# Chapter 7
# ENTROPY

# Clausius Inequality

- The Clausius inequality states that:

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

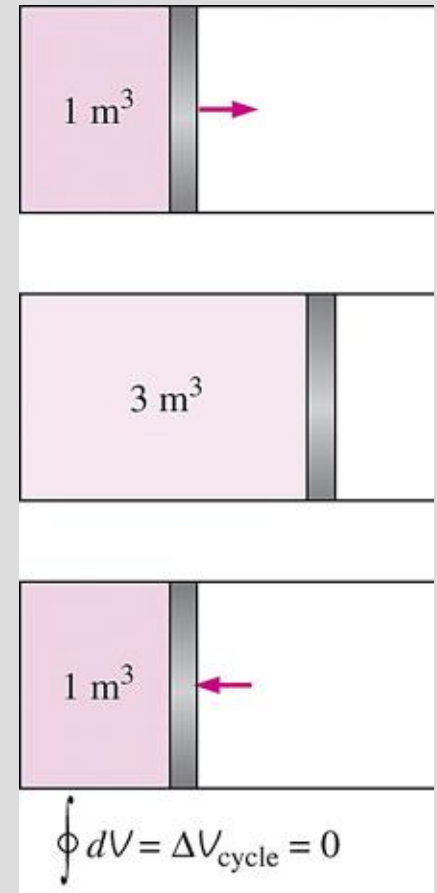- It can be shown that, for internally reversible cycles (e.g. Carnot cycle):

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

- It can also be shown that, for irreversible cycles:

$$\oint \left( \frac{\delta Q}{T} \right)_{\text{irr}} < 0$$
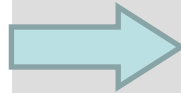
# Results of Clausius Inequality

- The cyclic integral of a quantity is zero only if that quantity is a property.

- *EXAMPLE*: Cyclic integral of volume.

- This means that $\left(\dfrac{\delta Q}{T}\right)_{\text{int rev}}$ is a property



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

# Definition of Entropy

- The formal definition of the property $\left(\dfrac{\delta Q}{T}\right)_{\text{int rev}}$ is:

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

- $S$ is a property called **entropy**.

- Entropy is an extensive property.

- Since entropy is a property, entropy change between two specified states is the same.
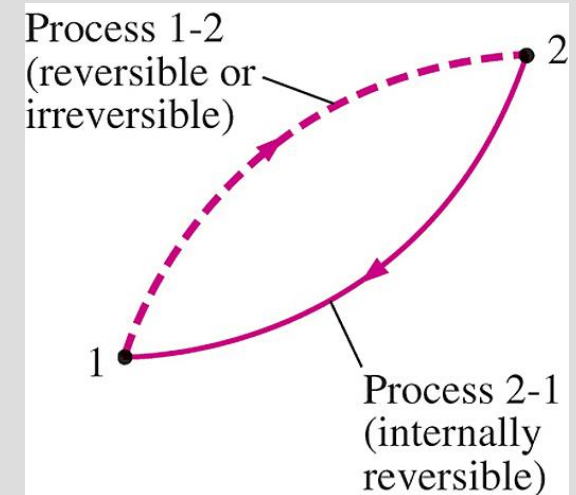
# Entropy Generation

- Assume we have a cycle consisting of two processes.

    - **Process 1-2 could be reversible or irreversible.**
    - **Process 2-1 is internally reversible.**

- According to Clausius inequality:

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

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

$$\implies S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

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

Process 1-2 (reversible or irreversible)

Process 2-1 (internally reversible)

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# Entropy Generation

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

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

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

- For an internally reversible process, $S_{gen} = 0$

$$S_{gen} \begin{cases} > 0 & \text{Irreversible process} \\ = 0 & \text{Reversible process} \\ < 0 & \text{Impossible process} \end{cases}$$
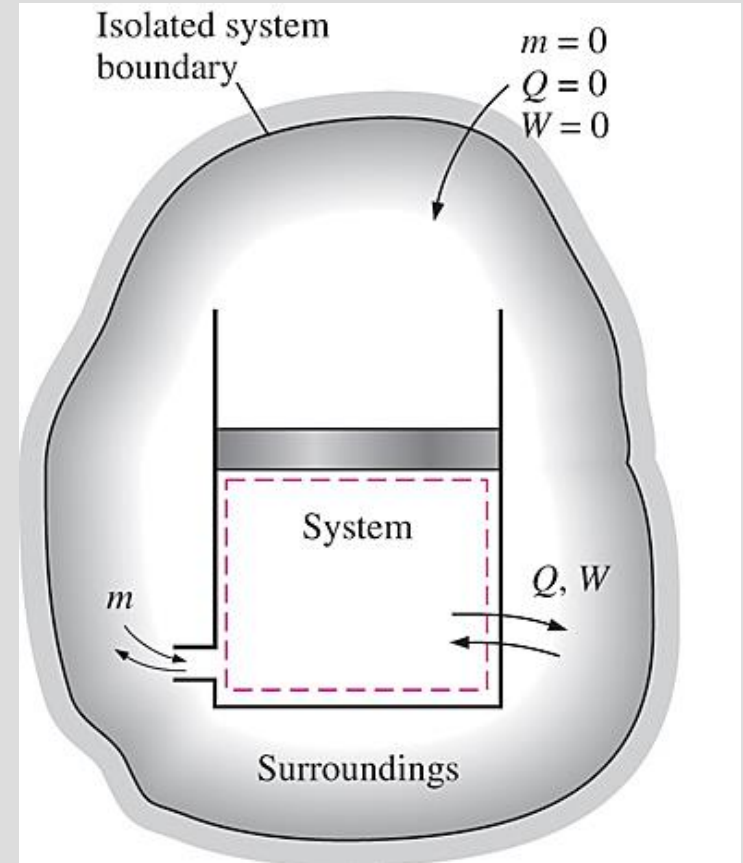
# The Increase of Entropy Principle

