

# CHAPTER 7

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## ENTROPY

# ENTROPY – The Clausius Inequality

- The Clausius inequality states that for for all cycles, reversible or irreversible, engines or refrigerators:

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

- For internally-reversible cycles:

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

- For Irreversible cycles:

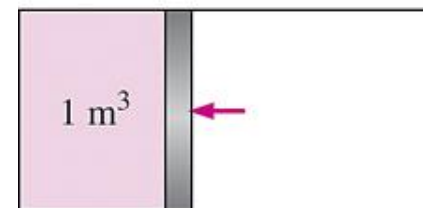
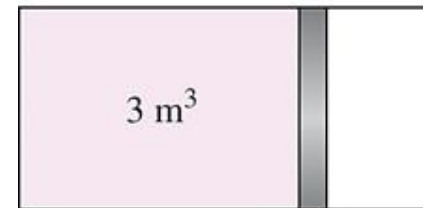
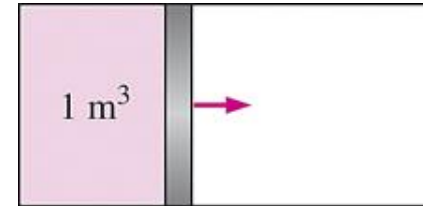
$$\oint \left( \frac{\delta Q}{T} \right)_{\text{irr}} < 0$$

# Implications of Clausius Inequality

- ❑ The cyclic integral of a quantity is zero only if that quantity is a property
- ❑ Example: Cyclic integral of volume

$$\oint dV = \Delta V_{cycle} = 0$$

- ❑ Therefore,  $(\delta Q/T)_{int.rev}$  must be an exact differential for a property



$$\oint dV = \Delta V_{cycle} = 0$$

# Definition of Entropy

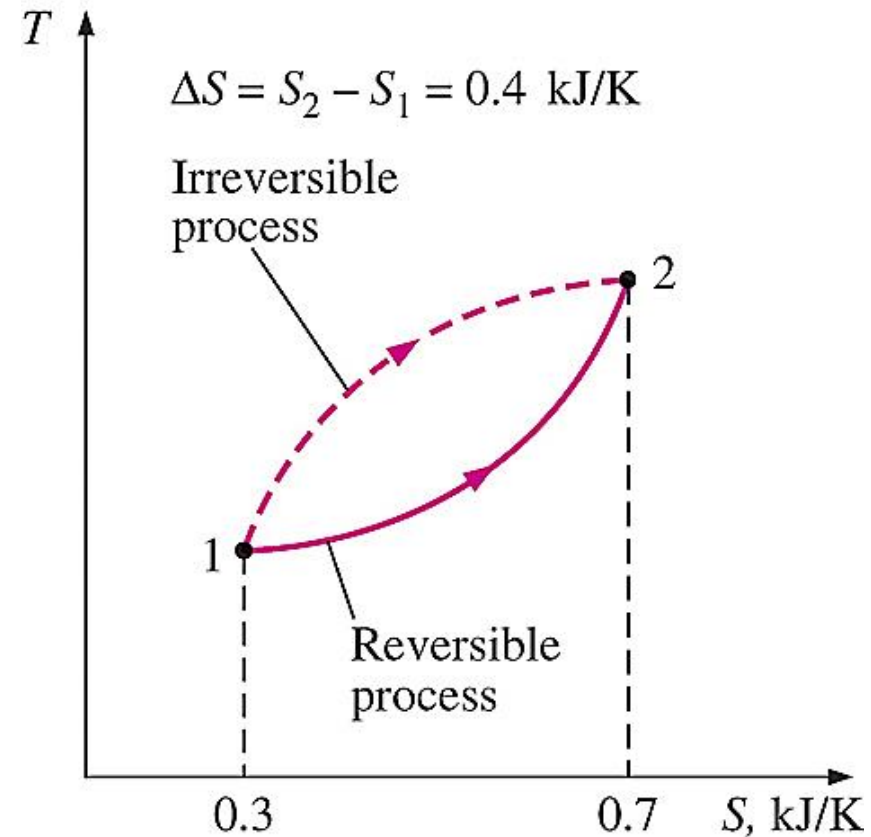
□ The formal definition of the property with an exact differential  $(\delta Q/T)_{\text{int.rev}}$  is:

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

- Entropy ("S") is an Extensive property (kJ/K)
- $s \equiv$  Specific entropy = Entropy per unit mass (kJ/kg-K) is an intensive property

# Entropy Change

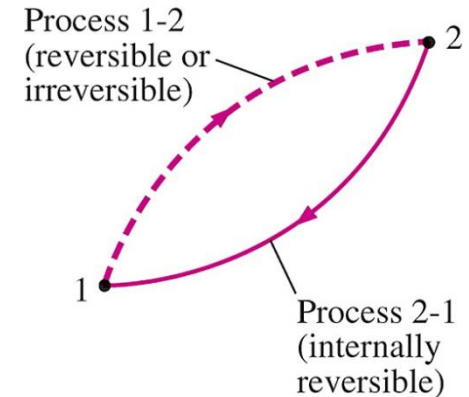
- ❑ The equilibrium state of a simple system is completely specified by any two independent intensive properties (e.g. Temp. & Entropy)
- ❑ Can show processes on a T-s diagram
- ❑ Entropy change between two specified equilibrium states is the same whether the process is reversible or irreversible.



# Entropy Generation

❑ Consider a cycle consisting of two processes

- Process 1-2 can be reversible or irreversible
- Process 2-1 is internally reversible



❑ According to Clausius Inequality

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

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

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

# Entropy Generation

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

- ❑ Some entropy is “generated” or “created” during an irreversible process due to the presence of irreversibilities
- ❑ The entropy generated  $S_{\text{gen}}$  is always  $\geq$  zero
- ❑ For an internally-reversible process,  $S_{\text{gen}} = 0$

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

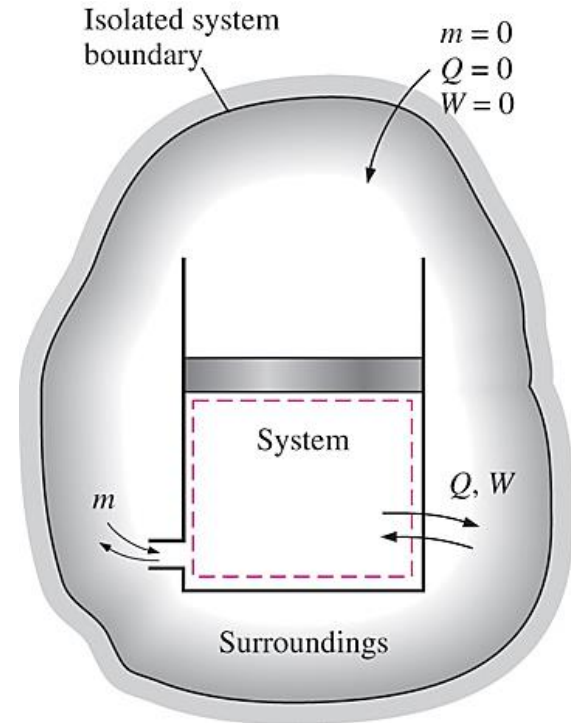
# The Increase in Entropy Principle

- The system and its surroundings form an “Isolated system,” therefore:

