Thermodynamics I
Chapter 6
Entropy

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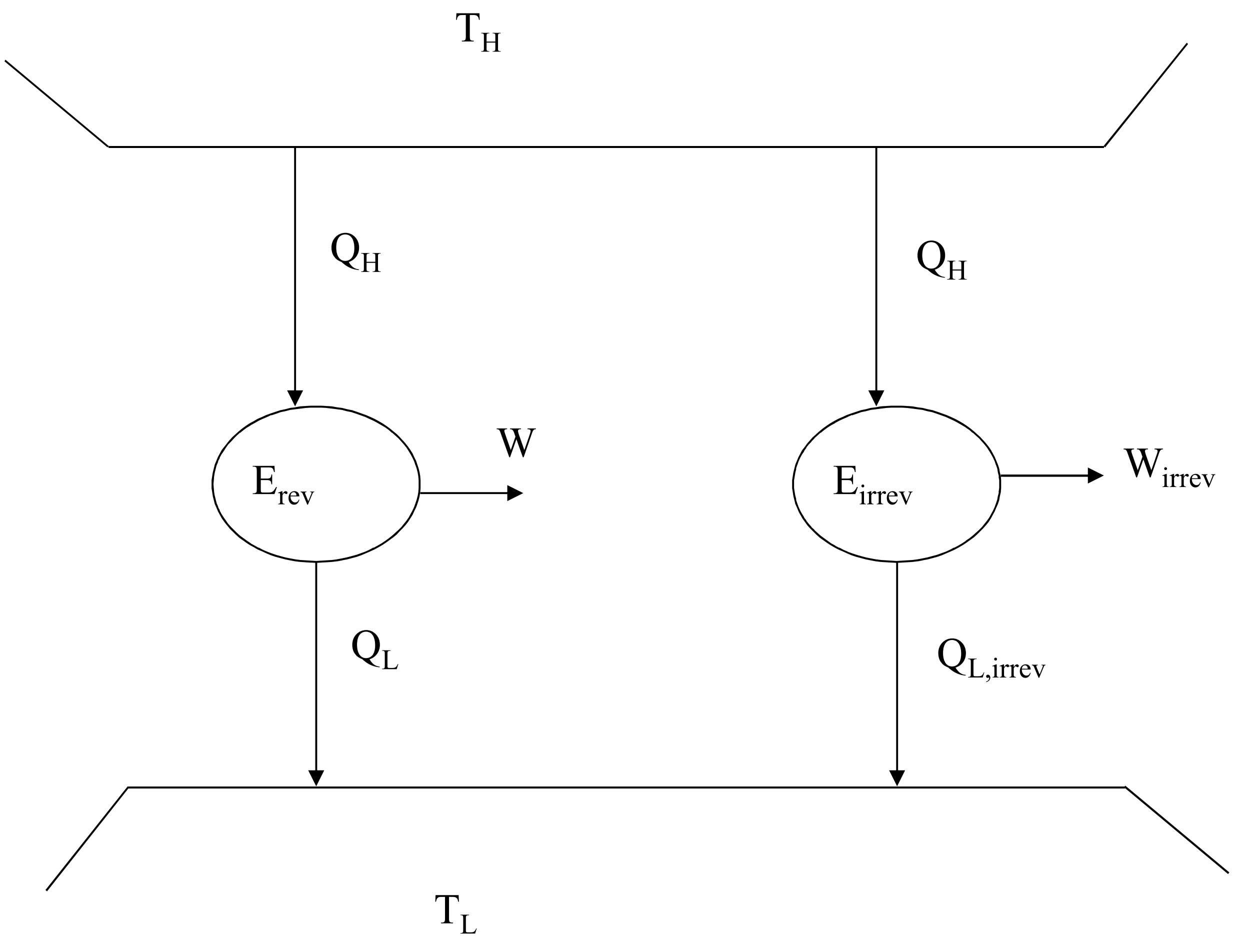
Entropy (Motivation)

The preferred direction implied by the 2nd Law can be better understood and quantified by the concept of entropy.