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \int_1^2 \frac{\delta Q}{T}^{\,0} + S_{\text{gen}}$$

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

The increase of entropy principle



Isolated system boundary

$m = 0$
$Q = 0$
$W = 0$

System

$m$

$Q, W$

Surroundings
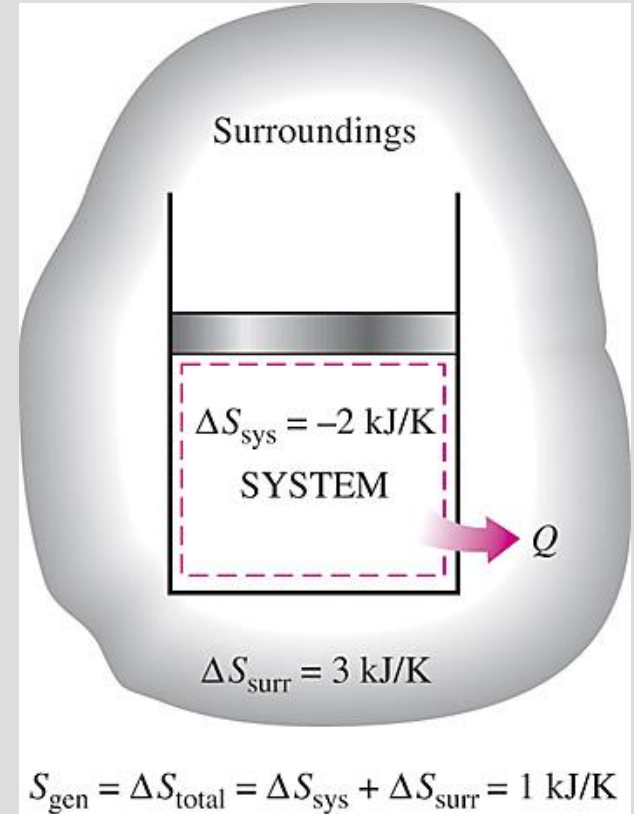
A system and its surroundings form an isolated system.

# Some Remarks About Entropy

- A process must proceed in the direction that complies with the increase of entropy principle. A process that violates this principle is impossible.

- Entropy is a *nonconserved property*, and there is *no* such thing as the *conservation of entropy principle*.



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

$$\Delta S_{sys} = -2 \text{ kJ/K}$$

SYSTEM

$$\Delta S_{surr} = 3 \text{ kJ/K}$$

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

# Some Remarks About Entropy

- The performance of engineering systems is degraded by the presence of irreversibilities.

- Entropy generation is a measure of the magnitudes of the irreversibilities during that process.

- Entropy generation 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).

- The unit of entropy is kJ/K.

- The unit of specific entropy is kJ/kg.K.
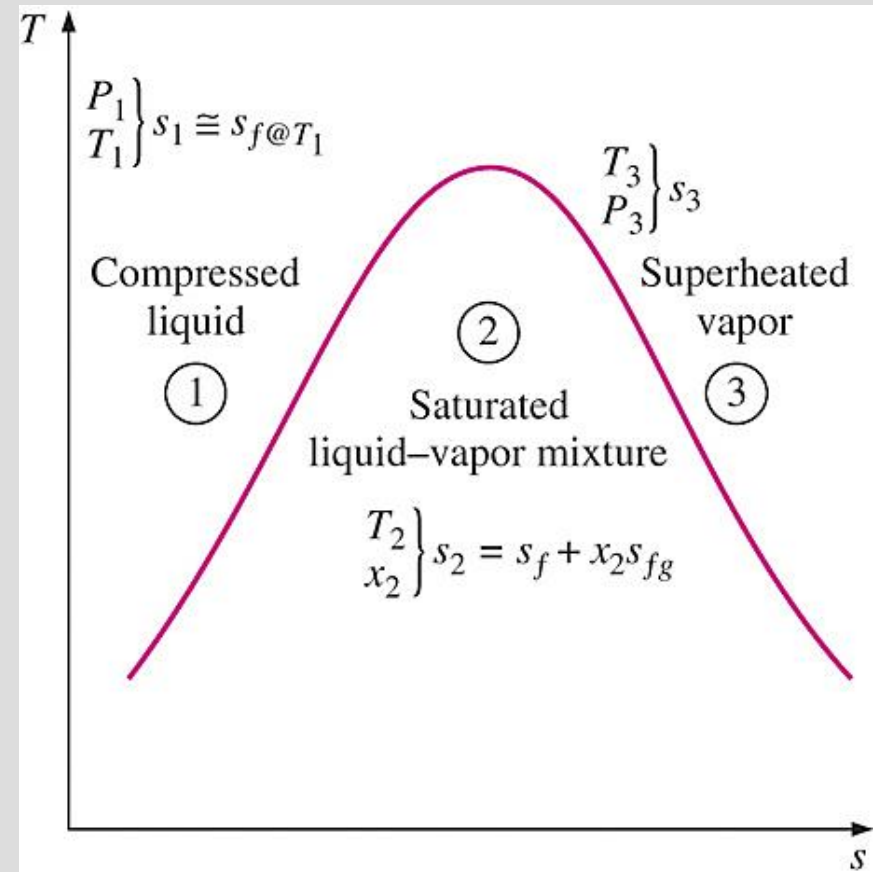
# Isentropic Processes