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}}$$

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

- Above relation is known as “the increase in entropy principle”

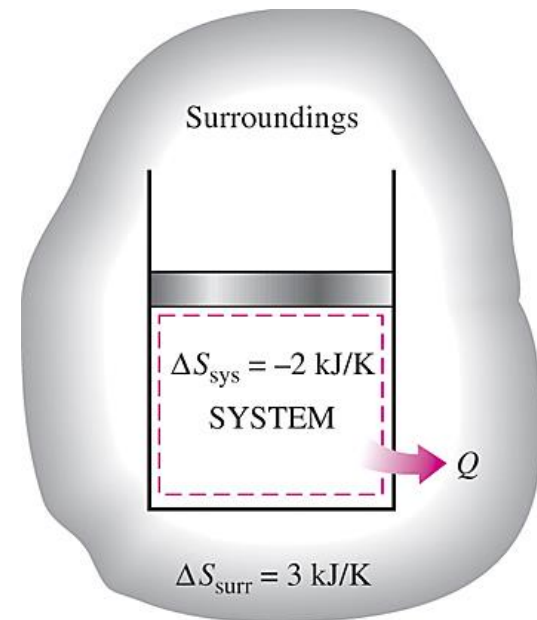




# The Increase in Entropy Principle

- ❑ All real processes must proceed in the direction that complies with the increase in entropy principle. A process that violates this principle is impossible.
- ❑ Entropy is a **non-conserved** property (i.e. no such thing as the conservation of entropy principle)

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



$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 1 \text{ kJ/K}$$

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

# The Increase in Entropy Principle



- ❑ The performance of engineering systems is degraded by the presence of irreversibilities.
- ❑ Entropy generation is a measure of the magnitude of the irreversibilities during the process.
- ❑ Entropy generation is used to establish criteria for the performance of engineering systems.

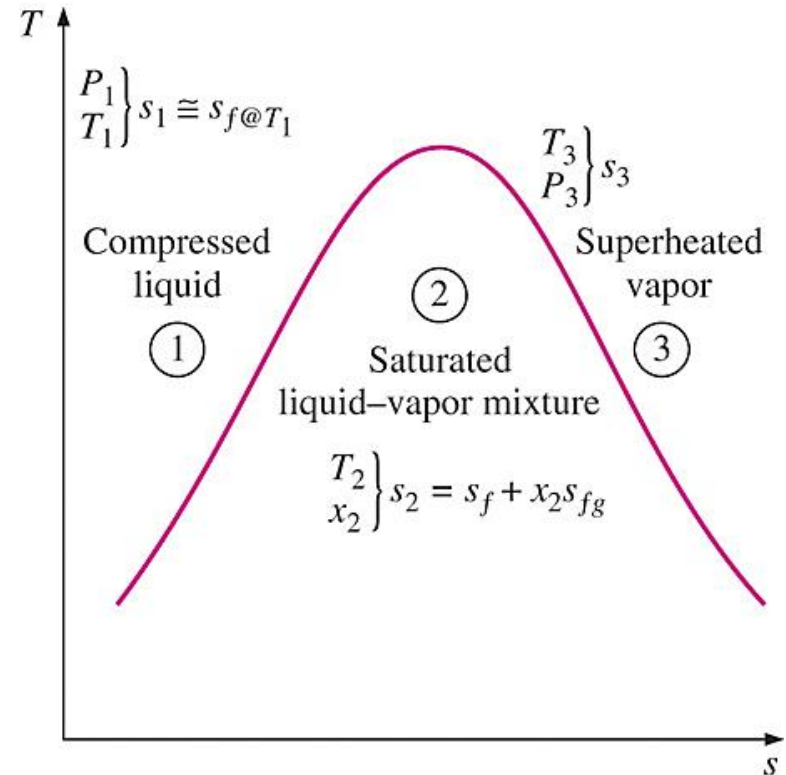
# LECTURE # 18



## Chapter 7 (Session #2): Entropy

# Entropy of a Pure Substance

- ❑ Entropy is a property; value of entropy of a system is fixed once the state of the system is fixed.
- ❑ The specific entropy of a pure substance (relative to a specified datum) is determined from the tables (like other properties).
- ❑ The unit of entropy is kJ/K.
- ❑ The unit of specific entropy is kJ/kg.K.



# PROPERTY TABLES



## ● Saturated Liquid and Saturated Vapor

- Known  $T_{\text{sat}}$  [Tables A-4 (water); A-11 (R134a)]
- Known  $P_{\text{sat}}$  [Tables A-5 (water); A-12 (R134a)]
- How to use for saturated Liquid-Vapor Mixture?

## ● Superheated Vapor

- Tables A-6 (water); A-13 (R134a)

## ● Compressed (subcooled) Liquid

- Table A-7 (water)

# PROPERTY TABLES --

## Saturated Liquid & Saturated Vapor

- Table A-4 (Water) -- **Examples:**

- **For  $T_{\text{sat}} = 50^{\circ}\text{C}$ :**

  - $s_f = 0.7038 \text{ kJ/kg.K}$ ;  $s_g = 8.0748 \text{ kJ/kg.K}$ ;  $s_{fg} = 7.3710 \text{ kJ/kg.K}$

- **For  $T_{\text{sat}} = 100^{\circ}\text{C}$ :**

  - $s_f = 1.3072 \text{ kJ/kg.K}$ ;  $s_g = 7.3542 \text{ kJ/kg.K}$ ;  $s_{fg} = 6.0470 \text{ kJ/kg.K}$

- **or  $T_{\text{sat}} = 373.95^{\circ}\text{C}$ :**

  - $s_f = 4.4070 \text{ kJ/kg.K}$ ;  $s_g = 4.4070 \text{ kJ/kg.K}$ ;  $s_{fg} = 0 \text{ kJ/kg.K}$

# PROPERTY TABLES --

## Saturated Liquid & Saturated Vapor



- Table A-5 (Water) -- **Examples:**

- **For  $P_{\text{sat}} = 75 \text{ kPa}$ :**

  - $s_f = 1.2132 \text{ kJ/kg.K}$ ;  $s_g = 7.4558 \text{ kJ/kg.K}$ ;  $s_{fg} = 6.2426 \text{ kJ/kg.K}$

- **For  $P_{\text{sat}} = 2.00 \text{ MPa}$ :**

  - $s_f = 2.4467 \text{ kJ/kg.K}$ ;  $s_g = 6.3390 \text{ kJ/kg.K}$ ;  $s_{fg} = 3.8923 \text{ kJ/kg.K}$