Entropy quantifies the 2nd Law and imposes the direction of processes.

Here we will study entropy and how processes will proceed only in the direction of increasing entropy.

Clausius Inequality



Consider two heat engines between the same temperatures

Consider $\frac{\delta Q}{T}$ of the whole cycle

(a) E_{rev}

$$\oint\left(\frac{\delta Q}{T}\right)_{rev} = \int\frac{\delta Q_H}{T_H} - \int\frac{\delta Q_L}{T_L}$$

$$= \frac{1}{T_H}\int\delta Q_H - \frac{1}{T_L}\int\delta Q_L$$

$$= \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

$$= 0$$

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

(b) E_{irrev} $$Q_{L,irrev} > Q_L$$

$$Q_{L,irrev} = Q_L + \Delta Q$$

$$\begin{aligned}
\oint \left(\frac{\delta Q}{T}\right)_{irrev} &= \frac{Q_H}{T_H} - \frac{Q_{L,\,irrev}}{T_L} \\
&= \frac{Q_H}{T_H} - \frac{Q_L + \Delta Q}{T_L} \\
&= \underbrace{\frac{Q_H}{T_H} - \frac{Q_L}{T_L}}_{=0} - \frac{\Delta Q}{T_L} \\
&= -\frac{\Delta Q}{T_L} < 0
\end{aligned}$$

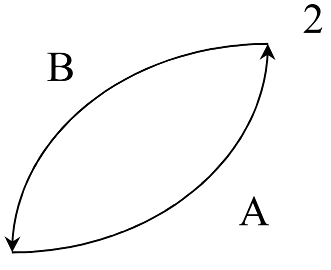
so $$\oint \left(\frac{\delta Q}{T}\right)_{irrev} < 0$$

Combined to be:

$$\boxed{\oint\left(\frac{\delta Q}{T}\right) \leqslant 0 \qquad \text{Clausius Inequality}}$$

$= 0$	if reversible
< 0	if irreversible
> 0	impossible

ENTROPY



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

$$\left.\begin{aligned}\int_1^2\left(\frac{\delta Q}{T}\right)_A&=-\int_2^1\left(\frac{\delta Q}{T}\right)_B\\&=\int_1^2\left(\frac{\delta Q}{T}\right)_B\end{aligned}\right\}$$

Does not depend on path; thermodynamic **property!**

Let's call this property **entropy, *S*** **[kJ/K]**

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

Entropy , ***S*** = extensive property [kJ/K]

Specific entropy, ***s*** = intensive property [kJ/kg.K]

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

We have actually defined entropy <u>change</u>

From statistical thermodynamics, entropy ~ measure of molecular **disorder**

Work is an ordered form of energy (High quality)

No *entropy transfer* along with work transfer

Heat is a disordered form of energy (Low quality)

Entropy is transferred along with heat transfer

> "Entropy = zero for pure crystal at 0 K"
>
> **Third Law of Thermodynamics**

Entropy with a 0 K reference is called *absolute entropy*

T-ds Relations

To find the relationship between δQ and T so that the integration of δQ/T can be performed

- From the **1^{st} Law** (neglecting KE & PE)

$$Q - W = U$$

$$\delta Q_{rev} - \delta W_{rev} = dU$$

$$\delta Q_{rev} = TdS$$

$$TdS - pdV = dU$$

$$\delta W_{rev} = pdV$$

$$TdS = dU + pdV$$

$$\boxed{Tds = du + pdv} \longleftarrow \quad \text{(a)}$$

- From the definition of **enthalpy**

$$h = u + pv$$

$$dh = du + pdv + vdp$$

$$du = dh - pdv - vdp$$

From (a)

$$Tds = du + pdv$$

$$= dh - pdv - vdp + pdv$$

$$\boxed{Tds = dh - vdp} \longleftarrow \text{(b)}$$

T-ds Relations

$$\longrightarrow \qquad \boxed{Tds = du + pdv}$$

$$\boxed{Tds = dh - vdp}$$

&

$$\boxed{ds = \frac{du}{T} + \frac{pdv}{T}}$$

$$\boxed{ds = \frac{dh}{T} - \frac{vdp}{T}}$$

Can be used for ΔS of any process (rev. & irrev.)
Can be used for open & closed system