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

$$\Delta s = 0 \quad \text{or} \quad s_2 = s_1$$
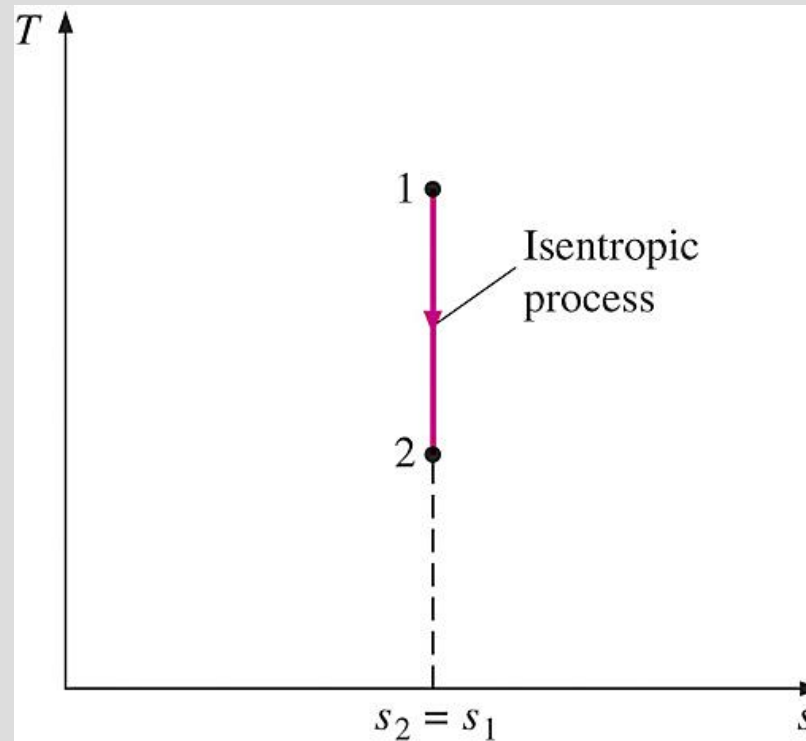
# Isentropic Processes

- If a process is internally reversible AND adiabatic, it is automatically isentropic.

**0 (adiabatic)**

**0 (internally reversible)**

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = \int_{1}^{2} \frac{\delta Q}{T} + S_{gen}$$

Steam

$s_1$

No irreversibilities
(internally reversible)

No heat transfer
(adiabatic)

$s_2 = s_1$
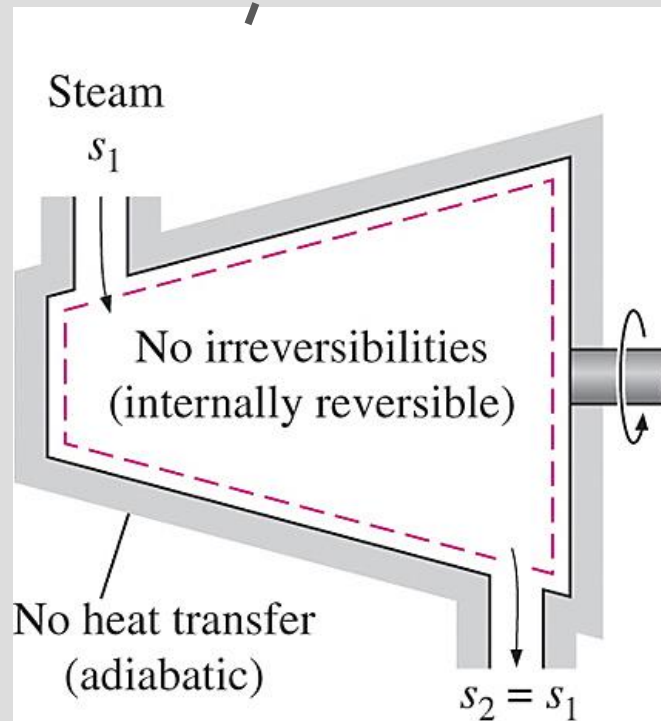
# Property Diagrams Involving Entropy
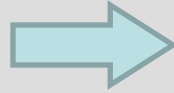
$$\delta Q_{\text{int rev}} = T\ dS \qquad \Longrightarrow \qquad Q_{\text{int rev}} = \int_{1}^{2} T\ dS$$
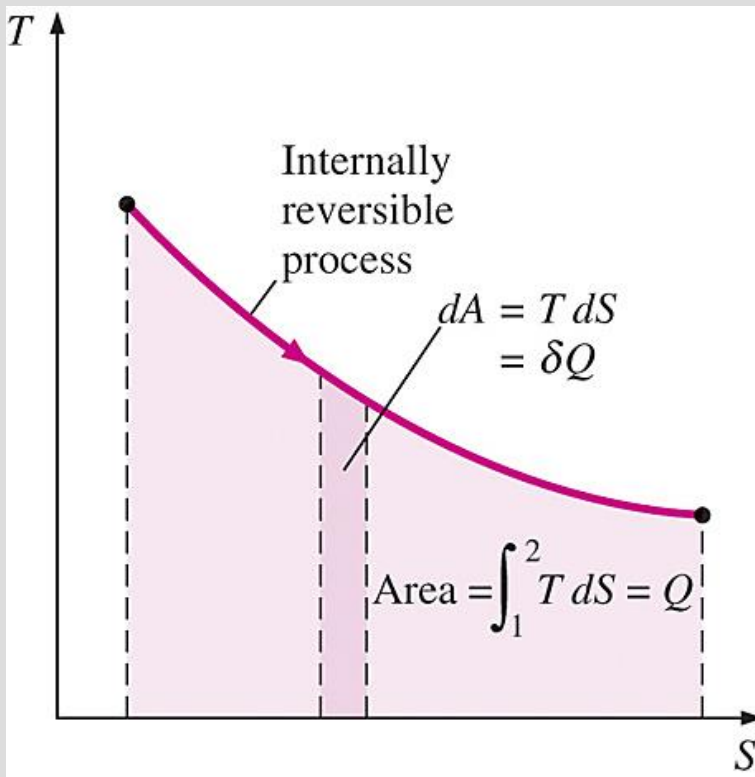


- On a *T-S* diagram, the area under the process curve represents the heat transfer for internally reversible processes.