- **For  $P_{\text{sat}} = 22.064 \text{ MPa}$ :**

  - $s_f = 4.4070 \text{ kJ/kg.K}$ ;  $s_g = 4.4070 \text{ kJ/kg.K}$ ;  $s_{fg} = 0 \text{ kJ/kg.K}$

# PROPERTY TABLES --

## Superheated vapor



- Example: Water (superheated vapor) at 200 °C and 0.1 MPa

- **Table A-6:**

$$v = 2.1724 \text{ m}^3/\text{kg}$$

$$u = 2658.2 \text{ kJ/kg}$$

$$h = 2875.5 \text{ kJ/kg}$$

$$s = 7.8356 \text{ kJ/kg K}$$



# PROPERTY TABLES --

## Compressed Liquid



- Example: Compressed Liquid Water at 200 °C and 10 MPa

- **Table A-7:**

$$v = 0.0011482 \text{ m}^3/\text{kg}$$

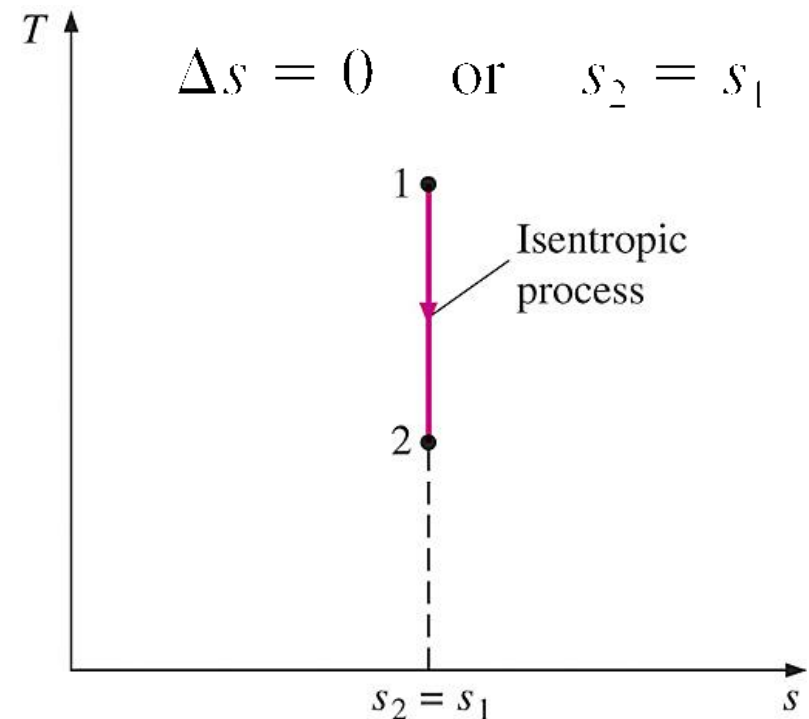
$$u = 844.32 \text{ kJ/kg}$$

$$h = 855.80 \text{ kJ/kg}$$

$$s = 2.3174 \text{ kJ/kg K}$$

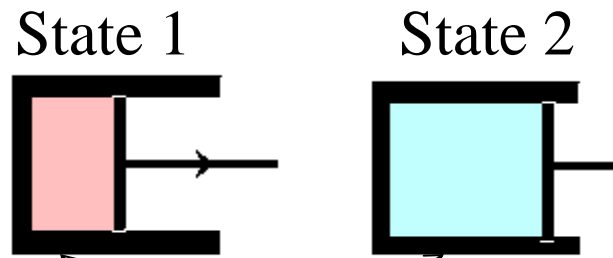
# Isentropic Processes

- ❑ A process during which the entropy remains constant is called an ***isentropic process***.
- ❑ An internally-reversible (i.e. frictionless) **adiabatic process** is automatically isentropic



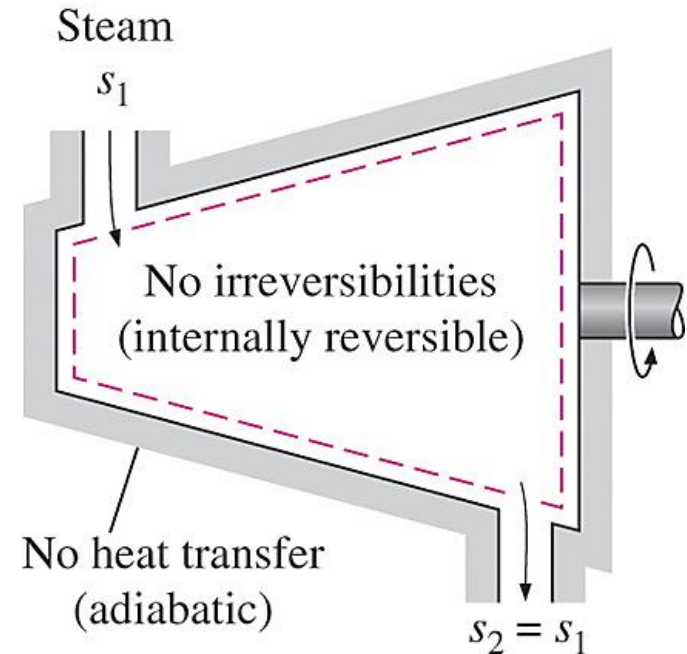
# Isentropic Processes

Closed System Undergoing Isentropic Expansion



No Heat Transfer and No Friction

Isentropic Expansion in Steady-Flow Open System (Turbine)

