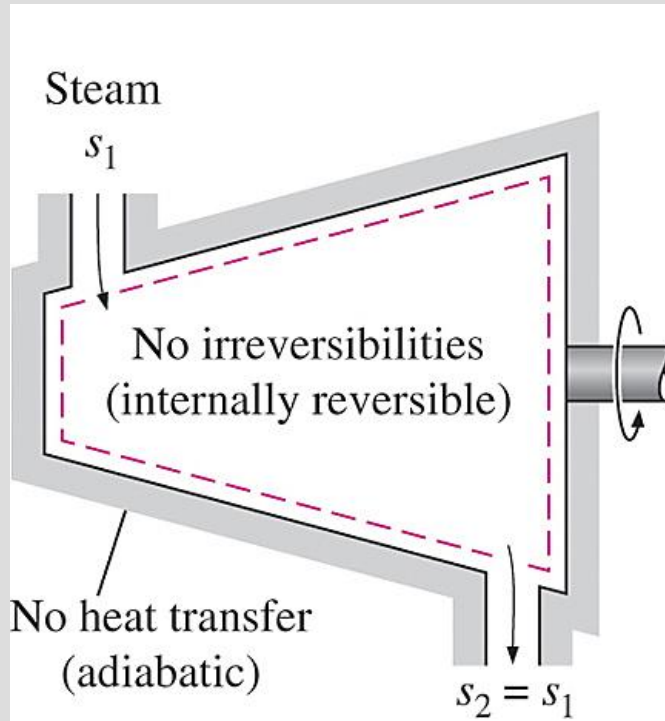
Entropy change

$$\Delta S = m\Delta s = m(s_2 - s_1) \quad (\text{kJ/K})$$



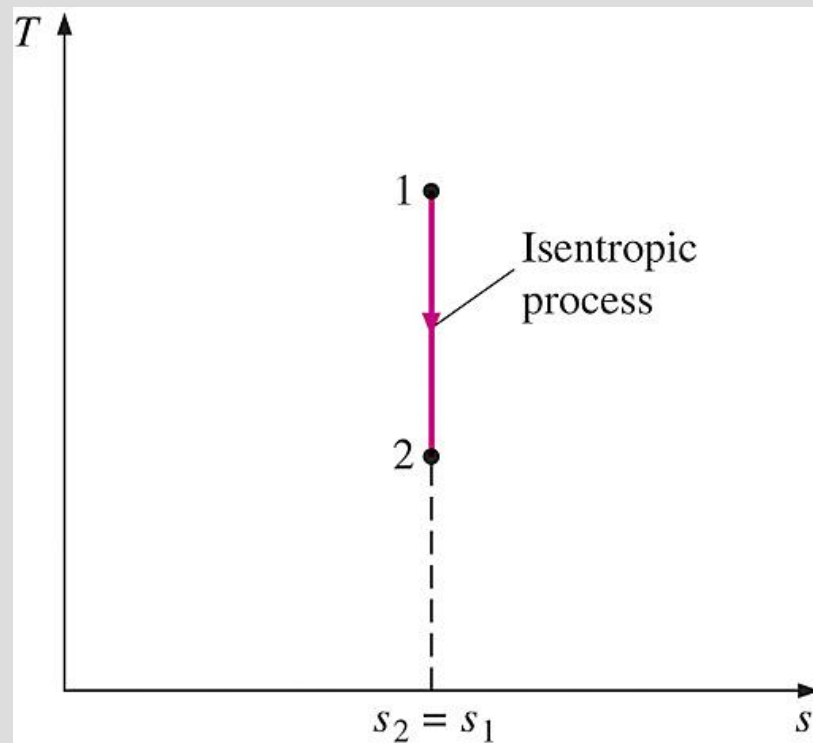
# ISENTROPIC PROCESSES

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



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

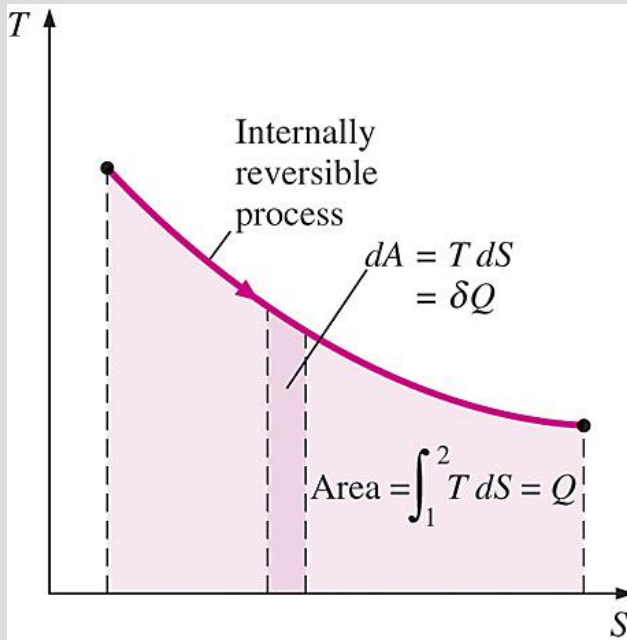
$$\Delta s = 0 \quad \text{or} \quad s_2 = s_1 \quad (\text{kJ/kg} \cdot \text{K})$$