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# 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.



Entropy, kJ/kg · K

GAS

LIQUID

SOLID

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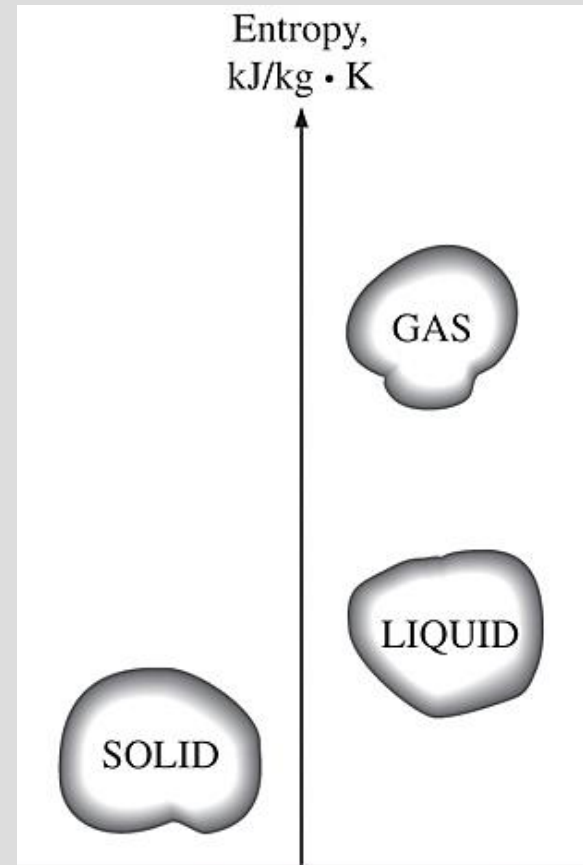
# Understanding Entropy

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

- This is called **the third law of thermodynamics**.



Pure crystal

$T = 0 \, K$
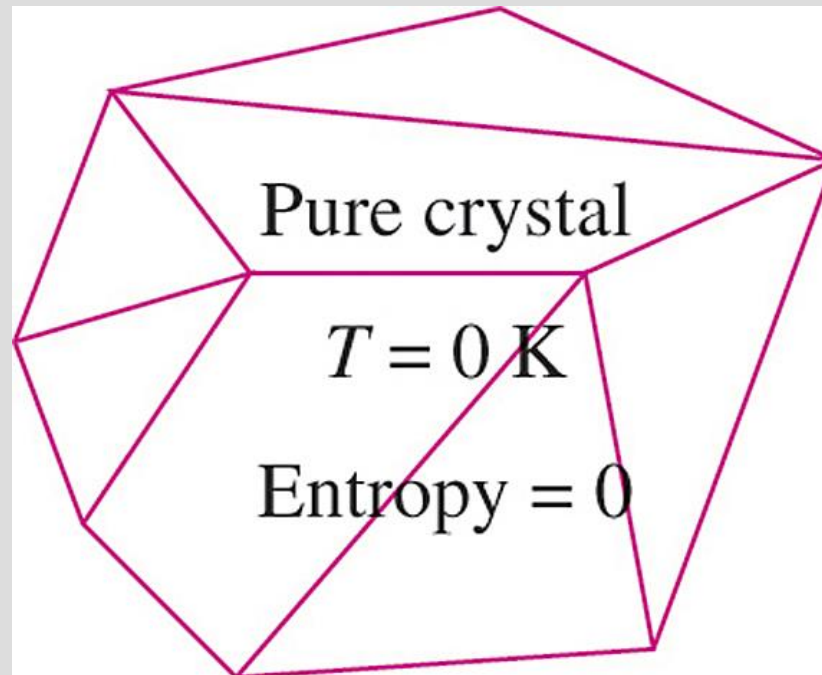
Entropy $= 0$

# 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.
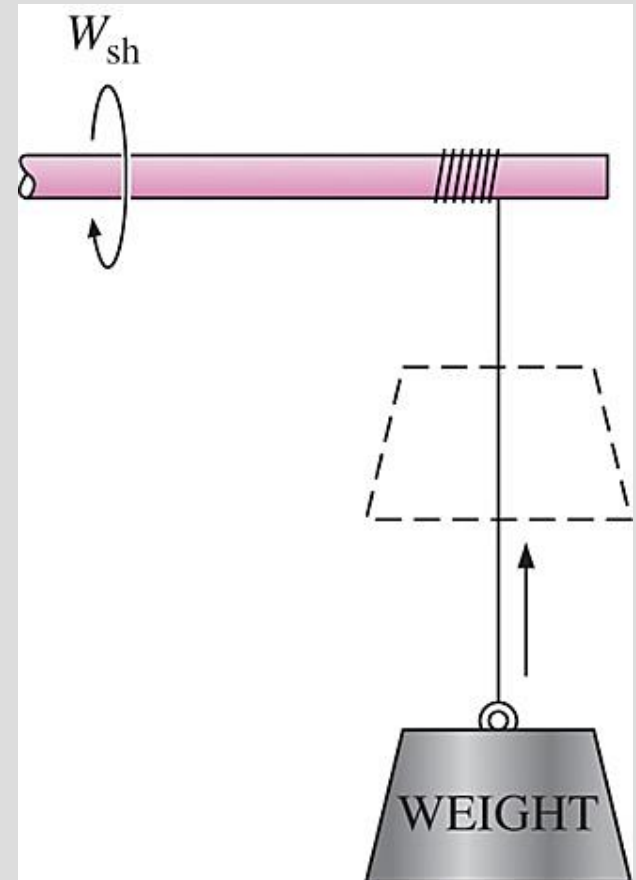
# Understanding Entropy