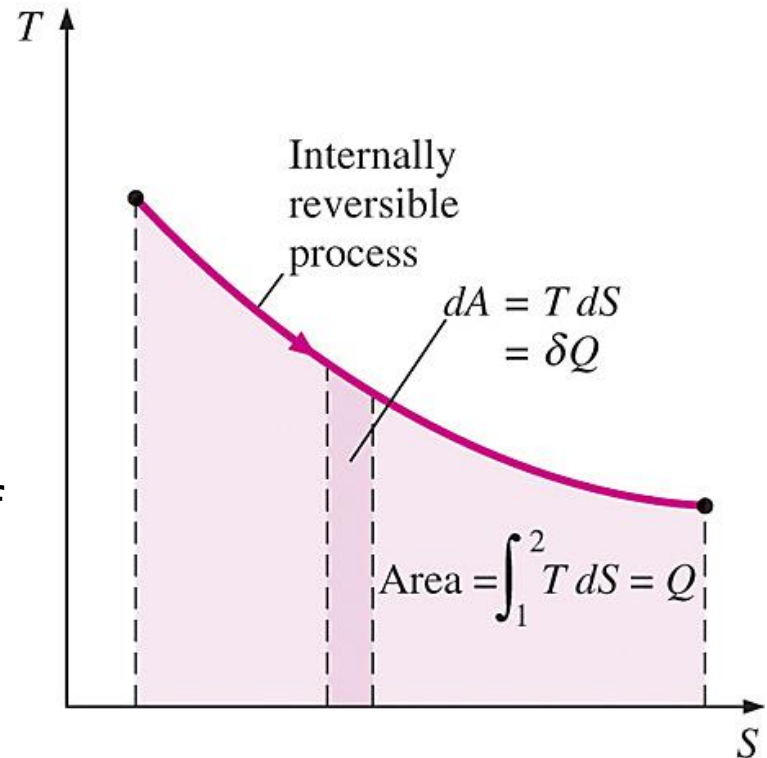


# Property Diagrams Involving Entropy

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

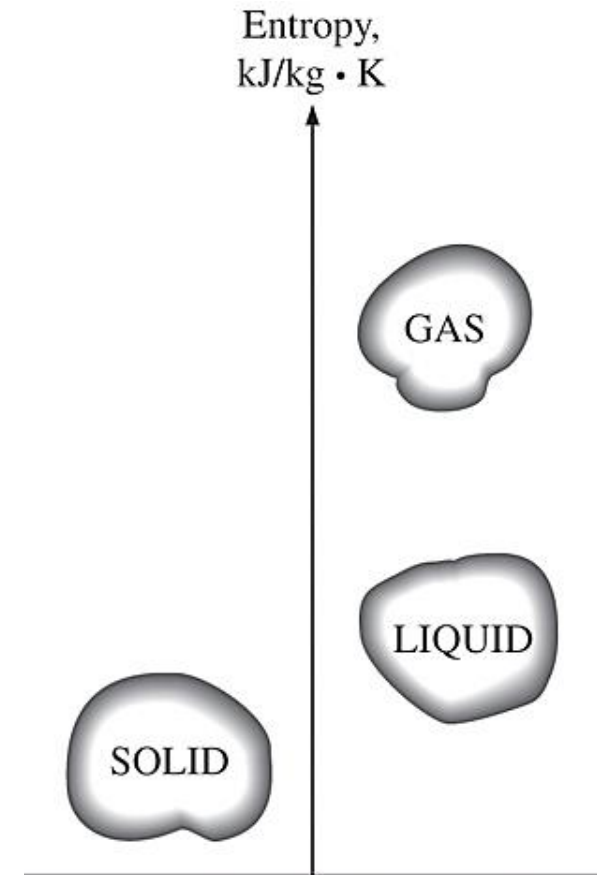
$$Q_{\text{int rev}} = \int_1^2 T dS$$

- For internally-reversible processes, the area under the process line on a T-S diagram represents the amount of heat transferred during the process.
- Reversible processes are shown as solid lines on the T-S diagram
  - Irreversible processes are shown as dashed lines on the T-S diagram



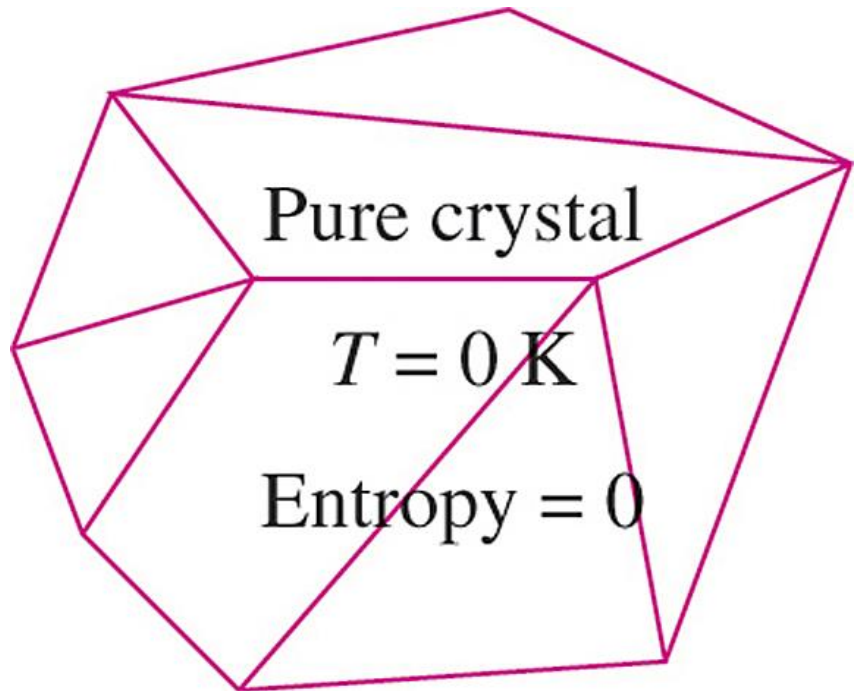
# Understanding Entropy

- ❑ Entropy is a measure of the level of molecular disorder of a substance.
- ❑ The higher the level of disorder, the higher the entropy.
- ❑ Gases have higher molecular disorder → they have higher entropy.
- ❑ The higher the level of disorder, the more disorganized energy becomes → the less useful effect it can have.



# Understanding Entropy

- A pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero.

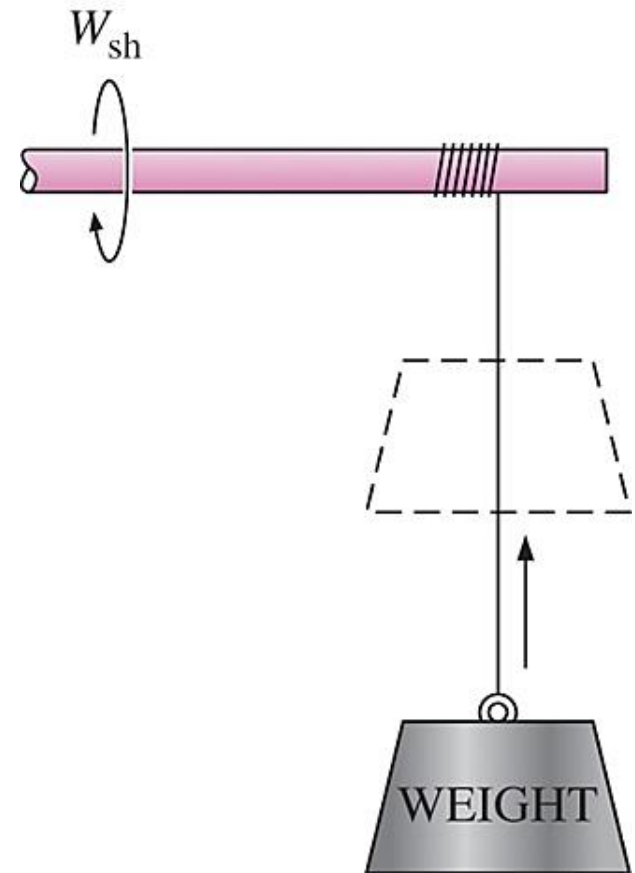


# Understanding Entropy

- ❑ Work is an organized form of transferring energy.
- ❑ All molecules are moving in the same direction.
  - Work does not involve entropy.