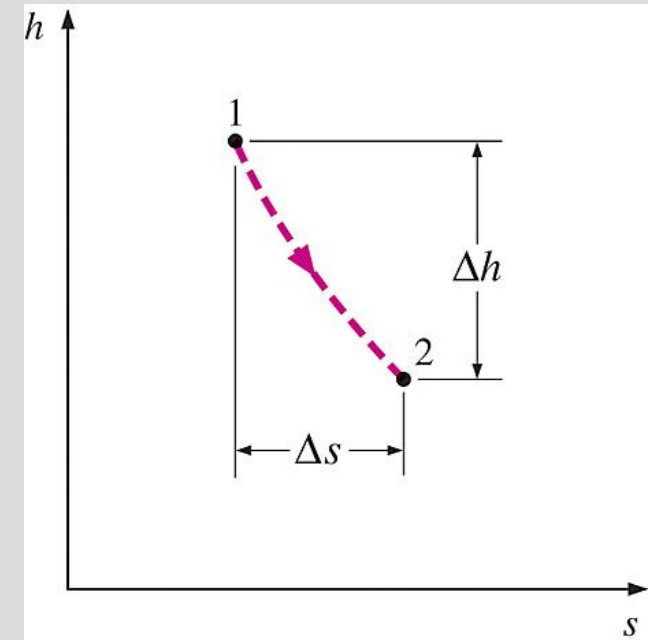
The isentropic process appears as a *vertical* line segment on a  $T$ - $s$  diagram.



# PROPERTY DIAGRAMS INVOLVING ENTROPY



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



For adiabatic steady-flow devices, the vertical distance  $\Delta h$  on an  $h$ - $s$  diagram is a measure of work, and the horizontal distance  $\Delta s$  is a measure of irreversibilities.

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

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

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

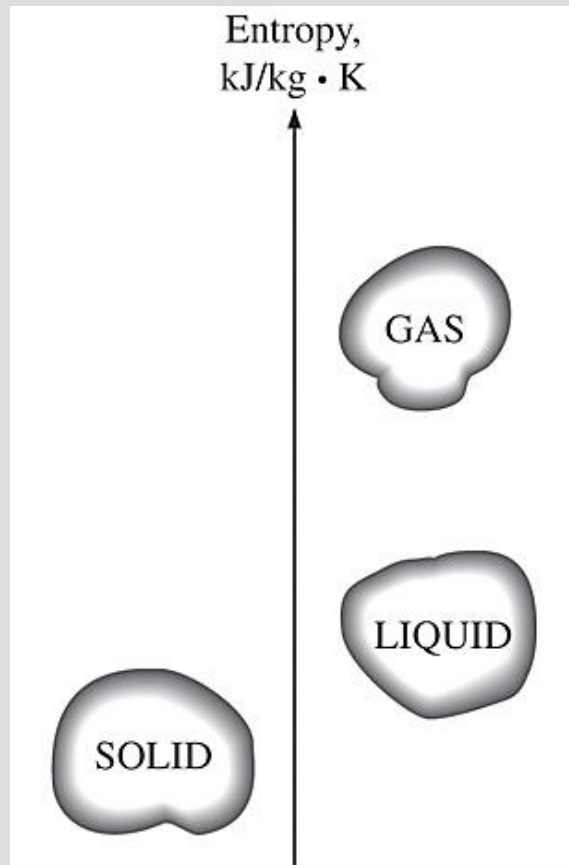
$$q_{\text{int rev}} = \int_1^2 T ds$$

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

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

**Mollier diagram:** The  $h$ - $s$  diagram

# WHAT IS ENTROPY?

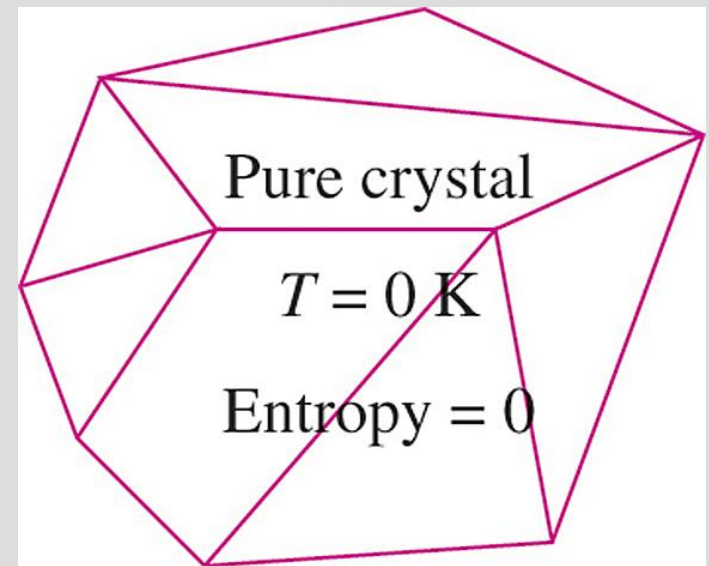


The level of molecular disorder (entropy) of a substance increases as it melts or evaporates.