- 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 to heat degrades energy.
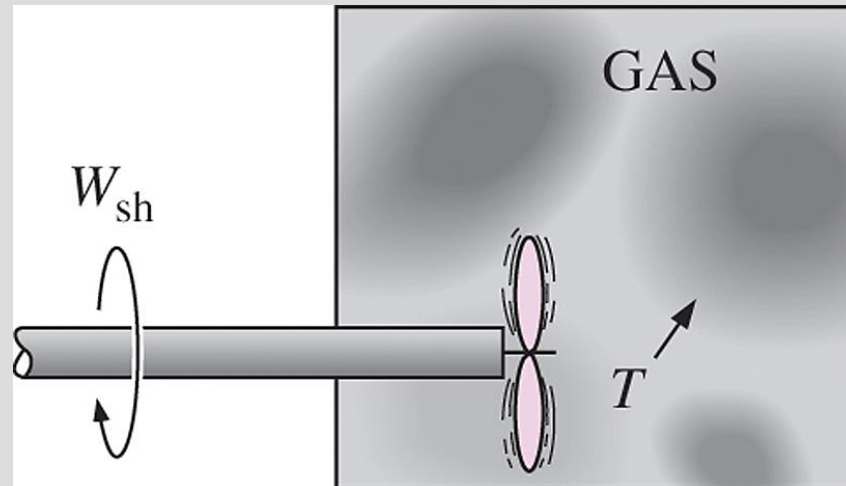
# Understanding Entropy

- During a heat transfer process between a hot and a cold body, the entropy of the hot body decreases, and the entropy of the cold body increases.

- Net entropy increases (according to the Increase of Entropy Principle).

  → Heat transfer always involves generation of entropy, and degrades energy.

HOT BODY
80°C
(Entropy decreases)

Heat

COLD BODY
20°C
(Entropy increases)
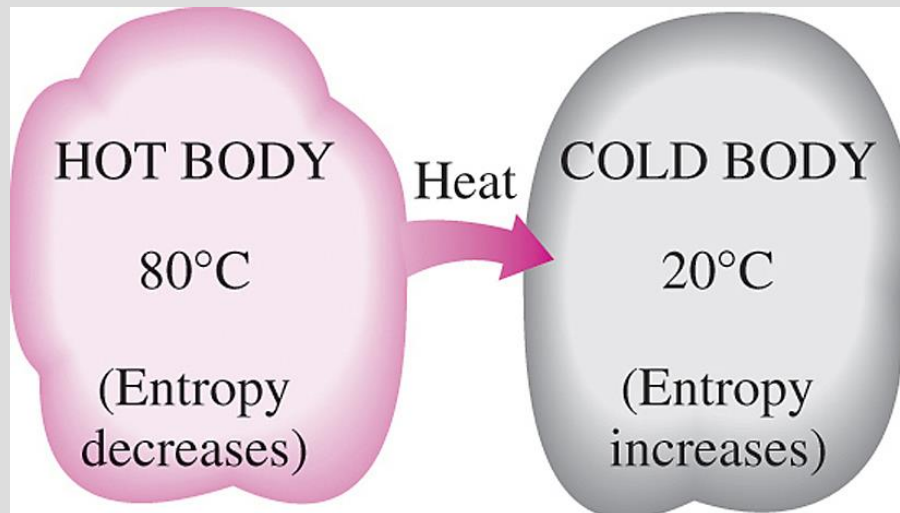
# THE *T ds* RELATIONS

- By applying the first law of thermodynamics on a system having an internally reversible process:

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

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

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

$$\Longrightarrow \quad T \, dS = dU + P \, dV \qquad \text{This is called the } \textbf{\textit{Gibbs Equation}}$$

**OR**

$$T \, ds = du + P \, dv \qquad \text{The } \textbf{\textit{First TdS Relation}}$$

# The *T dS* Relations

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

$$dh = du + P\,dv + v\,dP \atop T\,ds = du + P\,dv \Bigg\} \quad T\,ds = dh - v\,dP$$

- This is called the ***Second T dS equation***.

# The *T dS* Relations

- Dividing the two *T dS* equations by *T*, we get:

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

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

# Entropy Change of 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 ≈ 0

$$ds = \frac{du}{T} + \frac{P \, dv}{T} \quad^{0}$$ $$\Longrightarrow \quad ds = \frac{du}{T}$$

- We have seen earlier that, for liquids and solids:

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

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

# Entropy Change of Ideal Gases

- From the first *T ds* relation:

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

- We also know that, for ideal gases:

$$du = c_v\ dT$$

$$P = RT/v$$

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

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

# Entropy Change of Ideal Gases

- From the second *T ds* relation:

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

- We also know that, for ideal gases:

$$dh = c_p\, dT$$

$$P = RT/v$$

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

# Constant Specific Heats (Approximate Analysis)

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

- In this case:
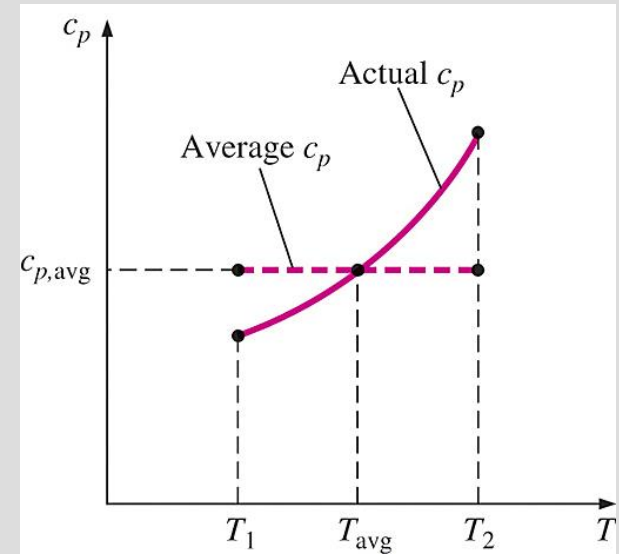
$$s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1} \longrightarrow s_2 - s_1 = c_{v,\text{avg}}\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

$$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1} \longrightarrow s_2 - s_1 = c_{p,\text{avg}}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

# Variable Specific Heats (Exact Analysis)

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

We choose absolute zero as the reference temperature and define a function $s°$ as

$$s° = \int_0^T c_p(T) \frac{dT}{T}$$

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

$$s_2 - s_1 = s_2° - s_1° - R \ln \frac{P_2}{P_1} \qquad (kJ/kg \cdot K)$$

| $T$, K | $s°$, kJ/kg $\cdot$ 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 $s^0$ represents only the temperature-dependent part of entropy.