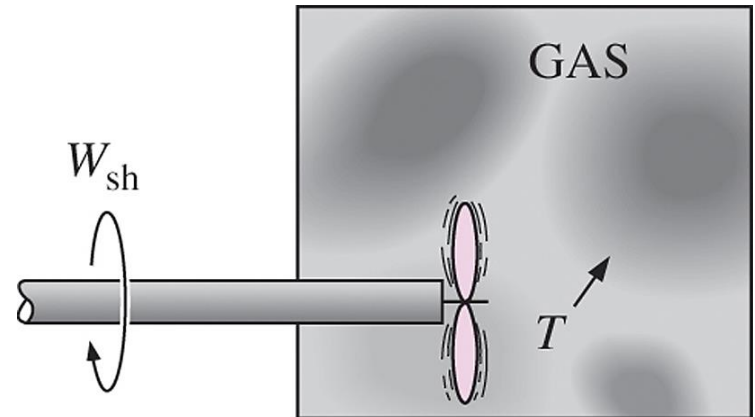
## EXAMPLE

- Raising a weight by a rotating shaft does not create any disorder (entropy)
- Energy is not degraded during this process.



# Understanding Entropy

- ❑ The paddle-wheel work done on a gas increases the level of disorder (entropy) of the gas.
  - Energy is degraded during this process.
  - Converting work into heat degrades energy

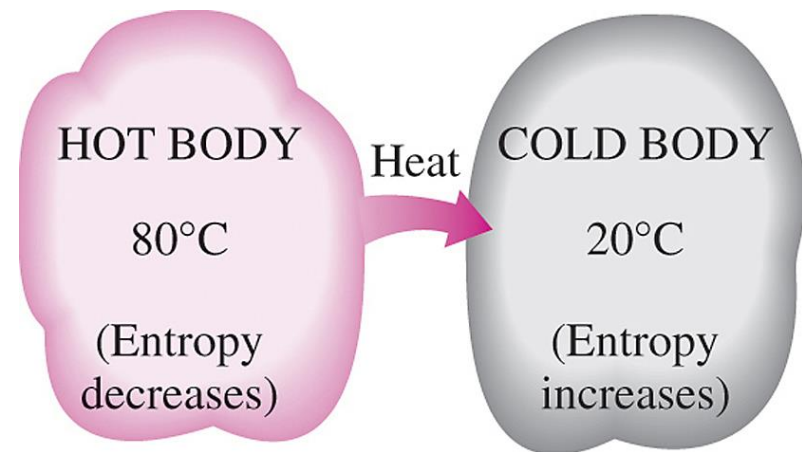


**FRICTION:** “dissipation of energy that otherwise could do work into a heating effect”



# Understanding Entropy

- ❑ During a heat transfer process between a hot and a cold body, the entropy of the hot body decreases, while the entropy of the cold body increases.
- ❑ Net entropy increases (according to the Increase of Entropy Principle).
  - Heat transfer across a finite temperature difference always involves generation of entropy, and degrades energy.



# The T- ds Relations

- Applying the first law of thermodynamics to a system undergoing an internally-reversible process:

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

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

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

$$T dS = dU + P dV$$

- Therefore,

$$T ds = du + P dv$$

- This is called the **First T ds Equation** or **Gibbs Equation**

# The T- ds Relations

- By applying the definition of enthalpy ( $h = u + Pv$ ) on the first  $T ds$  equation, we get:

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

- This is called the **Second T ds equation**

# The T- ds Relations

□ Dividing the two T- ds equations by T, we get:

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

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

□ Above relations can be used to determine changes in entropy

# Entropy Change for Liquids and Solids

- Liquids and solids can be approximated as *incompressible substances* since their specific volumes remain nearly constant during a process, i.e.  $dv \approx 0$

$$ds = \frac{du}{T} + \frac{P}{T} \cancel{dv} \xrightarrow{0} ds = \frac{du}{T}$$

- As shown earlier, for liquids and solids:

$$c_p = c_v = c \quad \text{AND} \quad du = c dT$$

$$\therefore ds = \frac{du}{T} = \frac{c dT}{T} \quad \Rightarrow \quad s_2 - s_1 = \int_1^2 c(T) \frac{dT}{T} \cong c_{\text{avg}} \ln \frac{T_2}{T_1}$$

# Entropy Change of Ideal Gases

□ From the first T ds relation:

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

□ Also, for ideal gases:  $du = c_v dT$  and  $P = RT/v$

□ Therefore,

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



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

# Entropy Change of Ideal Gases

□ From The second T ds relation:  $ds = \frac{dh}{T} - \frac{v dP}{T}$

□ Also, for ideal gases:  $dh = c_p dT$  and  $P = RT/v$

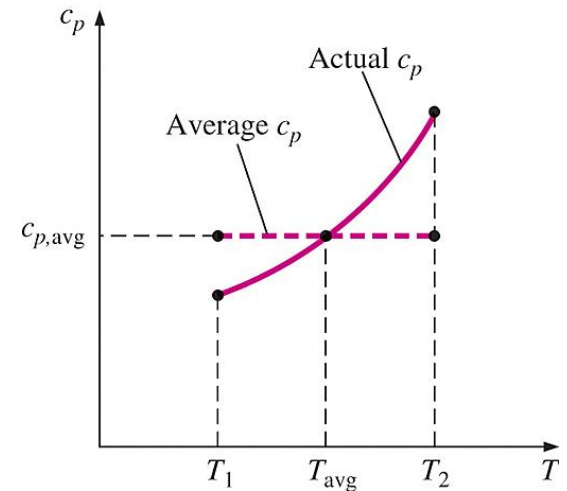
□ Therefore,

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

# Constant Specific Heat (Approximate Analysis)

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

□ In this case:



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

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

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

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



# Isentropic Process of Ideal Gases (Approximate Analysis)

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

➤ Therefore,  $\ln \frac{T_2}{T_1} = -\frac{R}{c_v} \ln \frac{v_2}{v_1} \Rightarrow \ln \frac{T_2}{T_1} = \ln \left( \frac{v_1}{v_2} \right)^{R/c_v}$

➤ For an ideal gas:  $R = c_p - c_v$   $k = c_p/c_v \Rightarrow R/c_v = k - 1$

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

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

# Reversible Steady Flow Work

- For a reversible steady flow process, the First Law can be written as:

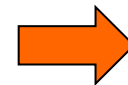
$$\delta q_{\text{rev}} - \delta w_{\text{rev}} = dh + dke + dpe$$

- We also know that:

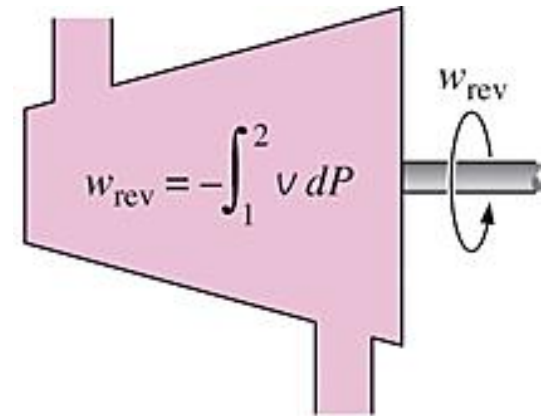
$$\left. \begin{array}{l} \delta q_{\text{rev}} = T ds \\ T ds = dh - v dP \end{array} \right\} \delta q_{\text{rev}} = dh - v dP$$

$$\therefore -\delta w_{\text{rev}} = v dP + dke + dpe \quad w_{\text{rev}} = - \int_1^2 v dP - \Delta ke - \Delta pe$$