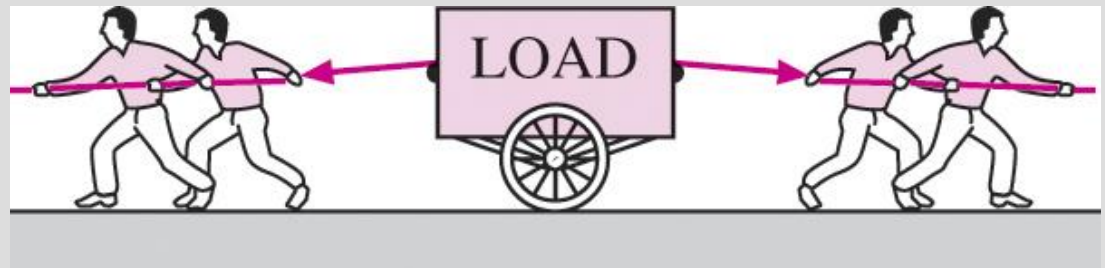
Boltzmann relation

$$S = k \ln p$$

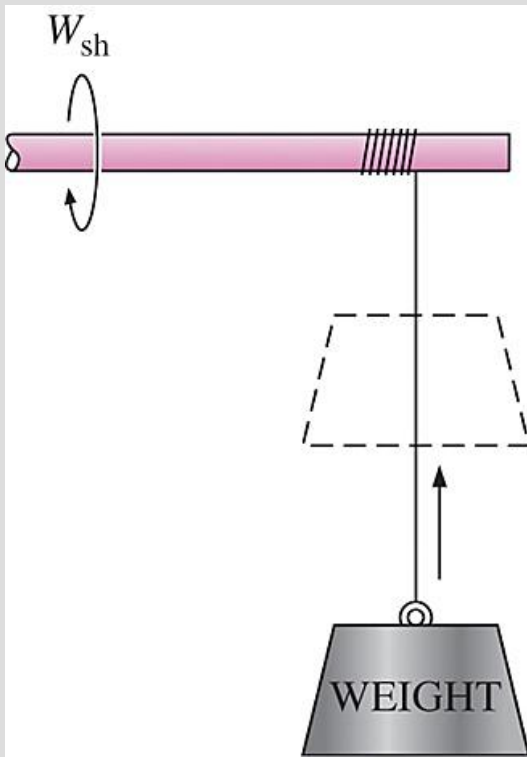
$$k = 1.3806 \times 10^{-23} \text{ J/K}$$



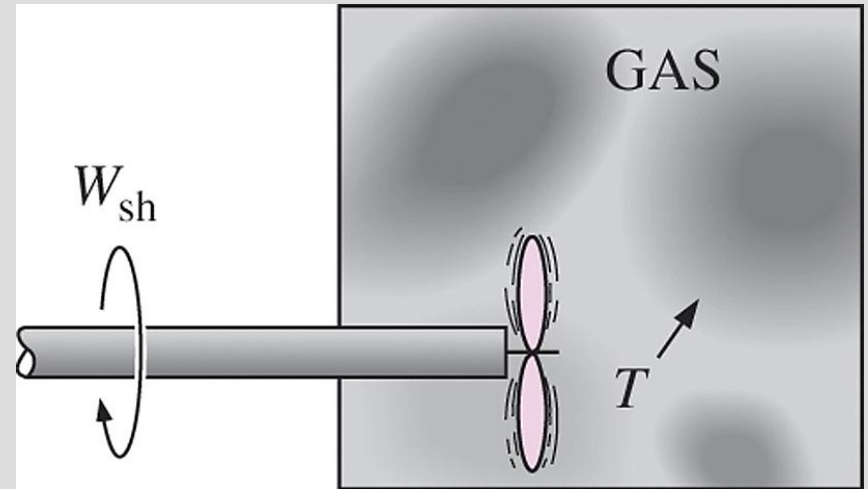
A pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero (**the third law of thermodynamics**).



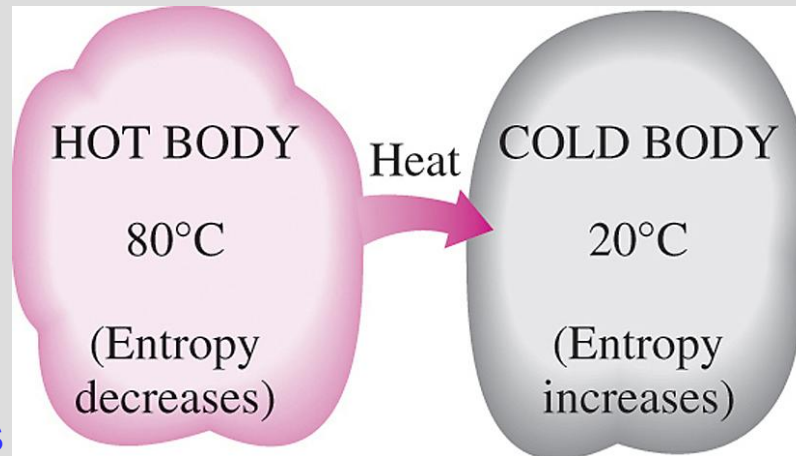
Disorganized energy does not create much useful effect, no matter how large it is.



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.

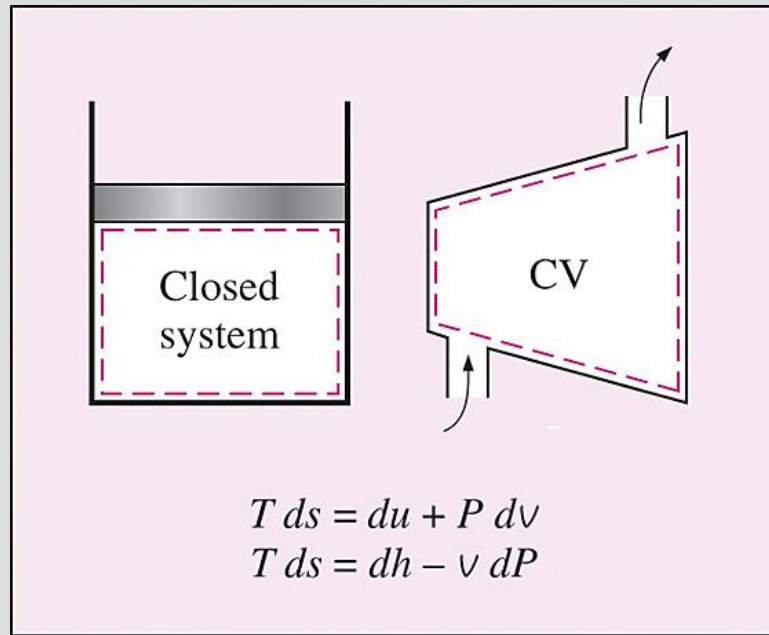


The paddle-wheel work done on a gas increases the level of disorder (entropy) of the gas, and thus energy is degraded during this process.