# Isentropic Processes of Ideal Gases
## Approximate Analysis

$$s_2 - s_1 = c_{v,avg} \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

- Setting this eq. equal to zero, we get

$$\ln \frac{T_2}{T_1} = -\frac{R}{c_v} \ln \frac{V_2}{V_1}$$ ⟹ $$\ln \frac{T_2}{T_1} = \ln \left( \frac{V_1}{V_2} \right)^{R/c_v}$$

- We know that: $$R = c_p - c_v \quad \text{and} \quad k = c_p/c_v$$

⟹ $$R/c_v = k - 1$$

⟹ $$\left( \frac{T_2}{T_1} \right)_{s=\text{const.}} = \left( \frac{V_1}{V_2} \right)^{k-1}$$

- Using a similar approach, it can be shown that:

$$\left( \frac{T_2}{T_1} \right)_{s=\text{const.}} = \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \quad \text{and} \quad \left( \frac{P_2}{P_1} \right)_{s=\text{const.}} = \left( \frac{V_1}{V_2} \right)^{k}$$

# Isentropic Processes of Ideal Gases
## Exact Analysis

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

$$\longrightarrow$$

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

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

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

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

- It is listed in Table A-17 for air

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

**TABLE A–17**

Ideal-gas properties of air

| $T$ K | $h$ kJ/kg | $P_r$ | $u$ kJ/kg | $v_r$ | $s^\circ$ kJ/kg·K |
|---|---|---|---|---|---|
| 200 | 199.97 | 0.3363 | 142.56 | 1707.0 | 1.29559 |
| 210 | 209.97 | 0.3987 | 149.69 | 1512.0 | 1.34444 |
| 220 | 219.97 | 0.4690 | 156.82 | 1346.0 | 1.39105 |
| 230 | 230.02 | 0.5477 | 164.00 | 1205.0 | 1.43557 |
| 240 | 240.02 | 0.6355 | 171.13 | 1084.0 | 1.47824 |
| 250 | 250.05 | 0.7329 | 178.28 | 979.0 | 1.51917 |
| 260 | 260.09 | 0.8405 | 185.45 | 887.8 | 1.55848 |
| 270 | 270.11 | 0.9590 | 192.60 | 808.0 | 1.59634 |
| 280 | 280.13 | 1.0889 | 199.75 | 738.0 | 1.63279 |
| 285 | 285.14 | 1.1584 | 203.33 | 706.1 | 1.65055 |
| 290 | 290.16 | 1.2311 | 206.91 | 676.1 | 1.66802 |
| 295 | 295.17 | 1.3068 | 210.49 | 647.9 | 1.68515 |
| 298 | 298.18 | 1.3543 | 212.64 | 631.9 | 1.69528 |
| 300 | 300.19 | 1.3860 | 214.07 | 621.2 | 1.70203 |
| 305 | 305.22 | 1.4686 | 217.67 | 596.0 | 1.71865 |
| 310 | 310.24 | 1.5546 | 221.25 | 572.3 | 1.73498 |
| 315 | 315.27 | 1.6442 | 224.85 | 549.8 | 1.75106 |
| 320 | 320.29 | 1.7375 | 228.42 | 528.6 | 1.76690 |
| 325 | 325.31 | 1.8345 | 232.02 | 508.4 | 1.78249 |
| 330 | 330.34 | 1.9352 | 235.61 | 489.4 | 1.79783 |
| 340 | 340.42 | 2.149 | 242.82 | 454.1 | 1.82790 |
| 350 | 350.49 | 2.379 | 250.02 | 422.2 | 1.85708 |

# Isentropic Processes of Ideal Gases
## Exact Analysis

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

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

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

- It is listed in Table A-17 for air

**TABLE A–17**

Ideal-gas properties of air

| T | h | | u | | s° |
|---|---|---|---|---|---|
| K | kJ/kg | $P_r$ | kJ/kg | $v_r$ | kJ/kg·K |
| 200 | 199.97 | 0.3363 | 142.56 | 1707.0 | 1.29559 |
| 210 | 209.97 | 0.3987 | 149.69 | 1512.0 | 1.34444 |
| 220 | 219.97 | 0.4690 | 156.82 | 1346.0 | 1.39105 |
| 230 | 230.02 | 0.5477 | 164.00 | 1205.0 | 1.43557 |
| 240 | 240.02 | 0.6355 | 171.13 | 1084.0 | 1.47824 |
| 250 | 250.05 | 0.7329 | 178.28 | 979.0 | 1.51917 |
| 260 | 260.09 | 0.8405 | 185.45 | 887.8 | 1.55848 |
| 270 | 270.11 | 0.9590 | 192.60 | 808.0 | 1.59634 |
| 280 | 280.13 | 1.0889 | 199.75 | 738.0 | 1.63279 |
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| 305 | 305.22 | 1.4686 | 217.67 | 596.0 | 1.71865 |
| 310 | 310.24 | 1.5546 | 221.25 | 572.3 | 1.73498 |
| 315 | 315.27 | 1.6442 | 224.85 | 549.8 | 1.75106 |
| 320 | 320.29 | 1.7375 | 228.42 | 528.6 | 1.76690 |
| 325 | 325.31 | 1.8345 | 232.02 | 508.4 | 1.78249 |
| 330 | 330.34 | 1.9352 | 235.61 | 489.4 | 1.79783 |
| 340 | 340.42 | 2.149 | 242.82 | 454.1 | 1.82790 |
| 350 | 350.49 | 2.379 | 250.02 | 422.2 | 1.85708 |