- When  $\Delta ke$  &  $\Delta pe$  are negligible



$$w_{\text{rev}} = - \int_1^2 v dP$$



# Remarks on Reversible Steady Flow Work

- ❑ The larger the specific volume, the greater the work produced (or consumed) by a steady-flow device.
- ❑ It can be shown that work-producing devices (e.g. turbines) deliver **more** work when they operate reversibly.
- ❑ It can also be shown that work-consuming devices (e.g. compressors) require **less** work when they operate reversibly.

$$w = -\int_1^2 v \, dP$$

# Reversible versus Irreversible Steady Flow Work

- Heat input and work output are positive

$$\delta q_{\text{act}} - \delta w_{\text{act}} = dh + dke + dpe \quad \text{Actual}$$

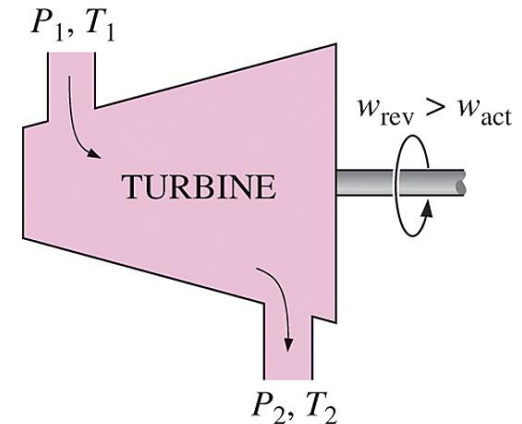
$$\delta q_{\text{rev}} - \delta w_{\text{rev}} = dh + dke + dpe \quad \text{Reversible}$$

- Since end states are the same:

$$\delta q_{\text{act}} - \delta w_{\text{act}} = \delta q_{\text{rev}} - \delta w_{\text{rev}} \quad \Rightarrow \quad \delta w_{\text{rev}} - \delta w_{\text{act}} = \delta q_{\text{rev}} - \delta q_{\text{act}}$$

$$\text{Since } \delta q_{\text{rev}} = T ds \text{ and } ds \geq \frac{\delta q_{\text{act}}}{T} \quad \Rightarrow \quad \frac{\delta w_{\text{rev}} - \delta w_{\text{act}}}{T} = ds - \frac{\delta q_{\text{act}}}{T} \geq 0$$

$$\therefore \boxed{w_{\text{rev}} \geq w_{\text{act}}}$$



Work-producing devices such as turbines deliver more work, and work-consuming devices such as pumps and compressors require less work when they operate reversibly.

# Remarks on Reversible Steady Flow Work

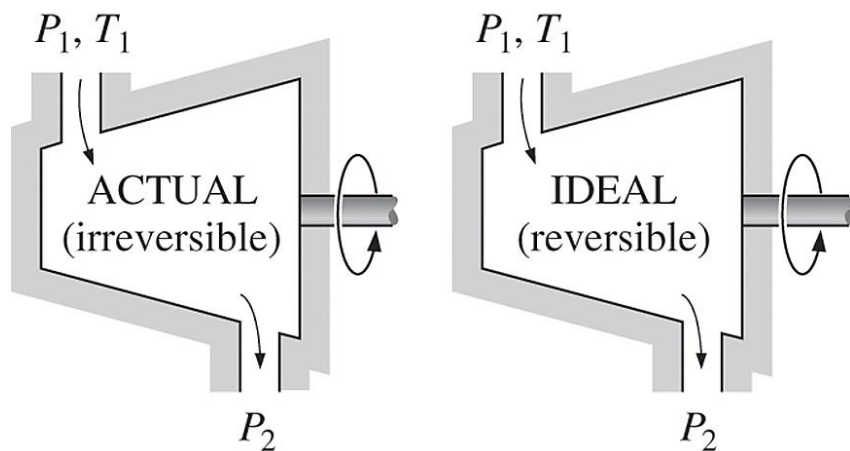
- If an **adiabatic** steady flow device (e.g. turbine, compressor, etc.) involves no irreversibilities:
  - **The process becomes isentropic.**
  - **The device will produce (or consume) reversible work**

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

0 (adiabatic)                      0 (internally reversible)

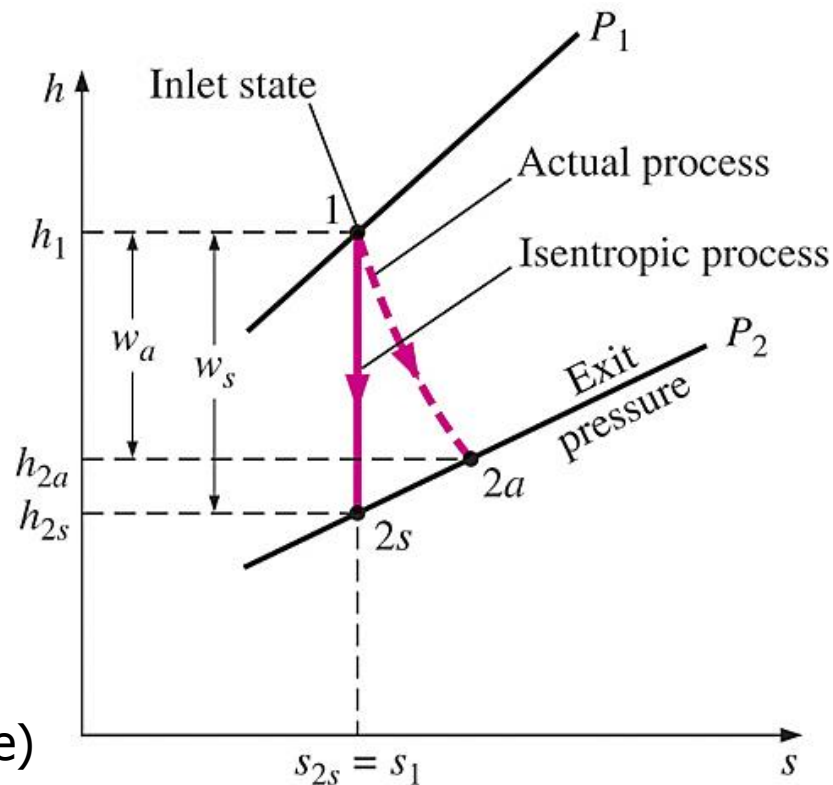
- In this case, reversible work can be used as a reference for the performance of the equivalent real devices.
- The comparison is made through a quantity called ***isentropic efficiency***.