During a heat transfer process, the net entropy increases. (The increase in the entropy of the cold body more than offsets the decrease in the entropy of the hot body.)

# THE $T ds$ RELATIONS



The  $T ds$  relations are valid for both reversible and irreversible processes and for both closed and open systems.

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

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

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

$$T dS = dU + P dV \quad (\text{kJ})$$

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

*the first  $T ds$ , or Gibbs equation*

$$h = u + Pv$$

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

*the second  $T ds$  equation*

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

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

Differential changes in entropy in terms of other properties

# ENTROPY CHANGE OF LIQUIDS AND SOLIDS

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

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 of an incompressible substance

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

# THE ENTROPY CHANGE OF IDEAL GASES

From the first  $T ds$  relation

$$ds = \frac{du}{T} + \frac{P dv}{T} \quad \begin{matrix} du = c_v dT \\ P = RT/v \end{matrix}$$

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$

$$s_2 - s_1 = \int_1^2 c_v(T) \frac{dT}{T} + R \ln \frac{v_2}{v_1}$$

From the second  $T ds$  relation

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

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

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

$$\begin{aligned} P v &= RT \\ du &= C_v dT \\ dh &= C_p dT \end{aligned}$$

A broadcast  
from channel IG.

# Constant Specific Heats (Approximate Analysis)

$$s_2 - s_1 = \int_1^2 c_v(T) \frac{dT}{T} + R \ln \frac{v_2}{v_1}$$



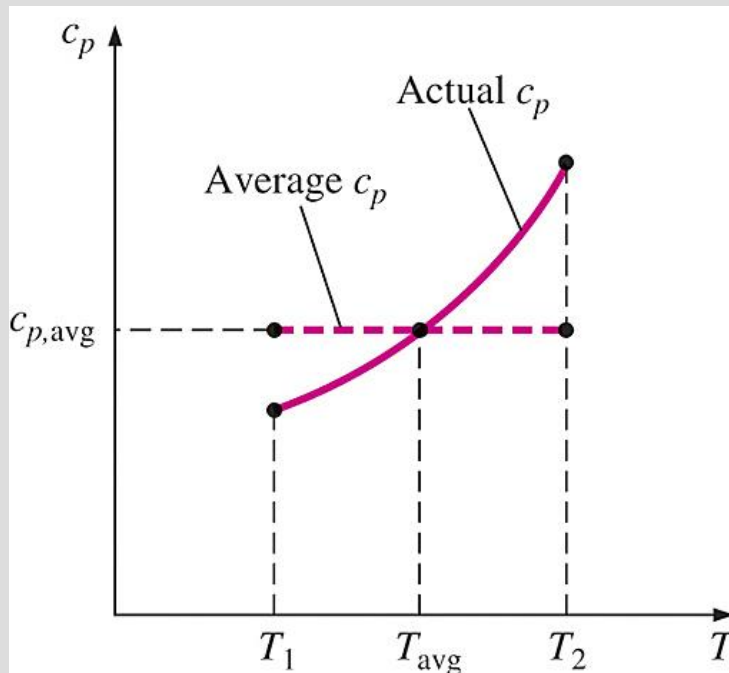
$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

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



$$s_2 - s_1 = c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

(kJ/kg · K)



Entropy change of an ideal gas on a unit-mole basis

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

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

Under the constant-specific-heat assumption, the specific heat is assumed to be constant at some average value.



# Variable Specific Heats (Exact Analysis)

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

$$s^\circ = \int_0^T c_p(T) \frac{dT}{T}$$

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

On a unit-mass basis

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

On a unit-mole basis

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

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

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

# Isentropic Processes of Ideal Gases

## Constant Specific Heats (Approximate Analysis)

$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

Setting this eq. equal to zero, we get

$$\ln \frac{T_2}{T_1} = -\frac{R}{c_v} \ln \frac{v_2}{v_1}$$

$$\ln \frac{T_2}{T_1} = \ln \left( \frac{v_1}{v_2} \right)^{R/c_v}$$

$$R = c_p - c_v, k = c_p/c_v$$

and thus  $R/c_v = k - 1$

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

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

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

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.

$$TV^{k-1} = \text{constant}$$

$$TP^{(1-k)/k} = \text{constant}$$

$$PV^k = \text{constant}$$

# Isentropic Processes of Ideal Gases

## Variable Specific Heats (Exact Analysis)

$$0 = s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1} \longrightarrow s_2^\circ = s_1^\circ + R \ln \frac{P_2}{P_1}$$

## Relative Pressure and Relative Specific Volume

$$\frac{P_2}{P_1} = \exp \frac{s_2^\circ - s_1^\circ}{R}$$

$\exp(s^\circ/R)$  is the relative pressure  $P_r$

$$\frac{P_2}{P_1} = \frac{\exp(s_2^\circ/R)}{\exp(s_1^\circ/R)}$$

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

$$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2} \longrightarrow \frac{v_2}{v_1} = \frac{T_2}{T_1} \frac{P_1}{P_2} = \frac{T_2}{T_1} \frac{P_{r1}}{P_{r2}} = \frac{T_2/P_{r2}}{T_1/P_{r1}}$$

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

$T/P_r$  is the relative specific volume  $v_r$

The use of  $P_r$  data for calculating the final temperature during an isentropic process.