# Reversible Steady Flow Work

- If a steady flow process is reversible, the 1$^{st}$ law can be written as:

$$\delta q_{rev} - \delta w_{rev} = dh + d\text{ke} + d\text{pe}$$
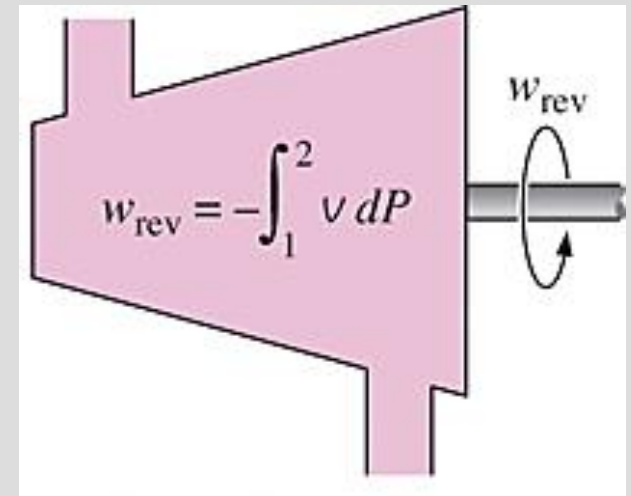
- In the mean time, we know that:

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



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

$$\Rightarrow \quad -\delta w_{rev} = v\,dP + d\text{ke} + d\text{pe}$$

$$\Rightarrow \quad w_{rev} = -\int_1^2 v\,dP - \Delta\text{ke} - \Delta\text{pe}$$

- When kinetic and potential energies are negligible

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

# 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.

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

$$W = -\int_1^2 V\, dP$$

$$W = -\int_1^2 V\, dP$$

# Proof that Steady-Flow Devices Deliver the Most and Consume the Least Work when the Process Is Reversible

Taking heat input and work output positive:

$\delta q_{act} - \delta w_{act} = dh + dke + dpe$ <span style="color:magenta">Actual</span>

$\delta q_{rev} - \delta w_{rev} = dh + dke + dpe$ <span style="color:magenta">Reversible</span>

$\delta q_{act} - \delta w_{act} = \delta q_{rev} - \delta w_{rev}$
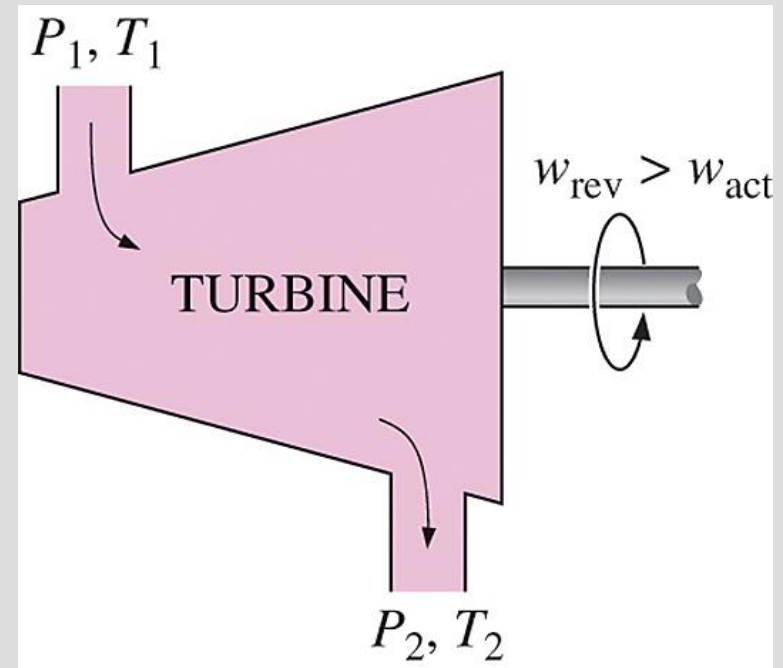
$\delta w_{rev} - \delta w_{act} = \delta q_{rev} - \delta q_{act}$

$\delta q_{rev} = T \, ds \qquad ds \geq \dfrac{\delta q_{act}}{T}$

$\dfrac{\delta w_{rev} - \delta w_{act}}{T} = ds - \dfrac{\delta q_{act}}{T} \geq 0$

$\partial w_{rev} \geq \partial w_{act}$

$w_{rev} \geq w_{act}$

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.



$P_1, T_1$

$w_{rev} > w_{act}$

TURBINE

$P_2, T_2$

A reversible turbine delivers more work than an irreversible one if both operate between the same end states.

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# Remarks on Reversible Steady Flow Work

- If an adiabatic device (e.g. turbine, compressor, etc.) involves no irreversibilities:

  - **The device will produce (or consume) reversible work.**
  - **The process becomes isentropic.**