# Isentropic Efficiencies of Adiabatic Turbines



$$\eta_T = \frac{\text{Actual turbine work}}{\text{Isentropic turbine work}} = \frac{w_a}{w_s}$$

$$\eta_T \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}} \quad (\text{Negligible } \Delta ke \text{ \& } \Delta pe)$$



# Isentropic Efficiencies of Adiabatic Pumps and Compressors

$$\eta_c = \frac{\text{Isentropic compressor work}}{\text{Actual compressor work}} = \frac{w_s}{w_a}$$

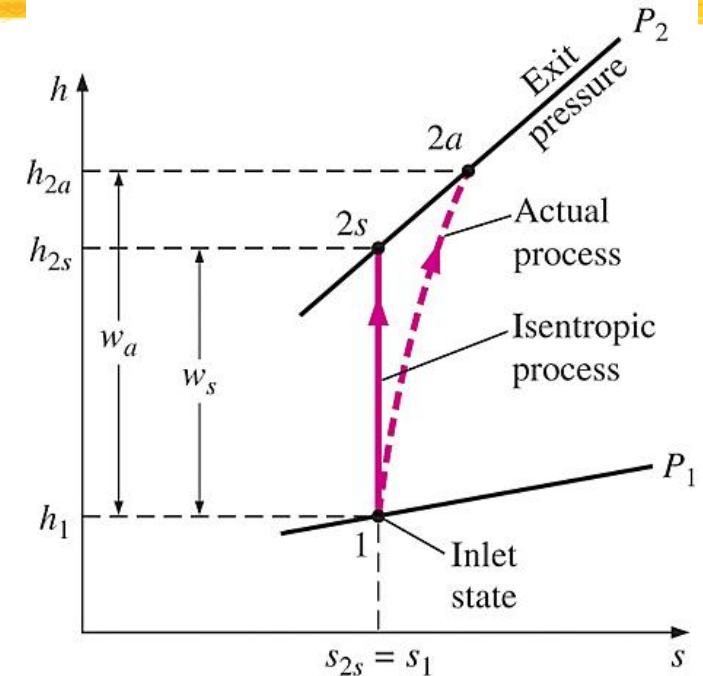
$$\eta_c \cong \frac{h_{2s} - h_1}{h_{2a} - h_1} \quad (\text{Negligible } \Delta ke \text{ \& } \Delta pe)$$

- For a pump, quantifying reversible (isentropic) work is simple:

$$w_{\text{rev}} = - \int_1^2 v \, dP$$

- Since  $v$  is nearly constant:  $w_{\text{rev}} = -v(P_2 - P_1)$

$$\therefore \eta_P = \frac{w_s}{w_a} = \frac{v(P_2 - P_1)}{h_{2a} - h_1}$$



# Isentropic Efficiency of Adiabatic Nozzles

- The purpose of the nozzle is to increase the KE of the fluid

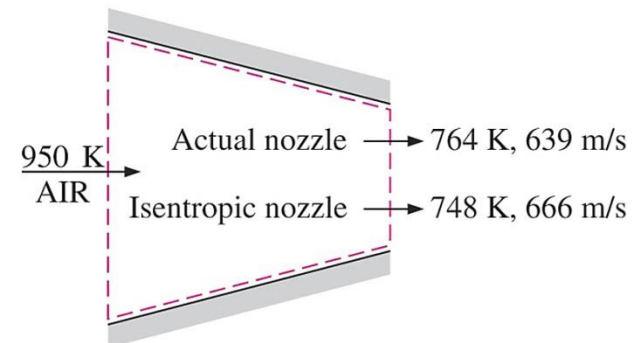
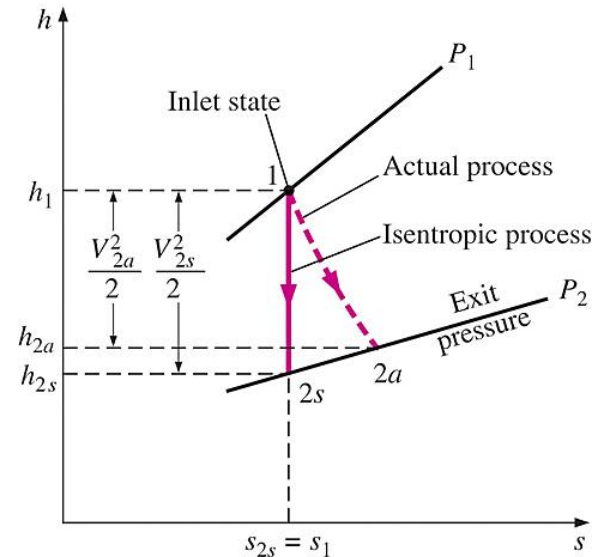
$$\eta_N = \frac{\text{Actual KE at nozzle exit}}{\text{Isentropic KE at nozzle exit}} = \frac{V_{2a}^2}{V_{2s}^2}$$

- If the inlet velocity of the fluid is small compared to the exit velocity, the First Law yields:

$$h_1 = h_{2a} + \frac{V_{2a}^2}{2}$$

- Therefore,

$$\eta_N \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$





# Entropy Balance

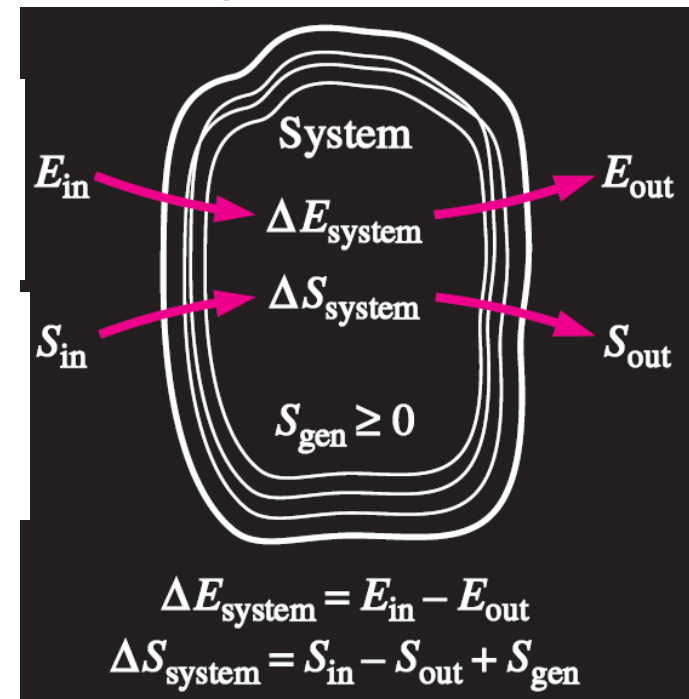
$$\left( \begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{entering} \end{array} \right) - \left( \begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{leaving} \end{array} \right) + \left( \begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{generated} \end{array} \right) = \left( \begin{array}{c}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

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

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

□ Entropy change of a system:

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



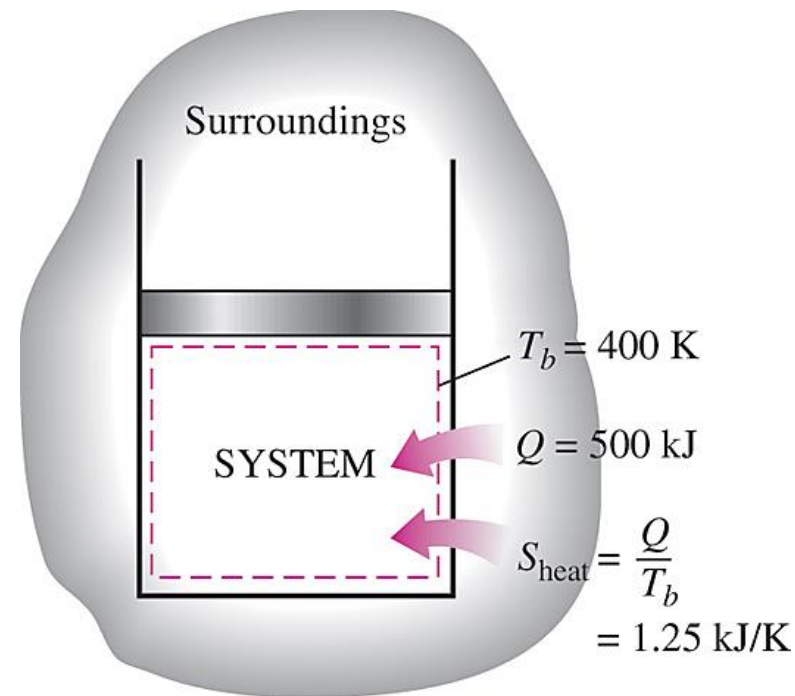
# Mechanisms of Entropy Transfer, $S_{in}$ and $S_{out}$

## 1. Entropy Transfer by Heat Transfer

- Heat transfer is always accompanied by entropy transfer in the amount of  $Q/T$ , where  $T$  is the boundary temp.

$$S_{\text{heat}} = \frac{Q}{T} \quad (T = \text{constant})$$

$$S_{\text{heat}} = \int_1^2 \frac{\delta Q}{T} \cong \sum \frac{Q_k}{T_k}$$

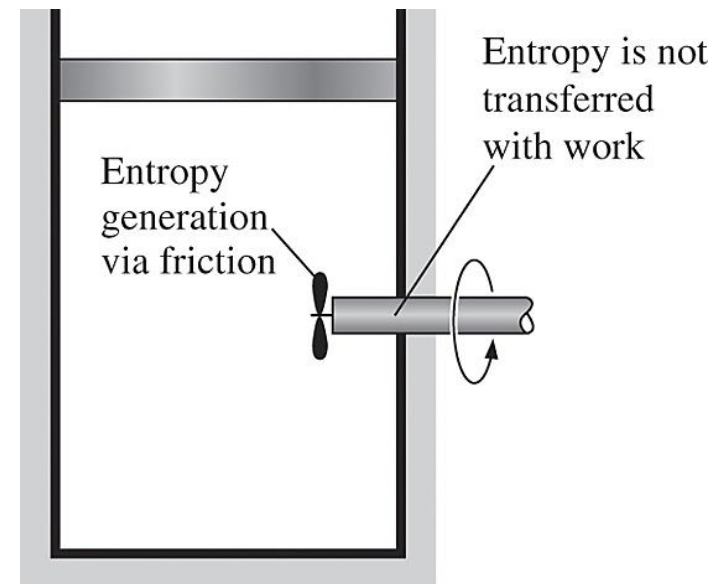


# Mechanisms of Entropy Transfer, $S_{in}$ and $S_{out}$

## 2. Entropy Transfer by **Work**

- No entropy accompanies work as it crosses the system boundary. But entropy may be generated within the system as work is dissipated into a less useful form of energy (a heating effect by friction)

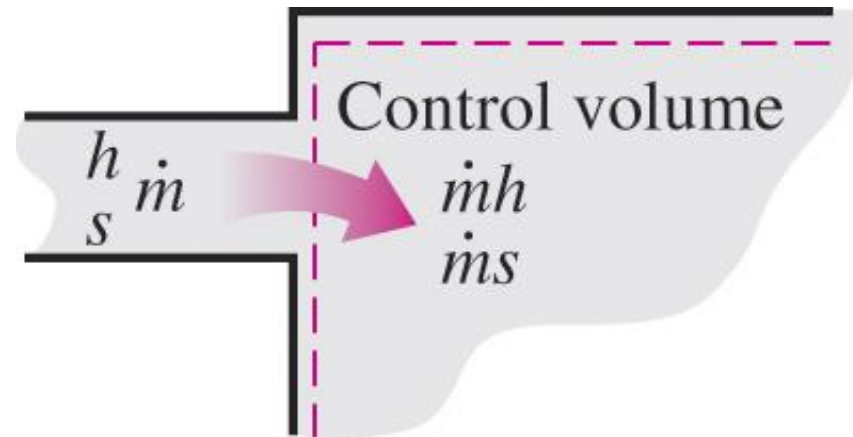
$$S_{work} = 0$$



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

## 2. Entropy Transfer by Mass

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



$$S_{\text{mass}} = \dot{m}s$$

# Closed Systems

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

- The entropy change of a closed system during a process equals the sum of the net entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries.

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

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

$$\Delta S_{\text{system}} = m(s_2 - s_1)$$

$$\Delta S_{\text{surr}} = Q_{\text{surr}}/T_{\text{surr}}$$

# Control Volumes

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

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

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

*Steady-flow:*

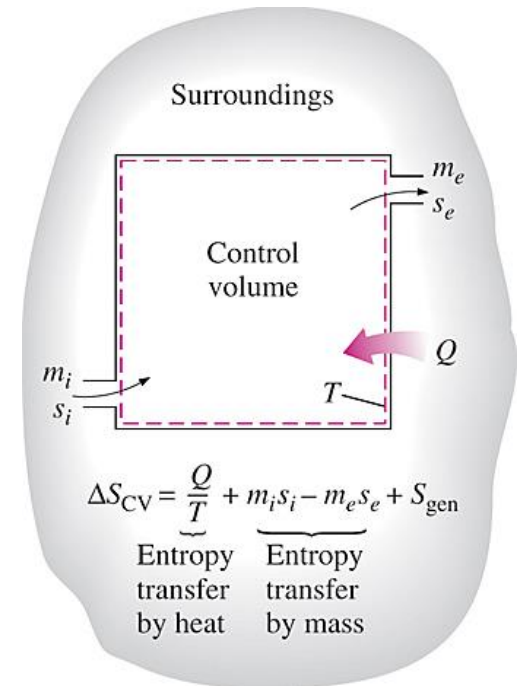
$$\dot{S}_{\text{gen}} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i - \sum \frac{\dot{Q}_k}{T_k}$$

*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:*

$$\dot{S}_{\text{gen}} = \dot{m}(s_e - s_i)$$



# Control Volumes

*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