The use of  $v_r$  data for calculating the final temperature during an isentropic process

Process: isentropic

Given:  $P_1$ ,  $T_1$ , and  $P_2$

Find:  $T_2$

$T$	$P_r$
.	.
.	.
.	.
$T_2$	← read $P_{r2} = \frac{P_2}{P_1} P_{r1}$
.	.
.	.
$T_1$	→ read $P_{r1}$
.	.
.	.
.	.

Process: isentropic

Given:  $v_1$ ,  $T_1$ , and  $v_2$

Find:  $T_2$

$T$	$v_r$
.	.
.	.
.	.
$T_2$	← read $v_{r2} = \frac{v_2}{v_1} v_{r1}$
.	.
.	.
$T_1$	→ read $v_{r1}$
.	.
.	.
.	.

# ENTROPY BALANCE

$$\left( \begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{entering} \end{array} \right) - \left( \begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{leaving} \end{array} \right) + \left( \begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{generated} \end{array} \right) = \left( \begin{array}{c} \text{Change in the} \\ \text{total entropy} \\ \text{of the system} \end{array} \right)$$

$$S_{\text{in}} - S_{\text{out}} + S_{\text{gen}} = \Delta S_{\text{system}}$$

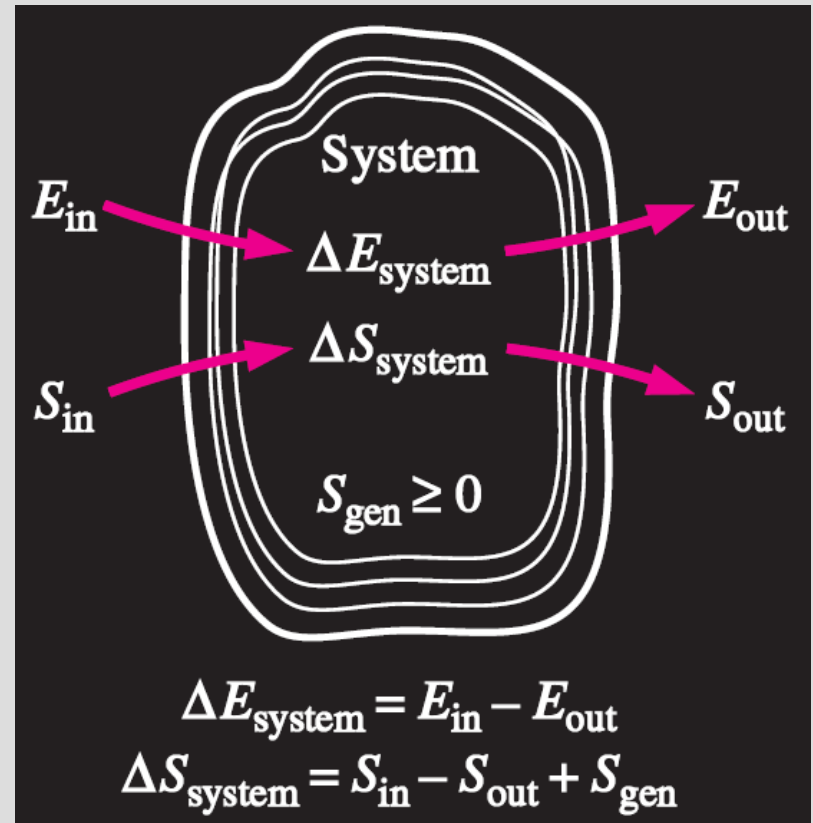
## Entropy Change of a System, $\Delta S_{\text{system}}$

$$\Delta S_{\text{system}} = S_{\text{final}} - S_{\text{initial}} = S_2 - S_1$$

When the properties of the system are not uniform

$$S_{\text{system}} = \int s \, \delta m = \int_V s \rho \, dV$$

Energy and entropy balances for a system.





# Mechanisms of Entropy Transfer, $S_{in}$ and $S_{out}$

## 2 Mass Flow

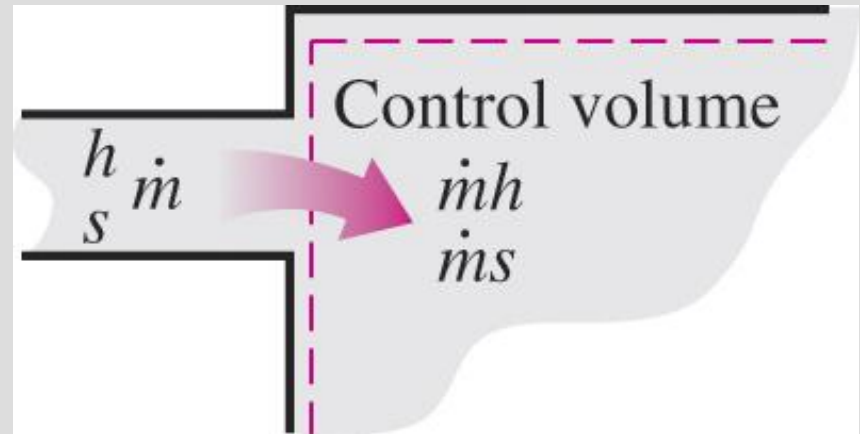
Entropy transfer by mass:

$$S_{\text{mass}} = ms$$

When the properties of the mass change during the process

$$\dot{S}_{\text{mass}} = \int_{A_c} s \rho V_n dA_c$$

$$S_{\text{mass}} = \int s \delta m = \int_{\Delta t} \dot{S}_{\text{mass}} dt$$



Mass contains entropy as well as energy, and thus mass flow into or out of system is always accompanied by energy and entropy transfer.