Entropy Change of Pure Substances

Can be obtained from Tds Relations in conjunction with other thermodynamic relations

For 2 phase substances like *water* and *R-134a*, use property tables

$\Delta S = S_2 - S_1$

For **ideal gas**, from *Tds relations*

$$ds = \frac{du}{T} + \frac{pdv}{T}$$

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

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

$$\boxed{\Delta s = s_2 - s_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}}$$

$$du = C_v dT$$

$$pv = RT \rightarrow \frac{p}{T} = \frac{R}{v}$$

Assume C_v=constant & integrate

Another relation,

$$dh = C_p dT$$

$$pv = RT \rightarrow \frac{v}{T} = \frac{R}{p}$$

Assume C_p =constant & integrate

$$ds = \frac{dh}{T} - \frac{vdp}{T}$$

$$ds = C_p \frac{dT}{T} - R\frac{dp}{p}$$

$$\int ds = \int C_p \frac{dT}{T} - \int R\frac{dp}{p}$$

$$\boxed{\Delta s = s_2 - s_1 = C_p \ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1}}$$

Entropy change

$$\Delta s = s_2 - s_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

$$\Delta s = s_2 - s_1 = C_p \ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1}$$

Both equations give the same result
Choose according to available data..

Isentropic Processes, *ΔS = 0*

For **ideal gases**, with constant C_p & C_v

$$\Delta s = C_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} = 0$$

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

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

$$\rightarrow \ln\frac{T_2}{T_1} = \ln\left(\frac{v_1}{v_2}\right)^{k-1}$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

$$C_p - C_v = R$$

$$k = \frac{C_p}{C_v}$$

$$\therefore \frac{R}{C_v} = k - 1$$

Another one

$$\Delta s = C_p \ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1} = 0$$

$$\ln\frac{T_2}{T_1} = \frac{R}{C_p}\ln\frac{p_2}{p_1}$$

$$= \ln\left(\frac{p_2}{p_1}\right)^{R/C_p}$$

$$= \ln\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}$$

$$C_p - C_v = R$$

$$\frac{R}{C_p} = \frac{C_p}{C_p} - \frac{C_v}{C_p} = 1 - \frac{1}{k}$$

$$\therefore \frac{R}{C_p} = \frac{k-1}{k}$$

Combined to become

$$\boxed{\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = \left(\frac{v_1}{v_2}\right)^{k-1}}$$

Isentropic process for
ideal gas,
constant C_p , C_v

Work for Open Systems

Reversible boundary work for *closed systems*

$$w_B = \int pdv$$

Open system reversible work, from 1st Law (single inlet/outlet)

$$\delta q_{rev} - \delta w_{rev} = dh + d\left(ke\right) + d\left(pe\right)$$

$$\cancel{dh} - vdp - \delta w_{rev} = \cancel{dh} + d\left(ke\right) + d\left(pe\right)$$

$$\delta q_{rev} = Tds$$

$$Tds = dh - vdp$$

$$\rightarrow \delta q_{rev} = dh - vdp$$

neglecting ke & pe, & rearrange;

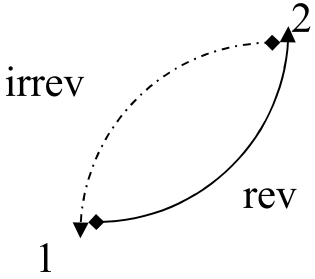
$$\delta w_{rev} = -vdp$$

$$w_{rev} = -\int_1^2 vdp$$

Reversible work for *open system*

Increase in Entropy Principle

- For reversible processes, entropy of universe (system surrounding) doesn't change, it is just transferred (along with heat transfer)
- In real processes, irreversibilities cause entropy of universe to increase
- Heat reservoirs don't have irreversibility
- To simplify analysis, assume irreversibilities to exist only inside the system under study.
- Inside the system, entropy *transfer* and *generation* occur.