**0 (adiabatic)**

**0 (internally reversible)**

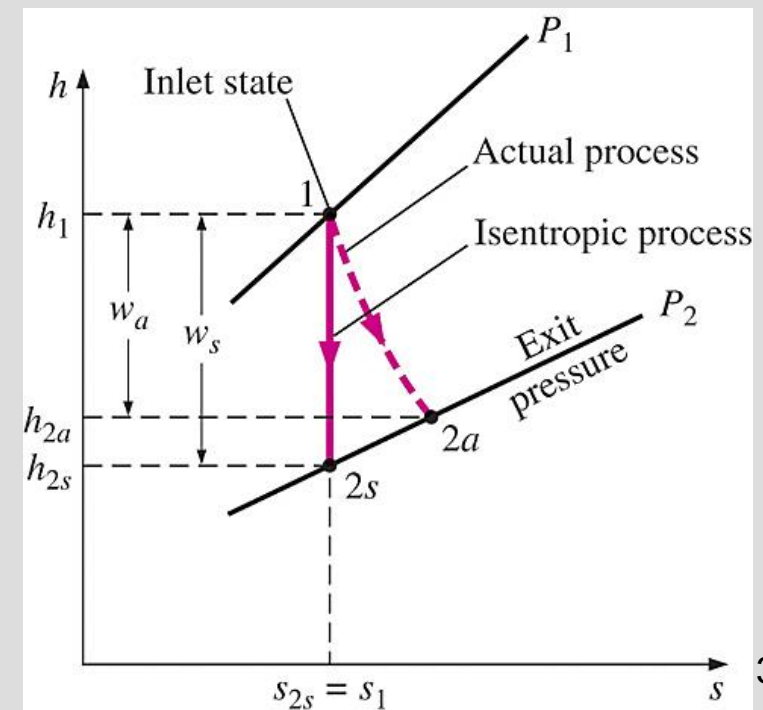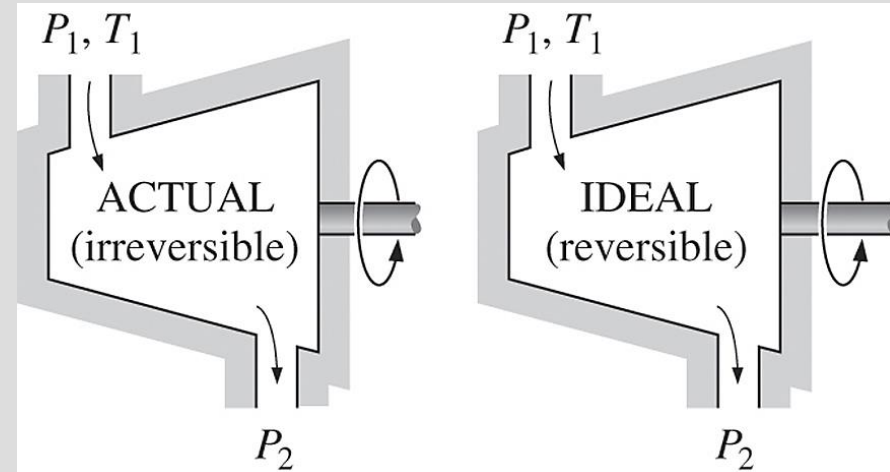$$\Delta S_{sys} = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

- 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 Efficiency of Turbines

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

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

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

# Isentropic Efficiency of Compressors and Pumps

$$\eta_C = \frac{\text{Isentropic compressor work}}{\text{Actual compressor work}} = \frac{w_s}{w_a}$$
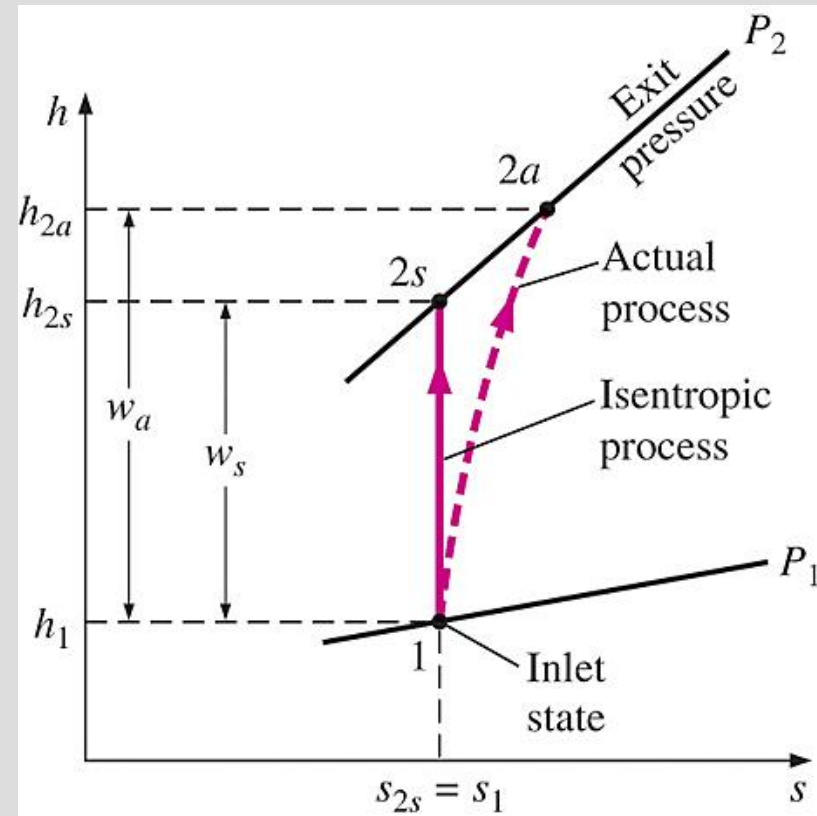
$$\eta_C \cong \frac{h_{2s} - h_1}{h_{2a} - h_1}$$

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

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

- The specific volume for liquids is nearly constant:

$$\Longrightarrow \quad w_{\text{rev}} = -v(P_2 - P_1) \quad \Longrightarrow \quad \eta_P = \frac{w_s}{w_a} = \frac{v(P_2 - P_1)}{h_{2a} - h_1}$$

# Isentropic Efficiency of Nozzles

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

- If the inlet velocity of the fluid is small relative to the exit velocity, the energy balance is:

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

Then,

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





950 K AIR

Actual nozzle → 764 K, 639 m/s

Isentropic nozzle → 748 K, 666 m/s