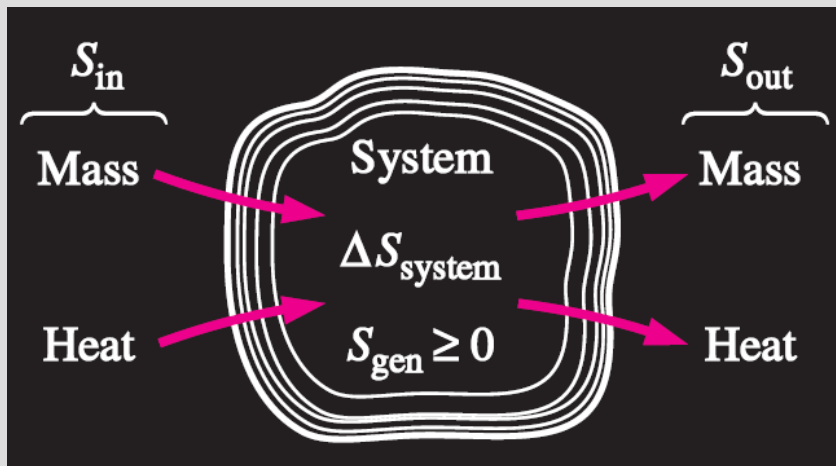
# Entropy Generation, $S_{\text{gen}}$

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

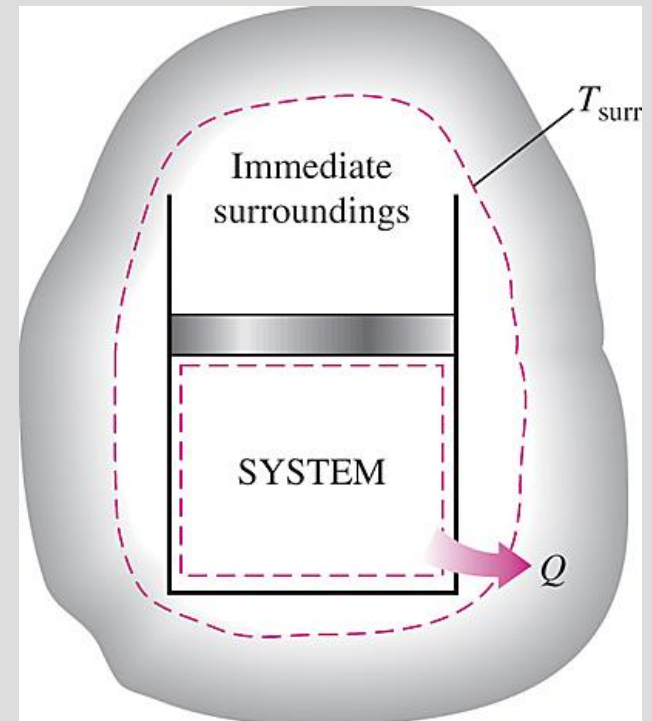
$$\underbrace{\dot{S}_{\text{in}} - \dot{S}_{\text{out}}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{\text{gen}}}_{\text{Rate of entropy generation}} = \underbrace{dS_{\text{system}}/dt}_{\text{Rate of change in entropy}} \quad (\text{kW/K})$$

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

Entropy generation outside system boundaries can be accounted for by writing an entropy balance on an extended system that includes the system and its immediate surroundings.



Mechanisms of entropy transfer for a general system.





# Closed Systems

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

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.

$$\text{Adiabatic closed system:} \quad S_{\text{gen}} = \Delta S_{\text{adiabatic system}}$$

$$\text{System + Surroundings:} \quad S_{\text{gen}} = \sum \Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\Delta S_{\text{system}} = m(s_2 - s_1) \quad \Delta S_{\text{surr}} = Q_{\text{surr}}/T_{\text{surr}}$$

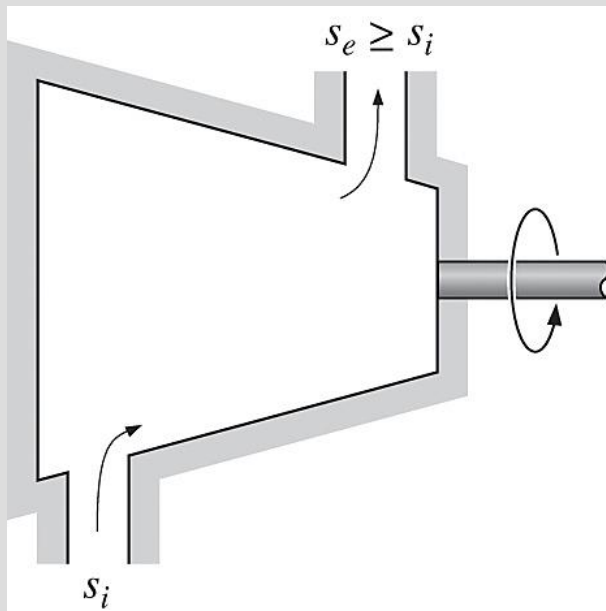
$$\sum \frac{Q_k}{T_k} + \sum m_i s_i - \sum m_e s_e + S_{\text{gen}} = (S_2 - S_1)_{\text{CV}} \quad (\text{kJ/K})$$

$$\sum \frac{\dot{Q}_k}{T_k} + \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \dot{S}_{\text{gen}} = dS_{\text{CV}}/dt \quad (\text{kW/K})$$

*Steady-flow:* 
$$\dot{S}_{\text{gen}} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i - \sum \frac{\dot{Q}_k}{T_k}$$