Irreversible cycle since one of the processes is irreversible

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

From Clausius Inequality;

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{irrev} + \underbrace{\int_2^1 \left(\frac{\delta Q}{T}\right)_{rev}}_{=\Delta S = S_2 - S_1} < 0$$

$$\rightarrow S_2 - S_1 + \int_1^2 \left(\frac{\delta Q}{T}\right)_{irrev} < 0$$

Rearrange

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

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

Generalize for all processes

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

$=$ when rev
$>$ when irrev
$<$ impossible

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

S_{gen}=*entropy generated*
$= 0$ when rev.
> 0 when irrev.
< 0 impossible

Entropy Generation for Closed System

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T_b} \right) + S_{gen}$$

Change of system entropy

Transfer of entropy (T where Q is transferred, usually at boundary

Entropy *generation*

S_{gen} is the measure of irreversibilities involved during process

$$S_{gen} = \Delta S_{total,universe} = \Delta S_{surrounding} + \Delta S_{system} \geq 0$$

ΔS surrounding or system may decrease (-ve), but ΔS total (surrounding + system) must be > 0

Entropy of universe always *increases* (Entropy increase principle)

No such thing as entropy conservation principle

For a process to occur, $S_{gen} > 0$

Entropy Generation for Closed System

$$\Delta S = S_2 - S_1 = \int \frac{\delta Q}{T_b} + S_{gen}$$

$$S_2 - S_1 = \frac{Q}{T_b} + S_{gen}$$

For multiple heat transfers at different temperatures

$$\boxed{S_2 - S_1 = \sum_{j=1}^{n} \frac{Q_j}{T_j} + S_{gen}}$$

Entropy Generation for Closed System

$$\frac{dS}{dt} = \sum_{j=1}^{n} \frac{\dot{Q}_j}{T_j} + \dot{S}_{gen}$$

In rate form

$$dS = \sum_{j=1}^{n} \frac{\delta Q_j}{T_j} + \delta S_{gen}$$

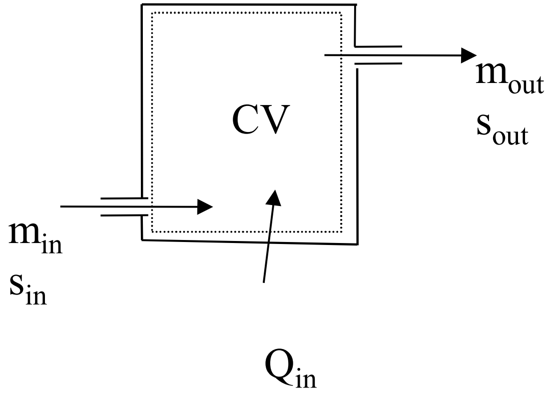
In differential form

δS_{gen} - depends on the process (friction, ΔT etc.)

- not a property

Entropy Generation for Open Systems

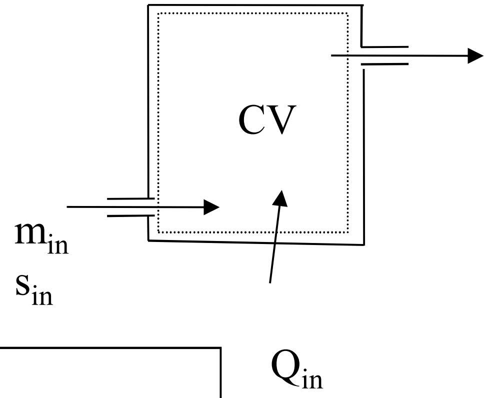
Apart from heat, **mass flows** also carry entropy along with them



$$\Delta S_{CV} = \sum_{j=1} \frac{Q_j}{T_j} + \sum S_{in} - \sum S_{out} + S_{gen}$$

$$\Delta S_{CV} = \sum_{j=1} \frac{Q_j}{T_j} + \sum ms_{in} - \sum ms_{out} + S_{gen}$$

Entropy Generation for Open Systems



$$\frac{dS_{CV}}{dt} = \sum_{j=1}^{n} \frac{\dot{Q}_j}{T_j} + \sum \dot{m}_{in} s_{in} - \sum \dot{m}_{out} s_{out} + \dot{S}_{gen}$$

Rate of *change* of system entropy

Rate of entropy *transfer*

Rate of entropy *generation*

Steady Flow Process

$$\frac{dm_{CV}}{dt} = 0 \rightarrow \boxed{\sum \dot{m}_{in} = \sum \dot{m}_{out}}$$

$$\frac{dS_{CV}}{dt} = 0$$

$$\cancel{\frac{dS_{CV}}{dt}} = \sum_{j=1} \frac{\dot{Q}_j}{T_j} + \sum \dot{m}_i s_i - \sum \dot{m}_o s_o + \dot{S}_{gen}$$

$$\boxed{0 = \sum_{j=1} \frac{\dot{Q}_j}{T_j} + \sum \dot{m}_i s_i - \sum \dot{m}_o s_o + \dot{S}_{gen}}$$

Steady Flow Process

single inlet/outlet;

$$0 = \sum_{j=1} \frac{\dot{Q}_j}{T_j} + \dot{m}_i(s_i - s_o) + \dot{S}_{gen}$$

$$s_i - s_o = \sum_{j=1} \frac{\dot{Q}_j / \dot{m}}{T_j} + \frac{\dot{S}_{gen}}{\dot{m}}$$

Reversible adiabatic process = isentropic process

Isentropic is not necessarily reversible adiabatic

Reversible process → $\boldsymbol{S_{gen} = 0}$

- Produces W_{max}
- Consumes W_{min}

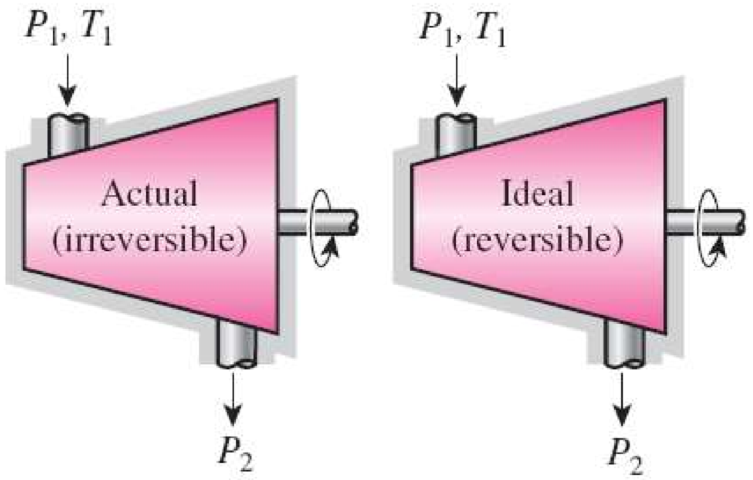
ISENTROPIC EFFICIENCIES OF STEADY-FLOW DEVICES

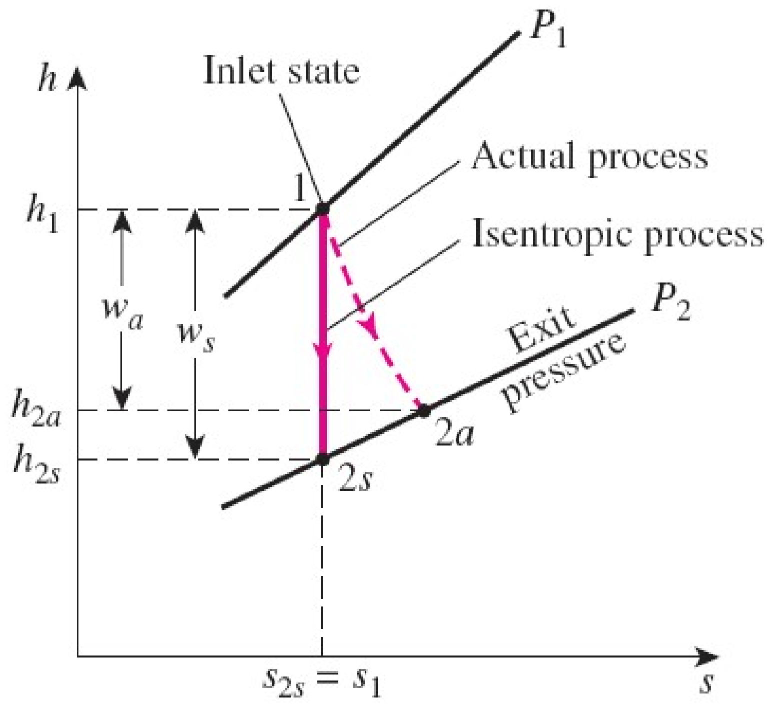
- Also known as *Adiabatic Efficiency* or *2nd Law Efficiency*
- The isentropic process involves no irreversibilities and serves as the ideal process for **adiabatic devices**.