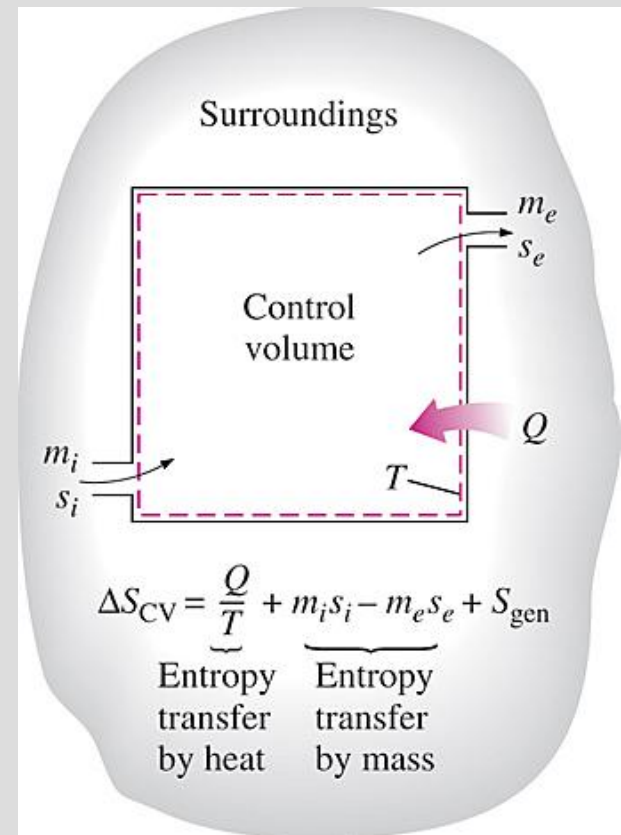
*Steady-flow, single-stream:* 
$$\dot{S}_{\text{gen}} = \dot{m}(s_e - s_i) - \sum \frac{\dot{Q}_k}{T_k}$$

*Steady-flow, single-stream, adiabatic:* 
$$\dot{S}_{\text{gen}} = \dot{m}(s_e - s_i)$$



The entropy of a substance always increases (or remains constant in the case of a reversible process) as it flows through a single-stream, adiabatic, steady-flow device.

## Control Volumes



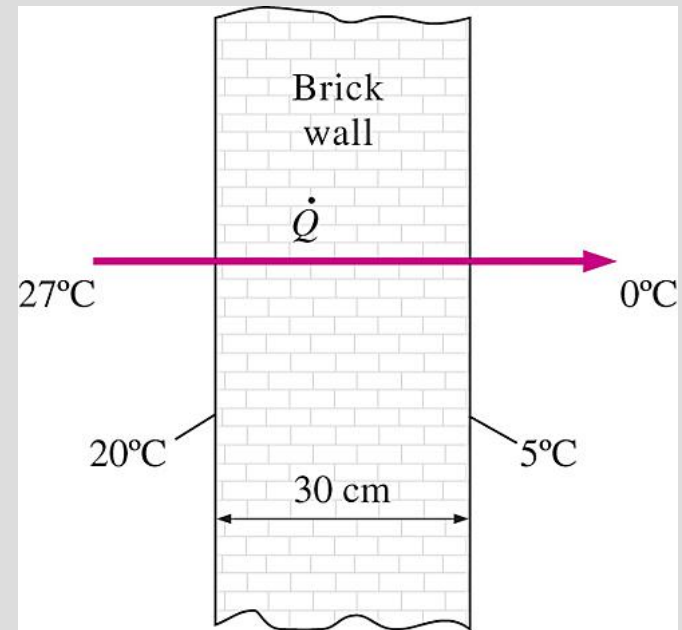
The entropy of a control volume changes as a result of mass flow as well as heat transfer.

# EXAMPLES

## Entropy balance for heat transfer through a wall

$$\underbrace{\dot{S}_{\text{in}} - \dot{S}_{\text{out}}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{\text{gen}}}_{\text{Rate of entropy generation}} = \underbrace{\frac{dS_{\text{system}}}{dt}}_{\text{Rate of change in entropy}} \xrightarrow{0 \text{ (steady)}}$$

$$\left(\frac{\dot{Q}}{T}\right)_{\text{in}} - \left(\frac{\dot{Q}}{T}\right)_{\text{out}} + \dot{S}_{\text{gen}} = 0$$

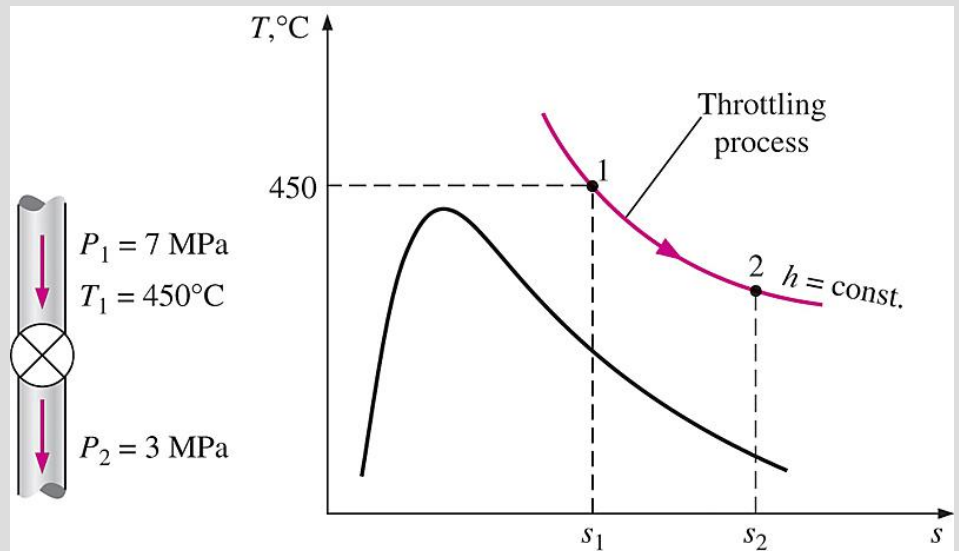


## Entropy balance for a throttling process

$$\underbrace{\dot{S}_{\text{in}} - \dot{S}_{\text{out}}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{\text{gen}}}_{\text{Rate of entropy generation}} = \underbrace{\frac{dS_{\text{system}}}{dt}}_{\text{Rate of change in entropy}} \xrightarrow{0 \text{ (steady)}}$$