Isentropic Efficiencies of Turbines

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

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





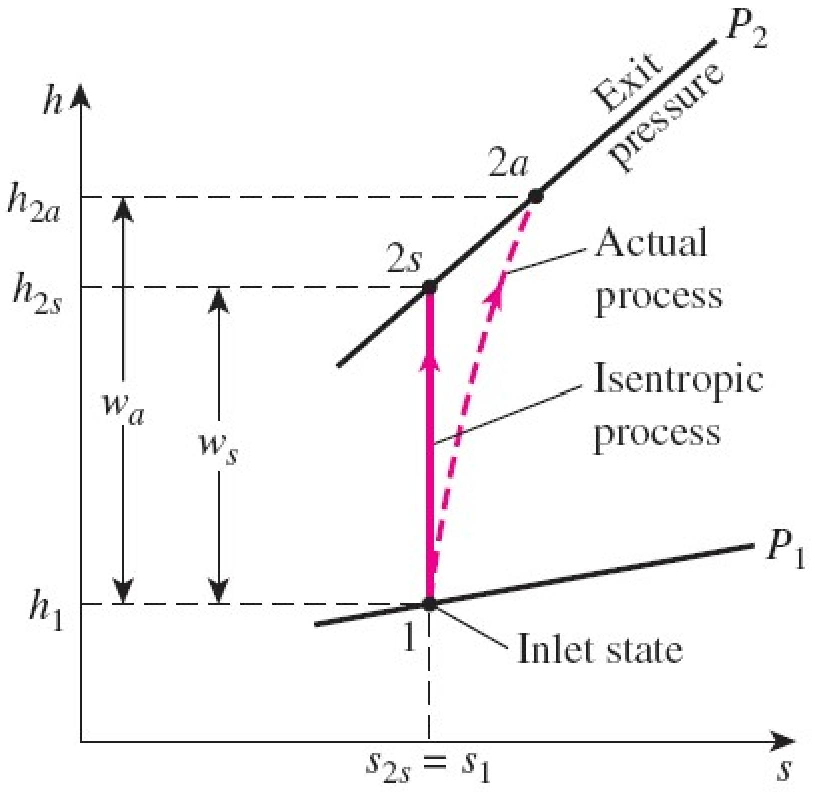
The *h-s* diagram for the actual and isentropic processes of an adiabatic turbine.

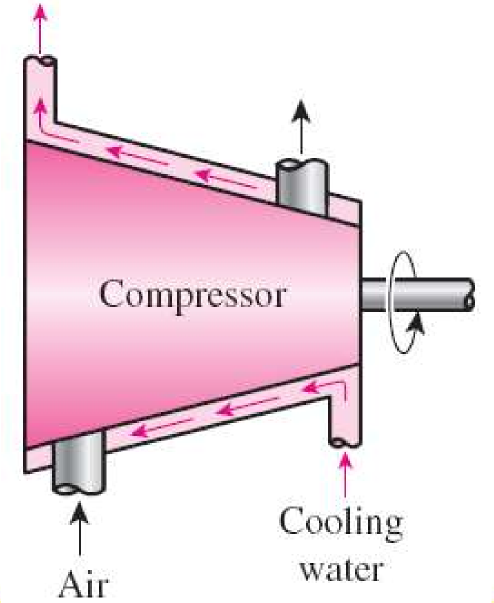
Isentropic Efficiencies of Compressors and Pumps

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

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

When kinetic and potential energies are negligible





Compressors are sometimes intentionally cooled to minimize the work input.

The *h-s* diagram of the actual and isentropic processes of an adiabatic compressor.

Isentropic Efficiency of Nozzles

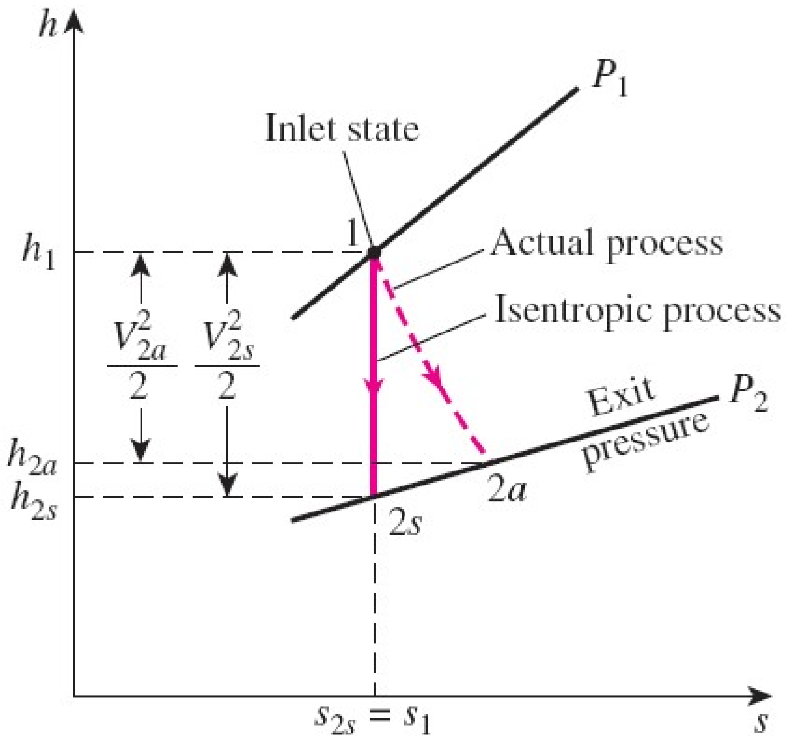
$$\eta_N = \frac{\text{Actual KE at nozzle exit}}{\text{Isentropic KE at nozzle exit}} = \frac{V_{2a}^2}{V_{2s}^2}$$

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

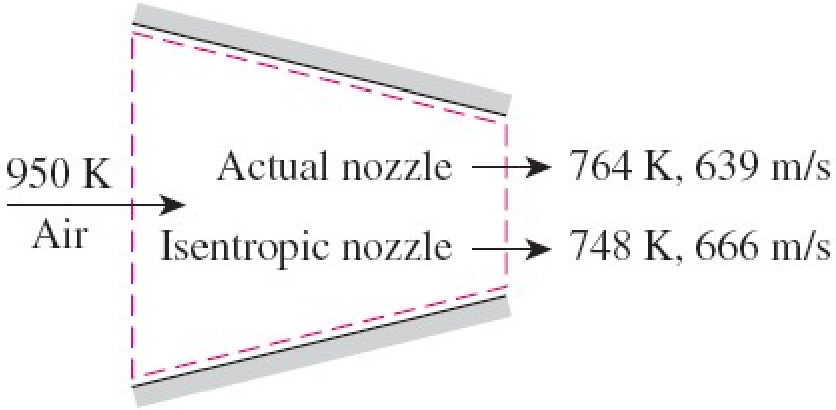
$$h_1 = h_{2a} + \frac{V_{2a}^2}{2}$$

Then,

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



The *h-s* diagram of the actual and isentropic processes of an adiabatic nozzle.



A substance leaves actual nozzles at a higher temperature (thus a lower velocity) as a result of friction.