$$\dot{m}s_1 - \dot{m}s_2 + \dot{S}_{\text{gen}} = 0$$

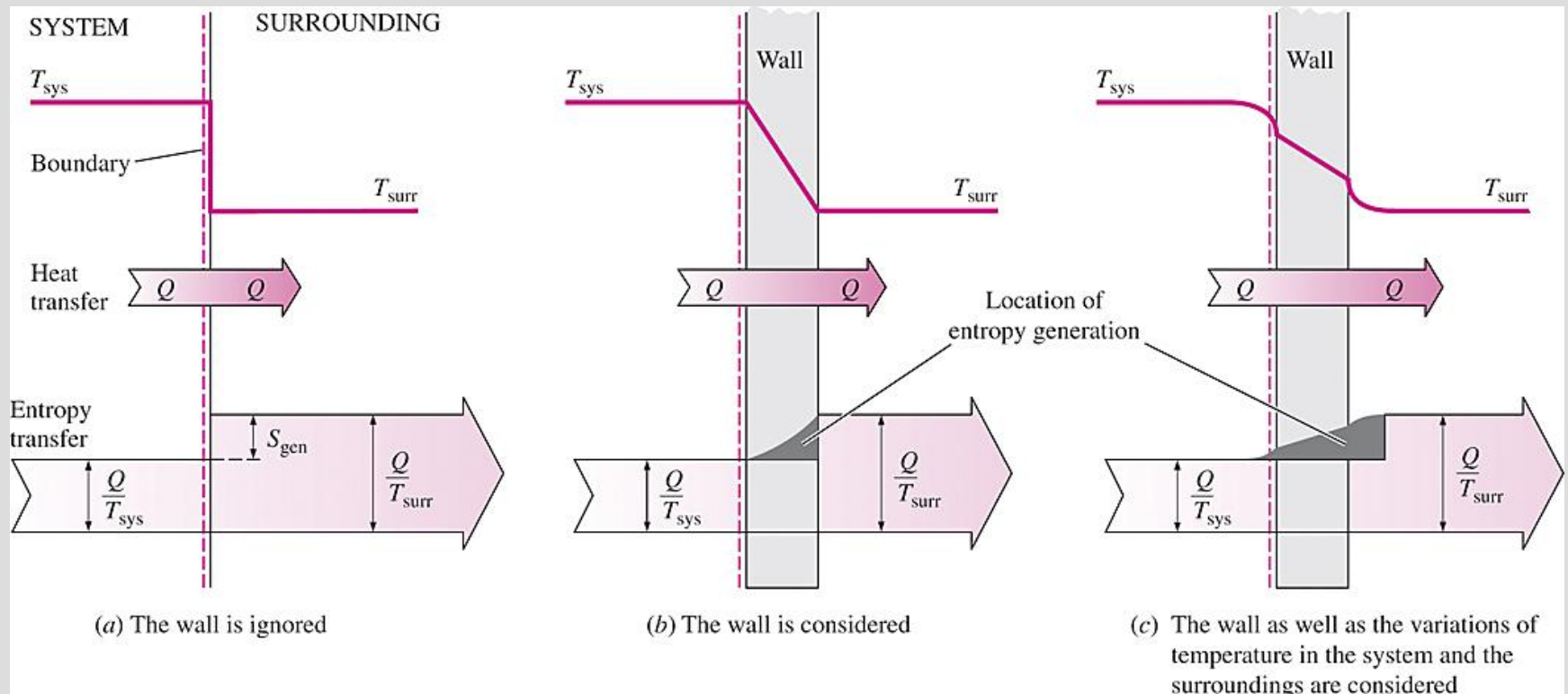
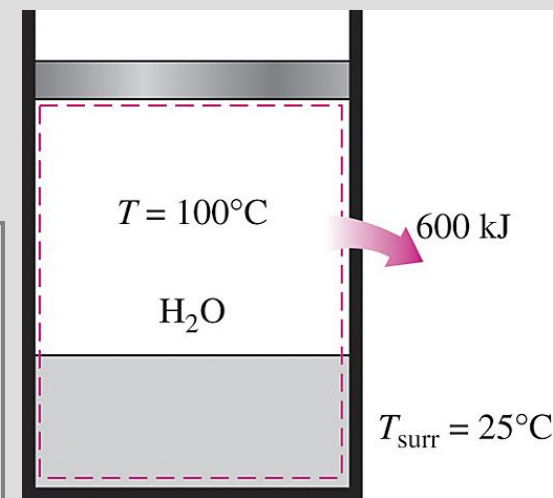
$$\dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1)$$



# Entropy generation associated with a heat transfer process

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{\text{gen}}}_{\text{Entropy generation}} = \underbrace{\Delta S_{\text{system}}}_{\text{Change in entropy}}$$

$$-\frac{Q_{\text{out}}}{T_b} + S_{\text{gen}} = \Delta S_{\text{system}}$$



Graphical representation of entropy generation during a heat transfer process through a finite temperature difference.